

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 is determined by Townsend 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 electrostatic force 'X', their velocity of downward fall is  $v_2$ , then  $\frac{v_1}{v_2} = \frac{mg}{mg - Xe}$  [Where  $m$  = mass of a drop,  $e$  = electronic charge,  $X$  = potential diff.,  $g$  = acceleration due to gravity]

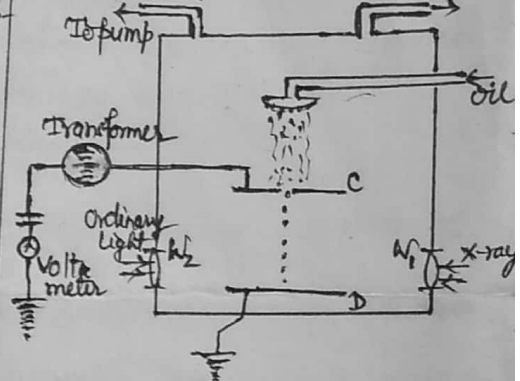
Thus, determining  $v_1$  &  $v_2$ , electronic charge can be calculated.

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:

$$\frac{v_1}{v_2} = \frac{mg}{mg - Xe} \quad (2) \quad \text{to Manometer}$$

Working principle: A cubical container/chamber, in which air is pumped out to create low pressure, used. Oil drops are charged through shower and oil drops are seen through microscope through window. 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  $4.8 \times 10^{-10}$  esu or  $1.6 \times 10^{-19}$  Coulomb.



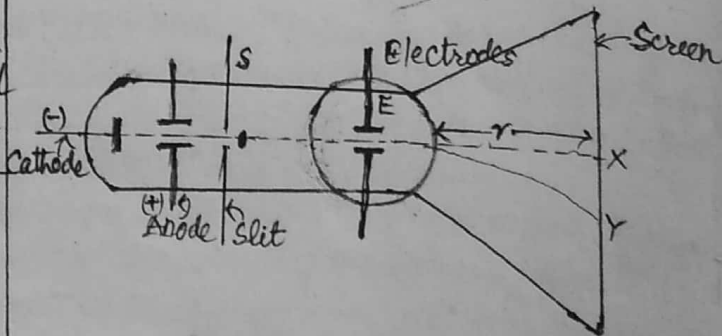
charge on electron is also calculated by following formula:  $e = F/N$  (Where  $F$  = faraday of electricity = 96500 coulombs = 9650 emu =  $9650 \times 3 \times 10^{10}$  esu,  $N$  = Avogadro's No. =  $6.023 \times 10^{23}$ )

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

→ 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 and it is so adjusted that the deflection is neutralised (return back from  $X$  to  $X$ ).



If  $m_e$ ,  $e$  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 ( $H$ ).

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

and,  $Hev = Xe$  ... (2)

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

Putting this 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  $1.7 \times 10^8$  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. ( $= \sum m_s, m_s = \text{Spin Q.No.}$ );  $2S+1$  = Spin multiplicity;  $L$  = Total or resultant orbital angular momentum quantum no. ( $= \sum m_l, m_l = \text{magnetic Q.No.}$ );  $J$  = 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 ( $d^2$ ) 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  $\uparrow \uparrow \square \square \square$
2. The total spin angular momentum quantum no. ( $S$ ) is known by  $\sum m_s$  (where  $m_s = \text{spin Q.No.}$ , generally unpaired electrons are taken consideration).  $m_s = +1/2$  for clockwise spin (1) and  $m_s = -1/2$  for anti clockwise spin (1). e.g., for  $d^2$  system,  $S = +1/2 + 1/2 = 1$ .
3. Then, spin multiplicity is known by  $(2S+1)$ . e.g., for  $d^2$  system, spin multiplicity =  $2 \times 1 + 1 = 3$ .
4. The total orbital angular momentum quantum no. ( $L$ ) is known by  $\sum m_l$  (where  $m_l = \text{magnetic quantum no.}$ ). 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:

