3. Atomic Structure

This chapter mainly deals with structure of Atom in its constituent particles and their characteristics like charge, mass etc.

Some Basic Forces

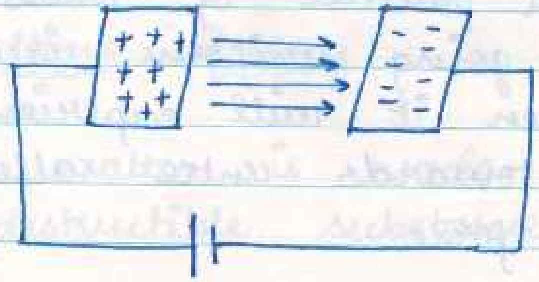
1] Electrostatic Force : When 2 charges q_1 & q_2 are separated by a distance, they will attract or repel each other depending upon sign of charge.
The magnitude of interaction is

$$F = \left| \frac{K q_1 q_2}{r^2} \right|$$

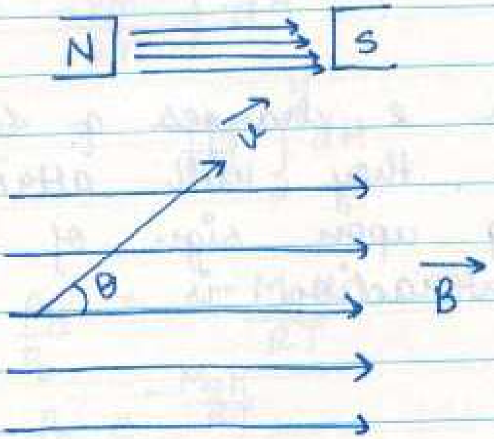
where,
$F \rightarrow$ mag. of force of interaction
$q_1, q_2 \rightarrow$ charges
$r \rightarrow$ distance of separation
$K \rightarrow$ constant $= 9 \times 10^9 \, Nm^2 c^{-2}$

2] Electric Forces : When a charge is placed in an electric field then it will experience a force equal to,

$$F = qE$$



3] Magnetic Force : when a charged particle is moving with velocity 'v' in magnetic field then it experiences a force called magnetic force and direction of net resultant force will be perpendicular to both $\vec{v}$ as well as $\vec{B}$.



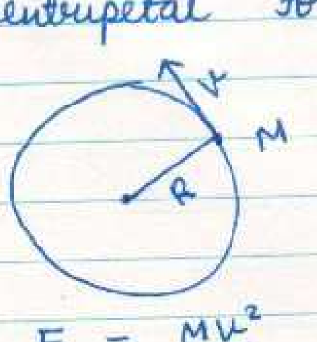
$$\vec{F} = q\,(\vec{v} \times \vec{B})$$

$$F = qvB\sin\theta$$

- If $\vec{v}$ is parallel to $\vec{B}$ $\Rightarrow \theta = 0 \Rightarrow F = 0$
- If $\vec{v}$ is $\perp^{er}$ to $\vec{B}$ $\Rightarrow \theta = 90° \Rightarrow F = qvB$ (Max.)

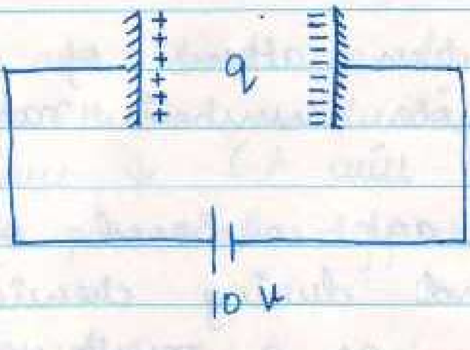
Direction and resultant force will be $\perp^{er}$ to both $\vec{v}$ as well as $\vec{B}$.

4] Centripetal Force : when a particle of mass 'M' is under going uniform circular motion then it will experience a force towards centre called centripetal force.



$$F_c = \frac{Mv^2}{R}$$

Note: If a charged particle is placed between 2 plates then its Kinetic Energy can be calculated using.



$KE = q \times V$

Q. Calculate KE of e^- placed in 10V P.D.

$\rightarrow KE = q \times V$
$= 1.6 \times 10^{-19} \times 10$
$= 1.6 \times 10^{-18}\ J = 10\ eV$

Note: $1\ eV = 1.6 \times 10^{-19}\ J$
$1\ MeV = 1.6 \times 10^{-13}\ J$

- Ionisation Potential :→ Minimum potential difference that must be applied to ionise an isolated gaseous atom.

* Various Theories about Atom :→

1] Dalton's Theory :

- All matter is made up of indivisible and indestructible substances called atoms.

- All atoms of an element are identical in all respects but they are different from atoms of other elements.

- compounds are formed when atoms of different elements combine in whole number ratio.

- Elements and compounds are composed of definite arrangement of atoms and during chemical changes those arrangements change, as a result chemical properties also change.

Drawbacks,

- Atom is not the fundamental particle, it consists of many subatomic particles.

- It does not give any information regarding the charge on atom.

• In 1830, Faraday established the presence of electrically charged particles inside the atom by carrying out electrolysis.

• An atom is neutral because it contains equal but opposite charge.

Discovery of Electrons :→

- Cathode Ray Experiment :

- Gases are bad conductors of electricity. To increase their conductivity,
  i) Pressure ↓ (λ will increase)
  ii) High potential difference is applied (ionisation)

Observations :

i) Cathode rays will move from cathode to anode.

ii) These rays are not visible but they can be detected by using florosent material (they spark or glow when hit)

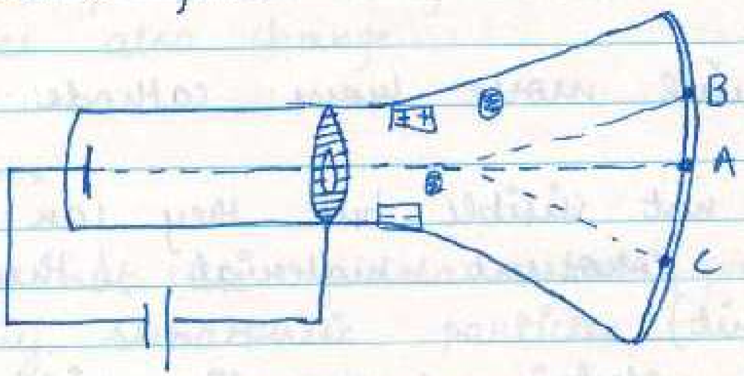
iii) In absence of electric & magnetic field, cathod rays travel in straight line.

iv) In presence of electrical or magnetic field, behaviour of cathode rays is same as expecte from negatively charged particles suggesting cathode rays consist of negatively charged particles calle es$^-$.

v) On changing gas inside the discharge tube, characteristics of cathode rays do not change. it means es$^-$ are basic constituent of all the atoms.

Calulation of e/m ratio for e^- by JJ Thomson :→

When perforated anode is used & high P.D. is applied then, in absence of electric & magnetic field, particles move in straight line. When electric field is applied, cathode ray particles strike at B. Now EF is switched off & MF is applied then particles strike at C. Now both are switched on simultaneously in such a way that electric force is counter balanced by magnetic force.



$$F_{\text{electric field}} = F_{\text{magnetic field}}$$

$$qE = qvB\sin 90^\circ \Rightarrow \boxed{v = \frac{E}{B}}$$

$$\text{KE of } e^- = \frac{1}{2}mv^2 = qV$$

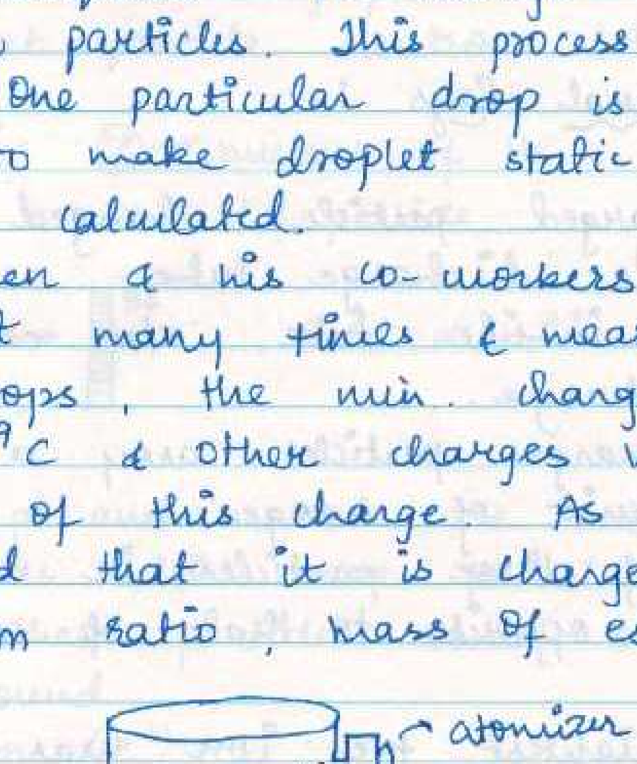
$$= \frac{1}{2}m_e\left(\frac{E}{B}\right)^2 = e \times V$$

$$\Rightarrow \frac{e}{m} = \frac{1}{2}\frac{E^2}{B^2V} = 1.758820 \times 10^{11}\ C\ kg^{-1}$$

· Determination of charge on es⁻:
By Mulliken Oil drop Experiment:

When small droplets of oil are sprayed b/w plates through a hole in upper plate. some droplets acquire -ve charge due to friction with air particles. This process can be n usin X-rays. One particular drop is choosen & EF is adjusted to make droplet static & charge on droplet is calulated.

Mulliken & his co-workers repeated this experiment many times & measured charge on many drops, the min. charge obtaind was 1.6×10^{-19} C & other charges were integral multiple of this charge. As a result it was concluded that it is charge possed by es⁻. Using e/m ratio, mass of es⁻ was also calulate



$$GF = BF + EF$$

$$M_{oil}\, g = M_{air}\, g + qE$$

$$d_{oil} \times \frac{4}{3}\pi r^3 = d_{air} \times \frac{4}{3}\pi r^3 + qE$$

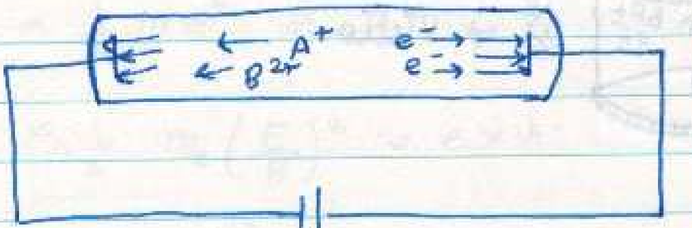
$$q = \frac{4/3\ \pi r^3 (d_{oil} - d_{air})}{E} = -1.6 \times 10^{-19} c$$

· Discovery of Proton :

when a perforated cathode was used then a stream of +ve particles comes out on backside of cathode & these are called canal rays or +ve charged rays.

Characteristics of Canal Rays :

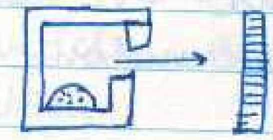
i) Nature of +ve charged particle, changed on changing gas inside discharge tube.
ii) On changing gas inside tube, e/m ratio of canal rays also change.
(iii) some of +ve charge particles carry a multiple of fundamental unit of charge.
(iv) The behaviour of these particles in magnetic or electric field is opposite to that of cathode rays.
v) The smallest & lightest +ve ion was obtained from hydrogen & was called proton.



· Discovery of Neutrons :→

When Chadwick bombarded Be^9 with α-particles then Be^9 were converted into C-12 and along with that a neutral particle having mass slightly greater than mass of proton is also emitted. He named that particle neutron. (1932).

He^{2+} $\left(\begin{smallmatrix}2p\\2n\end{smallmatrix}\right) \rightarrow$ nucleus of He
(α-particle)



$Be^9 + \alpha\,(He^{2+} \longrightarrow C_6^{12} + n +$ Energy

Note: e^-, p^+ and neutron are only sub-atomic stable particles which are found in nucleus. Other than these particles some other particles are also found,

i) Positron (e^+)
mass = 9.1×10^{-31} kg
Charge = 1.6×10^{-19} C
It is antiparticle of electron.

ii) Neutrino
Mass = negligible
Charge = 0

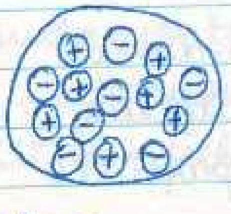
iii) π Meson : π^+, π^-, π^0
mass = (200 - 300) times mass of e^-

* Atomic Models :→

From above observations, it is clear that atom is no more indivisible. It consists of several sub-atomic particles and some models were proposed.

1] Thomson's Model of Atom (1898) :

Acc^n to it, an atom is spherical in which +ve charge is distributed uniformly and -ve charge is embedded just like seeds in watermelon or plum in pudding.

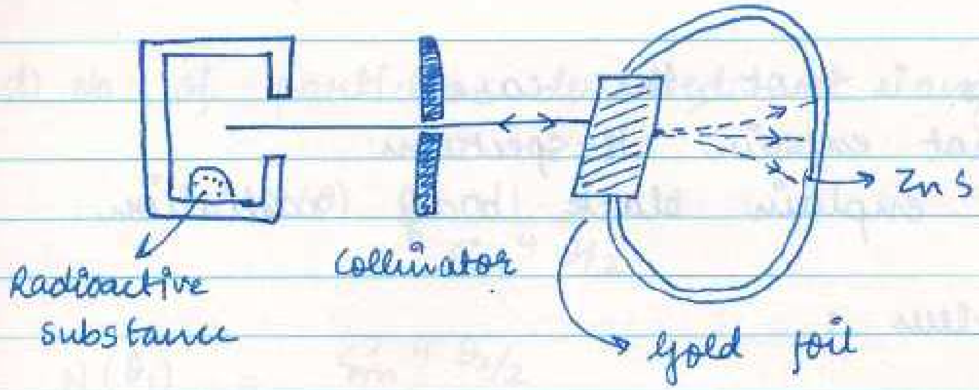


Advantage,
- It explains neutrality of atom

Drawbacks,
- It could not explain scattering of α-particles
- It could not explain H-spectrum
- It could not explain black body radiation.

2] Rutherford Model (1911 - 13) :

Rutherford bombarded gold foil with α-particles and he observed the trajectory of α-particles using detector.



Observations,

- Most α-particles went straight, it means maximum part of atom is empty
- A few α-particles got deviated from their path, due to repulsion of positively charged particle 'α' due to positive charge present inside atom.
- very few (one in a million) α-particles, retraced their path, it means that +ve charge inside the nucleus is highly dense and very small.

Rutherford proposed, an atom consists of highly dense positively charged nucles where most of the mass of an atom is concentrated. And negatively charged e^- revolve around nucleus just like planets revolve around sun. Necessary centripetal force is provided by coulombic attractions b/w nucleus and es$^-$.

Drawbacks,

- Accⁿ to Maxwell Theory, accelerating charged particles will emit EM waves, as a result, e^- will follow spiral path and will collide with nucleus, but this is not the case.

- It could not explain H-spectrum
- It could not explain black body radiation.

a) Radius of Nucleus :

$$R_{Nu} \propto A^{1/3}$$

$$R_{Nu} = R_0 A^{1/3}$$

where,

R_{Nu} → radius of nucleus
R_0 → Rutherford constant $(1.1 \times 10^{-15} m)$
A → Mass No.

rad. of atom = $10^{-10} m$
rad. of nucleus = $10^{-15} m$

b) Density of Nucleus :

$$d = \frac{Mass}{Volume} = \frac{Zm_p + (A-Z)M_n}{\frac{4}{3}\pi R_{Nu}^3} = \frac{AM_n}{\frac{4}{3}\pi R_0^3 A} = 2.98 \times 10^{17} \ kg/m^3$$

c) Impact Parameter :→ (b)

It is perpendicular distance of velocity vector of α-particle from the line passing through nucleus.

Angle of deviation $(\theta) \propto \frac{1}{b}$

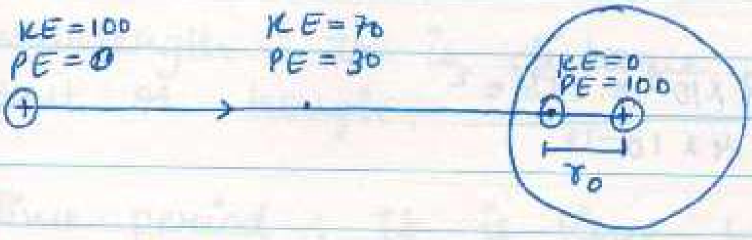
d) No. of particles deviated at angle θ :

$$N(\theta) \propto \frac{1}{\sin^4 \theta/2}$$

$$\frac{N(\theta_1)}{N(\theta_2)} = \frac{\sin^4 \theta_2/2}{\sin^4 \theta_1/2}$$

e) Distance of closest approach :

When a +ve charged particle is accⁿ towards another +ve charged particle, it KE energy is converted into PE and distance of closest approach, all KE is converted into PE.



At distance of closest approach,

$$KE = PE$$

$$\frac{1}{2} m u^2 = \frac{K q_1 q_2}{r_0}$$

where,

r_0 → distance of closest approach.

Q. An α particle of KE = 5.4 MeV is projected towards gold nucleus (Z = 79). Calculate distance of closest approach.

→ $5.4 \text{ MeV} = \frac{K \times 2e \times 79e}{r_0}$.

$\Rightarrow r_0 = \frac{158 \times \cancel{K} 9 \times 10^9}{\underset{0.6}{\cancel{5.4}} \times 10^6} = 158$

$5.4 \times 1.6 \times 10^{-13} = \frac{K q_1 q_2}{r_0} = \frac{9 \times 10^9 \times 2e \times 79e}{r_0}$

b) In above que. find KE of α particle when it was 4×10^{-12} m away from neucleus.

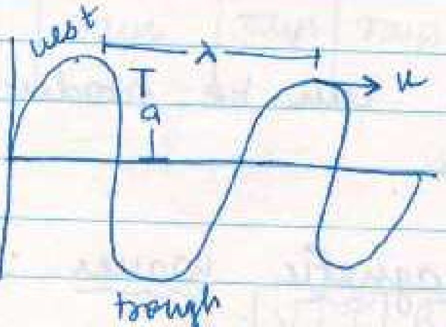
→ ~~PE~~ =
$5.4 \times 1.6 \times 10^{-19} = \underline{KE} + \frac{9 \times 10^9 \times 158 e^2}{4 \times 10^{-12}}$

Q. At what speed an α particle should be projected towards Mg nucleus such that it approaches nucleus upto 4×10^{-13} m.

→ $v^2 = \frac{9 \times 10^9 \times 2e \times \cancel{4}2e \times Z}{\underset{2}{\cancel{4}} \times 1.67 \times 10^{-27}} = \frac{9 \times 10^9 \times 12 \times 2.56 \times 10^{-38}}{1.67 \times 10^{-27}}$

* Some Basic Terms :→

1] Wave :→ It is periodic disturbance which cause transfer of energy and momentum from one point to another without actual transfer of matter.



a) Amplitude : Max. displacement of particle from its mean position.

b) Wavelength : It is distance between two successive crest or trough.

c) Time period : It is time taken to travel a distance equal to wavelength.

$$T = \frac{\lambda}{v}$$

d) Frequency : No. of waves passing through a point per unit time.

$$\underset{\text{freq.}}{\nu} = \frac{1}{T} = \frac{\overset{\text{velocity}}{v}}{\lambda} \quad s^{-1} \text{ or } Hz$$

e) Wave Number ($\bar{\nu}$) : It represents no. of waves present per unit length.

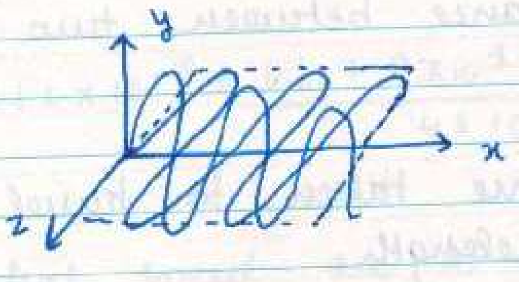
$$\vec{\nu} = \frac{1}{\lambda}$$

* Maxwell's Theory :→

Acc^n to it EM waves can be produced by oscillating charged particles.

• Characteristics of Electro-magnetic Waves :→

1] These waves consist of electric & magnetic field oscillating perpendicular to each Other as well as to the direction of propagation.



2] EM waves do not require any medium for propagation.

