CHAPTER 2

ATOMIC STRUCTURE

VALUES:

* e/m for electron = 1.7588×10^{11} C/kg
* Charge on electron = 1.6022×10^{-19} C or 4.8×10^{-10} e.s.u
* Mass of electron = 9.11×10^{-31} kg
* Max. e/m Ratio of canal Rays = 9.54×10^{7} C/kg
  (when H_2 gas is used in discharge tube)
* Mass of proton = 1.6726×10^{-27} kg
* Mass of neutron = 1.6749×10^{-27} kg
* Planck's constant = 6.6262×10^{-34} Js
* Speed of light, c = 3×10^{8} ms^{-1}
* Vacuum Permitivity, ϵ_0 = 8.85×10^{-12} $C^2 J^{-1} m^{-1}$
* Rydberg's constant, R = 1.0974×10^{7} m^{-1}

FORMULAS

1. $e/m = \frac{E}{B^2 r}$

2. $E = h\nu$ (ν: frequency)

3. $\nu = \frac{c}{\lambda}$

4. $E = hc\bar{\nu}$ ($\bar{\nu}$: wave number)

5. $mvr = \frac{nh}{2\pi}$

6. $r_n = n^2 (0.529) A^\circ$

7. $E_n = \frac{-1312.36}{n^2}$ kJ/mol

8. $\Delta E = +1312.36 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ kJ/mol

9. $\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) m^{-1}$

10. $\sqrt{\nu} = a(z - b)$ Moseley's Law

* In discharge tube, following experiments were performed:
  1. Discovery of Cathode Rays
  2. Discovery of Canal Rays
  3. Properties of cathode Rays and Canal Rays.

* Neutron → Discovered through Radioactivity

* Arrangement of fundamental particles came from spectral studies.

CATHODE RAYS

Name Cathode Rays → Goldstein
Name Electrons → Stoney

At 5000 - 10,000 V P = 1 atm Nothing happens
At 5000 - 10,000 V P = 0.1 mm Hg Uniform Glow + Fluorescense
At 5000 - 10,000 V P = 0.01 mm Hg Dark Space + Fluorescence

Uniform Glow → Due to excitation and de-excitation
Fluorescence → Due to ionization

* Cathode Rays are produced at:
  High Voltage and Low Pressure

* The exact voltage required for production of cathode rays depends on the length of the tube and the pressure inside the tube.

PROPERTIES OF CATHODE RAYS

Properties	Discovered by	Experiment
1. Negatively charged	J. Perine and J.J Thomson	Electric Field
2. Travels straight	Hittorf	Shadow of opaque object
3. K.E, P.E, Material Nature	William Crooke	Light Paddle Wheel
4. Bend of 90°	Thomson	Magnetic Field
5. e/m	Thomson	Simultaneous electric and magnetic field
6. Charge of e^-	Milikan	Oil drop

* Cathode Rays are reducing in nature

* Charge of e^- = $1.6 \times 10^{-19} C$
* Mass of e^- = $9.11 \times 10^{-31} kg$

MILIKAN OIL DROP METHOD

* In oil drop method, gas is ionized by X-Rays gun

* For measuring charge of electron

* Two Chambers :
  Upper chamber : → Filled with air
  → Pressure adjusted by vacuum pump

* Two electrodes attached with electricity to generate electric field in the space between the electrodes.

* Atomizer → For creating fine spray of oil droplets

* Arc lamp → To illuminate the space between electrodes

* Droplet fell under the force of gravity
  $v_1 \propto mg$

* After ionization of air:
  → The air between electrodes was ionized by X- Rays
  → Droplet got charged

→ Droplet moved upward against gravitational force with velocity V_2

$$V_2 \propto Ee - mg$$

E : electric field strength

e : charge of electron

$$\frac{V_1}{V_2} = \frac{mg}{Ee - mg}$$

From this "e" is calculated to be $1.6022 \times 10^{-19} C$

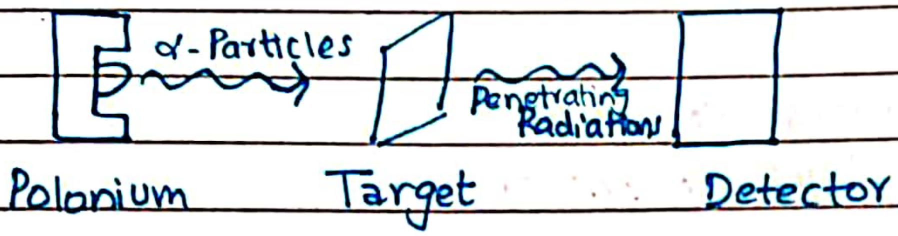
CANAL RAYS OR POSITIVE RAYS

* Cations
* Perforated cathode used in experiment
* Origin : collision of cathode rays with gas

* e/m of canal Rays is always less than that of cathode rays.

