B. Sc. II (Hons.) Paper III A (Inorganic Chem)

Group A Atomic Structure (By Dr. [illegible] Kumar, [illegible] College, [illegible])

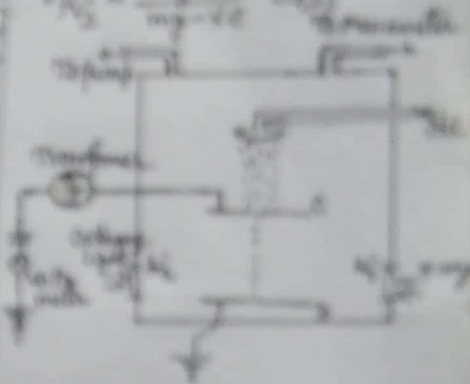
Determination of electronic charge by Millikan's method or Oil drop method

Charge on electron, i.e., electronic charge was determined by Thomson [illegible] in 1897 [illegible]. In 1903 Thomson invented a method to determine electronic charge, based on its principle: If ionised gas is passed through moist atmosphere, then by 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, then velocity of downward fall is v_2, then $\frac{v_1}{v_2} = \frac{mg}{mg + Xe}$ [Here m = mass of a drop, e = electronic charge, X = potential diff., g = acceleration due to gravity] —(1)

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

On this theory Millikan developed a method called Oil drop or Millikan'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, then oil drops are dropped through sprayer and oil drops are charged by X-rays through window. Oil drops are seen through microscope through window 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 [illegible] 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 Millikan) on electron is found to be 4.8×10^{-10} e.s.u. or 1.6×10^{-19} coulomb.

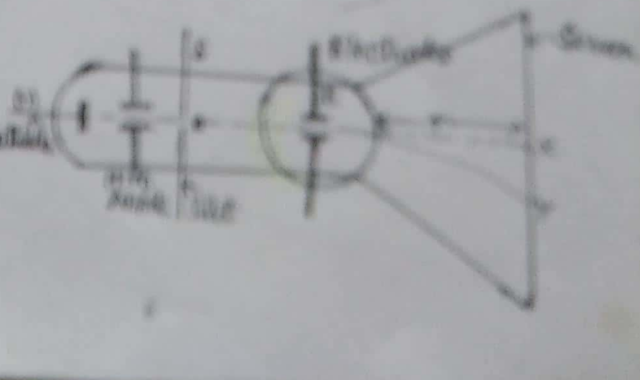
Charge on electron is also calculated by following formula, $e = F/N$ (where F = faraday of electricity = 96500 coulombs = 96500 e.m.u. = $96500 \times 3 \times 10^{10}$ e.s.u., N = Avogadro's no. = 6.023×10^{23})

$e = 96500 \times 3 \times 10^{10} / 6.023 \times 10^{23} = 4.802 \times 10^{-10}$ e.s.u.

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 rays, i.e., fast moving electrons. When high voltage electric field is applied in a highly evacuated bulb, a cathode ray (stream of fast moving electrons) 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 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).

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

and, $Hev = Xe$ ... (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:

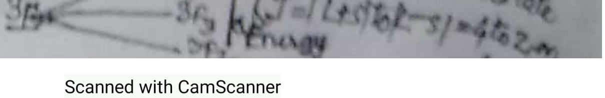
m_l = 0 [ ] s-orbital (l=0); m_l +1 0 -1 [| |] p-orbital (l=1); m_l +2 +1 0 -1 -2 [| | | |] d-orbital (l=2); m_l = +3 +2 +1 0 -1 -2 -3 [| | | | | |] f-orbital (l=3)

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 = $^3F_4$, $^3F_3$, $^3F_2$)

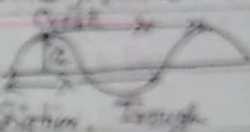


1. **Electromagnetic radiation:** In 1856, James Clark Maxwell stated that light, x-ray, γ-ray, heat etc. emit energy continuously in the form of waves or radiations & the energy is called radiant energy. These waves are associated with electric & magnetic fields, so called electromagnetic waves or radiations.

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

* **Increasing order of electromagnetic radiations w.r.t. wavelength** is Cosmic ray (10^{-16} m) < γ-ray (10^{-14} m) < x-ray (10^{-12} m) < UV (10^{-8} m) < Visible (10^{-7} m) < IR (10^{-6} m) < Microwaves (10^{-3} m) < Radio waves (10^{-1}–10^{4} m)

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 vaccum i.e. medium is not necessary for their propagation. (iv) The wavelengths of these radiations varies from 10^{-16} to 10^{4} m (v) They travel with the velocity of light ($\sim 3\times10^{8}\ ms^{-1}$)



Characteristic terms: 1. **Wavelength:** The distance between any two consecutive crests / troughs is called wavelength of electromagnetic radiation. It's denoted by symbol 'λ' (Lamda) & expressed in Å (angstrom), μ (micron), mμ (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's denoted by symbol (nu) ν and units are sec^{-1} or Hz.

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

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

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

* **Relation among wavelength / wavenumber / frequency & velocity:**

$$\nu = c/\lambda = c\bar{\nu}$$ (Where ν = frequency, c = velocity of light ($3\times10^{8}\ ms^{-1}$), λ = wavelength, $\bar{\nu}$ = wave number)

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. shows dual character i.e. particle (Corpuscular) as well as wave nature. The wave 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 [redacted] in the form of one 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)

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)

Or, $E = h\frac{c}{\lambda}$ — (2) (Since $c = \nu\lambda$ or $\nu = c/\lambda$)

(Where E = Energy, ν = frequency of electronic wave, λ = 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 eqn (2) & (3), $\frac{hc}{\lambda} = mc^2$ or, $\lambda = h/mc = h/p$ [$\because$ p (momentum) = mass x 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 of e: For particle nature – It has all characteristics of particle; mass, charge, energy & also momentum (ii) when it strikes a ZnS 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 particles e.g. electron. It stated as "It is impossible to measure, simultaneously both the position & momentum (v) 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 $h/4\pi$, i.e. $\Delta x \cdot \Delta p \geq h/4\pi$ or, $\Delta x \cdot m \times \Delta v \geq h/4\pi$ — (1)

(where Δx = uncertainty or error in determing its position, Δp = uncertainty in measuring momentum, Δv = uncertainty in measuring velocity, m = mass of particle) From eqn (1), it is evident that if Δx is small, i.e. the position of the particle is known almost exactly, Δp or Δv would be large i.e. there would be large uncertainty or error in its measured value.

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

3. Schrodinger's wave equation: In 1926, Ervin 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:

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

(Where ψ = wavefunction & represent amplitude of wave, m = mass of particle, E = total energy of particle describing wave motion, V = potential energy, h = Planck's Constant)