3] Light is also an example of EM wave

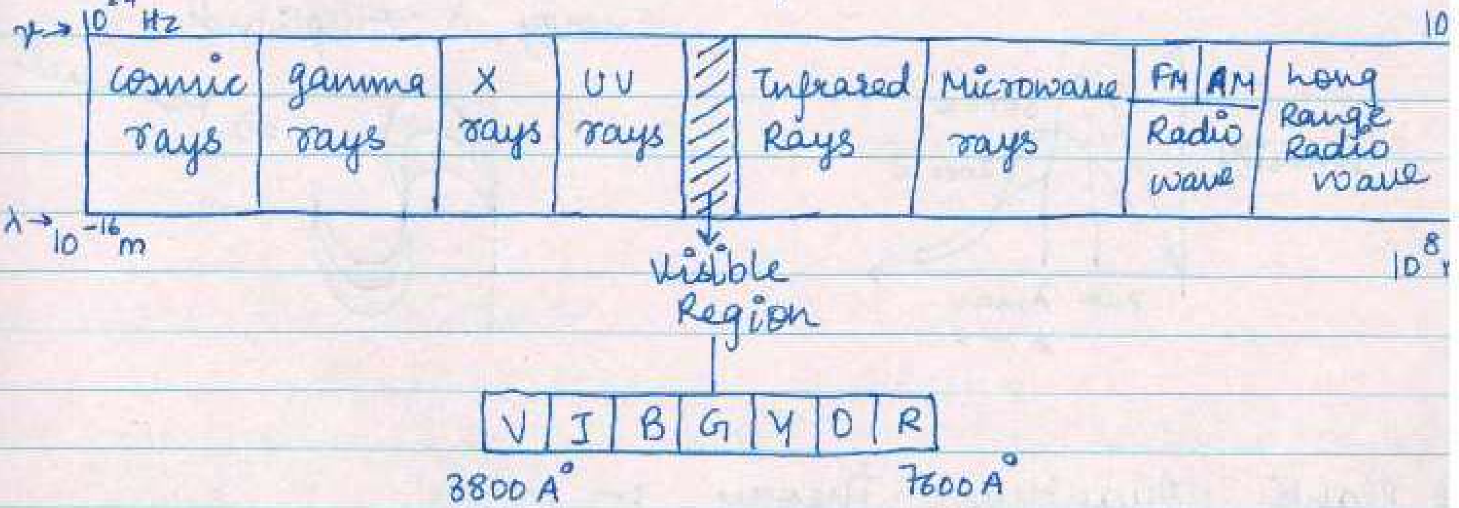
4] All EM waves travel with velocity,

$$c = 3 \times 10^{8}\ m/s$$

$$c = \nu\lambda \Rightarrow \nu = c/\lambda$$

$$\nu \propto 1/\lambda$$

- If all EM waves are arranged in increasing or decreasing order of frequency or wavelength then a spectrum is obtained and that spectrum is called EM radiation spectrum.



Drawbacks,

i) It could not explain black body radiations

ii) It could not explain photoelectric effect

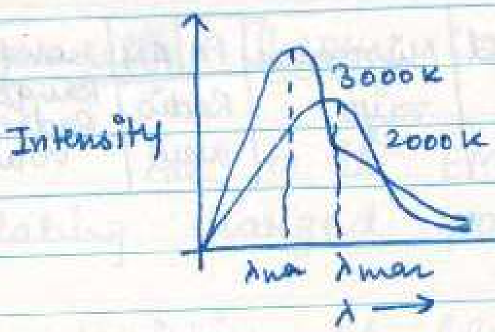
iii) It could not explain H-spectrum

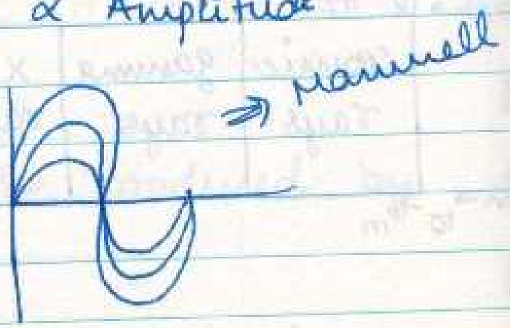
iv) It could not explain variations in specific heat capacities of solids.

- Black Body : It is the substance which can absorb or emit radiations of all ~~colours~~ wavelengths.

v) when we heat a body, it becomes dull red on further heating intensity of red colour increases and finally at high temperature, it becomes blueish

$$Energy \propto Amplitude^2$$





* Plank's Quantum Theory :→

Accⁿ to it, energy is transferred from one point to another point not in form of continuous waves but in form of discrete energy packets called Quanta and energy of each packet is fixed. It is given by,

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

where,

E_{photon} → Energy of 1 photon
ν → freq. of photon
c → velocity of light
λ → wavelength of photon
h → Plank's constant $(6.62 \times 10^{-34}\ J)$

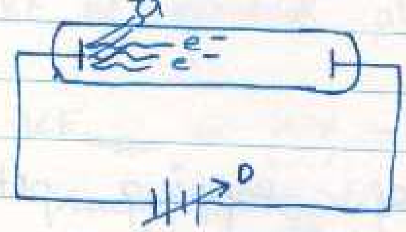
$$E_p = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{\lambda\ (m)} = J$$

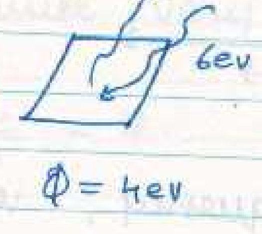
$$E_p = \frac{1240\ n\text{-}meV}{\lambda (nm)}$$

Q. Find energy of photon having wavelength 1 A°.

→ $E_p \cong 12400\ eV$

* Photoelectric Effect :→ When certain metals are exposed to radiations then some e⁻ are emitted from metal surface, these e⁻ are called photoelectrons and due to these e⁻ current is produced which is called photo current and this whole phenomena is called photoelectric effect.



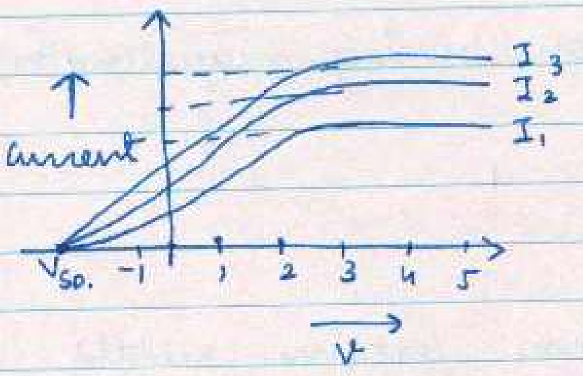


observation :→

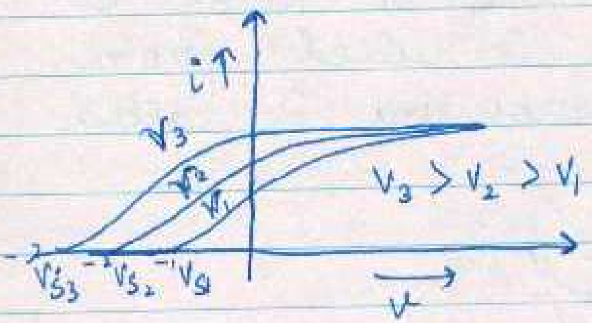
1) Intensity : • When PD ↑, value of photo current ↑ and it becomes max. at certain P.D. and value of that max. current is called saturation current.

• As intensity of radiation is ↑, value of saturation current ↑.

- On changing intensity, value of stopping potential remain same.
- There is 'I' in circuit even when no potential is applied.



2) Frequency :



- On changing frequency, value of stopping potential changes but value of saturation current remains unchanged.

3)

- Photo e^- are ejected from plate instantaneously when photons collide with metal surface.

· Work Function (ϕ) : Min. amt. of energy required to remove an e^- from metal plate.

Einstein Proposed (1905),

1) Energy of light is not distributed evenly. it is concentrated in form of bundles or packets of energy called photons.

2) Energy of each photon is fixed and given by,

$$E = \frac{hc}{\lambda}$$

3) Energy of photon cannot be given partially to an e^-. either photon will give up all energy or none.

4) KE of ejected photo e^- will vary from 0 to KE_{max}

$$KE_{max.} = \underbrace{h\nu}_{\text{energy of incident light}} - \phi = \frac{hc}{\lambda} - \phi$$

5] Photon will have zero rest mass and will travel with speed of light.

- Quantum yield :→

% Quantum yield = $\frac{\text{No. of } e^- \text{ ejected}}{\text{No. of photons incident}} \times 100$

- Stopping Potential (V_s) :→ It is the min. P.D. required to stop fastest moving e^-.

$$KE_{max} = q_e V_s .$$

- Thershold Frequency (ν_{th}) :→ Min. frequency of incident light to cause photoelectric effect.

$$E = \phi = h\nu_{th}$$

- Threshold Wavelenth (λ_{th}) :→ Max. wavelength of incident light at which photoelectric effect will take place. Above it no photoelectric effect will take place.

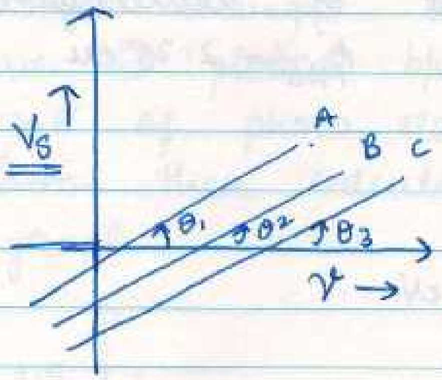
$$E = \phi = \frac{hc}{\lambda_{th}} .$$

H.W.

Q. Bank # 1 to 34

D.PP #16

Q. For ~~threshold~~ three metals A, B & C



Find relⁿ b/w θ_1, θ_2 & θ

$\Rightarrow e \times V_S = h\nu - \phi$

$\Rightarrow V_S = \frac{h}{e}\nu - \frac{\phi}{e}$

$\downarrow \; \downarrow \quad \downarrow$ $\qquad \therefore \theta_1 = \theta_2 = \theta_3.$

$\Rightarrow y = mx + c$

* Monochromatic source of light :→

This is source of light which emits radiations of single wavelength.

Q. Calculate no. of photons emitted by 60W bulb in 10 hrs. that emits light of wavelength 6620 A°.

$\longrightarrow \quad \phi = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{6.62 \times 10^{-6}} = \cancel{3}10^{-20} \; J = \cancel{6}2$

Total photons $= \frac{6\cancel{0} \times 10 \times 60 \times 60 \times 2}{10^{-20}}$

$= \cancel{720} \times 10^{24}$

$= 7.26 \times 10^{26}$ photons

Q. calculate KE of photoelectrons emitted by a sodium surface when light of wavelength 400 nm is incident on it. $\phi_{Na} = 2.28$ eV.

$\longrightarrow$ $KE = \frac{1240}{400} - 2.28$

$= 3.1 - 2.28 = 0.82$ eV

Q. Calculate the value of longest wavelength which can result in emission of photoelectron from a sodium surface. $\phi_{Na} = 2.5$ eV.

$\longrightarrow$ $2.5 = \frac{1240}{x}$

$\Rightarrow x = \frac{12400}{25} \Rightarrow 496$ nm

Q. UV light of $\lambda = 280$ nm is used in an experiment of photoelectric effect with Li ($\phi = 2.5$eV). Find
a) KE_{max} b) V_s.

$\longrightarrow$ $KE_{max} = \frac{1240}{280} - 2.5 = 4.43 - 2.5 = 1.93$

Q. A point source of 640 W emits light uniformly in all direction. a) Calculate no. of photons falling on sphere of r = 1cm at a distance of 5 km if $\lambda_p = 310$ nm.

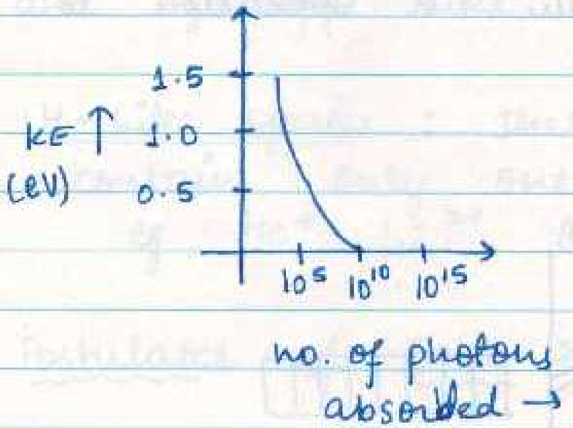
$\left(\frac{\frac{1}{100} \times 5000}{\frac{2 \times \pi \times 1}{10000}} \right.$

$\longrightarrow$ $640 = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{3.1 \times 10^{-7}}$ $\Rightarrow n \times 6.4 \times 10^{-19} = 640.$

$n = \frac{10^{21}}{25 \times 10^{5}}$ $= \frac{4 \times 10^{14}}{360}$

$\frac{10}{9} \times 10^{12}$

b) Power of source remains unchanged but no. of photons changes due to change in wavelength. A curve is plotted b/w no. of photons absorbed and KE of photo electrons emitted from sphere as given then calculate work function of sphere from graph.



$\underline{\underline{0.4}}$ eV

$10^9 \times E_i = 10^{10} \times E_f$

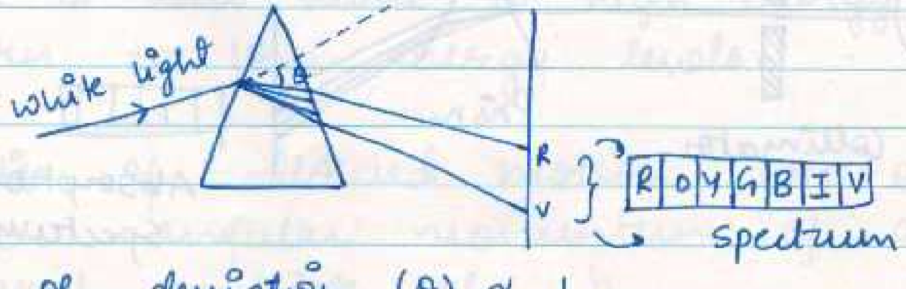
$\Rightarrow E_f = \phi = 0.1 \times 4 = \underline{\underline{0.4\ eV}}$

$P = 640\ J/s$

$\phi = \frac{640 \times}{10^{10}} = \frac{64}{10^9} = \frac{6.4 \times 10^{-}}{1.6 \times 10^{-1}}$

$4 \times 10^{11}\ J$

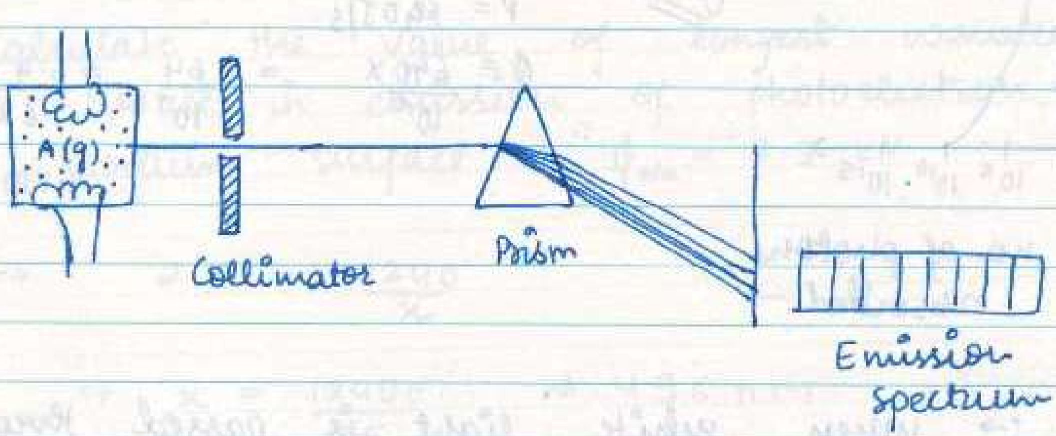
* Dispersion :→ when white light is passed through the prism then it splits up into all different wavelengths of seven colours and this phenomena is called dispersion.
When this dispersed light is received on photographic film or white paper, a pattern is obtained and is called spectrum of white light.



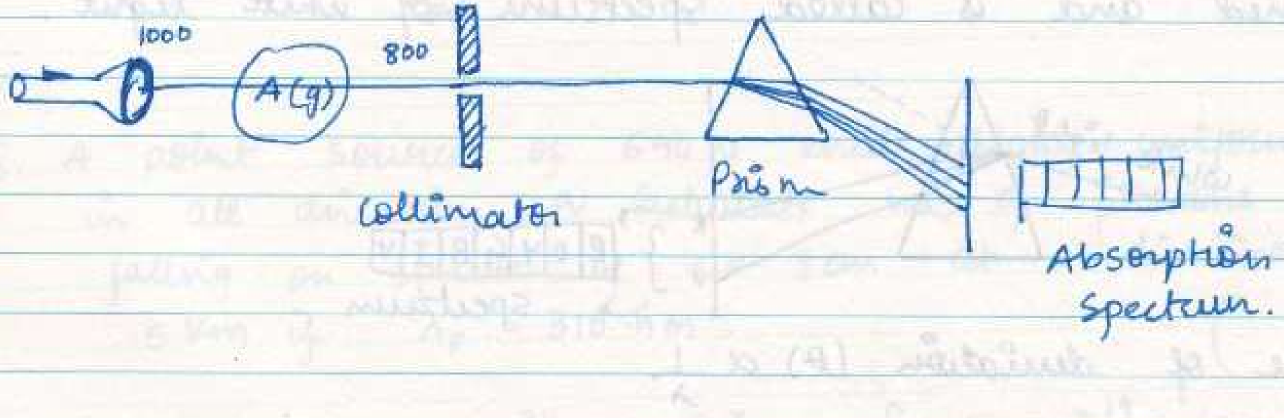
Angle of deviation (δ) $\propto \frac{1}{\lambda}$

H.W.
in 1 → 6 to 15

1] Emission Spectrum :→ When a gaseous sample is heated, then electrons present in atoms or molecules get excited and when that heater is switched off, those e^- will return to ground state by emitting ~~waw~~ radiations of diff. wavelng & when those radiations are passed through prism & obtained on photographic film, a spectrum is obtained.



2] Absorption Spectrum :→ When a light is incident on gaseous sample & is passed through a prism where dispersion takes place and after that it is received on photographic film. The spectrum obtained in this case is called absorption spectrum.



* Bohr's Model :→

1] Bohr used planck's quantum theory and its concept of quantization of energy.

2] Bohr's model is applicable only for hydrogen and hydrogen like species.

H-Like species : These are the ions which contain only one electron.
eg, He^+, Li^{2+}, Be^{3+}, etc.

- Postulates of Bohr :→

1] e^- revolve around nucleus in circular path which are stationary these are called orbits or energy levels and these have fixed radius.

2] When an e^- is moving in a particular energy level, its energy is quantised or fixed. An e^- will absorb or emit radiations when it will move to high energy levels or return to low energy levels.

3] States of allowed motion are only those where angular momentum of an e^- is integral multiple of $\frac{h}{2\pi}$

- Calculation of
i) radius of n^{th} orbit (r_n)
ii) velocity of e^- in n^{th} orbital (V_n)
iii) Time period of revolution (T) of e^-
iv) Frequency of revolution (ν) of e^-
v) Total energy of e^- in n^{th} orbital.

a) Radius of n^{th} orbital (r_n) :-

When an e^- is moving around nucleus then necessary C.P.F is provided by electrostatic attraction.

$$\frac{m_e V_n^2}{r_n} = \frac{K(Ze)e}{r_n^2}$$

$$\Rightarrow r_n = \frac{KZe^2}{m_e V_n^2} \quad \therefore \quad \left\{ \begin{aligned} m_e V_n r_n &= \frac{nh}{2\pi} \\ \Rightarrow V_n &= \frac{nh}{2\pi m_e r_n} \end{aligned} \right\}$$

$$\Rightarrow r_n = \frac{KZe^2}{m_e \times \dfrac{n^2h^2}{4\pi^2 m_e^2 r_n^2}}$$

$$\cancel{r_n} = \frac{4\pi^2 m_e r_n^{\cancel{2}} \cdot KZe^2}{n^2h^2}$$

$$\Rightarrow r_n = \frac{n^2h^2}{4\pi^2 m_e KZe^2} = \frac{h^2}{4\pi^2 K m_e e^2}\left(\frac{n^2}{Z}\right)$$

$$= 0.529 \times \frac{n^2}{Z} \; A^\circ$$

Q. Calculate value of r_1, r_2 & r_3 for H atom.

→ $r_1 = 0.529 \times 1$ A°

$r_2 = 0.529 \times 4$ A°

$r_3 = 0.529 \times 9$ A°

- From this we can conclude, orbits are not equidistant.