DISCOVERY OF NEUTRON (RADIOACTIVITY)

Radioactivity → James Chadwick



$m = 1.0087$ amu

* Highest penetration power

* Neutrons are 1842 times heavier than electron

PLANCK'S QUANTUM THEORY

* Radiation emitted or absorbed by a body is in discontinuous form.

* Energy Radiations → Quanta
  In case of light → Photon

* Each radiation is associated with a specific frequency, which increases with temperature.

$$E = hf$$

* Energy is quantized

$$E = nhf$$

Wave Number : Number of waves per unit length.
It is the reciprocal of wavelength

$$E = hc\bar{\nu}$$

BOHR'S ATOMIC RADIUS

* orbits or shells
* Energy:
  - → Fixed in an orbit
  - → Radiate energy when ~~one~~ electron moves to lower energy level
  - → Absorb energy when electron moves to higher energy level

$$\Delta E = E_2 - E_1 = hf$$

* Angular momentum of electron (mvr) in the hydrogen atom is quantized

$$mvr = \frac{nh}{2\pi}$$

For 1^{st} shel : $\frac{h}{2\pi}$

For 2^{nd} shell = $\frac{h}{\pi}$

For 3^{rd} shel = $\frac{3h}{2\pi}$

BOHR'S RADIUS

$$r_n = n^2 (0.529) A^\circ$$

MCQ. Ratio of radii of second and third Bohr orbit of hydrogen atom is :

Ans ⇒ 4 : 9

Explanation :

$$r_n \propto n^2$$

$$\frac{r_2}{r_3} = \frac{n_2^2}{n_3^2}$$

$$\frac{r_2}{r_3} = \frac{2^2}{3^2}$$

$$\frac{r_2}{r_3} = \frac{4}{9}$$

* RADIUS OF MONOELECTRONIC SPECIES

H, He^{+1}, Li^{+2}, Be^{+3}

$r \propto \frac{1}{V^2}$ $\quad$ $V \propto \frac{1}{\sqrt{r}}$

MCQ : Electrons revolve with fastest speed in

✓a) K $\quad$ b) L $\quad$ c) M $\quad$ d) N

* Correct order of spacing

$$r_4 - r_3 > r_3 - r_2 > r_2 - r_1$$

RYDBERG'S CONSTANT

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c}$$

$$R = 1.0974 \times 10^7 m^{-1}$$

ENERGY OF ORBIT

* Energy of an orbit
  → Increase with increase in Z
  → Decrease with decrease in Z

* Energy of an orbit can never be positive

$$E_n = -\frac{1312.26}{n^2} \text{ kJ/mol}$$

$$E_n = \frac{-13.6}{n^2} \text{ eV}$$

→ n is principal quantum number which can never be zero. If we make 'n' infinity value of E would become zero

→ The total energy of atomic electron is less than zero

* Excitation energy is less than ionization energy.
* Energy of H-atom in ground state is negative

* As we go away from nucleus energy gap b/w successive orbit decreases.

SPECTRUM

* Extent of Bending:

Radiation of high frequency (shorter wavelength) bends to greater extent and vice versa.

V I B G Y O R

→ Increasing wavelength

→ Decreasing frequency

* Spectrometer: Device for detecting and analyzing wavelengths of electromagnetic radiation.

Violet → 400 - 420

Indigo → 420 - 460

Blue → 460 - 510

Green → 510 - 580

Yellow → 580 - 600

Orange → 600 - 630

Red → 630 - 750

MCQ: Which photon bend to greater extent
✓a) Violet b) Red

* Order of increasing frequency and Decreasing Wavelength
1. Radio ~~freque~~ Waves
2. Micro waves
3. Infra red
4. Visible Light
5. Ultraviolet
6. X-Rays
7. Gamma Rays

Hint: Roman Men Invented Very Unusual X-Ray Guns

* Two Types Of Spectrum
1. Line Spectrum / Atomic Spectrum
2. Continuous Spectrum

* CONTINUOUS SPECTRUM:
→ No clear boundary
→ Colours partially overlap

Examples:
1. Rainbow
2. Nuclear Boundaries

* LINE SPECTRUM

→ clear boundaries
→ atomic (gaseous)

- Sodium (Na) imparts yellow colour
- Strontium gives red colour
- Potassium (K) gives violet colour

The line spectrum may be:
(i) Line Absorption Spectrum
(ii) Line Emission Spectrum

(i) LINE ABSORPTION SPECTRUM

When white light consisting of wavelengths 380nm-760nm is passed through a sample of substance, it may absorb certain wavelengths of radiation.

The spectrum of this radiation from which some wavelengths have been absorbed, will show certain dark lines in a bright background.

