

ENGG. CHEMISTRY

**1ST & 2nd
SEM**

All Branch

Under SCTE&VT, Odisha

PREPARED BY



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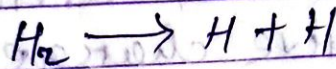
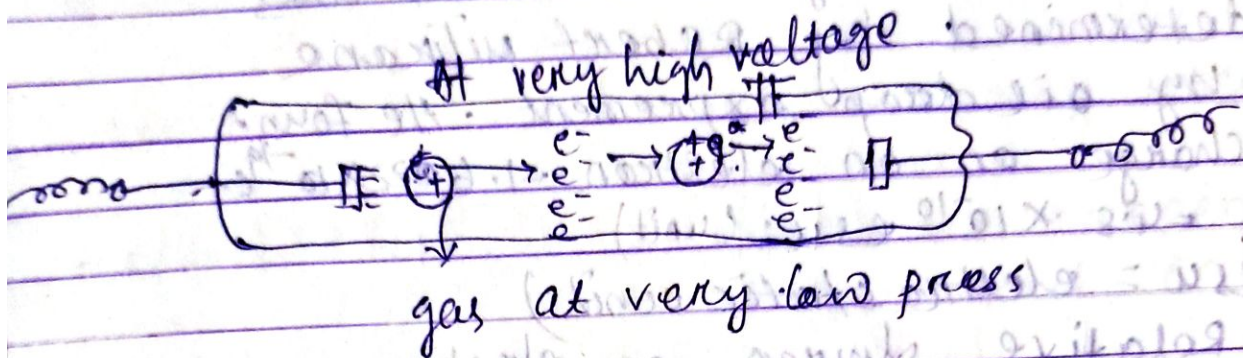
STRUCTURE OF ATOM

- There are 3 fundamental particles of atom.

electron, neutron, proton.

Electron:-

It was 1st discovered by J.J. Thomson in cathode ray experiment.



- Cathode ray initially starts from the atom collides to the atom, the flow of the cathode ray continue. This is flow of -vely charged particles. This particles are called as electron by Seddy.

- when cathode ray strikes against
- ① metal - produces heating effect.
 - ② fluorescent screen - produce fluorescence.
 - ③ with spin wheel - gives mechanical effect.
 - ④ with photographic plate - fogged.
 - ⑤ Against heavy metal anti-cathode - produce x-ray.

Specific charge (e/m)
Determined by J.J. Thomson.

He found its value

- A specific charge (e/m) for cathode ray is independent to the nature of the cathode material and gas used in discharged tube.

- Absolute charge of electron was determined by Robert Millikan by oil drop experiment. He found charge on an electron $-1.6022 \times 10^{-19} \text{ C}$
 $= 4.8 \times 10^{-10} \text{ esu (unit)}$

(esu = electrostatic unit)

= Relative charge on electron = unit negative charge

- Mass of an electron was found $9.1 \times 10^{-31} \text{ kg} = 9.1 \times 10^{-28} \text{ g}$

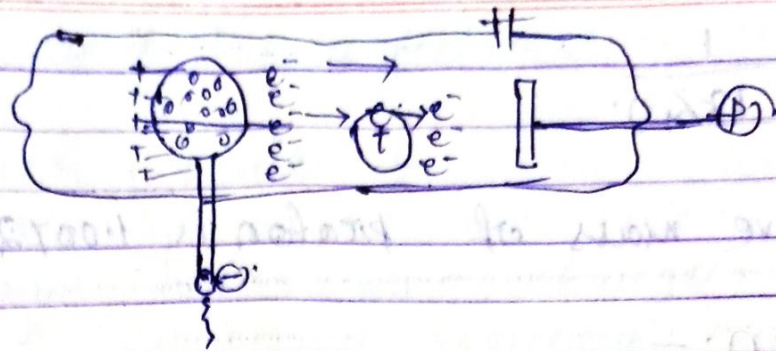
- On increasing the velocity of electron, mass of electron increases called reduced mass of $e^- (m')$

$$m' = \frac{m_{\text{rest}}}{\sqrt{1 - (v/c)^2}}$$

- If velocity of electron becomes equal to velocity of light, then reduced mass become infinity.

Proton:—

It was discovered by E. Goldstein during canal ray or β ray expt.



All the properties of canal ray / +ve ray
 except following properties.

- +ve ray cannot produce x-ray when strike against heavy metal.
- specific charge on proton e/m depends on the nature of gas used in discharged tube.
- As the atomic mass of the element (gas) increase then e/m decreases. Therefore maximum e/m is found in case of H.

$$E/m = +9.579 \times 10^4 \text{ C/g}$$

- Absolute charge on proton $+1.6022 \times 10^{-19} \text{ C}$
 (or) $+4.8 \times 10^{-10} \text{ esu}$.

- Absolute mass of proton.

$$= 1.672 \times 10^{-24} \text{ g}$$

$$= 1.672 \times 10^{-27} \text{ kg}$$

$$\frac{(e/m)_e}{(e/m)_p} = 1840:1$$

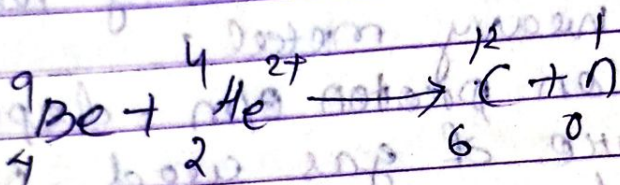
$$(e/m)_p$$

$$\frac{m_e}{m_p} = \frac{1}{1840}$$

Relative mass of proton is 1.0072 amu

Neutron: -

- Discovered by James Chadwick by bombarding α -ray on Be plate.



- Due to chargeless particle neutron was discovered at last.
 - Absolute mass of neutron $= 1.675 \times 10^{-27} \text{ kg}$
 - Neutron is the heaviest fundamental particle.
 - Its relative mass is 1.00866 amu
 - It has specific and relative charge is 0.
- Compare

- Specific charge of α, p, e, n

$$e/m \quad \frac{2}{4} < \frac{1}{1} < \frac{1}{1/1840} < 0$$

e/m order $n < \alpha < p < e$

- Neutron, Proton, nucleus & electron all spin in their nuclear axis. Therefore in case of clock wise

spin $+\frac{1}{2}$ and $+$ or anticlockwise $-\frac{1}{2}$

Plum pudding Model:—

- Atom is spherical and entire sphere is formed with $+$ ve charge & e^- are embedded around the center like raisin in the plum pudding & seeds in watermelon.
- This model only explains electrically neutral nature of atom, but failed to explain α -scattering experiment.