Q. Calculate :

i) $\frac{(r_1)_H}{(r_2)Li^{2+}} = \frac{0.53}{0.53 \times 4/3} = \frac{4}{3} \quad \frac{3}{4}$

ii) $\frac{(r_2)Li^{2+}}{(r_1)Be^{3+}} = \frac{0.53 \times 4/3}{0.53 \times 1/4} = \frac{16}{3}$

iii) $\frac{(r_1)He^{+}}{(r_2)Li^{2+}} = \frac{0.53 \times 1/2}{0.53 \times 4/3} = \frac{3}{8}$

b) Velocity of e^- in n^{th} orbit (V_n)

$$m_e v_n r_n = \frac{nh}{2\pi}$$

$$\Rightarrow V_n = \frac{nh}{2\pi m_e r_n} = \frac{hz}{2\pi m_e n} = \frac{h}{2\pi m_e}\left(\frac{z}{n}\right) \times \frac{1}{0.529}$$

$$= \left(\frac{2\pi k e^2}{h}\right) \times \frac{z}{n}$$

$$V_n = 2.188 \times 10^6 \left(\frac{z}{n}\right) \text{ m/s}$$

$$= \frac{c}{137} \times \left(\frac{z}{n}\right)$$

c) Time Period of revolution (T)

$$T = \frac{2\pi r_n}{V_n} = \frac{\cancel{2}\cancel{\pi} \times \frac{h^2}{4\cancel{\pi^2}\cancel{k} m_e \cancel{e^2}} \times \frac{n^2}{Z}}{\frac{\cancel{2}\cancel{\pi}\cancel{k}\cancel{e^2}}{h} \times \frac{Z}{n}}$$

$$= \frac{n^3 h^3}{k^2 Z^2 \cdot 4 m_e \pi^2} = \frac{h^3}{k^2 4 m_e \pi^2}\left(\frac{n^3}{Z^2}\right)$$

$$T \propto \frac{n^3}{Z^2}$$

d) Frequency of revolution (ν_n):

$$\nu = \frac{1}{T}$$

$$\nu = \frac{4\pi^2 m_e k^2}{h^3} \times \left(\frac{Z^2}{n^3}\right)$$

$$\nu \propto \frac{Z^2}{n^3}$$

e) Total Energy of e^- in n^{th} orbital (E_n):

When an e^- is revolving then it will have kinetic energy as well as potential energy.

$$TE = KE + PE$$

$$KE = \frac{1}{2} m_e V_n^2$$

$$\Rightarrow \frac{m_e v_n^2}{\cancel{r_n}} = \frac{kze^2}{r_n^{\cancel{2}}}$$

$$\therefore KE = \frac{1}{2} m_e v_n^2 = \frac{kze^2}{2r_n}$$

$$PE = -\frac{kq_1q_2}{r_n} = -\frac{kze^2}{r_n}$$

$$\therefore TE = \frac{kze^2}{2r_n} - \frac{kze^2}{r_n} = -\frac{kze^2}{2r_n}$$

$$\Rightarrow \boxed{TE = -KE = \frac{PE}{2}}$$

$$E_n = -\frac{kze^2}{2 \times h^2} \times 4\pi^2 m_e k e^2 \times \frac{z}{n^2}$$

$$= -\frac{2\pi^2 m_e e^4 k^2}{h^2} \times \frac{z^2}{n^2}$$

$$E_n = -13.6 \times \frac{z^2}{n^2} \text{ eV/atom}$$

$$= -13.6 \times 1.6 \times 10^{-19} \frac{z^2}{n^2} = -2.18 \times 10^{-18} \frac{z^2}{n^2} \text{ J/atom}$$

- Why Total Energy is Negative ?

Here we assume PE of system to be zero when neucleus & e^- were present at infinite distance. But when they attract each other, work is done by system & energy of system will decrease and hence it becomes negative.

H.W.
Q. Bank = 35 to 60

TE -ve means, an e^- is in influence of nucleus.

Q. For H-atom calculate :

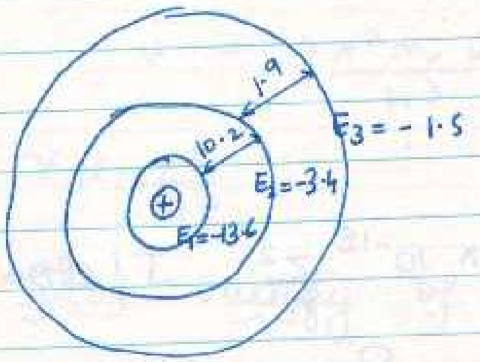
i) $E_1 = -13.6$ eV

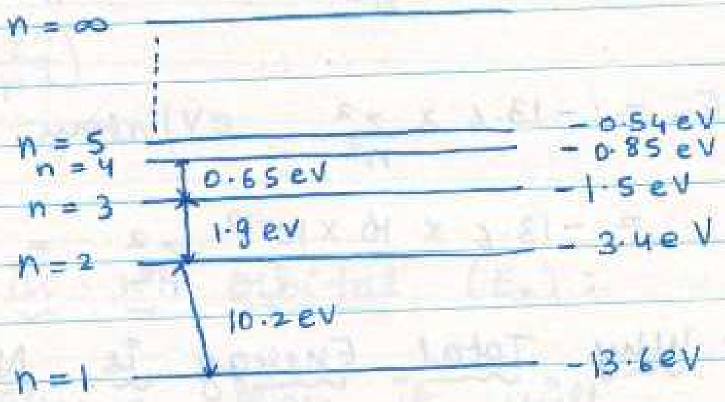
ii) $E_2 = -13.6 \times \frac{Z^2}{n^2} = \frac{-13.6}{4}$ eV

iii) $E_3 = \frac{-13.6}{9}$ eV

iv) $E_4 = \frac{-13.6}{16}$ eV

v) $E_5 = \frac{-13.6}{25}$ eV





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

Energy gap b/w two successive levels keep on decreasing as energy level increases.

n=1 ground state
n=2 1st enited state
n=3 2nd encited state
n=8 7th enited state.

- **Ionisation Energy** : Amt. of Energy req. to remov an e^- from influence of nucleus.

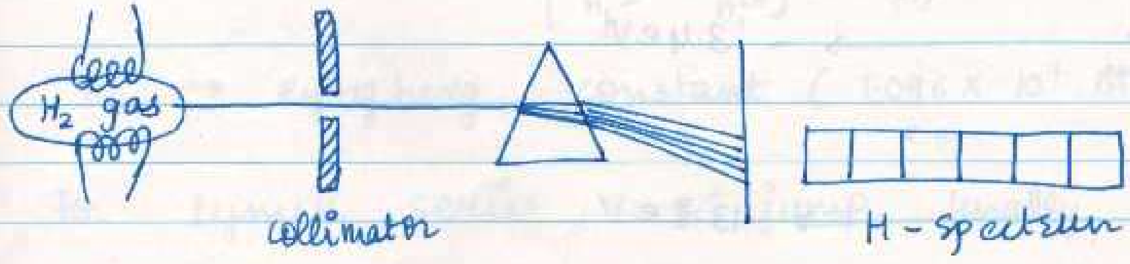
$IE = +13.6 \times \frac{Z^2}{1^2}$ eV/atom

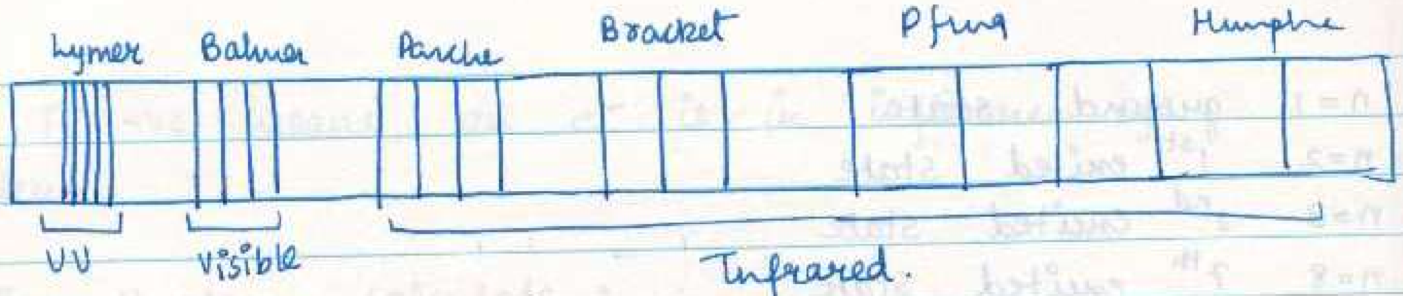
$IE = K \times \frac{Z^2}{1^2}$ eV/atom

$E_n = -K \times \frac{Z^2}{n^2}$ eV/atom

Q. Calculate TE, KE & PE of e^- in H atom in
(i) I orbit = -13.6 ; +13.6 ; -27.2
(ii) II orbit = -3.4 ; 3.4 ; -6.8
(iii) III orbit = -1.5 ; ~~0.75~~ 1.5 ; [illegible] 3

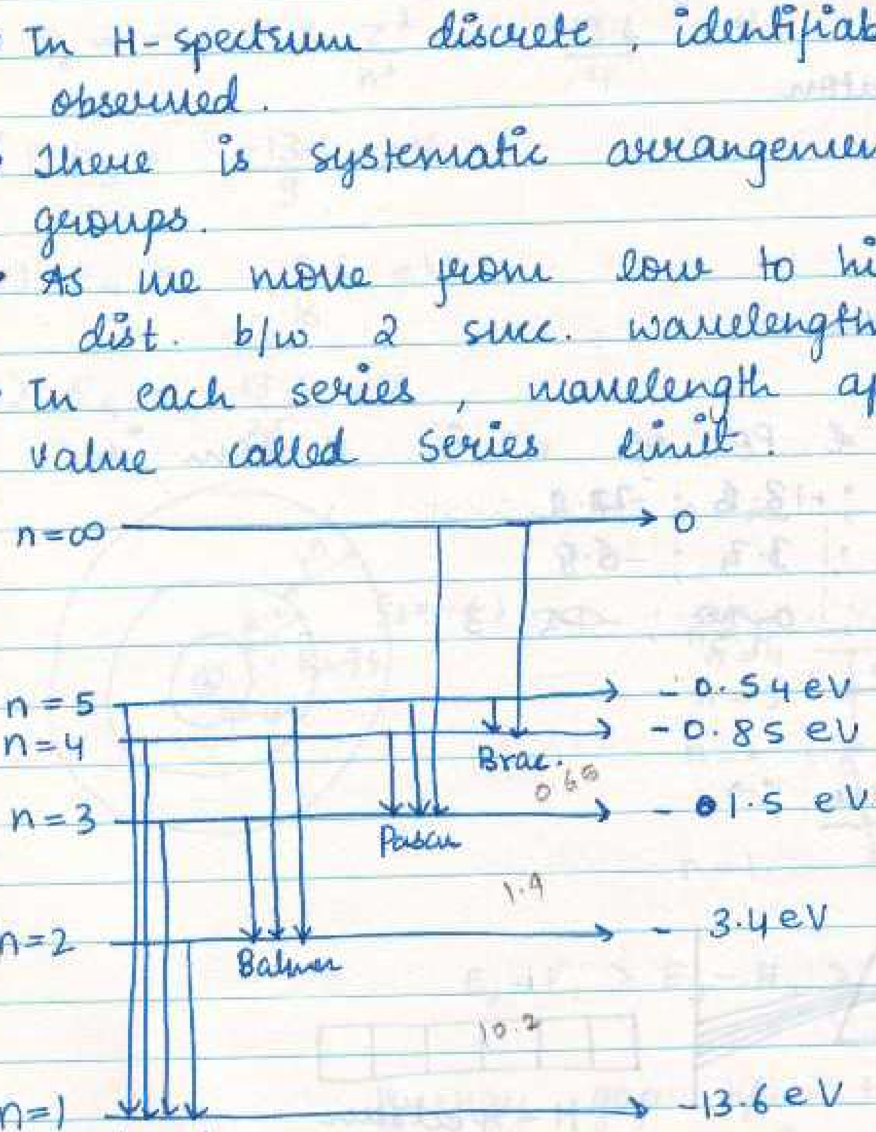
* Hydrogen Spectrum :→





Observations,

- In H-spectrum discrete, identifiable wavelengths were observed.
- There is systematic arrangement of wavelength in groups.
- As we move from low to high wavelength, dist. b/w 2 succ. wavelengths increases.
- In each series, wavelength approaches a particular value called series limit.



LBPBPu

- For lymer series ,

first wavelength $(H_\alpha) = \frac{1240}{\Delta E} = \frac{1240}{10.2}$ nm

second wavelength $(H_\beta) = \frac{1240}{E_3 - E_1} = \frac{1240}{12.1}$ nm

last wavelength $(H_\infty) = \frac{1240}{E_\infty - E_1} = \frac{1240}{13.6}$ nm

$$E_n = \frac{-2\pi^2 m k^2 e^4 Z^2}{n^2 h^2}$$

$$\Delta E = E_i - E_f = \frac{2\pi^2 m k^2 e^4}{h^2} \times Z^2 \times \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

ΔE = Energy of photon emitted / absorbed

$$\Delta E = E_{Photon} = \frac{hc}{\lambda} = \frac{2\pi^2 m k^2 e^4}{h^2} \times Z^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$$\Rightarrow \frac{1}{\lambda} = \frac{2\pi^2 m k^2 e^4}{h^3 c} \times Z^2 \times \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$$= R_H \times Z^2 \times \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$R_H \rightarrow$ Rydberg constant ($1.096 \times 10^7 \ m^{-1}$)

For lymer series , e^- jump finally to $n=1$

$$\frac{1}{\lambda} = R_H \times Z^2 \left[\frac{1}{1^2} - \frac{1}{n_i^2}\right]$$

For I line (H_α),

$$\frac{1}{\lambda_I} = R_H \times Z^2 \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

For II line (H_β),

$$\frac{1}{\lambda_{II}} = R_H \times Z^2 \left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

For last line,

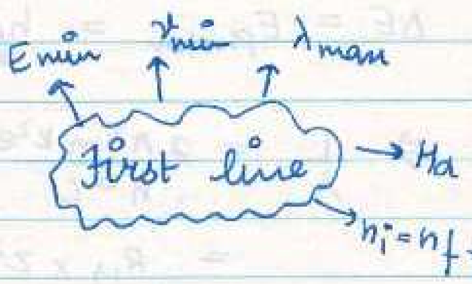
$$\frac{1}{\lambda_{last}} = R_H \times Z^2 \left[\frac{1}{1^2} - \cancelto{0}{\frac{1}{\infty^2}}\right]$$

- For Balmer Series,

e^- jump finally to $n = 2$

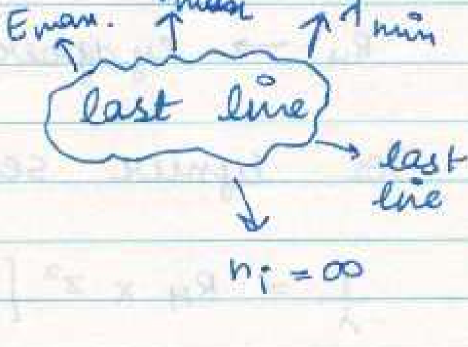
$$\frac{1}{\lambda} = R_H \times Z^2 \times \left[\frac{1}{2^2} - \frac{1}{n_i^2}\right]$$

$n_i = 3, 4, 5, \ldots \infty$



For I line,

$$\frac{1}{\lambda_I} = R_H \times Z^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$



For last line,

$$\frac{1}{\lambda_{line}} = R_H \times Z^2 \left[\frac{1}{2^2} - \cancelto{0}{\frac{1}{\infty^2}}\right]$$

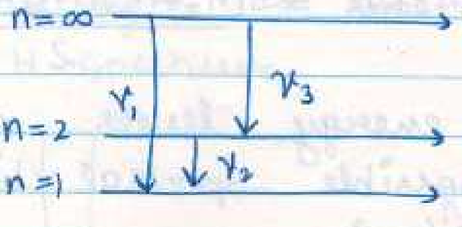
Q. The energy level of an atom for I, II and III level are E, $\frac{4E}{3}$ and 2E respectively. A photon of wavelength 'λ' is emitted for a transition 3 to 1. What will be wavelength of emmission for transition 2 to 1.

→ 3 λ.

$\lambda = \frac{hc}{E}$; $\lambda' = \frac{hc}{E/3}$ ⇒ $\underline{\underline{\lambda' = 3\lambda}}$.

Q. Let ν_1 be the frequency of series limit of lymer series, ν_2 be the freq. of first line of lymer series and ν_3 be the series limit frequency of Balmer series. Then find rel^n between ν_1, ν_2 and ν_3.

→ $\nu_2 < \nu_1$

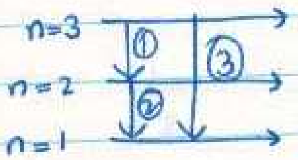


$E_1 = E_2 + E_3$

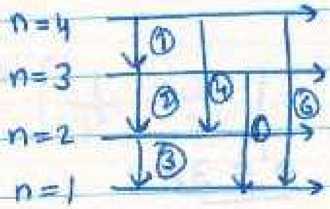
$\Rightarrow \nu_1 = \nu_2 + \nu_3$.

- Calculation of number of spectral lines :→

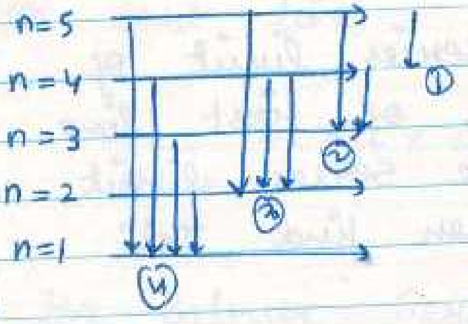
Case I : If suff. no. of atoms are present so that all possible transitions can take place.



③



⑥



⑩ . no. of lines

a) If transition occurs b/w energy levels n_2 and n_1 then max. possible spectral lines $= \frac{(n_2-n_1)(n_2-n_1+1)}{2}$

b) If transition occurs b/w energy levels n and ground state then max. possible spectral lines are $= \frac{n(n-1)}{2}$

Q. A gaseous sample of H atoms is taken in which sufficient no. of H atoms are present. Then calculate spectral lines that can be obtained if

a) ~~([illegible])~~ ~~3~~ $\frac{(11-3)(11-3+1)}{2} = 36$

b) ~~40~~ $11\frac{(11-1)}{2} = 55$

c) 9.

H.W.
Ex. 1 :→ 16 to 39
DPP next.

Case II : If sufficient no. of atoms are not present.

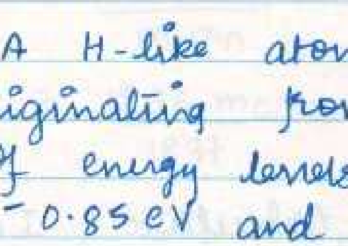
Q. Calculate max. no. of photons that can be emitted when in gaseous sample only 2 H are present & both are in 10^{th} excited state.

→ 10 + 5 = 15

Q. Calculate min. no. of atoms req. for all possible transitions b/w n=4 & n=1.

→  ④.