(ii) LINE ~~ABSOR~~ EMISSION SPECTRUM

When the substance, that has absorbed radiation (energy), emits it in the form of radiation and a spectrum is obtained, it is called line emission spectrum.

It consist of bright lines in a dark background

* To Find Number Of Spectral Lines

$$\text{Number of Spectral lines} = \frac{n(n-1)}{2}$$

MCQ: Number of spectral lines when electron is emitted from $n_2 = 5$ to ground state

$$\frac{5(5-1)}{2} = \frac{5(4)}{2} = \frac{20}{2}$$

$= 10$ lines

SPECTRAL SERIES FOR HYDROGEN

1. LYMAN SERIES

LBPBP

- → U-V Region
- → $n_2 = 2, 3, 4, 5 \ldots$
- → $n_1 = 1$

2. BALMER SERIES

- → Visible Region
- → $n_2 = 3, 4, 5 \ldots$
- → $n_1 = 2$

3. PASCHEN SERIES

- → Near IR Region
- → $n_2 = 4, 5, 6, 7$
- → $n_1 = 3$

4. BRACKETT SERIES

- → Mid IR Region
- → $n_2 = 5, 6, 7$
- → $n_1 = 4$

5. PFUND SERIES

- → Far IR Region
- → $n_2 = 6, 7$
- → $n_1 = 5$

* DEFECTS IN BOHR'S THEORY

→ cannot explain spectrum of more complicated atoms (multi electron system)

→ Cannot explain multiplicity of spectral lines

→ Cannot explain Zeeman effect (effect of magnetic field)

→ cannot explain stark effect (effect of electric field)

→ Doesnot follow Heisenberg's Uncertainty Principle

X-RAYS

* Electromagnetic Radiations
* Very high frequency (shorter wavelength)
* Wavelength Range: 10^{-2} A° to 10^{+2} A° (0.01nm to 10nm)

METHODS OF PRODUCING X-RAYS

1. Roentgen Method
2. Coolidge Method
3. By Using Betatron

ROENTGEN METHOD

Pressure : 0.01 mm Hg
Voltage : 30,000 to 50,000 V
Cathode Shape : Concave
X-Rays Origin : Anode
Source of e^- : Cathode (Ionization)

PROPERTIES OF X-RAYS

1. Travel in straight Line like ordinary light
2. Neutral
3. Can ionize gases
4. Produce fluorescence in substances like rock salt, uranium, glass, compounds of calcium and barium
5. Show reflection and refraction
6. Diffracted by crystalline substances
7. Can Penetrate through substances
8. Blacken photographic plates

* Which property depend on intensity of X-Rays
  a. Ionization of gases by X-Rays
  b. Blackening of photographic plates

CHARACTERISTIC X-RAYS (INNER-SHELL TRANSITIONS)

* Three Types
  K_α, K_β, K_γ

* Inner-shell transitions emit photons of frequency beyond the ultraviolet region and are known as X-Rays.

* If $n_1 = 1$ → X-Rays belong to K-series

K_α : L → K
K_β : M → K
K_γ : N → K

ENERGY ORDER

$$K_\gamma > K_\beta > K_\alpha$$

K-series X-rays are more energetic than any other series.

MOSELEY'S LAW

* The frequencies of emitted X-rays increase regularly with the number of positive charge on the nuclei of target elements, used as anode.

* Wavelengths of X-rays are the characteristics of each element, used as anode.

* Number of Lines in X-rays spectrum depends on:
  1. Nature of target material (Nuclear charge)
  2. Excitation voltage

$$\sqrt{\nu} = a(Z-b)$$

ν : frequency
a : proportionality constant
b : screening constant

* Number and frequency of X-rays depend on:
  Nature of anode

a : Proportionality Constant
Unit : Hz
Depends upon element

b : Screening Constant
→ b is unitless
→ b increase from top to bottom
→ b almost remain constant from left to right

* As b increase, I.E decrease

$$I.E \propto \frac{1}{b}$$

QUANTUM NUMBERS

* De-Broglie's Prediction:

Atomic particles (like electron) could have both wave-like and particle-like properties

* De-Broglie → predicted matter should behave like wave
* Davison and Germer → experimentally proved that electrons behaved like wave
* First wave property shown was → Diffraction

$$\lambda = \frac{h}{mv}$$

* Atomic Orbital : A definite region in the three dimentional space around the nucleus, where there is maximum probability of finding an electron of a specific energy.