α -scattering experiment:—

- On the basis of α -scattering experiment Rutherford proposed nuclear model of atom.
- 99% inner part of the atom is hollow.
- All massive particles (proton & neutrons) are concentrated at the centre of the atom in very small volume. This is called nucleus of the atom.

$$\frac{\text{Diameter of Atom } r_{\text{atom}}}{\text{Diameter of nucleus } r_{\text{nucleus}}} = \frac{10^{-8} \text{ cm}}{10^{-13} \text{ cm}} = \frac{10^{-10} \text{ m}}{10^{-15} \text{ m}} = 10^5$$

$$r_{\text{atom}} = 10^5 \times r_{\text{nucleus}}$$

$$V = \frac{4}{3} \pi r^3, \quad \frac{\text{Vol. of atom}}{\text{Vol. of nucleus}} = \frac{r_{\text{atom}}^3}{r_{\text{nucleus}}^3} = (10^5)^3$$

$$\text{Size of atom} = 10^{15} \times \text{size of nucleus}$$

Defects:-

- According to Maxwell's theory of electromagnetic radiation when an electron revolves around the nucleus, it releases electromagnetic waves continuously. Radius of curvature decreases, electron falls at its nucleus. But this doesn't happen.
- Electron if releases energy continuously, atomic spectrum should be continuous.
- Atomic spectrum is found discontinuous spectrum.

Electromagnetic waves:-

waves having no particle associated with electric field & magnetic field & \perp to each other, & \perp to the direction of propagation. Having constant velocity 3×10^8 m/sec, needs no medium to propagate are called electromagnetic waves.

- These have same velocity ^{but} frequency & wavelength are different.

Electromagnetic Spectrum:

when ^{EM}waves having no particle are arranged in increasing order of wave length & decreasing order of frequency & energy a series of waves obtain called electromagnetic spectrum.

Cosmic Ray.

Gamma ray

x-ray

v.v ray

visible ray

I.R rays.

Microwaves.

Radiowaves.

Radha me Mira ko Invite

kiya. Ultra. Red. X-ray. Gamma ray

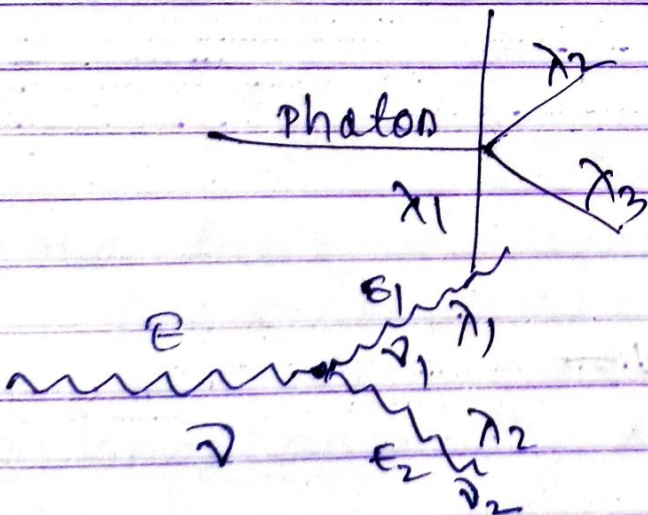
$$\lambda \uparrow \nu \downarrow = E \downarrow$$

$$\lambda = c/\nu \quad , \quad c = \lambda \times \nu$$

$$\nu = c/\lambda \quad E = h \cdot \nu$$

$$E = h \cdot c/\lambda$$

$$h = 6.625 \times 10^{-34} \text{ (J.s)}$$



$$\frac{1}{\lambda} = \frac{1}{\lambda_2} + \frac{1}{\lambda_3}$$

Acc^d to law of conservatⁿ of energy.

$$E = E_1 + E_2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$h\nu = h\nu_1 + h\nu_2$$

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda = \lambda_1 + \lambda_2$$

$$\frac{1}{\lambda} = \frac{\nu_1 + \nu_2}{\lambda_1 \lambda_2}$$

$$\lambda = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$$

$$E_1 = h\nu_1 = hc/\lambda_1$$

$$E_2 = h\nu_2 = hc/\lambda_2$$

$$\frac{E_1 + E_2}{E_2} = \frac{\nu_1 + \nu_2}{\nu_2} = \frac{\lambda_2}{\lambda_1}$$

A molecule E_1

A $K.E.$ A $K.E.$

$$E = h\nu + K.E. \quad \nu = N$$

$$2K.E. = E - h\nu$$

$$K.E. = \frac{E - h\nu}{2}$$

Photo electric effect! -

incident radiation E

λ photoelectron

metal surface.

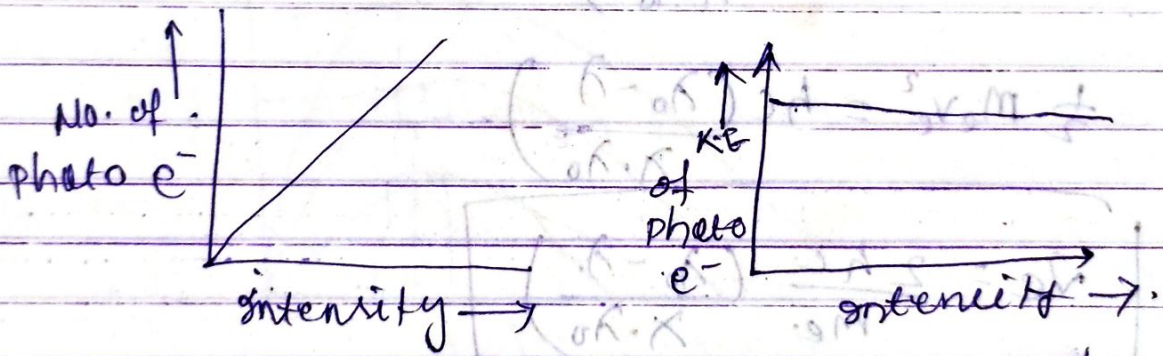
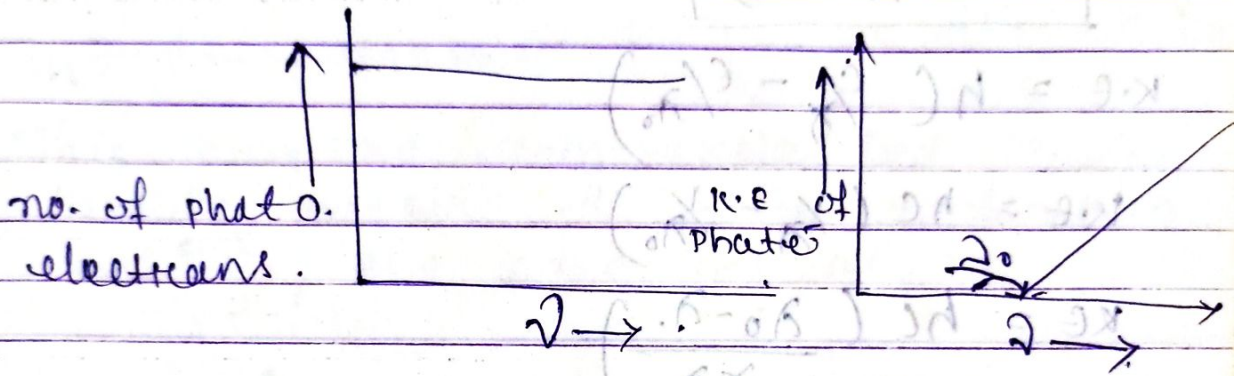
①

Threshold frequency (ν_0)

Minimum frequency of incident radiation which can eject electron.