Q. What transaction in He^+ would have same wavelength as Paschen wavelength n=5 to n=3 in H spectrum.

→ 

He^+ 10 to 6
Be^{2+} 20 to 12

$\frac{1}{9}-\frac{1}{25}$

-0.54
-1.5
0.96

$E_1 = \frac{-13.6 \times z^2}{n^2}$

Q. A H-like atom is observed to emit 6 wavelength originating from all possible transition b/w group of energy levels. These levels have energies b/w -0.85 eV and -0.544 eV (including both of these levels)

a) 3
b) 15 to 12
c) $9R_H\left(\frac{1}{16}-\frac{1}{25}\right) = 159$ nm

$-13.6 \times \frac{4^2}{n^2} = \frac{-13.6}{16}$

$\frac{25\times16}{20}$ 16 20 $\frac{9\times16}{12}$ $\frac{9\times25}{256}$ 15 4 16×25

$-13.6 \times \frac{16}{n} =$

H.W.
Q.B. ⇒ 61 to 80

Q. Suppose in Bohr's model of H-atom instead of electrostatic force some other force is acting b/w e^- & nucleus which causes P.E. to vary as $\frac{-K}{6r^6}$. Assuming Bohr's Quantisation to be true,

a) Derive expression of radius of nth orbit

b) Derive expression of TE in nth orbit.

$$\longrightarrow \quad F = \frac{-K}{6r_n^6} \quad \Rightarrow \quad r_n^6 = \frac{-K}{6F}$$

—x—

a) $$\longrightarrow \quad F = -\frac{du}{dr} = \frac{-K}{r^7}$$

$$\Rightarrow \frac{m v_n^2}{\cancel{r_n}} = \frac{-K}{r_n^{\cancel{7}\,6}} \quad \Rightarrow \quad r_n^6 = \frac{-K}{m v_n^2}$$

$$\Rightarrow r_n^4 = \frac{4\pi^2 m_e K}{h^2} \times \frac{1}{n^2}$$

b) $$\longrightarrow \quad TE = KE + PE$$

$$= \frac{1}{2} m v_n^2 - \frac{K}{6r^6}$$

$$= \frac{K}{2r_n^6} - \frac{K}{6r_n^6}$$

• Concept of reduced Mass :

Till now we have assumed nucleus to be static.

$$\because E_n = \frac{-2\pi^2 m_e k^2 e^4}{h^2} \times \frac{Z^2}{n^2}$$

If we use above formula to calculate IE of hydrogen & deuterium then it will be same but actually ionisation energy of dueterium is slightly greater than IE of H. Actually nucle is not static. Nucleus as well as e⁻ both are moving but COM of system will (close to) coincide with COM of nucleus because nucleus is very heavy as compared to e⁻. In such a case combined system can be represented by single mass called reduced mass.

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}$$

where,

μ = reduced mass

m_e = mass of e⁻

m_n = mass of neutron

$m_p \approx m_n = 1836\, m_e$

$$E_n = \frac{2\pi^2 k^2 e^4 z^2}{n^2 h^2} \times \mu$$

$$r_n = \frac{h^2 n^2}{4\pi^2 k z e^2} \times \frac{1}{\mu}$$

$$v_n = \frac{2\pi k e^2}{h} \times \frac{z}{n} \times \frac{\mu}{m_e}$$

For H,

$$1/\mu = \frac{m_e + m_n}{m_e m_n}$$

$$\mu = \frac{1836\, m_e}{1837}$$

For D,

$$\mu = \frac{2 \times 1836 \times m_e}{3673}$$

$IE_D > IE_H$

- **Drawbacks of Bohr's Model,**

1) It is applicable only for H & H-like species, not for multielectronic species.

2) It could not explain why angular momentum was integral multiple of $\frac{h}{2\pi}$

3) Bohr could not explain fine spectrum of H-atom

4) In H-spectrum, single line was actually a doublet which proves that e^- will have two possible spins (clockwise & anti)

5) When magnetic field was applied, spectral lines were splitted into many lines and this effect is called zeeman effect. It is due to presence of sub energy levels within energy levels.

6) Bohr assumed orbits to be circular path with fixed radius but actually we talk about orbit in terms of probability & it is spherical in shape.

* De Broglie Hypothesis :→

Acc^n to de Broglie, every moving Obj. is asso. with a wave called matter wave. And a particle showing wave character as well as particle character. is said to be showing dual nature.

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

where,

λ → de Broglie wavelength
p → momentum
m → mass of particle
v → velocity

Q. Calculate de Broglie wavelength,

a) of an e⁻ moving with velocity 10^6 m/s.

$$\rightarrow \lambda = \frac{6.63 \times 10^{-34}}{10^6 \times 9.1 \times 10^{-31}} = 0.71 \, A^\circ$$

b) of a cricket ball of mass 0.5 Kg moving with v = 20m/s.

$$\rightarrow \lambda = \frac{6.63 \times 10^{-34}}{0.5 \times 20} = 6.63 \times 10^{-35}$$

de Broglie Hypothesis is applicable for microscopic as well as macroscopic objects but it is significant for microscopic objects.

$$KE = E = \frac{1}{2}\frac{m^2v^2}{m} = \frac{p^2}{2m}$$

$$p = \sqrt{2ME} \longrightarrow KE$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2ME}} = \frac{h}{mv}$$

Case I : If a charged particle is placed in a potential difference of 'V' volt

$$KE = E = qV$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2ME}} = \frac{h}{\sqrt{2MqV}}$$

Case II : If particle is neutral

$$KE = E = \frac{3}{2}KT$$

$$\lambda = \frac{h}{\sqrt{2M \times 3/2\, KT}} = \frac{h}{\sqrt{3MKT}}$$

Case III : If charged particle is an e^-

$$m = m_e \; ; \; q = e$$

$$\lambda = \frac{h}{\sqrt{2m_e eV}} = \sqrt{\frac{150}{\underset{\substack{\downarrow \\ \text{voltage}}}{V}}}\ A^\circ = \frac{12.27}{\sqrt{V}}\ A^\circ$$

H.W.
Ex.1 ⇒ 40 to
Q.B. ⇒ 61 to

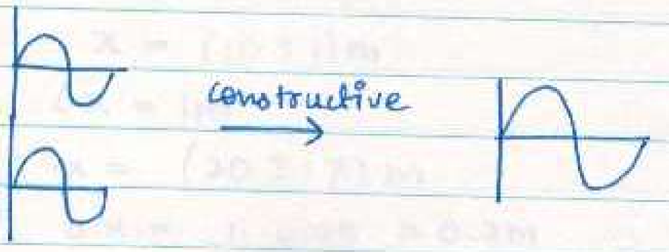
Q. Calculate de Broglie wavelength of ~~the~~ He atom moving with 10^4 m/s velocity.

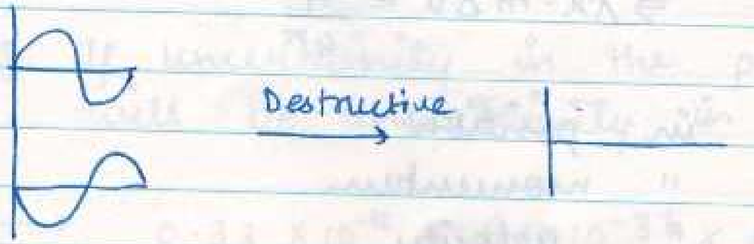
$\rightarrow \lambda = \frac{h}{mu} = \frac{6.62 \times 10^{-34}}{4 \times 1.6 \times 10^{-27} \times 10^4}$

Q. Calculate de Broglie wavelength of an e^- accelerated through a P.D. of
a) 75 V → $\sqrt{2}$ A°
b) 400 V → $\sqrt{3/8}$ A°

- **Justification of Angular Momentum :→**

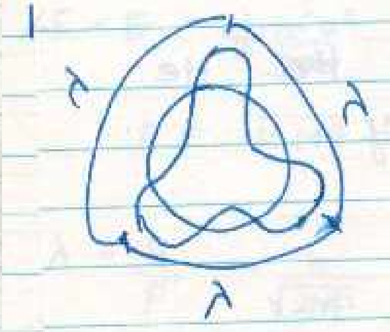
If we assume an e^- to be matter wave then it should interfere constructively when fitted into circumference.





I orbit

II orbit



3^{rd} orbit

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

$$\Rightarrow 2\pi r_n = n \times \frac{h}{mv}$$

$$\Rightarrow m v_n r_n = n \frac{h}{2\pi}$$

$$L = m v_n r_n = n \times \frac{h}{2\pi}$$

* Heisenberg Uncertainity Principle :→

Accⁿ to it, it is impossible to measure position as well as momentum of a moving sub-atomic particle simultaneously with 100% accuracy.

There will always be some uncertainity in position and momentum.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \approx \frac{h}{4\pi}$$

$\Delta p = \Delta(mv) = m\Delta v$ $\Rightarrow \Delta x \cdot m\Delta v = \frac{h}{4\pi}$

where,

Δx → uncertainity in position

Δp → " momentum

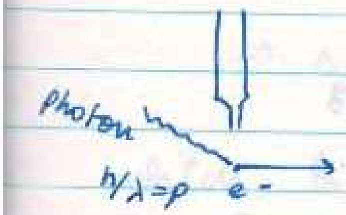
Δv → " velocity

m → mass of particle.

Momentum of photon $= \frac{h}{\lambda}$

- change in momentum of particle will be in range 0 to h/λ.

- uncertainity in position $(\Delta x) = \lambda$ (wavelength of light used)



In order to locate a sub-atomic particle we have to incident some light or photons over it & when they will collide with it they will change velocity & momentum of particle.

For numerical purpose,

$x = (10 \pm 1)\,m$

$\Delta x = 1\,m$

$x = (20 \pm 1\%)\,m$

$\Delta x = \frac{1}{100} \times 20 = 0.2\,m$

Q. If uncertainity in the position is 0.33 pm. What will be uncertainity in velocity of e^-.

$\longrightarrow \quad 0.33 \times 10^{-12} \times 9.1 \times 10^{-31} \times \Delta v = \frac{6.63 \times 10^{-34}}{4\pi}$

$\Rightarrow \Delta v = \frac{6.63 \times 10^{9}}{4\pi \times 9.1 \times 0.33} = 1.78 \times 10^{8}\,m/s$

Q. If H^+ is accelerated to 6.62×10^6 m/s. If error is ±1% in velocity. Then find uncertainity in position.

$$\longrightarrow \quad 6.\cancel{6}2 \times 10^4 \times \overset{1.6}{\cancel{9.1}} \times 10^{-27} \times \Delta x = \frac{6.\cancel{6}2 \times 10^{-34}}{4\pi}$$

$$\Rightarrow \Delta x = \frac{10^{-17}}{4\pi \times \underset{1.6}{\cancel{9.1}}} = \frac{100 \times 10^{-13}}{12.56 \times \cancel{9.1}\ 1.6}$$

Q. Calulate uncertainity in velocity and momentum of particle of mass 6.62×10^{-27} kg if uncertain in its position is 1 A°.

$$\longrightarrow \quad \Delta \ 10^{-10} \times 6.\cancel{6}2 \times 10^{-27} \times \Delta v = \frac{6.\cancel{6}2 \times 10^{-34}}{4\pi}$$

$$\Rightarrow \Delta v = \frac{1000}{4\pi} = \frac{250}{\pi}$$

$$\Delta p = 6.62 \times 10^{-27} \times \frac{250}{\pi}$$

Q. If uncertainity in position and momentum are equal, show that UC in velocity is $\frac{1}{2M}\sqrt{\frac{h}{\pi}}$

$$\longrightarrow \quad \Delta p \cdot \Delta x = \frac{h}{4\pi}$$

$$\Rightarrow \Delta p = \sqrt{\frac{h}{4\pi}} \Rightarrow \Delta v = \frac{1}{2M}\sqrt{\frac{h}{\pi}}$$

Q. Prove that an e⁻ cannot exist inside the nucleus.

$$\overset{\nearrow 10^{-15}}{\Delta x} \times 9.1\times10^{-31} \times \Delta v = \frac{6.63\times10^{-34}}{4\pi}$$

$$\Rightarrow \Delta v = 10^{12} \times \frac{6.63}{4\pi\times9.1} \approx 5.7\times10^{10}\ \text{m/s}$$

which is more than light and is not possible. Hence, e⁻ cannot exist inside the nucleus.

Q. Prove that,

a) $\Delta x \cdot \Delta \cancel{g} \lambda = \frac{\lambda^2}{4\pi}$ where,

ΔE = uncertainity in KE

b) $\Delta x \cdot \Delta E = \frac{hv}{4\pi}$

v = velocity of particl

$p = \sqrt{2ME}$

$\rightarrow$ a) $\rightarrow \Delta x \cdot \Delta(h/p)$ $\Delta P = \frac{h}{\lambda} \Rightarrow \left|\frac{dp}{d\lambda}\right| = \frac{h}{\lambda^2}\,\Delta x$

$$\Rightarrow \Delta x \times \frac{\cancel{h}}{\lambda^2}\,\Delta\lambda = \frac{\cancel{h}}{4\pi}$$

$$\Rightarrow \Delta x \cdot \Delta\lambda = \frac{\lambda^2}{4\pi}$$

b) $\rightarrow E = \frac{p^2}{2M} \Rightarrow \sqrt{2EM} = p \Rightarrow \frac{dp}{dE} = \frac{-1}{2\sqrt{2EM}}$

$$\frac{dp}{dE} = \frac{1}{v}$$

$$\Rightarrow \Delta x \cdot \Delta E = \frac{hv}{4\pi}$$

* Quantum Wave Mechanical Model :→

This model assumes that every sub-atomic particle is associated with a matter wave.

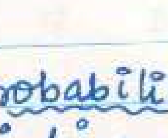
- To represent a wave, we need a wave function. $\psi(x, y, z, t)$
- This wave function represents spatial distribution of particles.
- This wave function contains all dynamic information regarding the particle it represents. eg : velocity, p, KE, etc.
- -ve value of 'ψ' has no physical significance. Both +ve & -ve region of wave function represent to the region where probability of finding an e^- is max.

* **Probability Density** (ψ^2) :→ represents probability of finding an e^- per unit volume or at a point.

$$\psi^2 = \frac{\text{Probability}}{\text{Volume}} \quad (m^{-3})$$

* **Probability** ($\psi^2 dv$) :→ It represents probability of finding an e^- in a given region

$$dv = \frac{4}{3}\pi(R+dr)^3 - \frac{4}{3}\pi R^3$$



$\Rightarrow P = \psi^2 4\pi R^2 dr$

* Schrodinger wave Equation :→

$$\underbrace{\frac{-h^2}{8\pi^2 M_e}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right)}_{KE} + \underbrace{V(\psi)}_{PE} = \underbrace{E(\psi)}_{TE}$$

$m_e \rightarrow$ mass of e^-.

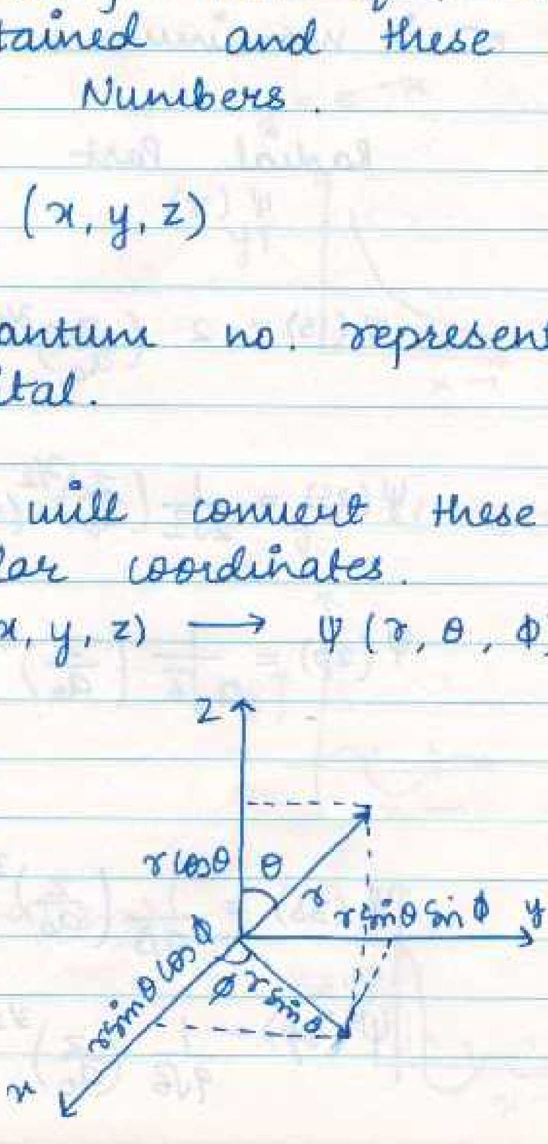
During solving this eq^n, three constans, n, l, m were obtained and these constants are called Quantum Numbers.

$\psi_{n,l,m}(x, y, z)$

This quantum no. represents wave function of an orbital.

Now we will convert these cartesian coordinates into Polar coordinates.

$\psi(x, y, z) \longrightarrow \psi(r, \theta, \phi)$



$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

$$\psi(x,y,z) = \underset{\substack{\downarrow \\ \text{radial Part} \\ \downarrow \\ \text{depends on} \\ (n,\,l)}}{\underline{\psi(r)}}\ \underset{\substack{\downarrow \\ \text{Angular Part} \\ \downarrow \\ \text{depends on} \\ (l,\,m)}}{\underline{\psi(\theta,\phi)}}$$

H.W.

DPP # 18

Ex. 1 60 to 63

R.B. 19 to 33 ; ~~1~~, ~~2~~, ~~3~~, 5, 8 to 10

- **Orbital** : It is 3D space around nucleus where probability of finding an e^- is maximum.

Angular Part $\psi(\theta,\phi)$	Radial Part $\psi(r)$
$\psi(s) = \sqrt{\frac{1}{4\pi}}$	$\psi(1s) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma/2}$
$\psi(p_x) = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi$	$\psi(2s) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\sigma)\, e^{-\sigma/2}$
$\psi(p_y) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi$	$\psi(2p) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma\, e^{-\sigma/2}$
$\psi(p_z) = \sqrt{\frac{3}{4\pi}} \cos\theta$	
$\psi(d_{z^2}) = \sqrt{\frac{5}{16\pi}}\,(3\cos^2\theta - 1)$	$\psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(6-6\sigma+\sigma^2)\, e^{-}$
$\psi(d_{xz}) = \sqrt{\frac{15}{4\pi}} \sin\theta \cos\theta \cos\phi$	$\psi(3p) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(4-\sigma)\,\sigma \cdot e^{-\sigma/}$

H.W.
DPP #19

$\psi(d_{yz}) = \sqrt{\frac{15}{4\pi}} \sin\theta \cos\theta \sin\phi$ $\quad$ $\psi(3d) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \cdot \sigma^2 \cdot e^{-\sigma/2}$

$\psi(d_{x^2-y^2}) = \sqrt{\frac{15}{4\pi}} \sin^2\theta \cos 2\phi$

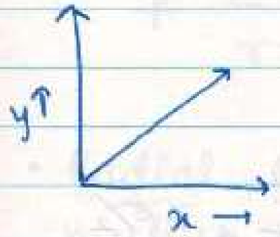
$\sigma = \frac{2Zr}{na_0}$; $a_0 = \frac{h^2}{4\pi^2 me^2} = 0.53$ Å

$\psi(d_{xy}) = \sqrt{\frac{15}{4\pi}} \sin^2\theta \sin 2\phi$

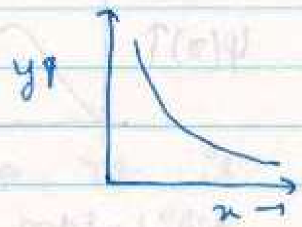
* Radial part depends on n, l
whereas angular part depends on l, m.