$m_l = 0$	$m_l +1 \ 0 \ -1$	$m_l +2 \ +1 \ 0 \ -1 \ -2$	$m_l +3 \ +2 \ +1 \ 0 \ -1 \ -2 \ -3$
$\square$	$\square \square \square$	$\square \square \square \square$	$\square \square \square \square \square$
s-orbital ( $l=0$ )	p-orbital ( $l=1$ )	d-orbital ( $l=2$ )	f-orbital ( $l=3$ )

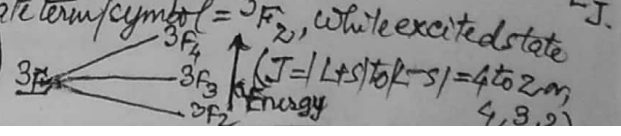
L-value	0	1	2	3	4	5
Spectroscopic Symbol	S	P	D	F	G	H

e.g., for  $d^2$  system,  $\uparrow \uparrow \square \square \square$  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.

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

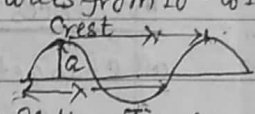


Electromagnetic radiation: In 1856, James Clark Maxwell stated that light, x-ray, γ-ray, heat etc. emit energy continuously in the form of waves or radiations & the energy is called radiant energy. These waves are associated with electric & magnetic fields, so called electromagnetic waves or radiations.

Different types of electromagnetic waves differ with respect to wavelength or frequency.

\* Increasing order of electromagnetic radiations w.r. to wavelength is Cosmic ray ( $10^{-16}m$ ) < γ-ray ( $10^{-10}m$ ) < x-ray ( $10^{-12}m$ ) < UV ( $10^8m$ ) < Visible ( $10^7m$ ) < IR ( $10^6m$ ) < Microwaves ( $10^2m$ ) < Radiowaves ( $10^3-10^4m$ )

Characteristics of electromagnetic radiations: (i) They emit energy continuously in the form of radiations or waves (ii) In these radiations, electric & magnetic components are always perpendicular to each other. They are also perpendicular to the direction in which the wave is travelling. (iii) They can travel even in vacuum i.e. medium is not necessary for their propagation (iv) The wavelengths of these radiations varies from  $10^{-16}$  to  $10^2m$  (v) They travel with the velocity of light ( $\approx 3 \times 10^8 ms^{-1}$ )



Characteristic terms: 1. Wavelength: The distance between any two consecutive crests or troughs is called wavelength of electromagnetic radiation. It is denoted by symbol 'λ' (Lambda) & expressed in Å (Angstrom), μ (micron), mm (millimicron), pm, nm (nanometer), mm, cm or m (SI) etc.

2. Frequency: The number of the wave lengths (oscillations) which pass through a point in one second is called frequency. It is denoted by symbol (ν) and unit is  $sec^{-1}$  or Hz.

3. Amplitude: The height of the crest or depth of trough in electromagnetic wave is called amplitude. It is denoted by symbol 'a' & its unit is of length (i.e. Å, m)

4. Wave number: The number of wave lengths which can be accommodated in one cm length along the direction of propagation is called wave number. It is denoted by symbol  $\bar{\nu}$  (nu bar) & expressed in reciprocal unit of length i.e.  $cm^{-1}$  or  $m^{-1}$ . ( $\bar{\nu} = \frac{1}{\lambda}$ )

5. Velocity: The linear distance travelled by the wave in one sec. is called velocity. It is denoted by symbol c & expressed in  $cm sec^{-1}$  or  $m sec^{-1}$ .