② Work function (W_0) = minimum energy of incident radiation which can eject e⁻.

$$W_0 = h\nu_0$$



- On the basis of work function

C < K < Na < Li < Zn < Cu < Ag < Fe < W < Pt

Explanation: - (By Einstein)

Case-1

$$E < W_0$$

$$\nu < \nu_0$$

no photoelectric effect.

Case-2

$$E = W_0$$

$$\nu = \nu_0$$

Photoelectron is ejected with zero K.E.

Case-III

$$E > W_0$$

$$\lambda > \lambda_0$$

Photoelectron is ejected with some K.E.

$$E = W_0 + K.E.$$

$$K.E. = E - W_0$$

$$K.E. = h\nu - h\nu_0$$

$$K.E. = h(\nu - \nu_0)$$

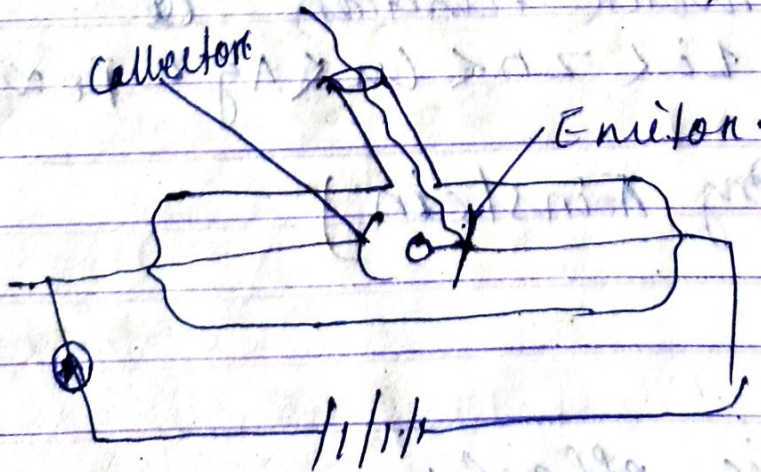
$$K.E. = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

$$K.E. = hc \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)$$

$$K.E. = hc \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)$$

$$\frac{1}{2} m_e v_e^2 = hc \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)$$

$$v_e = \frac{2hc}{m_e} \left(\frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)$$



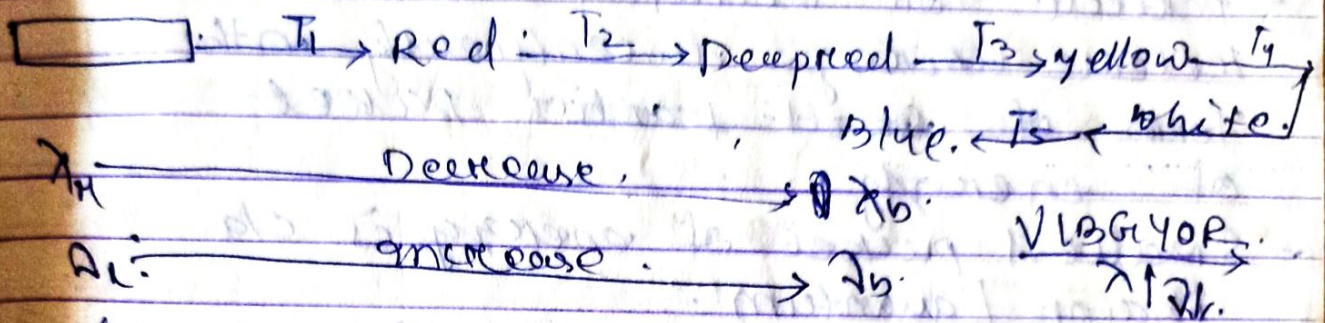
Stopping potential = $e \cdot V$

Therefore $K.E. = e \cdot V$

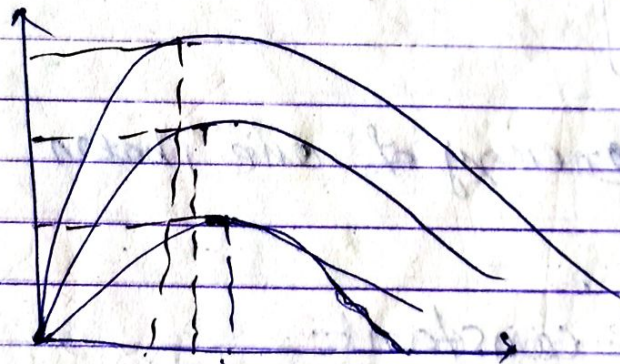
$$\frac{1}{2} m_e v_e^2 = eV$$

Black body radiation: -

The ideal body which can absorb or emit radiation of all types of frequency.



This can be only explained by the particle nature of ~~radiation~~ radiation, not ^{entirely} by the wave nature.



Important points: -

Wave nature of radiation only explains interference of light & diffraction of light.

- Following effects can only be explained if we consider particle nature of radiation.

① Black body effect.

② Photo electric effect.

③ Compton effect.

- (a) Variation of heat capacity on increasing temp.
- (c) Discontinuous spectrum of fusion.

Planck quantum theory.

- particle or oscillator, absorb or release energy discontinuously in the form of small particle packet of energy.
 - Smallest packet of energy is called photon / quantum.
 - Energy of quantum is directly proportional to frequency.
- $E \propto \nu$

$$E = h\nu$$

This is energy of one photon or one quantum.

$$E = hc/\lambda$$

h = Planck's constant.

$$= 6.625 \times 10^{-34} \text{ J/Sec.}$$

$$E = \frac{hc}{\lambda} \quad \left. \begin{array}{l} \text{meter/Sec} = 3 \times 10^8 \text{ m/Sec.} \\ \text{meter} \end{array} \right\}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$1 \text{ \AA} = 10^{-10} \text{ m.}$$