* Graphs :→

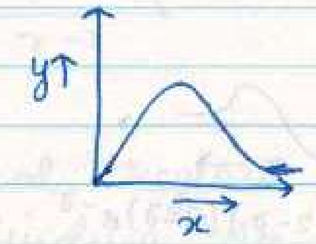
$y = x$



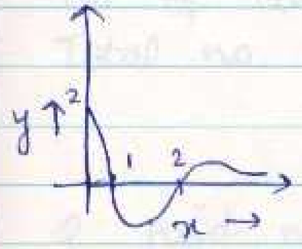
$y = e^{-x}$



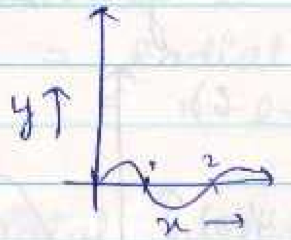
$y = xe^{-x}$



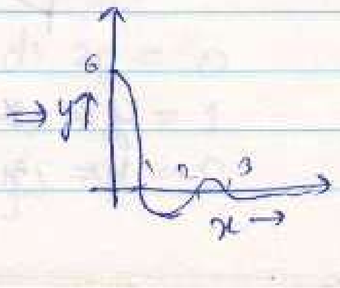
$y = (1-x)(2-x)e^{-x}$



$y = x(1-x)(2-x)e^{-x}$

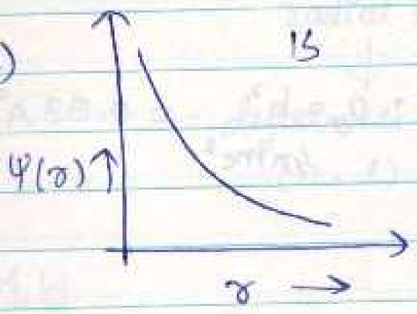


$y = (1-x)(2-x)(3-x)e^{-x}$

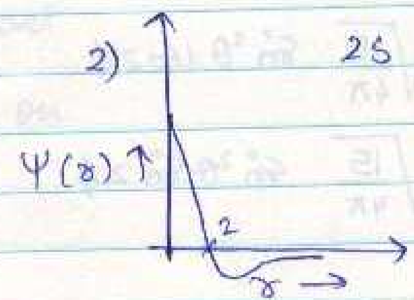


- Graph b/w $\psi(r)$ V/S r

1)



2)

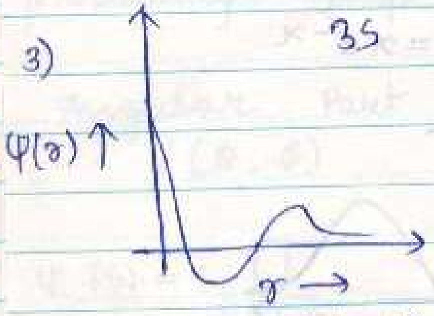


$\psi(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Kr}$

$\psi(r) = (2-r)\,e^{-r}$

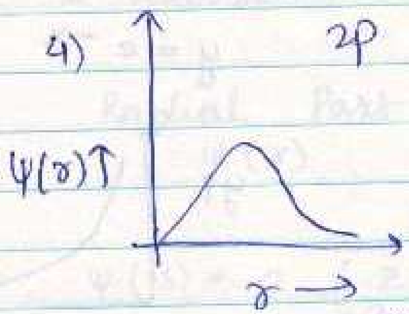
$y = K e^{-x}$

3)



$\psi(r) = (2-r)(3-r)e^{-r}$

4)

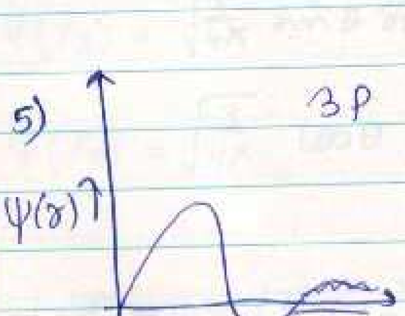


$\psi(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$

$= K \cdot K'r \cdot e^{-Kr}$

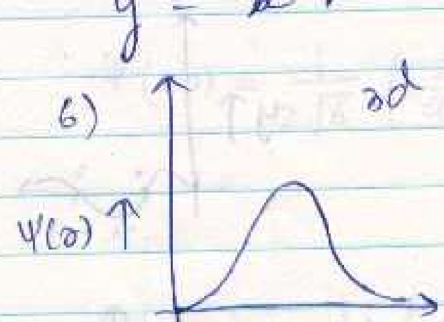
$y = x \cdot K^{-x}$

5)



$y = K(4-r)\cdot r\, e^{Kr}$

6)

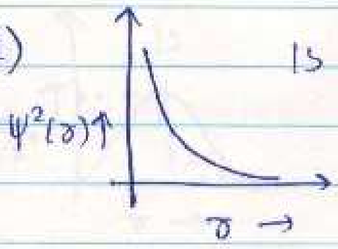


$y = K \cdot r^2 \cdot e^{-Kr}$

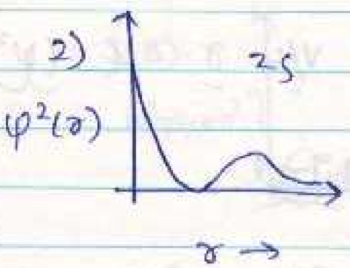
$y = x^2 \cdot e^{-Kx}$

• Graph b/w $\psi^2(r)$ vs r :→

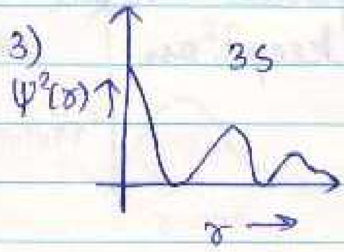
1)



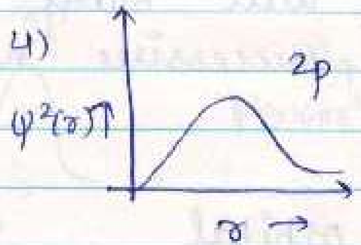
2)



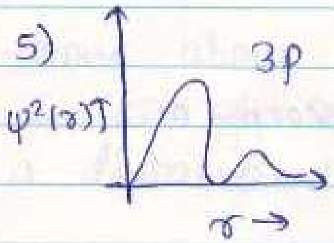
3)



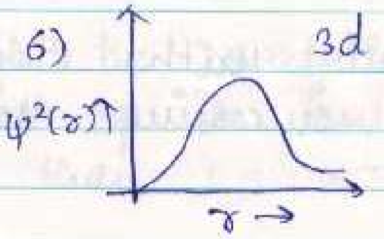
4)



5)



6)



• Radial Node :→ It is spherical region around nucleus where probability of finding an e^- is zero.

No. of radial Node = $n-l-1$
No. of angular Node = l
Total no. of node = Radial node + angular node
= $n-l-1+l = n-1$

Q. Find no. of radial nodes in

a) 1s = 0
b) 2s = 1
c) 3s = 2
d) 2p = 0
e) 3p = 1
f) 3d = 0

- Some imp points :-

for $\psi(r)$ v/s r & $\psi^2(r)$ v/s r

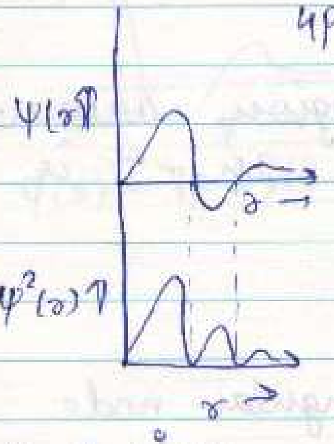
for s orbital

a) graph ~~will~~ will start with some finite value.
b) height of successive maxima will keep on decreasing.

for p & d orbital

a) graph starts with origin (nucleus)
b) height of successive maxima will keep on decreasing.

4-1-1

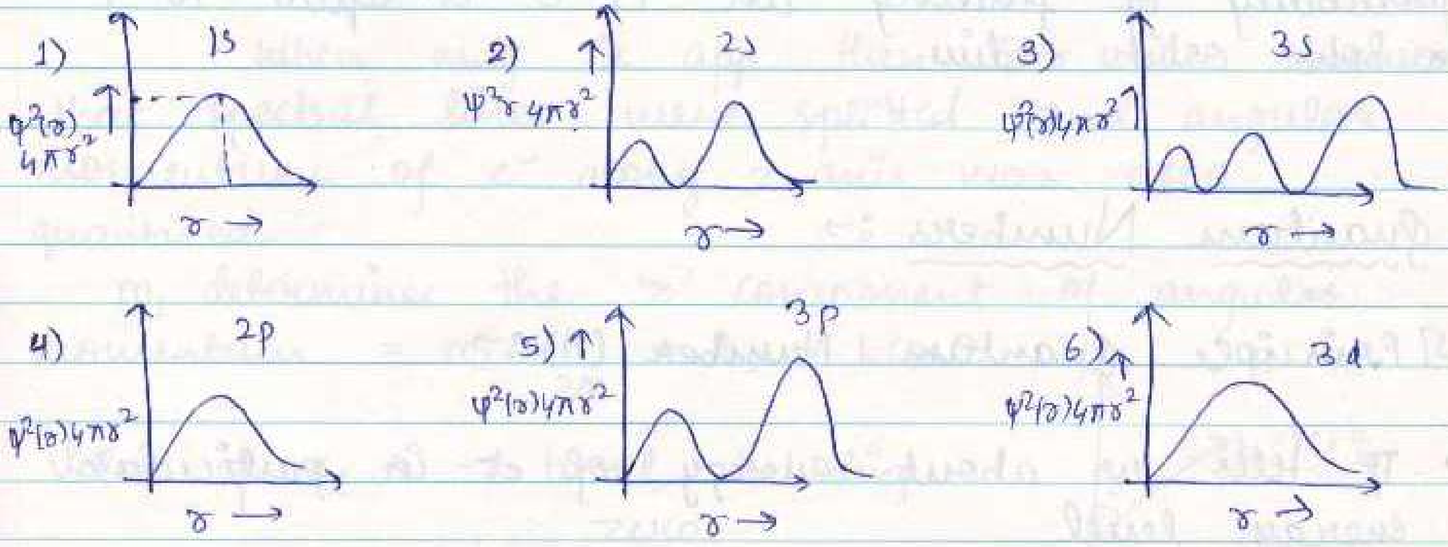


Conclusion,

From above graph it can be concluded that probability of finding 's' e^- is more close to nucleus as compared 'p' & 'd' orbitals. So we can say, penetration effect of 's' towards nucleus is more.

ns > np > nd > nf

- Graph b/w probability distribution function $[\psi^2(r)4\pi r^2]$ v/s r



From above graph it can be concluded that an e^- of 2s spends most of its time ~~dos~~ at a distance much larger than 1s e^-.

Q. For 1s e^-, find distance at which probability of finding an e^- is maximum for H-atom

$\rightarrow \quad \psi(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma/2} \; ; \; \sigma = \frac{2Zr}{na_0}$

$\Rightarrow \quad \frac{d(\psi^2 4\pi r^2)}{dr} = 0 \Rightarrow \frac{d}{dr}\left[4\times\left(\frac{Z}{a_0}\right)^3 \times e^{-\sigma} \times 4\times\pi\times r^2\right] = 0$

$\Rightarrow 4\left(\frac{Z}{a_0}\right)^3 \times e^{-\sigma} \times \frac{2Z}{na_0} \times 4\times\pi\times 2r = 0$

$\Rightarrow \frac{4}{a_0^3} \times e^{-r/a_0} \times \frac{2}{a_0} \times 4\times\pi\times 2r = 0$

$\Rightarrow \underline{\underline{r = a_0}}$

From above result it is clear that max. probability of finding an 1s e^- is equal to 1st r Bohr orbit radius.

- **Quantum Numbers** :→

1] Principle Quantum Number (n) :→

- It tells us about energy of e^- in particular energy level.
- As value of 'n' ↑, Energy ↑.
- Value of 'n' = 1 to ∞.
- It is used to determine orbit angular momentum $= \underline{n} \times \frac{h}{2\pi}$

2] Azimuthal Quantum Number (l) :→

- Values to 'l' can be 0 to (n-1)
- It tells us about shape of Orbitals
- It tells us about orbital angular momentum $= \sqrt{l(l+1)} \times \frac{h}{2\pi}$

$$s = 0$$

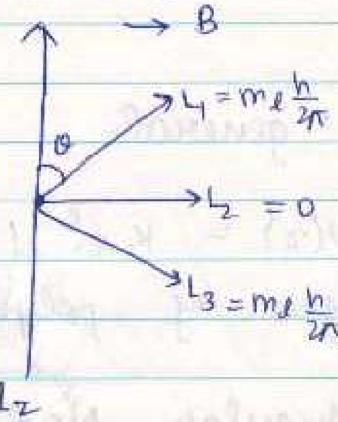
$$p = \frac{\sqrt{2}h}{2\pi}$$

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

3] Magnetic Quantum Number (m_l) :→

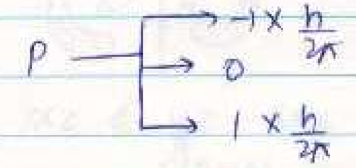
When mag. is app. then it was observed that spectral lines were splitted and angular momentum of e^- along z-axis was also quantised.

m_l determines the 'z' component of angular momentum. $= m_l \times \frac{h}{2\pi} = L_z = L\cos\theta$

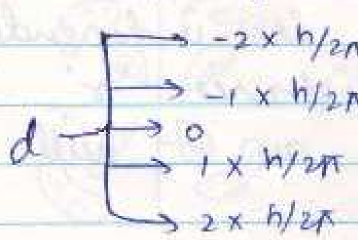


Value of m_l ⇒ $-l$ to $+l$ including zero.

For p,
$l = 1$, $m_l = -1, 0, 1$



For d,
$l = 2$, $m_l = -2, -1, 0, 1, 2$



Calculation of θ for P,

$$L_z = L\cos\theta$$

$$\frac{h}{2\pi} = \sqrt{2} \times \frac{h}{2\pi} \times \cos\theta$$

$$\Rightarrow \theta = 45^\circ.$$

4] Spin Quantum Number :→

An e^- while moving around nucleus also revolves around its own axis and this property should not be taken to be actual

H.14
3(A)

spinning motion. It is better to regard it as inter-sive property like charge, mass, and this quantum mechanical state has no physical analogous.

spin values are $+1/2$, $-1/2$.

- Magnetic moment = $\sqrt{n(n+2)}$ BM
  ↳ no. of unpaired e^-

In general,

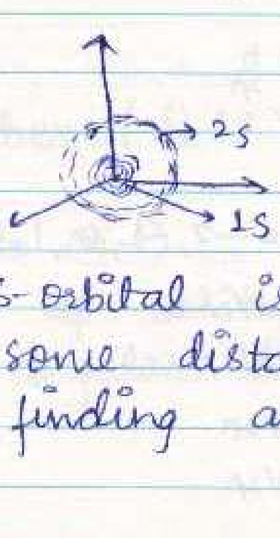
$$\psi(r) = K r^{l}\,(\text{polynomial in } r)^{n-l-1}\, e^{-r}$$

degree of polynomial = $n-l-1$ = no. of radial nodes.

* Angular Nodes :→

① For s-orbital

$$\psi(\theta,\phi) = \sqrt{\frac{1}{4\pi}}$$

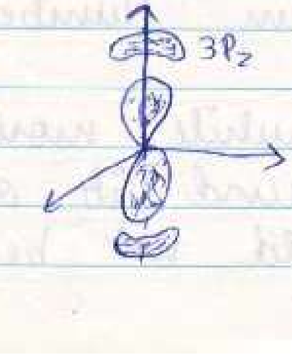


angular wave funᶜⁿ of s-orbital is independent of θ / ϕ, as a result at some distance 'r' from nucleus probability of finding an e^- will be same.

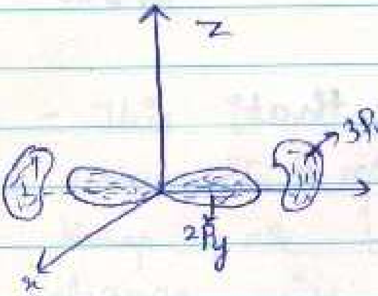
② For p-orbital

For P_z,

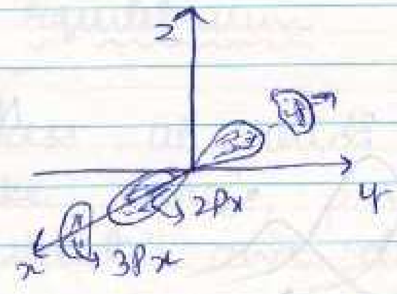
$$\psi(\theta,\phi) = \sqrt{\frac{1}{3\pi}}\cos\theta$$



xy plane is nodal plane or ang. plane



xz is nodal plane or angular node

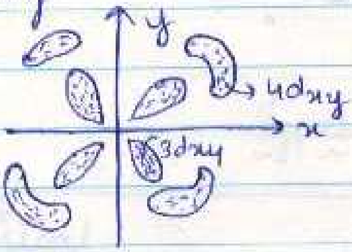


yz is nodal Plane or angular node

③ For d-orbital

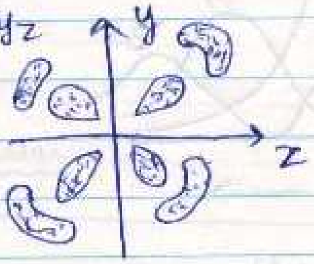
$l = 2 =$ no. of angular nodes

a) dxy



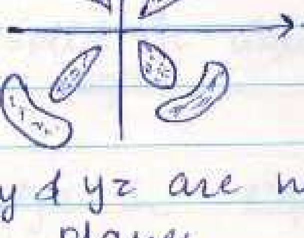
xz & yz are nodal planes

b) d_{yz}



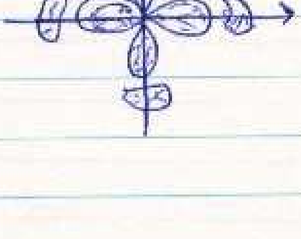
xy & xz are nodal planes

c) d_{xz}

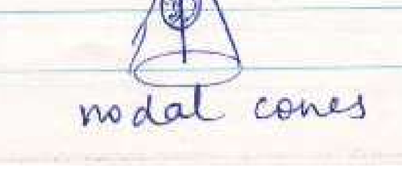


xy & yz are nodal planes

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

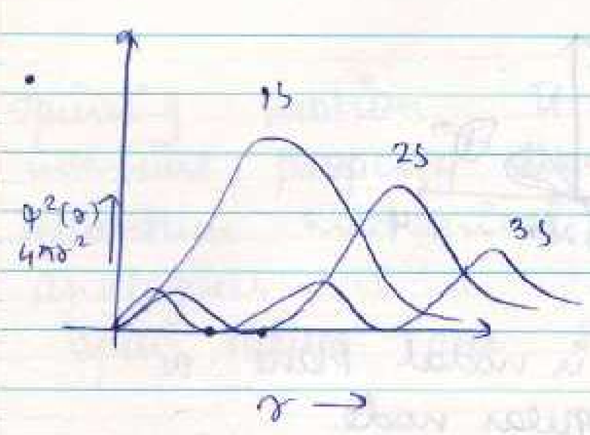


e) d_{z^2}

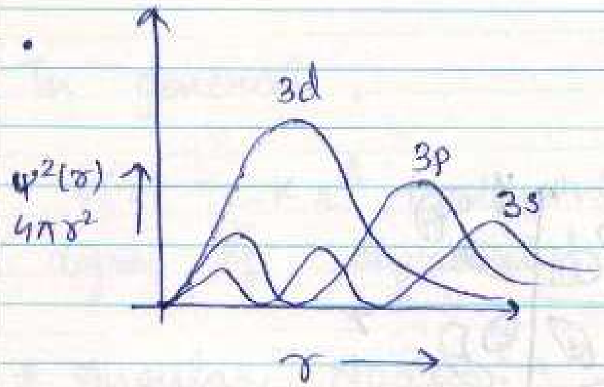


nodal cones

Ex.2
Ex.3(A)
Ex.1
DPP #20



Not necessary that nodes of 2s & 3s coincide.

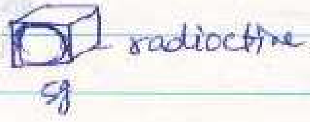


- Probability of finding a 3d e^- near nucleus is more!

4. Chemical Equilibrium

- This is state of a process at which various properties of system like conc^n, partial pressure, temp, etc becomes constant and does not change with time.

100 ml



Crystallization $\underset{0.1 g/s}{\overset{0.1 g/s}{\rightleftharpoons}}$ Dissolution

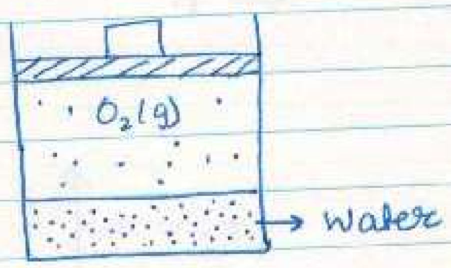
Types of Equilibrium

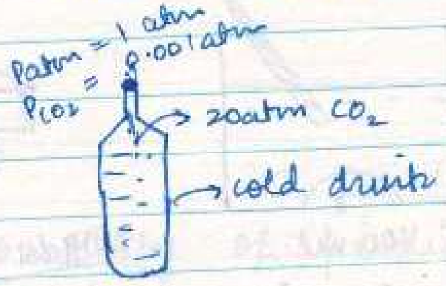
- Physical equilibrium
  - Phase equilibrium
    - Solid-liquid Eq.
      $H_2O(s) \rightleftharpoons H_2O(l)$
    - liquid-gas Eq.
      $H_2O(l) \rightleftharpoons H_2O(g)$
    - Solid-gas Eq.
      $CO_2(s) \rightleftharpoons CO_2(g)$
  - solid in liquid solution
    eg: sugar in water
  - Gas in liquid solution
    eg: $O_2(aq.)$
- Chemical Equili.
  - Homogeneous Equilibrium
  - Hetergeneous Equilibrium

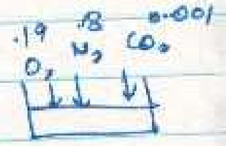
Gas in liquid :→

Henry's Law :→

Accⁿ to it, solubility of gas is directly proportional to partial pressure of gas over solvent.