\* Relation among wavelength/wave number, frequency & velocity:

$$c = \lambda \nu = c \bar{\nu} \quad \left( \text{where } \nu = \text{frequency, } c = \text{velocity of light } (3 \times 10^8 ms^{-1}), \lambda = \text{wavelength, } \bar{\nu} = \text{wave number} \right)$$

Wave mechanical Concept of the Atom:

1. de-Broglie's equation (wave-particle dualism (or) Dual behaviour of matter): In 1923, Louis de-Broglie (French physicist) advanced the hypothesis that all forms of matter like electron, proton, neutron, atom, molecule etc. show dual character i.e. particle (Corpuscular) as well as wave nature. The waves associated with such particles is called a 'matter wave' which is different from electromagnetic wave.

He gave co-relation between momentum (particle nature) and wavelength (wave nature) of a moving particle in the form of an equation, known as de-Broglie's wave equation. According to the relation,  $\lambda = \frac{h}{mv} = \frac{h}{p}$  (where λ = wavelength, p = momentum, m = mass of particle, v = velocity)

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Derivation: The de-Broglie equation can be easily derived using Einstein mass-energy relationship. Consider the case of an electron. If it is supposed to have wave nature. Its energy will be given by  $E = h\nu$  (Planck's equation)

$$\text{or, } E = h \frac{c}{\lambda} \quad (\text{Since } c = \nu\lambda \text{ or } \nu = c/\lambda)$$

(Where  $E =$  Energy,  $\nu =$  frequency of electronic wave,  $\lambda =$  wavelength,  $c =$  velocity of light  
 $h =$  Planck's Constant)

On the other hand, if electron is supposed to have particle nature, its energy is given by Einstein mass-energy relation,  $E = mc^2$  — (3)

From eq. (2) & (3),  $\frac{hc}{\lambda} = mc^2$  or,  $\lambda = \frac{h}{mc} = \frac{h}{p}$  [ $\because p = \text{mass} \times \text{velocity} (mc)$ ]

This is the de-Broglie's wave equation.

Limitations: (i) It is true only for microscopic particles (e.g. e, p, n). It has no relevance for moving semimicro or macroparticles e.g. ball.

Evidences to support wave & particle nature or dual nature: For particle nature — It has all characteristics of particle; mass, charge, energy & also momentum (ii) It strikes a zinc coated plate/screen, a bright spot (scintillation) is produced. (iii) Black body radiation & photoelectric effect. For wave nature — (i) Davison & Germer expt (ii) Thomson expt.

2. Heisenberg Uncertainty principle: In 1927, Werner Heisenberg (German physicist) developed the uncertainty principle which is an important consequences of the dual nature of ~~microscopic~~ <sup>microscopic particles e.g.</sup> electron. It stated as "It is impossible to measure simultaneously both the position & momentum of a microscopic particle (e.g. electron) with absolute accuracy or certainty."

The product of uncertainty (or error in measurement) in position & uncertainty in momentum of a microscopic particle is always constant & is equal to or greater than  $\frac{h}{4\pi}$ , i.e.  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$  or,  $\Delta x \cdot m \cdot \Delta v \geq \frac{h}{4\pi}$  — (1)

(Where  $\Delta x =$  uncertainty or error in determining its position,  $\Delta p =$  uncertainty in measuring momentum,  $\Delta v =$  uncertainty in measuring velocity,  $m =$  mass of particle) From eq. (1), it is evident that if  $\Delta x$  is small, i.e. the position of the particle is known almost exactly,  $\Delta p$  or  $\Delta v$  would be large i.e. there would be large uncertainty or error in its measured value.

This principle has no impact on <sup>our</sup> daily life since it is concern with microscopic particles, not macroparticles.

3. Schrodinger's wave equation: In 1926, Erwin Schrodinger (Austrian physicist) proposed that since an electron behave as a wave, it should obey the same equation of motion which all other known types of waves obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron wave propagating in three dimensions (x, y & z) in space. This wave equation is known as Schrodinger's wave equation & is written as:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

(Where  $\psi =$  wave function & represent amplitude of wave,  $m =$  mass of particle,  $E =$  total energy of particle describing wave motion,  $V =$  potential energy,  $h =$  Planck's constant)