* Four Quantum Numbers
  1. Principal Quantum Number (n)
  2. Azimuthal Quantum Number (l)
  3. Magnetic Quantum Number (m)
  4. Spin Quantum Number (s)

(1–3) Derived from Schrodinger's Wave Equation

PRINCIPLE QUANTUM NUMBER (n)

Values of n = 1, 2, 3, 4, 5, 6, 7

Max. No. of electrons in a shell = $2n^2$

* Principal Quantum number can never be zero or negative

* n is upto infinity

* MAX ACCOMODATION OF ELECTRONS ($2n^2$)

1. K-shell → $2e^-$
2. L-shell → $8e^-$
3. M-shell → $18e^-$
4. N-shell → $30e^-$

H^+ → vacant
H → $1e^-$
He → $2e^-$

Size → n
Shape → l
x, y, z orientation → m
spin → s

AZIMUTHAL QUANTUM NUMBER (l)

Values :

$l = 0$ to $n-1$

e.g when $n = 1$, $l = 0$

$n = 2$, $l = 0, 1$

$n = 3$, $l = 0, 1, 2$

$n = 4$, $l = 0, 1, 2, 3$

When $l = 0$ → s-subshell → spherical

$l = 1$ → p-subshell → dumbbell shape

$l = 2$ → d-subshell → sausage shape

$l = 3$ → f-subshell → complicated

* Maximum number of electrons in a subshell = $2(2l+1)$

s = 2

p = 6

d = 10

f = 14

* The letters s, p, d and f has been taken from the old spectroscopic terms:

sharp, principal, diffused, fundamental

MAGNETIC QUANTUM NUMBER (m)

→ orbital
→ explains magnetic properties of electron

* VALUES OF 'm'

$-l$ through 0 to $+l$

e.g

If $l = 1$, $m = -1, 0, +1$
If $l = 2$, $m = -2, -1, 0, +1, +2$
If $l = 0$, $m = 0$ → (still one orbital)

As $l = 1$ is p-subshell so m exist as p_x, p_y, p_z
As $l = 2$ is d-subshell so $m = d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$

Max number of orbitals in an orbit $= n^2$

* Magnetic Quantum Number arises in magnetic field

* No. of orbitals in a subshell $= 2l + 1$
* No. of orbitals in an orbit $= n^2$

SPIN QUANTUM NUMBER (s)

* Describe the spin of an electron on its axis

* Spin either:

  clockwise = $-1/2$

  anticlockwise = $+1/2$

* Direction of spin can be found out by the application of an external magnetic field

* Two electrons in the same orbital:

  Spin = 0

* Parallel spins → (↑↑)
* Antiparallel or pair up spins → (↑↓) or (↓↑)

* No. of spectral lines = No. of subshells in a shell

SHAPES OF ORBITALS.

* Orbitals have:
  a. No physical existence
  b. No fixed boundaries

NODE

Where probability of finding an electron is minimum.

To Find Total Number Of Nodes:

Total Number Of nodes = $n-1$

* The 1s orbital has no nodes.
* The 2s orbital has one radial node
* The 3s orbital has two radial nodes

* All the 2p ($2p_x$, $2p_y$, $2p_z$) orbitals have a single angular node
* All the 3d orbitals have two angular nodes.

The number of nodes is always one less than the principal quantum number.

Nodes $= n-1$

- As $n = 1$, the 1s orbital has no nodes
- The 2s and 2p orbitals have one node
- The 3s, 3p, 3d orbitals have two nodes.

ANGULAR NODES

The number of angular nodes is always equal to orbital angular momentum quantum number, l

No. of angular nodes $= l$

RADIAL NODES

The number of radial nodes = total number of noder ~~by~~ minus number of angular nodes :

Radial Nodes $= (n-1) - l$

Example

* In 2s orbital

As $n = 2$, $l = 0$

No. of nodes $= 2 - 1 = 1$

Angular nodes $= 0$

Radial nodes $= (2-1) - 0 = 1$

AUFBAU PRINCIPLE
(THE BUILDING UP PRINCIPLE)
(n+l RULE)

* Electrons are first filled in sub energy levels having lower n+l value

* If two orbitals have the same n+l value, the one having lower 'n' value will be filled up first

1s, 2s, 2p, 3s, 3p, 4s, 3d

PAULI'S EXCLUSION PRINCIPLE

* No two electrons in an atom can have the same set of four quantum numbers.

* No two electrons in an orbital have same spin

* An orbital can never be occupied by more than two electrons.

* Two electrons in same orbital have:
  → Same 3 quantum numbers

HUND'S RULE

If degenerate orbitals are available (orbitals of same energy), and more than one electrons are to be filled in them, they should be placed in different orbitals with same spin, rather than to put them in the same orbital with opposite spins.

STABILITY OF ORBITAL

p^6 (Completely filled) > p^3 (Half filled) > Partial

d^{10} > d^5 > partial

f^{14} > f^7 > Partial

MCQ: Removal of electron is difficult from:

a) | ↑ | ↑ | |

✓ b) | ↑ | ↑ | ↑ |

c) | ↑↓ | ↑ | ↑ |