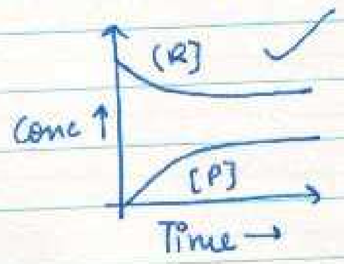


Partial pressure of gas $\propto$ solubility of gas

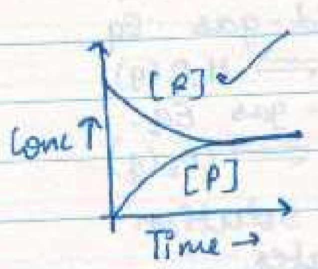
Q. Identify the graph which represents equilibrium

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} P$$

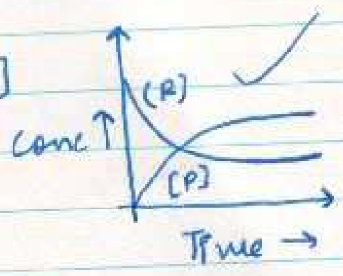
a)



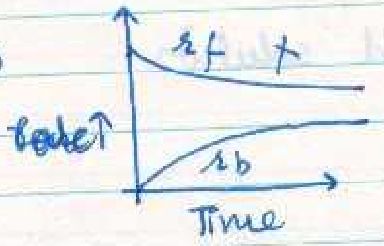
b)



c]



d)



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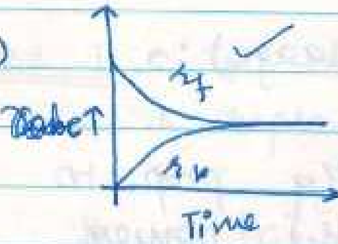
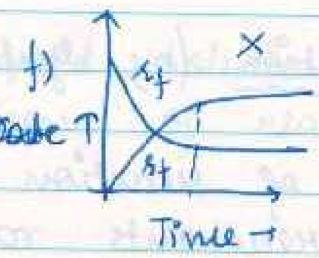
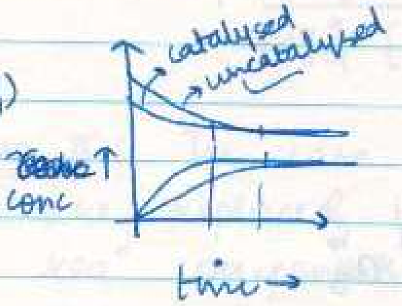
e)





g)



* Characteristics of Equilibrium :→

- It is dynamic in nature.
- At eq. rate of forward as well as backward reaction becomes equal.
- At eq. conc. of partial pressure of reaction components becomes constant
- Eq. can be achieved from both directions.

eq. :→	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	$+ Cl_2(g)$
$t=0$	1		0	0
$t=t_{eq.}$	0.3		0.7	0.7
$t=0$	0		1	1
$t=t_{eq.}$	0.3		0.7	0.7

- Catalyst helps in achieving eq. quickly but it does not alter eq. conc. or partial pressure.
- If reaction components involve gases then eq. can be achieved only in closed vessels.

- **Law of Mass Action** (by Guldberg & Waage) :-

Acc^n to it, rate of reaction is directly prop. to active mass of reactants raised to the power their stoichiometric coefficients.

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

rate of forward rea^n $(r_f) \propto a_A^a \, a_B^b$

$$r_f = K_f \, a_A^a \, a_B^b$$

rate of backward rea^n $(r_b) \propto a_C^c \, a_D^d$

$$r_b = K_b \, a_C^c \, a_D^d$$

where,

r_f, r_b → rate of forward & backward rea^n resp.

K_f, K_b → rate constants for forward & backward rea^n resp.

a_A, a_B, a_C, a_D → active masses of A, B, C & D

At equilibrium

$$r_f = r_b$$

$$K_f \, a_A^a \, a_B^b = K_b \, a_C^c \, a_D^d$$

$$K_{eq} = \frac{K_f}{K_b} = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$$

K_{eq} → equilibrium constants (depends only on temp.)

Case I : In case of liquid solutions, active mass is replaced by conc. of reac^n components

$$K_c = \frac{[C]_{eq}^{c}\,[D]_{eq}^{d}}{[A]_{eq}^{a}\,[B]_{eq}^{b}}$$

Case II : In case of aq. rea^n components, active masses are replaced by conc. or partial pressure of rea^n components.

$$K_p = \frac{P_{C_{eq}}^{c}\,P_{D_{eq}}^{d}}{P_{A_{eq}}^{a}\,P_{B_{eq}}^{b}} \quad ; \quad K_c = \frac{[C]_{eq}^{c}\,[D]_{eq}^{d}}{[A]_{eq}^{a}\,[B]_{eq}^{b}}$$

Case III : In case of pure solid, pure liquid or excess solvent, active mass remains constant or is replaced by unity.

$H_2O(l) \rightleftharpoons H_2O(g)$ $\quad K_p = P_{H_2O}$ = VP of water

$H_2O(s) \rightleftharpoons H_2O(g)$ $\quad K_p = P_{H_2O}$ = VP of ice

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\quad K_p = P_{CO_2}$; $K_c = [CO_2]$

$H_3COOH(aq.) + H_2O(l) \rightleftharpoons CH_3COO^-(aq.) + H_3O^+(aq.) \Rightarrow K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ is

$H_3(aq.) + H_2O(l) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.) \Rightarrow K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$

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- $CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$

$$\Rightarrow K_c = \frac{[H_2O][CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

$K_{eq.}$ → K_p, K_c } True equilibrium constant depend only on temp.

K_x :→

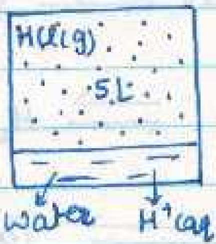
$$aA + bB \rightleftharpoons cC$$

$$K_x = \frac{x_C^{\,c}}{x_A^{\,a}\, x_B^{\,b}}$$

x_A, x_B, x_C → Mole fraction of A, B & C resp.

K_{pc} :→

$$HCl\,(g) \rightleftharpoons H^+\,(aq.) + Cl^-\,(aq.)$$



$[HCl] = \frac{n_{HCl}}{5}$

$[H^+] = \frac{n_{H^+}}{1}$

not uniform

$$K_{pc} = \frac{[H^+][Cl^-]}{P_{HCl}\ (bar/atm)}$$

Units of K_p & K_c :→

$$aA\,(g) \rightleftharpoons bB\,(g)$$

$K_p = \frac{P_B^{\,b}}{P_A^{\,a}} = (atm)^{b-a}$; $K_c = \frac{[B]^b}{[A]^a} = [M]^{b-a}$

units of eq. constants depends on stoichiometry of reactants.

K_p° & K_c° are unitless and dimensionless quantities.

$$K_p^\circ = \frac{\left(\frac{P_B}{1\ bar}\right)^b}{\left(\frac{P_A}{1\ bar}\right)^a} \quad ; \quad K_c^\circ = \frac{\left(\frac{[B]}{M}\right)^b}{\left(\frac{[A]}{M}\right)^a}$$

- Relationship b/w K_p and K_c :→

$$aA \rightleftharpoons bB$$

$$K_p = \frac{(P_B)^b}{(P_A)^a} \quad ; \quad K_c = \frac{[B]^b}{[A]^a}$$

$$P_B = \frac{n_B}{V}RT = [B]RT$$

$$P_A = \frac{n_A}{V}RT = [A]RT$$

$$\therefore K_p = \frac{([B]\,RT)^b}{([A]\,RT)^a}$$

$$\Rightarrow K_p = \frac{[B]^b}{[A]^a} \times (RT)^{b-a}$$

$\Rightarrow K_p = K_c\,(RT)^{\Delta n_g}$; where Δn_g = moles of gaseous product − moles of gaseous reactants

Q. Write relⁿ b/w K_p & K_c for :→

a) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

→ $K_p = K_c(RT)$

b) $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$

→ $K_p = K_c$

c) $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

→ $K_p = K_cRT$

d) $NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq.) + OH^-\,(aq.)$

→ K_p is not defined. (∵ no gas)

e) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

→ $K_P = \frac{K_c}{R^2T^2}$

* Types of Reactions :→

1) Reversible reactions
2) Irreversible reactions

· Reversible reactions : These are reactions which do not go upto completion.
For eg,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2(g)$$

t=0 1M 0 0
t=t 0.3M 0.7M 0.7M

· Irreversible reactions :→ These are reaction which go upto almost completion.
For eg,

- Neutralisation Rxn,

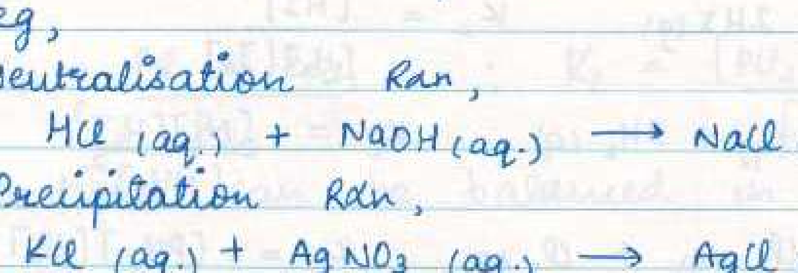
$$HCl_{(aq.)} + NaOH_{(aq.)} \longrightarrow NaCl_{(aq.)} + H_2O(l)$$

- Precipitation Rxn,

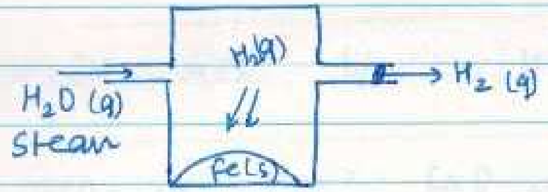
$$KCl_{(aq.)} + AgNO_{3(aq.)} \longrightarrow AgCl_{(s)}\downarrow + KNO_{3(aq.)}$$

Note :→ 1) Strictly speaking, all reactions are reversible and the reactions which goes upto almost completion are called irreversible reactions.

2) A reversible rxn can be converted into irreversible rxn and vice versa.



$CaCO_3 \longrightarrow CaO_{(s)} + CO_2(g)$ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$



$4H_2O(g) + 3Fe(s) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

* Types of Chemical Equilibrium :→

i) Homogenous equilibrium :→ In it all reactants and products are present in same phase.

a) Gas Phase :→

- $H_{2(g)} + I_2(g) \rightleftharpoons 2HI(g)$ $\quad K_c = \frac{[HI]^2}{[H_2][I_2]}$
- $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\quad K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$
- $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b) Liquid Phase :→

- $NH_4OH(aq.) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$ $\quad K_c = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$
- $CH_3COOH(aq.) + H_2O(l) \rightleftharpoons CH_3COO^-(aq.) + H_3O^+(aq.)$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

ii) Heterogeneous Equilibrium :→ In it reactants and products will be present in more than one phases.

eg,

- $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

$K_p = P_{CO_2}$ $\quad K_c = [CO_2]$ ~~[illegible]~~

~~[illegible]~~

· Characteristics of equilibrium constant (K_{eq}) :→

- It is defined only for balanced chemical reaction.

eg: $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_p = \frac{P_{Cl_2} \times P_{PCl_3}}{P_{PCl_5}} \; ; \; K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

* reactions can be balanced in infinite ways.

- Expression of eq. constant involves conc. or partial pressure at equilibrium.

- Value of eq. constant does not change on changing initial conc. of reactants. It only depends on temp.

	$PCl_{5(g)}$	$\rightleftharpoons PCl_{3(g)}$	$+ Cl_{2(g)}$
t = 0	1 M	0	0
t = teq.	0.3M	0.7M	0.7M
t = 0	2M	0	0
t = teq.	2 − x	x	x

$$K_{eq} = \frac{0.7 \times 0.7}{0.3}$$

- If reaction is reversed then $K_{eq.}$ constant changes as follows

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} \qquad K'_{eq} = \frac{[PCl_5]_{eq.}}{[Cl_2]eq.[PCl_3]eq.} = \frac{1}{K_{eq}}$$

- If a reaction is multiplied by a factor then its $K_{eq.}$ changes as follows

$$2PCl_{5}(g) \rightleftharpoons 2PCl_{3}(g) + 2Cl_{2}(g) \qquad K'_{eq} = \frac{[PCl_3]^2_{eq}[Cl_2]^2_{eq.}}{[PCl_5]^2_{eq.}} = K^2_{eq}$$

- If two reactions are added then their $K_{eq.}$ get multiplied

$$\begin{array}{ll} A_{(g)} \rightleftharpoons B(g) + C(g) & K_1 = \frac{[B][C]}{[A]} \\ B_{(g)} \rightleftharpoons D(g) & K_2 = \frac{[D]}{[B]} \\ \hline A(g) \rightleftharpoons C(g) + D(g) & \end{array}$$

$$\hookrightarrow K_3 = \frac{[C][D]}{[A]} = K_1 \times K_2.$$

- If one reaction is subtracted from other then ~~their~~ $K_{eq.}$ changes as follows

$$\begin{array}{ll} A(g) + B_{(g)} \rightleftharpoons C_{(g)} & K_1 = \frac{[C]}{[A][B]} \\ D_{(g)} + B(g) \rightleftharpoons E_{(g)} & K_2 = \frac{[E]}{[D][B]} \\ \hline A(g) + E(g) \rightleftharpoons C(g) + D(g) & K_3 = \frac{[C][D]}{[A][E]} = \frac{K_1}{K_2} \end{array}$$

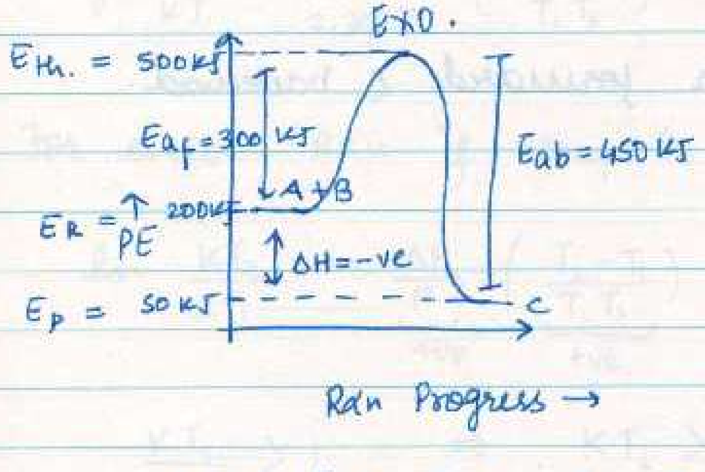
- If we use catalyst then it does not alter eq. conc., partial pressure or K_{eq}.

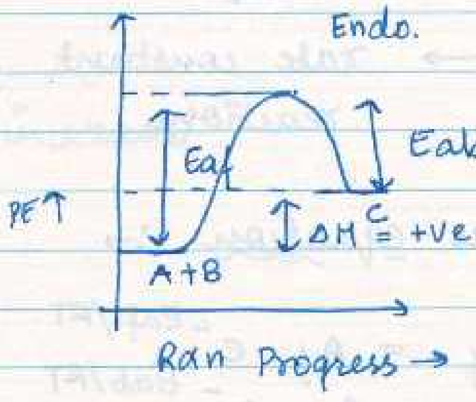
* Effect of Temperature on K_{eq} :→

· **Threshold Energy** : Min. PE that should be possessed by reactant molecules so that they can get converted into products.

· **Activation Energy** : Min. amt. of KE possessed by reactant molecules so that they can get converted into product or they can cross threshold barrier.

$$A + B \longrightarrow C$$





$$\Delta H = E_{af} - E_{ab} = E_p - E_R$$

if $\Delta H < 0$ ⇒ Process is exothermic

if $\Delta H > 0$ ⇒ Process is endothermic

E_{af} & E_{ab} ⇒ activation energy for forward & backward rxn resp.

E_p, E_R → PE of product & Reactants resp.

- $R \xrightleftharpoons[\text{exo.}]{\text{Endo.}} P \quad \Delta H = +100 \text{ KJ/mol}$

  $P \xrightleftharpoons[\text{endo.}]{\text{exo.}} R \quad \Delta H = -100 \text{ KJ/mol}$

- $R \xrightleftharpoons[r_b]{r_f} P$

Rate of forward Rxn $(r_f) = K_f [R]$
Rate of backward Rxn $(r_b) = K_b [P]$
At equilibrium,
$r_f = r_b$
$K_f [R] = K_b [P]$

$$K_{eq} = \frac{K_f}{K_b} = \frac{[P]eq.}{[R]eq.}$$

K_b, K_f → rate constant for forward & backward reactions

- Arrhenius equation :→

$$K_f = A_f \, e^{-Eaf/RT}$$
$$K_b = A_b \, e^{-Eab/RT}$$

$$K_{eq} = \frac{A_f \, e^{-Eaf/RT}}{A_b \, e^{-Eab/RT}} = A \, e^{-(Eaf - Eab)/RT}$$

$$K_{eq} = A \, e^{-\Delta H/RT}$$

A_f, A_b → Arrhenius constants for forward & backward reactions respectively.

Assuming A and ΔH to be temp. independent

$$\ln K = \ln A - \frac{\Delta H}{RT}$$

At Temp. T_1

$$\ln KT_1 = \ln A - \frac{\Delta H}{RT_1} \quad \text{—— ①}$$

At Temp. T_2

$$\ln KT_2 = \ln A - \frac{\Delta H}{RT_2} \quad \text{—— ②}$$

② - ①

$$\ln \frac{KT_2}{KT_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Rightarrow \log \frac{KT_2}{KT_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

For endo. Rxn if temp. is increased

$$\ln \frac{KT_2}{KT_1} = \underbrace{\frac{\Delta H}{R}}_{+ve}\left(\underbrace{\frac{T_2 - T_1}{T_1 T_2}}_{+ve}\right)$$

$$\frac{KT_2}{KT_1} > 1 \quad \Rightarrow \quad KT_2 > KT_1$$

★ Increase in temperature favours endothermic process

* Higher the value of Keq., higher will be the yield of Reaction.

- In case of endo. Rxn, yield will ↑ on increasing temperature (coz keq ↑).

* Application of Keq. :→

- Keq. is used in determination of,
  i) extent of Rxn
  ii) direction of Rxn
  iii) eq. conc. or partial pressure.

A] Extent of Reaction :→

$$R \rightleftharpoons P \qquad K_{eq} = \frac{[P]_{eq}}{[R]_{eq}} = 1000$$

$t=0$ 1001M 0

$t=t_{eq}$ 1 M 1000M

$$A \rightleftharpoons B \qquad K_{eq} = \frac{[B]}{[A]} = \frac{1}{1000} = 10^{-3}$$

$t=0$ 1001M 0

$t=t_{eq}$ 1000M 1M

if $K > 10^3$ ⇒ almost all reactant will get converted into product

if $K < 10^{-3}$ ⇒ negligible amt. of reactant will get converted into product

if $10^{-3} < K < 10^3$ ⇒ considerable amt.

Note: Coeff. of Reactants & product should be

B] Direction of Reaction :→

$R \rightleftharpoons P$ $K = 100 = \frac{[P]eq.}{[R]eq.}$

t = 0 10M 20M

Reaction quotient $= Q = \frac{[P]_t}{[R]_t} = \frac{20}{10} = 2$

if $Q < K \Rightarrow$ Rxn will move in forward direcⁿ
if $Q > K \Rightarrow$ " " " " backward "
if $Q = K \Rightarrow$ Rxn is at equilibrium.

C] Eq. conc. or partial pressure :→

Keq. helps in determination of Eq. conc. of partial pressures

Q. Calculate eq. conc. of $H_{2(g)}$, $I_2(g)$ and $2HI(g)$. If initially 2 moles of each $H_2(g)$ & $I_2(g)$ are taken in 10 L vessel.