The energy absorbed or emitted is integral multiple of $h\nu$

$$\Delta E = n h \nu$$

, $n = 1, 2, 3, 4, \dots$

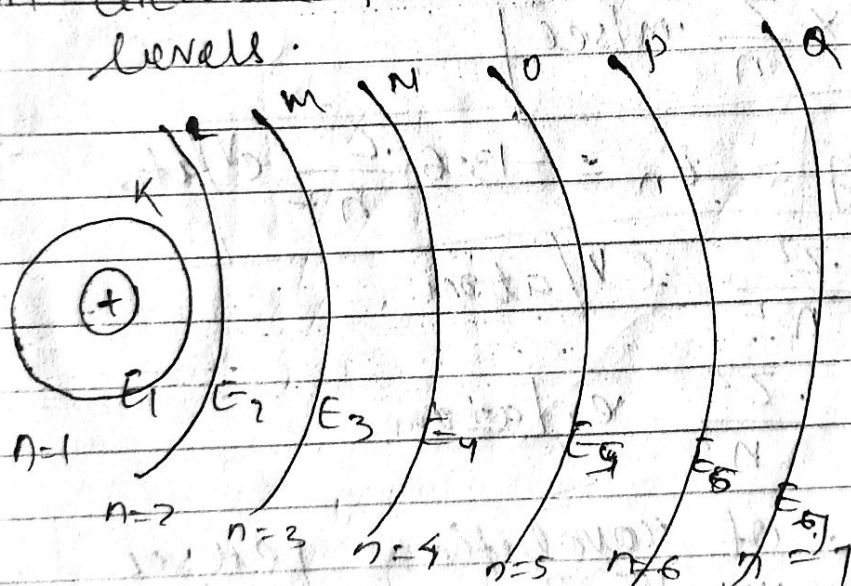
This is called quantisation of energy

$$\text{No. of photons} = \frac{\text{Total energy (J)}}{\text{Energy of photon (J)}}$$

$$\text{Energy of 1 mol-photon} = N_A \cdot h \nu$$

Bohr's atomic theory :-

① Electrons are revolving around the nucleus in circular path called shells or energy levels.



② Energy of constant cells are also called stationary orbits.

$$E_1 < E_2 < E_3 < E_4 < E_5 \dots$$

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > \dots$$

- When electron jumps from one orbit to another orbit it absorbs or releases energy.

$$\Delta E = E_2 - E_1$$

- Angular momentum of e^- in n th orbit i.e.

$$m_e v_e r_n = \frac{n h}{2\pi}$$

$$\text{No. of orbit} = n$$

1st, 2nd, 3rd

$$r_n = 0.53 \frac{n^2}{Z} \text{ \AA}$$

$$v_n = 2.19 \times 10^6 \frac{Z}{n} \text{ m/sec}$$

$$\text{Total energy} = E_n = -13.6 \frac{Z^2}{n^2} \text{ eV/atom}$$

$$P.E = -27.2 \frac{Z^2}{n^2} \text{ eV/atom}$$

$$K.E = +13.6 \frac{Z^2}{n^2} \text{ eV/atom}$$

• $f_n =$ no. of revolution per sec

$$f_n = 6.66 \times 10^{15} \frac{Z^2}{n^3} \text{ per sec}$$

$$T_n = 1.5 \times 10^{-16} \frac{n^3}{Z^2}$$

$$\text{Total energy} = \frac{-kze^2}{4\pi r_n}$$

$$k = \frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ N/m}^2$$

$$P.E = \frac{-kze^2}{r_n}, \quad K.E = \frac{kze^2}{2r_n}$$

Limitations on Bohr's theory:—

- ① This theory only explains mono electronic atom and ion spectrum.
- ② This theory cannot explain Zeemann's effect and Stark effect.

Zeemann's effect:—

When spectrum taken under electric field line spectrum is converted into fine line spectrum.

Stark effect:—

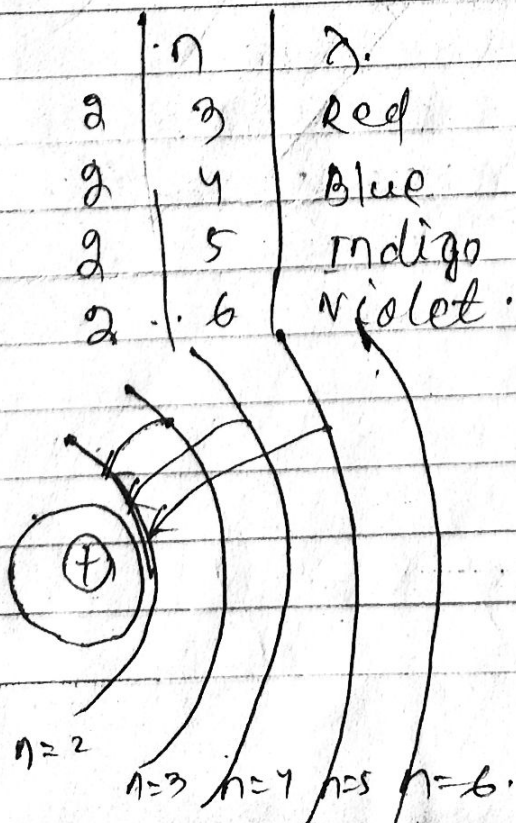
When a spectrum is obtained under electric field line spectrum converted into fine line spectrum.

H-spectrum:

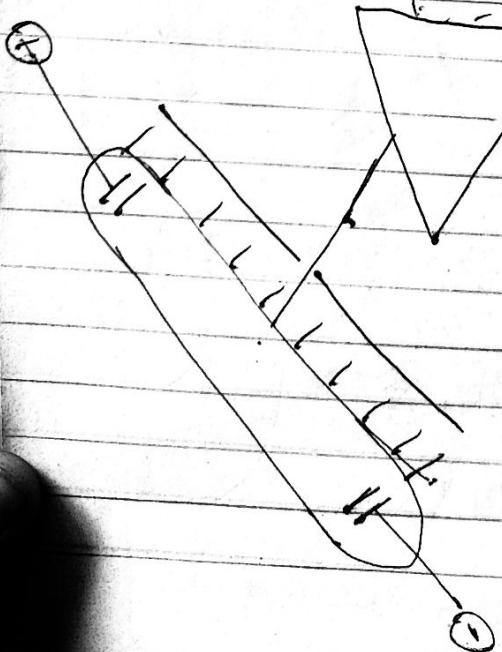
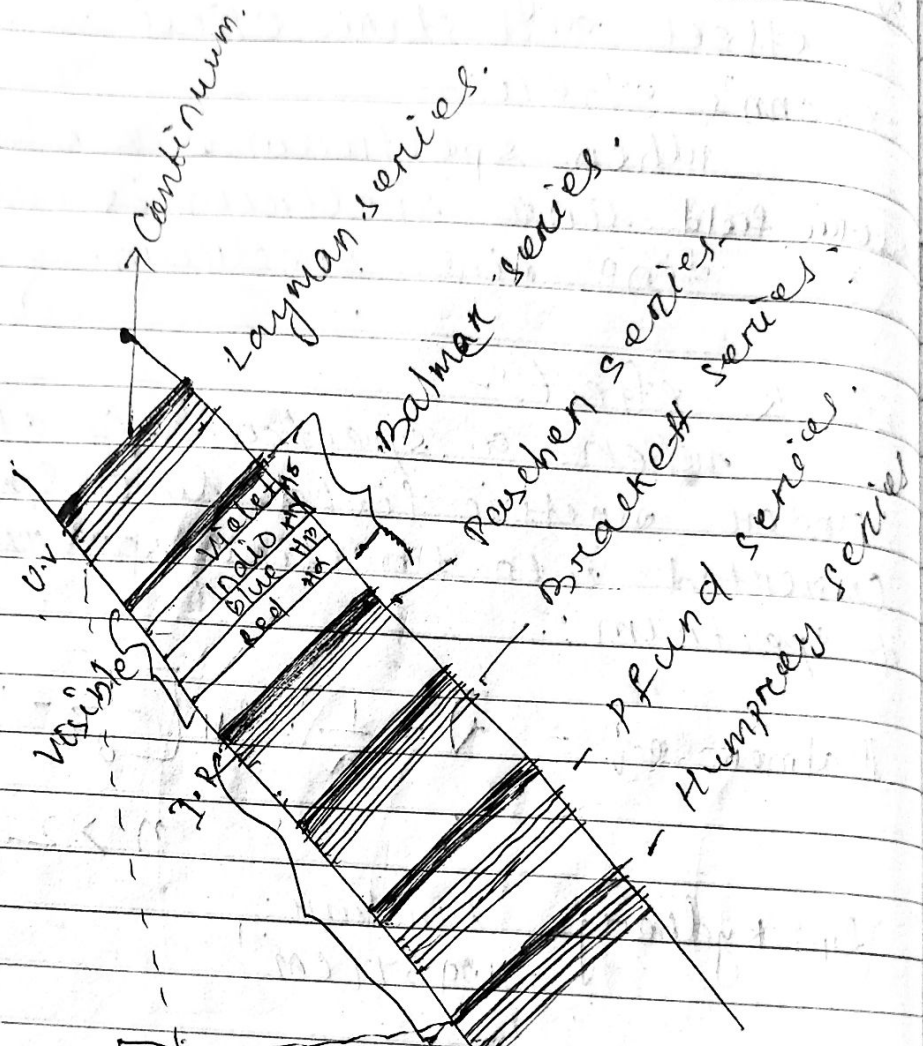
$$\text{Balmer eqn} = \frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad \text{--- (1)}$$

$n > 2$

$R_H = \text{Rydberg's constant}$
 $= 109677 \text{ cm}^{-1}$



Lal Babu RO
Pan bahut
Pasand
Hai.



② Ritz principle of combination:-

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

③ Bohr's equation:-

$$\bar{\nu} = \frac{1}{\lambda} = R_H \cdot Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

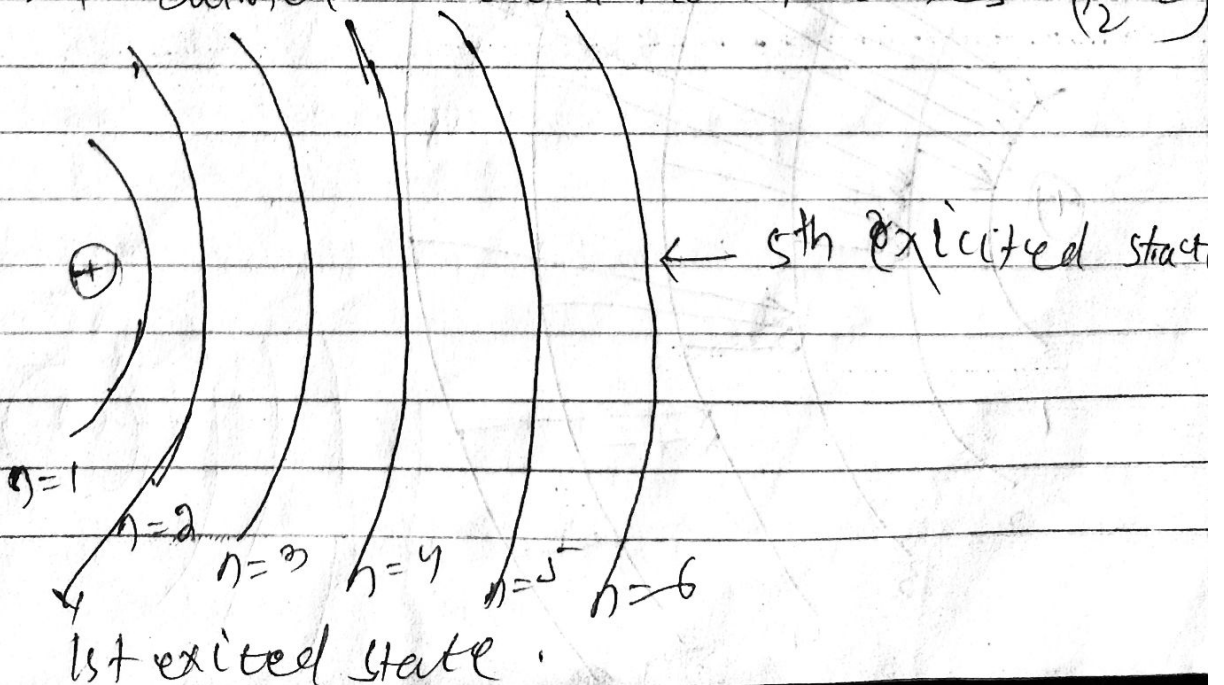
n_1	n_2		
1	2, 3, ... ∞	Lyman series	U.V.
2	3, 4, ... ∞	Balmer series	visible region
3	4, 5, ... ∞	Paschen	near I.R
4	5, 6, ... ∞	Brackett	middle I.R
5	6, 7, ... ∞	Pfund	Far I.R
6	7, 8, ... ∞	Humphrey	V. Far I.R

No. of lines in spectrum.

① Total lines = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

② No. of lines in particular series = $(n_2 - n_1)$

③ In Balmer series, No. of lines = $(n_2 - 2)$



for e^- :

$$h = 6.625 \times 10^{-34} \text{ J}\cdot\text{sec}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$\lambda = \frac{12.26 \times 10^{-10}}{\sqrt{V_{\text{volt}}}} \text{ meter}$$

$$\lambda = \frac{12.26}{\sqrt{V_{\text{volt}}}} \text{ \AA} \quad \text{--- (8)}$$

- 1st time de-broglie wave eqⁿ was confirmed by Davison & Germer.

- No. of e^- waves on an orbit? -

from Bohr's theory: -

$$m_e v_e r_n = \frac{n h}{2\pi}$$

$$m_e v_e = \frac{n h}{2\pi r_n} \quad \text{--- (9)}$$

from de broglie wave eqⁿ.

$$\lambda = \frac{h}{m_e v_e}$$

$$\therefore m_e v_e = \frac{h}{\lambda} \quad \text{--- (10)}$$

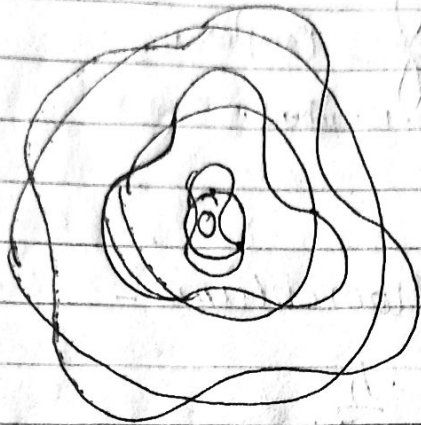
$$\frac{nh}{2\pi m v} = \frac{h}{\lambda}$$

$$n\lambda = 2\pi r_n$$

(3)

circumference of n^{th} orbit.