$H_{2(g)} + I_2(g) \rightleftharpoons 2HI(g)$ $K = 100 = \frac{[HI]^2_{eq}}{[H_2]_{eq}[I_2]_{eq}}$

t = 0 0.2 M 0.2M 0

2 2 0

$\frac{2-x}{10}$ $\frac{2-x}{10}$ $\frac{2x}{10}$ $\therefore x =$ ~~8/x~~ $5/3$

$20 = 12x$

$[H_2]_{eq} = [I_2]_{eq} = \frac{2-5/3}{10} = 1/30\,M$

$[HI]_{eq} = \frac{1}{3}\,M$

b) In above problem if initially 5 moles of $HI(g)$ were taken then calculate eq. conc. of $H_2(g)$, $I_2(g)$ & $HI(g)$

$K = 100$

$$\longrightarrow \quad H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$\begin{array}{llll} t=0 & 0 & 0 & 5 \\ t=t & \frac{x/2}{10} & \frac{x/2}{10} & \frac{5-x}{10} \end{array}$$

$$100 = \frac{\left[\frac{5-x}{10}\right]^2}{\left[\frac{x/2}{10}\right]\left[\frac{x/2}{10}\right]} \Rightarrow x/2 = \frac{5-x}{10} \Rightarrow x = \frac{5-x}{5}$$

$$x = 5/6.$$

$[H_2]_{eq} = \frac{1}{24}\ M = [I_2]_{eq}$

$[HI]_{eq} = \frac{5-5/6}{10} = \frac{25}{60}\ M$

- if K is very small :-

Q. calculate eq. conc. of $PCl_5(g)$, $PCl_3(g)$ & $Cl_2(g)$ if initially only 1 mol of $PCl_5(g)$ is taken in 10 L vessel.

$$\longrightarrow \quad PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K = 10^{-5}$$

$$\begin{array}{llll} t=0 & 1 & 0 & 0 \\ & \frac{1-x}{10} & \frac{x}{10} & \frac{x}{10} \end{array}$$

$$\Rightarrow \frac{1}{10^5} = \frac{\left[\frac{x}{10}\right]^2}{\left[\frac{1-x}{10}\right]} \Rightarrow \frac{1-x}{10^6} = \frac{x^2}{100}$$

$$10^4 x^2 + x - 1 = 0$$

$$x = \frac{-1 \pm \sqrt{1+4\times10^4}}{2\times10^4} \Rightarrow x \approx \frac{1}{100}$$

if K is very large :

Q.

→ $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $K = 10^5$

t=0   1mol   0   0

t=t $\frac{1-x}{10}$ $\frac{x}{10}$ $\frac{x}{10}$

$\Rightarrow 10^5 = \frac{x^2/10^{\cancel{2}}}{1-x/\cancel{10}} \Rightarrow 10^6(1-x) = x^2$

$\Rightarrow x^2 + 10^6 x - 10^6 = 0$

$x = \frac{-10^6 \pm \sqrt{10^{12}+4\times10^6}}{2}$

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

t=0   1   0   0

t=t   0   1   1

t=teq $\frac{x}{10}$ $\frac{1-x}{10}$ $\frac{1-x}{10}$

$\Rightarrow 10^5 = \frac{1}{10}\times\frac{1}{10} / x/_{10} \Rightarrow x = 10^{-6}$

$\therefore [PCl_5]eq = 10^{-7}$ M

$[PCl_3]eq = 0.1$ M $= [Cl_2]eq$.

Q. If initially 0.11 M of A and 0.01M of B are taken then calculate equilibrium conc. of A & B.

V = 100

→ $C_{(s)} \rightleftharpoons B(aq) + A(g)$ $K = 10^{-8}$.

t=0   0   ~~0.01~~ 1   ~~0.11~~ 11

t=t $\frac{x}{100}$ $\frac{1-x}{100}$ $\frac{11-x}{100}$

10^{-7} 0.1

~~0.11~~

$10^{-6} = \frac{(1-x)(11-x)}{x}$

$\Rightarrow x10^{-6} = 11 - 12x + x^2$

$\Rightarrow x^2 - x(12 + \cancel{10^{-6}}) + 11 = 0$

$x = \frac{12+10}{2}$ $x = 11$

Q. If 1L of 0.4 M $AgNO_3$ is mixed with 1L of 4.4 M NH_3 (aq.) solution and following Rxn takes place

$$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) \quad K = 10^{10}$$

Find eq. conc. of Ag^+ (aq), NH_3 (aq.) & $Ag(NH_3)_2^+$ (aq.).

→ $Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.)$

	Ag^+	$2NH_3$	$Ag(NH_3)_2^+$
t=0	0.4	4.4	
t=t	x	3.6	0.4
t=teq.	x	3.6 + x	0.4 - x

$$\frac{0.4 - x}{(x)(3.6 + x)} = 10^{10} \quad \therefore x = \frac{1}{9} \times 10^{-9}$$

H.W.

Ex. 1 ⇒ 1 to 10.

Q1. In a vessel the following equilibrium is established.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

If initially the $CO_2(g)$ is taken at 10 atm with excess of C(s). $K_p = 100 \times 10^3$ calculate partial pressure of $CO(g)$

→ $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

	$C(s)$	$CO_2(g)$	$2CO(g)$
t=0		10 atm	
		10 - x	2x

$$10^3 \, \overset{25}{\cancel{100}} = \frac{4x^2}{10 - x}$$

$$10^3(250 - 25x) = x^2$$

$$x^2 + 25x - 250 = 0$$

$\underline{\underline{20}}$ atm.

V.D. of PCl_5 = 57.7

Q2. In 10L vessel NH_4HS (s) is taken & dissociates as

$$\underset{\substack{2\,mol \\ 2-x}}{NH_4HS_{(s)}} \rightleftharpoons \underset{x}{NH_{3}\,(g)} + \underset{x}{H_2S_{(g)}}$$

If 102 g of NH_4HS is taken at 300 K pressure developed If 50% of solid dissociates then calculate the value of K_p.

$$\longrightarrow \quad K_p = K_c\,(RT)^2$$
$$= 0.01 \times (0.0821 \times 300)^2$$
$$= (2.463)^2$$

Q3. Tor At 40°c & 2 atm pressure N_2O_4 (g) dissociates as

$$\underset{\substack{2\,atm \\ 10\,atm}}{\overset{a}{N_2O_4\,(g)}} \overset{0.25}{\rightleftharpoons} \underset{1}{2\,NO_2\,(g)}$$

(a) If degree of dissociation is 0.25 then find K_p.

$$\rightarrow \quad K_p = \frac{1}{1.5} = 2/3 \text{ atm}.$$

b) If pressure of reaction mixture becomes 10 atm, then what will be degree of dissociation.

$$\longrightarrow \quad \frac{2}{3} = \frac{4x^2}{10-x} \quad \Rightarrow 20 - 2x = 12x^2$$
$$\Rightarrow 10 - x = 6x^2 \Rightarrow 6x^2 + x - 10 = 0$$

* Relationship b/w $\underline{K_p}$, $\underline{K_x}$ and $\underline{P_{Total, eq}}$

* Degree of Dissociation :→ It represents the extent to which a particular compound dissociates into products.

- It is represented by "α".
- It is defined only when single reactant is present.

eg,

i) $$CaCO_{3}(s) \xrightleftharpoons{\alpha=0.2} CaO(s) + CO_{2}(g)$$

t=0 a=10 mol

$$10 - 10\times0.2 \qquad 10\times0.2 \qquad 10\times0.2$$

$$a - a\alpha \qquad a\alpha \qquad a\alpha$$

ii) $$PCl_{5}(g) \xrightleftharpoons{\alpha} PCl_{3}(g) + Cl_{2}(g)$$

$t=0$ a $-$ $-$

$t=t_{eq.}$ $a(1-\alpha)$ $a\alpha$ $a\alpha$ $n_T = a(1+\alpha)$

$$M_{avg.} = \frac{W_T}{n_T} = \frac{\cancel{a} \times M_T}{\cancel{a}(1+\alpha)} = \frac{208.5}{(1+\alpha)}$$

$$VD_{min} = \frac{M_{avg.}}{2}$$

q. If initially only $N_2O_4(g)$ is taken and it dissociates ~~to~~ 20% at equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate Mavg & VD of mixture.

→ $$M_{avg} = \frac{92}{(1+0.2)} = \frac{920}{12}$$

$$VD_{mix} = \frac{460}{12}$$

q. Write expression for total moles

a) $A(g) \overset{\alpha}{\rightleftharpoons} B(g) + 2C(g)$

$t=0$ a

$t=t$ $a(1-\alpha)$ $a\alpha$ $2a\alpha$ $n_t = a(1+2\alpha)$

b) $A(g) \overset{\alpha}{\rightleftharpoons} 2B(g) + 3(g)$

$t=0$ a

$t=t$ $a(1-\alpha)$ $2a\alpha$ $3a\alpha$ $n_t = a(1+4\alpha)$

c) $2A \overset{\alpha}{\rightleftharpoons} B + 3C$

$t=0$ a

$t=t$ $a(1-\alpha)$ $\frac{a\alpha}{2}$ $\frac{3a\alpha}{2}$ $n_t = a(1+\alpha)$

d) $3A \overset{\alpha}{\rightleftharpoons} B + 4C$

$t=0$ a

$t=t$ $a(1-\alpha)$ $\frac{a\alpha}{3}$ $\frac{4a\alpha}{3}$ $n_t = a + \frac{2}{3}a\alpha$

Q. Calculate DOD of $NH_{3}(g)$ if VD of mixture at eq. is 6.5 & initially only NH_3 was taken.

— $$2NH_{3}(g) \rightleftharpoons N_{2}(g) + 3H_{2}(g)$$

$t=0$ $\quad a$

$t=t$ $\quad a(1-\alpha) \qquad \frac{a\alpha}{2} \qquad \frac{3a\alpha}{2} \qquad n_t = a(1+\alpha)$

$13 = M_{avg}$.

$\Rightarrow 13 = \frac{17}{(1+\alpha)} \qquad \Rightarrow \alpha = 4/13$

For dissociation,

$$A_n \rightleftharpoons nA$$

$t=0$ $\quad a$

$t=t$ $\quad a(1-\alpha) \qquad na\alpha \qquad n_T = a(1-\alpha+n\alpha)$

$$M_{avg} = \frac{W_T}{n_T} = \frac{a \times M_T}{a(1-\alpha+n\alpha)}$$

$$\frac{M_T}{M_{avg}} = \frac{VD_T}{VD_{avg}} = 1+\alpha(n-1)$$

$$\alpha = \frac{M_T - M_{avg}}{M_{avg}(n-1)} \quad ; \quad \alpha = \frac{VD_T - VD_{avg}}{VD_{avg}(n-1)}$$

For association,

$$nA \rightleftharpoons A_n$$

$t = 0 \quad a$

$t = t \quad a - a\alpha \qquad \frac{a\alpha}{n} \qquad n_T = a\left(1 - \alpha + \frac{\alpha}{n}\right)$

$$M_{avg} = \frac{W_T}{n_T} = \frac{M_T}{(1 - \alpha + \alpha/n)}$$

$$\frac{VD_T}{VD_{min}} = \frac{M_T}{M_{avg}} = 1 + \alpha\left(\frac{1}{n} - 1\right)$$

$$\alpha = \frac{M_T - M_{avg}}{M_{avg}\left(\frac{1}{n} - 1\right)} \quad ; \quad \alpha = \frac{VD_T - VD_{min}}{VD_{min}\left(\frac{1}{n} - 1\right)}$$

* Relationship between K_P, K_x & $P_{Total\,eq}$:→

Case I : If $\Delta ng \neq 0$

$$A(g) \rightleftharpoons B(g) + C(g)$$

$t = 0 \quad a \qquad 0 \qquad 0$

$t = t \quad \frac{a(1-\alpha)}{a(1+\alpha)}P_T \qquad \frac{a\alpha}{a(1+\alpha)}P_T \qquad \frac{a\alpha}{a(1+\alpha)}P_T \qquad n_T = a(1+\alpha)$

$\qquad x_A P_T \qquad x_B P_T \qquad x_C P_T$

$$K_p = \frac{P_B \times P_C}{P_A} = \frac{x_B \times x_C}{x_A} \times P_T^{\,1}$$

$$\Rightarrow K_p = K_x \, P_T^{\,\Delta ng}$$

if $\Delta n_g \neq 0 \Rightarrow K_x$ will depend on temp. & $P_{Total\,eq}$.

Case II : If $\Delta n_g = 0$

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

$t=0$ $\quad a$

$t=t$ $\quad \frac{a(1-\alpha)}{a} \times P_T \qquad \frac{\frac{a\alpha}{2}}{a} \times P_T \qquad \frac{\frac{a\alpha}{2}}{a} \times P_T \qquad n_T = a$

$\qquad x_{HI} \cdot P_T \qquad x_{H_2} \cdot P_T \qquad x_{I_2} P_T$

$$K_p = \frac{x_{H_2} \cdot x_{I_2}}{x_{HI}^2} \Rightarrow K_p = K_x.$$

if $\Delta n_g = 0 \Rightarrow K_p = K_x \Rightarrow K_x$ will depend only on temp.

• Relationship b/w K_p, α & $P_{T\,eq}$:-

Case I : If $\Delta n_g \neq 0$

$$A_{(g)} \xrightleftharpoons{\alpha} B_{(g)} + C_{(g)}$$

$t=0$ $\quad a$

$t=t$ $\quad \frac{a(1-\alpha)}{a(1+\alpha)} P_T \qquad \frac{a\alpha}{a(1+\alpha)} P_T \qquad \frac{a\alpha}{a(1+\alpha)} P_T \qquad n_T = a(1+\alpha)$

$$K_p = \frac{\alpha^2}{1-\alpha^2} P_T$$

if $\Delta n_g \neq 0 \Rightarrow$ "α" depends on P_T & temp.
if $\Delta n_g \neq 0 \Rightarrow$ To determine K_p we need α & P_T

Case II : If $\Delta ng = 0$

$$\begin{array}{lcccc} & 2HI_{(g)} & \rightleftharpoons & H_{2(g)} & + \; I_{2(g)} \\ t=0 & a & & & \\ t=t & \frac{a(1-\alpha)}{a}.P_T & & \frac{a\alpha}{a.2} P_T & \frac{a\alpha}{a.2} P_T \end{array} \qquad n_T = a$$

$$K_p = \frac{\alpha^2}{4(1-\alpha)^2}$$

if $\Delta ng = 0 \Rightarrow$ 'α' depends only on temp.

if $\Delta ng = 0 \Rightarrow$ To determine K_p we need α only

- Relationship b/w K_c, α and Volume (V) :→

Case I : If $\Delta ng \neq 0$

$$\begin{array}{lcccc} & A_{(g)} & \rightleftharpoons & B_{(g)} & + \; C_{(g)} \\ t=0 & a & & 0 & 0 \\ t=t & \frac{a(1-\alpha)}{V} & & \frac{a\alpha}{V} & \frac{a\alpha}{V} \end{array} \qquad n_T = a(1+\alpha)$$

$$\boxed{K_c = \frac{a\alpha^2}{V(1-\alpha)}}$$

To determine K_c, we need a, α & V

Case II : If $\Delta n_g = 0$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$t = 0$ $\quad a$

$t = t$ $\quad \frac{a(1-\alpha)}{v} \qquad \frac{a\alpha}{2V} \qquad \frac{a\alpha}{2V}$

$$\Rightarrow \boxed{K_c = K_p = \frac{\alpha^2}{4(1-\alpha)^2}}$$

To determine K_c we only need 'α'.

Q. At a given temp. $PCl_5(g)$ dissociates 20% at 4 atm eq. pressure. Calculate the pressure at which PCl_5 dissociated by 50% at same temp.

$\longrightarrow$ ~~K_p~~ $\Rightarrow$ $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$t = 0$ $\quad a \qquad 0 \qquad 0$

$t = t$ $\quad \frac{a(1-\alpha)}{a(1+\alpha)} P_T \qquad \frac{a\alpha}{a(1+\alpha)} P_T \qquad \frac{a\alpha}{a(1+\alpha)} P_T$

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P_T$$

$$K_p = \frac{0.04}{0.96} \times 4 = \frac{16}{96} = \frac{0.25}{0.75} \times P_T$$

$$= \frac{1}{6} = \frac{1}{3} \times P_T$$

$$\therefore P_T = 0.5 \text{ atm}$$

Q. Calculate Kp from given data :

**

$$\overset{2}{NH_2COONH_4}(s) \rightleftharpoons \underset{2p}{\overset{4}{2NH_{3(g)}}} + \underset{p}{\overset{2}{CO_2}}(g)$$

If total pressure at eq. was found to be 6 atm.

→ ~~Kp~~ = ~~α~~ $2p + p = 6$

$$K_p = P^2_{NH_3} \times P_{CO_2}$$

$$= 4p^2 \times p = 4p^3 = \underline{\underline{32}}$$

Q. At a given temp. DOD of HI is 0.2 . Calculate the no. of moles of each substance if 2 moles of each $H_2(g)$ & $I_2(g)$ are added to 10L vessel at same temp.

$$K_p = K_c = \frac{\alpha^2}{4(1-\alpha)^2}$$

→ $2HI_{(g)} \underset{}{\overset{0.2}{\rightleftharpoons}} H_{2(g)} + I_{2(g)}$

$$K_c = \frac{0.04}{4 \times 0.64}$$

$t = 0$ $\quad 0 \quad 2 \quad 2$

$t = t_{eq.}$ $\quad 0.4x \quad 2-(0.2)x \quad 2-(0.2)x$

$\therefore 0.2, 0.4, 0.4$

$K_c =$

Q. A mixture of SO_2, SO_3 & O_2 gases is maintained in a 10L flask at a certain temp.

$$2SO_{2}(g) + O_{2}(g) \rightleftharpoons 2SO_{3}(g) \quad K_c = 100$$

If the no. of moles of $SO_2(g)$ & $SO_3(g)$ in flask at eq. are equal, then how many moles of O_2 are present at eq.

$\longrightarrow$ $2SO_{2}(g) + O_{2}(g) \rightleftharpoons 2SO_{3}(g)$

$K_c = 100 = \dfrac{[\cancel{SO_3}]^2}{[\cancel{SO_2}]^2 \cdot [O_2]}$ $\Rightarrow$ moles of O_2 = $\underline{\underline{0.1}}$.

Q. Consider the following equilibria at 300 K

$$\overset{2}{2A}(g) + \overset{0.05}{H_2O}(g) \rightleftharpoons \overset{2}{C}(g) + \overset{2}{3D}(g) \quad K_p = 3\times10^{22}\ \text{atm}$$

The equilibrium was attained in a container by taking A, C & D at partial pressure of 2 atm each along with large amt. of liquid water. If VP of water at 300 K is $\frac{38}{760} = 0.05$ atm then calculate pp of A when equilibrium gets estab..

$\rightarrow$ K_p = 3×10^{22} = ~~$\frac{[illegible]}{4\times 0.05}$~~ $\quad K_p = K_x \times P_T^{\Delta ng}$

$2A$	$+ H_2O$	$\rightleftharpoons$ $C(g)$	$+ 3D(g)$
2	0.05	2	2
0	0.05	3	5
2p	0.05	3−p	5−3p

$\Rightarrow 3\times10^{22} = \dfrac{(5-3p)^3 \cdot (3-p)}{(2p)^2 \times 0.05}$

Q. For the rxn

$3p = 6$

$$A_{(g)} \rightleftharpoons 2B_{(g)}$$

$p \qquad 2p$

The equilibrium PP of A & B are 4 bar & 2bar respectively. If the equilibrium mixture is slowly & isothermally compressed to 12 bar maintaining equilibrium then the new equi. pressure (in bar) of B(g) becomes ___ ?

[Take $\sqrt{184} = 13.5$]

$$\longrightarrow \quad K_p = \frac{P_B^2}{P_A} = \frac{4}{4} = 1 = \frac{(P^2}{12-P}$$

$$\Rightarrow P^2 + P - 12 = 0$$

$$\Rightarrow P = \underline{3}$$

H.W.

Ex.2 ⇒ 1, to 22

R.B. ⇒ 1 to 4, 6, 7, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27,

DPP # 23, 24

* Le-Chatelier's Principle :→

Accⁿ to it, if a system at equilibrium is subjected to a change in concentration, partial P., volume or temp. then system will move in a direction where it can nullify effect of change.

We will study effect of

i) change in conc.

ii) change in total pressure at eq.

iii) Addition of inert gas

iv) Addition of catalyst
v) Change in temp.