λ = wavelength of e^- wave.



No. of orbit.

No. of e^- inside \rightarrow

1

1

2

2

3

3

4

4

No. which characterised position, shape, size, energy, orientation & spin of an electron are c/a quantum no.

- Principal quantum no. (n) - (Bohr)

- Q. no. characterised no. of shells, radius, velocity of e^- , angular momentum of e^- , etc.



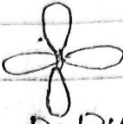
$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \dots$

Shell = K L M N O \dots

Azimuthal quantum no. :- (l) - (Sommerfeld)
 $l = 0 \dots (n-1)$ Elliptical shell
 sub shell.

This characterizes shell, subshell, shape of orbital.

$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \dots$
 subshell = s p d f g

 spherical
 Dumbbell
 Complex
 D. Dumbbell

Orbital angular momentum :-

$$\sqrt{l(l+1)} \cdot \frac{h}{2\pi}$$

$$= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} \quad (h\text{-dinec})$$

eg:- for e^- in 3d-subshell.

$$O.A.M = \sqrt{2(2+1)} \cdot \frac{h}{2\pi}$$

$$= \sqrt{6} \cdot \frac{h}{2\pi}$$

No. of orbitals in a subshell :-

$$= \sum_{l=0}^{l=n-1} (2l+1)$$

eg d-subshell no. of orbitals.

$$= 2 \times 2 + 1 = 5$$

No. of e^- in subshell

$$= 2(2l+1)$$

in d-sub shell $= 2(2 \times 2 + 1) = 10.$

Magnetic quantum no. - (m)

- Proposed by Linde to explain Zeeman's effect and Stark effect.
- This characterised the orientation.

$$m = -l \dots 0 \dots +l$$

$$l=0 \rightarrow s, m=0$$

$$l=1 \rightarrow p, m = -1, 0, +1$$

$P_x \quad P_z \quad P_y$

$$L=2 \rightarrow d, m = -2, -1, 0, +1, +2$$

$$= d_{xy}, d_{yz}, d_{z^2}, d_{xz}, d_{x^2-y^2}$$

Spin q. no.

(S) - Goudemith, Uhlenbous & Gerlach
to explain double line spectrum

$$S = +\frac{1}{2} \uparrow$$

$$S = -\frac{1}{2} \downarrow$$

Spin angular Momentum :-

$$= \sqrt{S(S+1)}\hbar$$

$$\therefore \text{Always } S = +\frac{1}{2}$$

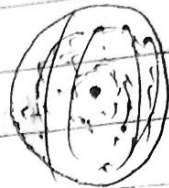
Orbital:-

3D space around the Nucleus where there is max^m probability (90-95%) of finding an electron is called orbital.

① 4 types of orbital.

S-orbital:-

- Spherical in shape.



Node / nodes:-

The plane / space where e⁻ density / probability is zero called Node.

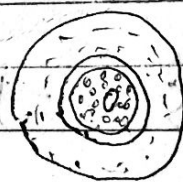
① Radial node or spherical node.

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

② Angular node or spherical nodal plane.

$$= l$$

① for 2s-orbital:-

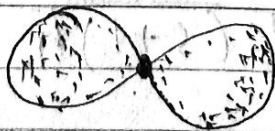


$$\text{Radial node} = 2 - 0 - 1 = 1$$

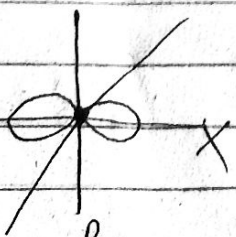
$$\text{Ang. node} = 0$$

② p-orbital:-

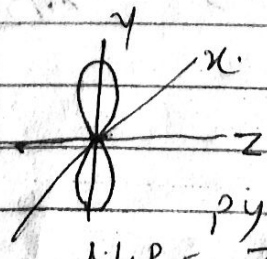
It is of 3 types.



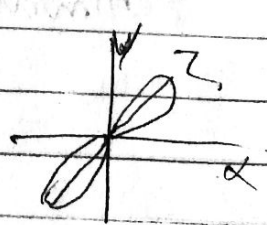
shape of orbital



p_x
N.P = yz plane



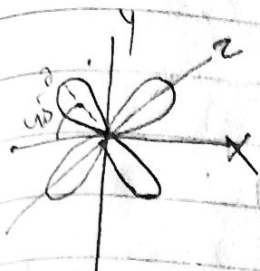
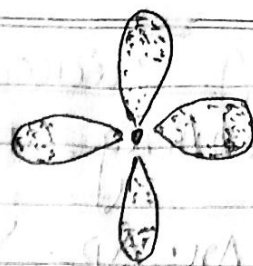
p_y
N.P = ZX



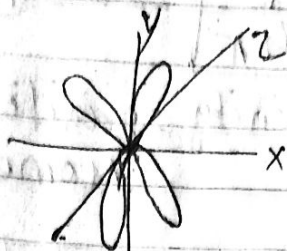
p_z
N.P = XY

d-orbital .. double dumbbell.

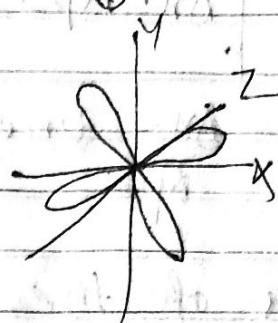
s - eyes.



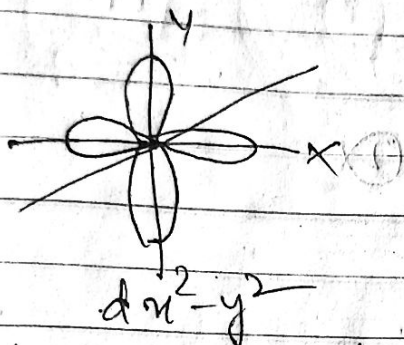
d_{xy}
N.P = (xz, yz)



d_{yz}
N.P = (xy, zx)

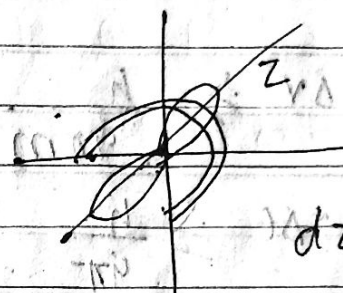


d_{zx}
N.P = (yz, xy)



$d_{x^2-y^2}$

2 nodal planes betⁿ axes.



d_{z^2}

No. nodal plane
Having two conical nodes
(rough nut) Plane
(Baby Soother)

f-orbitals.

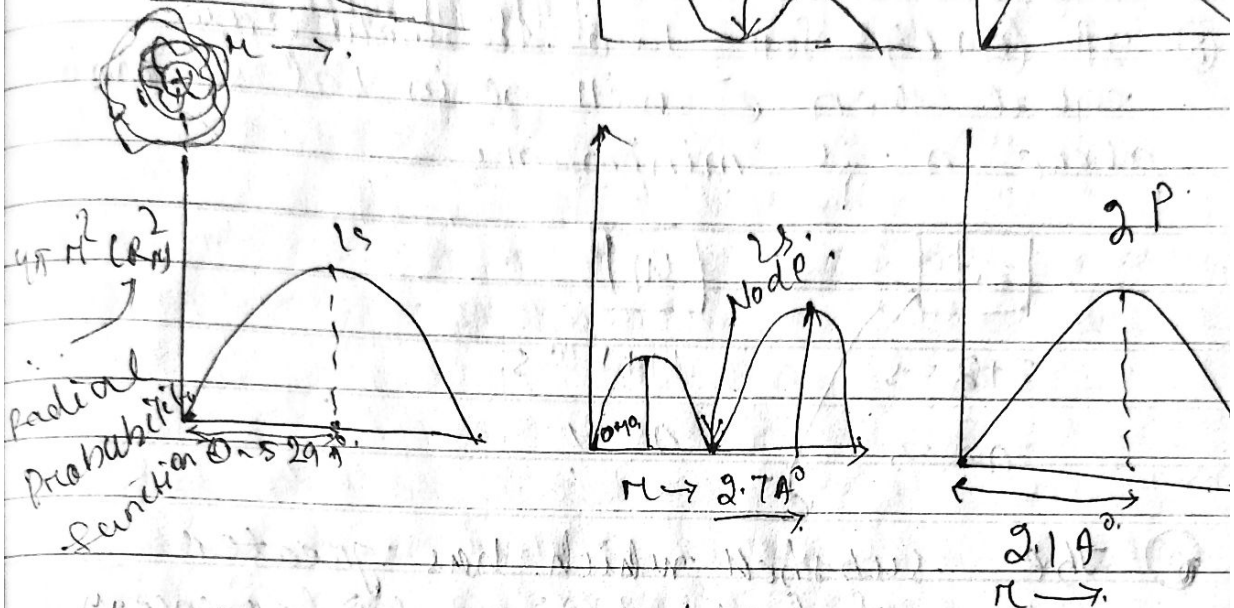
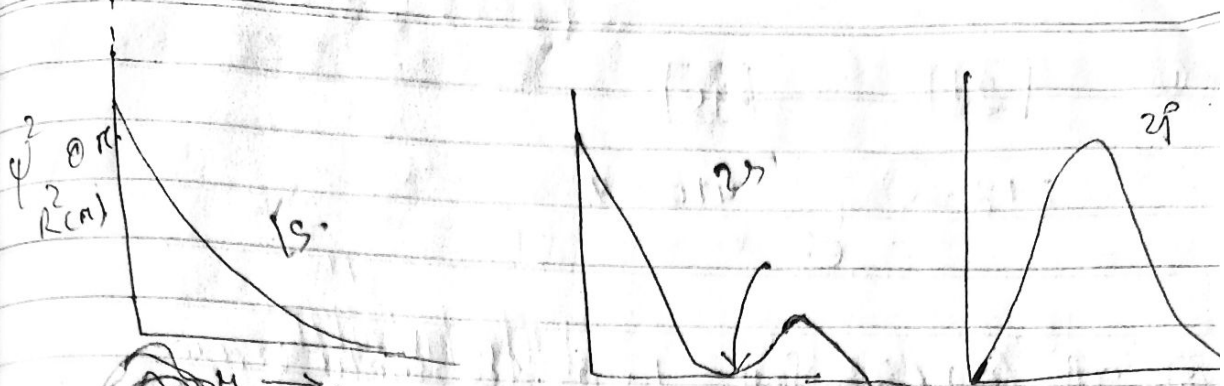
7 types of f orbital.

- Triple dumbbell or complex shape.

Dt. 23.07.15

Heisenberg Uncertainty Principle :-

It is impossible to determine exact position and exact velocity or momentum of an "electron or



no. of peaks = $(n - l)$

No. of minima = $(n - l + 1)$

27.07.15

Electronic Configuration :-

Subshell wise configuration :-

Aufbau Principle :-

- e^- has tendency to occupy that subshell which has lowest energy state

- $K < L < M < N < \dots$

$s < p < d < f < \dots$

$(n + l)$ Rules :-

e^- will go in that substance where $(n + l)$ is minimum.

①

3d

4s

$$3+2=5$$

$$4+0=4$$

e⁻

② If $(n+l)$ for two subshells are equal then e⁻ will go in that subshell where n is minimum.

3d

4p

$$3+2=5$$

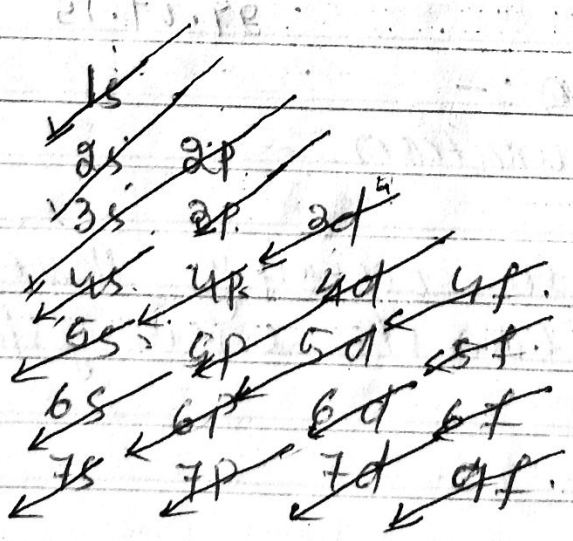
$$4+1=5$$

$$n=3$$

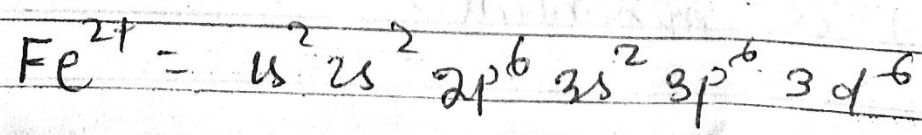
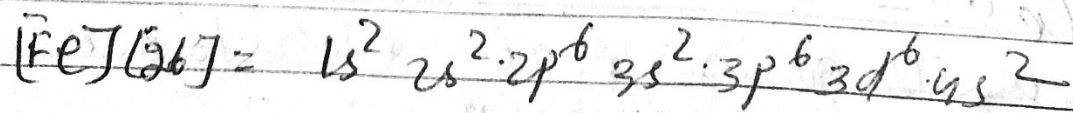
$$n=4$$

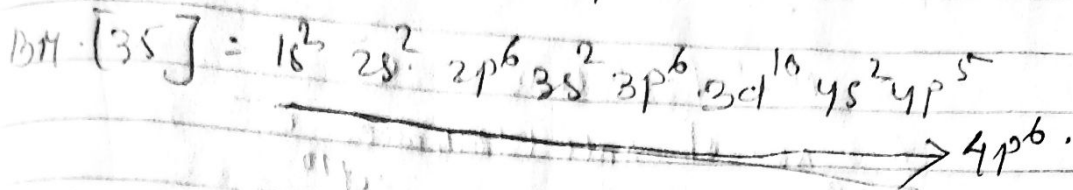
e⁻

③ The subshell which has greater value of $(n+l)$ having higher energy state. But if $(n+l)$ are equal then which has higher value of n will have greater energy state.