- Effect of change in concentration :→

If this rea^n is carried out in 1 L container

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

$t = t_{eq}$ 10 M   20 M   20 M $K_c = \frac{20 \times 20}{10} = 40$

if we add 10 mol of Cl_2

$t = t$ 10 M   20 M   30 M $Q_c = \frac{30 \times 20}{10} = 60$

if we add 10 mol of PCl_5

$t = t$ 20 M   20 M   20 M $Q_c = 20$ M

if $Q < K \Rightarrow$ Rxn will move in forward direc^n
if $Q > K \Rightarrow$ Rxn will move in backward dire^n

Q. For the given rxn no. of moles at eq. of A, B, C & D are found to be 4, 4, 2, & 8 resp. in 1 L cont. If 18 mol of D are added, calculat no. of moles of A, B, C & D at new eq.

→ $A + B \rightleftharpoons C + D$ $K_c = 1$ $\frac{(26-x)(2-x)}{(4+x)(4+x)} = 1$

4   4   2   8

4   4   2   26 $Q_c = \frac{52}{16}$

$4+x$ $4+x$ $2-x$ $26-x$

18   18   [illegible]   [illegible]

- In above case we added 18 moles by but only 1 mole was reacted. So compensation is not 100%.

But for the following Rxn compensation will be 100%.

$$\overset{\leftarrow 1\,Mol}{}$$

$$A_{(s)} \rightleftharpoons \underset{\underset{\curvearrowleft\ 3M}{2M}}{B_{(aq)}} \qquad K_c = 2$$

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)} \qquad K_c = [CO_2]$$

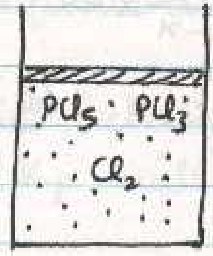
$$K_p = P_{CO_2}$$

- Effect of change in Total pressure at Eq. :-

- If total pressure is changed by changing volume of container

$$PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$



$$P_{PCl_5} = n_{PCl_5} \times \frac{RT}{V}$$

$$P_{PCl_3} = n_{PCl_3} \times \frac{RT}{V}$$

$$P_{Cl_2} = n_{Cl_2} \times \frac{RT}{V}$$

$$P_T = n_T \times \frac{RT}{V}$$

- if total pressure of system is ↑ by decreasing volume then system will try to ↓ total pressure by moving in a direcⁿ where total gaseous moles are less.

Q. For the rxn,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

The no. of moles at eq. was found to be 2, 6 & 4 resp. at 10 atm pressure. Calculate new eq. partial pressure & no. of moles if eq. is establishd at a total pressure of 50 atm.

→ [illegible] = [illegible] * $K_p = 1$[illegible]2

$x^2 - 10x + 24 = 120 + 60x$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \frac{(4-x)(6-x)}{(2+x)5} = 10$$

52.84

$x^2 - 70x - 96 = 0$

$\frac{2\overset{x}{\uparrow}}{5} \qquad \frac{6-x}{5} \qquad \frac{4-x}{5}$

$$\xrightarrow{\quad x \quad}$$

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \Rightarrow K_p = 10$$

$\frac{2}{12} \times 10 \qquad \frac{6}{12} \times 10 \qquad \frac{4}{12} \times 10$

$\frac{2+x}{12-x} \times 50 \qquad \frac{6-x}{12-x} \times 50 \qquad \frac{4-x}{12-x} \times 50$

$$\Rightarrow 10 = \frac{(6-x)(4-x) \times 50}{(12-x)(2+x)} \quad ; x = 2$$

At new eq. 20 atm 20 atm 10 atm

At old eq. 1.67 atm 5 atm 3.33 atm

At new eq.		At old eq.
P_{PCl_5}	>	P_{PCl_5}
P_{PCl_3}	>	P_{PCl_3}
P_{Cl_2}	>	P_{Cl_2}
$[PCl_5]$	>	$[PCl_5]$
$[PCl_3]$	>	$[PCl_3]$
$[Cl_2)$	>	$[Cl_2]$

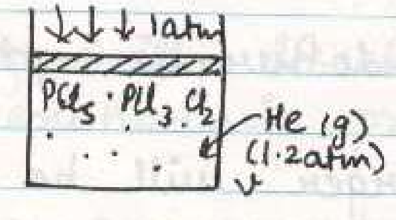
- Values of P.P. & conc. at new eq. are greater than their values at previous equilibrium. So we can say, effect of volume will dominate. Coz volume was ↓ as a result, P.P. & conc are higher.

- **Addition of Inert Gas :→**

Inert gas can be added under two conditions
- At constant volume
- At constant pressure.

i) **At constant Volume :→**

If inert gas is added at constant volume, then there will be no effect on equilibrium



As volume will not change, PP wont, hence K_p will be constant.

ii) **At constant Pressure :→**

If inert gas is added at constant pressure, then rxn will move in a direction where total no. of gaseous moles are more.

- **Effect of Temperature** :→

On changing temp., value of eq. constant (Keq.) changes.

$$A \underset{exo}{\overset{endo}{\rightleftharpoons}} B + C \qquad K_{eq.} = \frac{[B][C]}{[A]}$$

For endothermic Rxn,
if temp. ↑

$$\ln \frac{KT_2}{KT_1} = \underbrace{\underset{\oplus}{\frac{\Delta H}{R}} \underset{\oplus}{\left(\frac{T_2 - T_1}{T_1 T_2} \right)}}_{\oplus} \Rightarrow \frac{KT_2}{KT_1} > 1$$

$$\Rightarrow \boxed{K_{T_2} > K_{T_1}}$$

* For endo. rxn, on ↑ temp. value of Keq. increases. It means rxn will move in direction of product.

* Increase in temp. favours endothermic process.

* Larger the value of "Keq." larger will be the yield of rxn, so, on ↑ temp. we can say yield of endothermic rxn will ↑.

* On ↑ temp., rate of forward as well as backward rxn will ↑.

* All dissociation Reactions are endothermic.

$$\left.\begin{aligned} &PCl_5(g) \xrightleftharpoons[\text{exo}]{\text{endo}} PCl_3(g) + Cl_2(g) \\ &N_2O_4(g) \xrightleftharpoons[\text{exo}]{\text{endo}} 2NO_2(g) \end{aligned}\right\} \begin{array}{l} \Delta H = +ve \\ \text{endothermic} \end{array}$$

$$\left.\begin{aligned} &N_2(g) + 3H_2(g) \xrightleftharpoons[\text{endo}]{\text{exo}} 2NH_3(g) \\ &H_2(g) + I_2(g) \xrightleftharpoons[\text{endo}]{\text{exo}} 2HI(g) \end{aligned}\right\} \begin{array}{l} \Delta H = -ve \\ \text{exothermic} \end{array}$$

* All combustion rxn are exothermic except combustion of nitrogen.

$$\left.\begin{aligned} &CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l) \\ &CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g) \end{aligned}\right\} \begin{array}{l} \Delta H = -ve \\ \text{exothermic} \end{array}$$

* Generally dissolution of gas in water is exothermic process.

$$\text{gas} + \text{water} \xrightleftharpoons[\text{endo}]{\text{exo}} \text{Solution}$$

$$O_2(g) + H_2O(l) \xrightleftharpoons[\text{endo}]{\text{exo}} O_2(aq.)$$

* Solubility of salt in water can be endothermic or exothermic.

If solubility is endothermic it means on ↑ temp. solubility will ↑

$$CaCl_2(s) + H_2O \xrightleftharpoons[\text{exo}]{\text{endo}} Ca^{2+}_{(aq.)} + 2Cl^-_{(aq.)}$$

H.W.
DPP #25
Ex. 1 ⇒ 39 to 51

Ex. 2 ⇒ 23 to 39, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52

* Dissolution of sugar in water is endothermic process.

• Effect of Catalyst :→

Catalyst ↑ the rate of forward as well as backward rxn to the same extent by providing an alternative path with lower activation energy. But it does not alter eq. conc., P.P. or K eq.

* Phase Diagram of Water :→

Evaporation

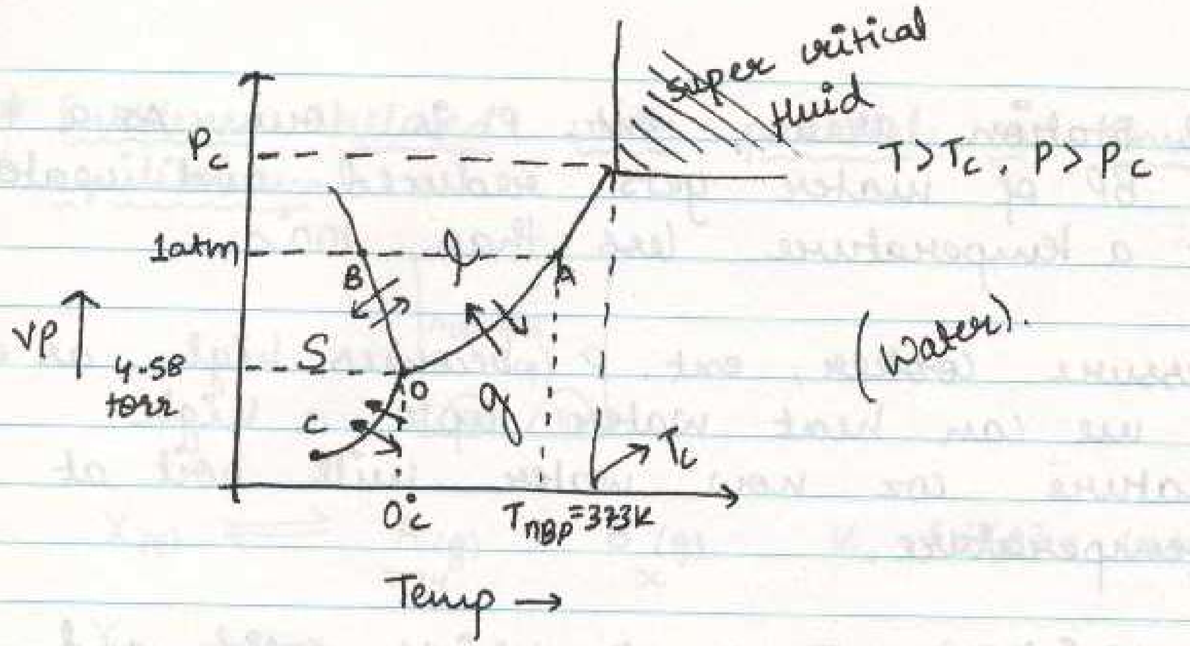
$H_2O(l) \overset{endo}{\rightleftharpoons} H_2O(g) \quad K_p = P_{H_2O} = VP$

Sublimation

$H_2O_{(s)} \overset{endo}{\rightleftharpoons} H_2O_{(g)} \quad K_p = P_{H_2O} = VP$

Fusion

$H_2O_{(s)} \overset{endo}{\rightleftharpoons} H_2O(l)$



where

OA → represents eq. b/w liquid & gas
OB → " " " solid & liquid
OC → " " " solid & gas
O → Triple point

- Triple Point :→ Point at which all 3 phases i.e. solid, liquid & gas are in equilibrium with each other.

- Boiling Point :→ It is the temperature at which VP of liquid becomes equal to external pressure.
  - If ext. P is 1 atm → Normal BP
  - If ext. P is 1 bar → Standard BP
  - As P ext. ↑, BP ↑

Q. Normal BP of water will be always greater than standard BP of water.

→ True.

H.W Ex.1, Ex.2, Ex.3(A)

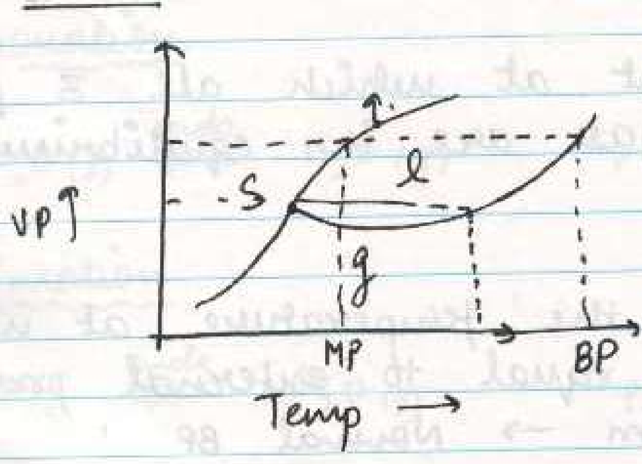
- In hill station areas, ext. P is low. As a result BP of water gets reduced and water boils at a temperature less than 100°C.

- In Pressure cooker, ext. P becomes high as a result we can heat water upto a high temperature coz now water will boil at high temperature.

- **Melting Point** :→ Temp. at which solid and liquid are in equilibrium.

  - On ↑ $P_{ext.}$ MP of water ↓

For CO_2



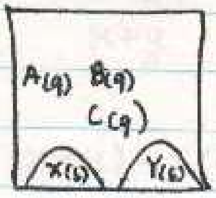
$CO_2(s) \rightleftharpoons CO_2(l)$

on ↑ P, rxn will move in backward direction i.e. solid will be formed.

- On ↑ $P_{ext.}$, rxn will move in a direction where density is more.

  If we ↑ P, then constituent particles will move in a direcⁿ where they can settle in less volume.

* Problems related with parallel or simultaneous equilibrium :-



$$X_{(s)} \rightleftharpoons \underset{x+y}{A_{(g)}} + \underset{x}{B_{(g)}} \qquad K_c = [A][B] = (x+y)x$$

$$Y_{(s)} \rightleftharpoons \underset{x+y}{A(g)} + \underset{y}{C(g)} \qquad K_c = [A][C] = (x+y)y.$$

Q. Two solids X & Y dissociates into gaseous products at certain temperature as follows in separate vessels :

$$X(s) \rightleftharpoons \underset{P_1}{A(g)} + \underset{P_1}{C(g)} \qquad K_{P_1} = P_1^2 = 400$$

$$\Rightarrow 2P_1 = 40$$

$$Y(s) \rightleftharpoons B(g) + C(g) \qquad K_{P_2}$$

At given temperature, pressure over excess solid X is 40 mm & total pressure over solid Y is 60 mm. Calculate

a) Values of K_{P_1}, K_{P_2} (in mm of Hg)

b) The ratio of moles of A & B in vapor state over mixture of X & Y.

c) Total pressure of gases over a mixture of X & Y.

→ $K_{P_1} = 400$ mm ; $K_{P_2} = 900$ mm

b) → $K_{p_1} = (P_1+P_2)\cdot P_1 = 400$

$K_{p_2} = (P_1+P_2)\cdot P_2 = 900$

$\therefore$ ratio $= 4/9$

c) → $P_T = P_A + P_B + P_C$

$= P_1 + P_2 + P_1 + P_2 = 2(P_1+P_2) = 2\sqrt{1300}$ torr.

* Problems related with sequential Equilibrium :→

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)} \qquad K_{c_1} = \frac{x(x-y)}{a-x}$$

$t=0 \quad a$

$t=t \quad a-x \qquad x \qquad x-y$

$$C_{(g)} \rightleftharpoons D_{(g)} \qquad K_{c_2} = \frac{y}{x-y}$$

$x-y \qquad y$

Q. When 1 mol of $A_{(g)}$ is introduced in a closed rigid 1L vessel maintained at constant temp. the following equilibria are established.

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)} \qquad K_{c_1}$$

$$C_{(g)} \rightleftharpoons B_{(g)} + D_{(g)} \qquad K_{c_2}$$

The pressure at eq. is twice the initial pressure calculate $\frac{K_{c_2}}{K_{c_1}}$ if $\frac{[C]_{eq}}{[B]_{eq}} = \frac{1}{5}$

$$\rightarrow \quad \underset{1-x}{A_{(g)}} \rightleftharpoons \underset{x+y}{B_{(g)}} + \underset{x-y}{C_{(g)}} \qquad K_{c_1} = \frac{(x+y)(x-y)}{1-x}$$

$$\underset{x-y}{C_{(g)}} \rightleftharpoons \underset{x+y}{B_{(g)}} + \underset{y}{D_{(g)}} \qquad K_{c_2} = \frac{(x+y)\,y}{x-y}$$

$$2 = (1-x) + (x+y) + (x-y) + y$$

$$\Rightarrow x+y = 1$$

$$\frac{x-y}{x+y} = \frac{1}{5}$$

$$\frac{K_{c_1}}{K_{c_2}} = \frac{(x-y)^2}{y(1-x)} = \underline{4}$$

* Production of ammonia :→

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe(s)} 2NH_{3}(g) \qquad \Delta H = -ve$$

In production of ammonia, high pressure is favourable for production of NH_3. & low temperature is favourable.
But if we keep temperature low then r_f as well as r_b will be very low. To rectify this problem, we use iron as catalyst.

Function of catalyst :→

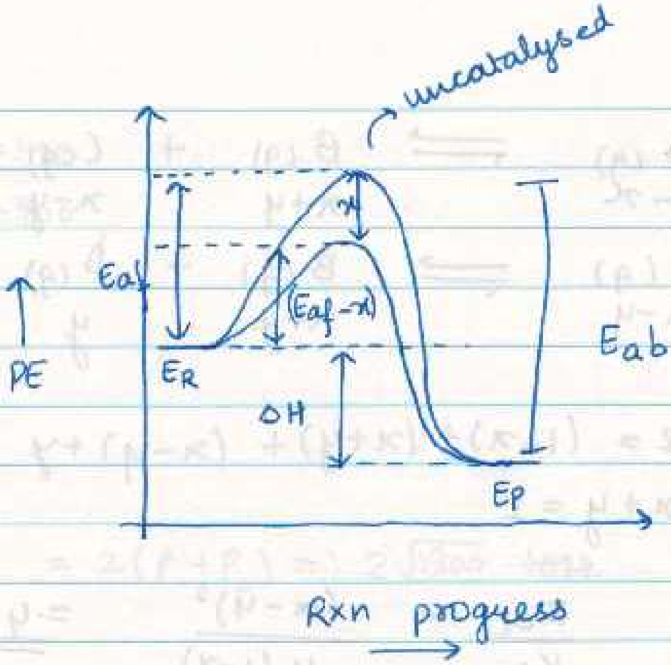
Catalyst ↑ the rate of forward rxn as well as backward rxn to the same extent as a result K_{eq} remains unchanged.

Uncatalysed Rxn :→

$$R \rightleftharpoons P$$

Catalysed Rxn :→

$$R \underset{}{\overset{\text{catalysed}}{\rightleftharpoons}} P$$



Uncatalysed,

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = A e^{-(E_{af}-E_{ab})/RT} = \frac{[P]_{eq}}{[R]_{eq}}$$

$$K_{eq} = A e^{-\Delta H/RT} \quad \text{— ①}$$

Catalysed,

$$K_{eq} = \frac{k_f'}{k_b'} = \frac{A_f e^{-(E_{af}-x)/RT}}{A_f e^{-(E_{ab}-x)/RT}} = \frac{A_f e^{-E_{af}/RT} e^{x/RT}}{A_f e^{-E_{ab}/RT} e^{x/RT}}$$

$$K_{eq} = A e^{-\Delta H/RT} \quad \text{—②}$$

Note : ① = ② but rate ↑ (by factor $e^{x/RT}$).

- Catalyst cannot alter ΔH, ΔG or K_{eq}.
- catalyst does not alter eq. conc. or eq. partial pressure.

- Catalyst can increase rate of spontaneous rxn but it cannot turn a non-spontaneous rxn into spontaneous rxn.

- Catalyst participates in the rxn qualitatively not quantitavely.

Q. 0.4 mol each of $A_{2}(g)$ and $B_{2}(g)$ are introduced in a sealed flask and heated 3000 K where following equilibrium was established :

$$A_{2}(g) + B_{2}(g) \rightleftharpoons 2AB(g)$$

At equilibrium mole % of AB was found to be 50
At equilibrium 0.4 mol of C_2 are added which reacts with A_2 to establish another equilibrium

$$A_{2}(g) + C_{2}(g) \rightleftharpoons 2AC(g)$$

At new eq. mol % of AB becomes $\frac{16}{1.2}$ %. Find
a) Keq for I Rxn = 4
b) Keq for II Rxn = 1

→ $A_2 + B_2 \rightleftharpoons 2AB$

$0.4-x \quad 0.4-x \quad 2x$

$0.2+y-y' \quad 0.2+y \quad 0.4-2y$

$A_2 + C_2 \rightleftharpoons 2AC$

$0.2-y' \quad 0.4-y' \quad 2y'$
$+y$

$\frac{2x}{0.8} \times 100 = 50 \Rightarrow x = 0.2$

$\frac{\overset{0.4}{\cancel{0.4}} - 2y}{1.4} = \frac{16}{120}$

$48 - 240y = 22.4$

$y = \frac{25.6}{240}$