Sub shell	
s	= 2
p	= 6
d	= 10
f	= 14

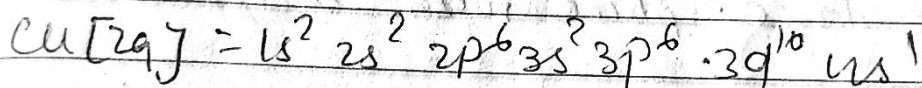
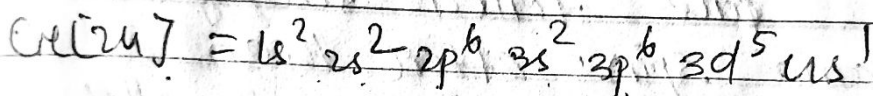




- Aufbau principle is violated in the cases:

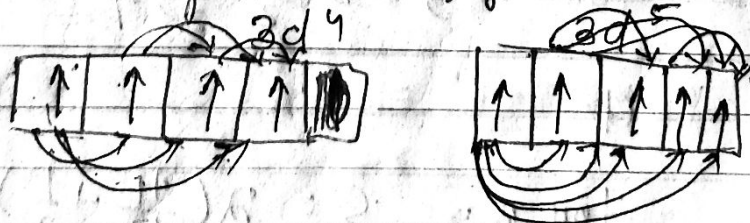
(1) for mono electronic atom or ions.

$\text{H} [1] \Rightarrow 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$
 - If an element has d^4 electrons it becomes d^5 . If it has d^9 then it is d^{10} because half filled and give more stable electronic configuration.



Half & Completely Filled subshell will be more stable.

- more symmetric arrangement
- lower energy state due to higher exchange energy.



No. of exchange = 6

$$= \frac{4(4-1)}{2} + 0$$

$$= \frac{4 \times 3}{2} = 6$$

No. of exchange = 10.

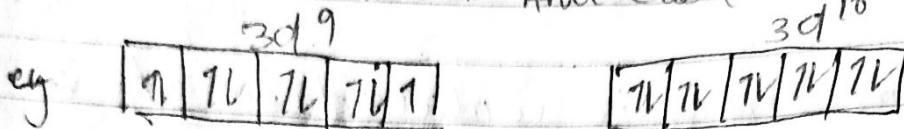
Higher exchange energy lower energy state (more stable)

$$\frac{5(5-1)}{2} = 10$$

$$\text{No. of exchange} = \frac{c(c-1)}{2} + \frac{A(A-1)}{2}$$

c = No. of clockwise e^-

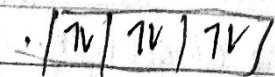
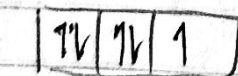
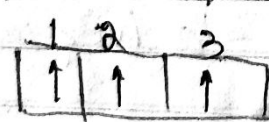
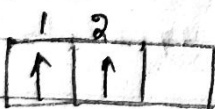
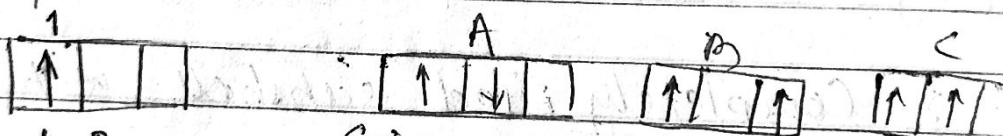
A = No. of Anti clockwise e^-



$$\begin{aligned} \text{No. of exchange} &= \frac{5(5-1)}{2} + \frac{4(4-1)}{2} \\ &= 10 + 6 = 16 \end{aligned} \quad \left| \quad \begin{aligned} &= \frac{5(5-1)}{2} + \frac{5(5-1)}{2} \\ &= 10 + 10 = 20 \end{aligned} \right.$$

Orbital wise Configuration:-
(Hunds rule of max^m multiplicity)

- In case of degenerate orbital
1st ~~orb~~ filled singly
with same spin. after then
pairing take place with antiparallel
spin.



Spin multiplicity

$$S = 2(\sum s + 1)$$

for A = 5 = $2(\frac{+1}{2} - \frac{1}{2}) + 1$

for B = 3 = $2(\frac{+1}{2} + \frac{1}{2}) + 1$

for C = 5 = $2(\frac{+1}{2} + \frac{1}{2}) + 1$

= 3

for C = 5 = $2(\frac{+1}{2} + \frac{1}{2}) + 1$

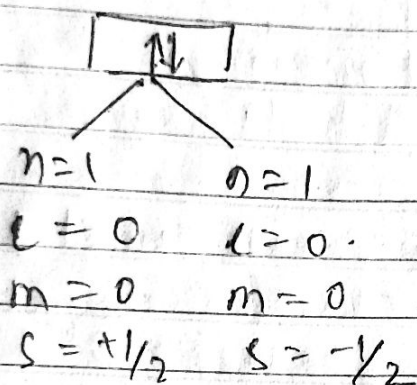
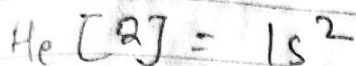
= 3

Angular multiplicity - $L = \sum m$. $\{m = +1, 0, -1\}$
 For B = $1, 1, 0, -1 = 0$
 For C = $L = 1$

Max^m the value of spin multiplicity & angular multiplicity will be more correct configuration orbital wise.

Pauli's exclusion principle:-

No two electrons in an atom can have same values of all quantum nos.



Calculation of magnetic moment:-

- by spin only formula:-

- Mag. moment, $\mu = \sqrt{n(n+2)}$ B.M.

n = no. of unpaired e^- in d-orbitals

$Fe^{3+} = 3d^5 = \sqrt{5(5+2)} = \sqrt{35}$ B.M.
 $= 5.91$ B.M.

$3d^3 = \sqrt{3(3+2)} = \sqrt{15}$ B.M. = 3.9 B.M.

⇒ Before decimal no. indicate unpaired e^- .

- which rule violate.
 valid.

3s 3p — Aufbau principle