DIAS

All India TEST – SERIES CSE – 2024

Physical – 1

Syllabus -: Atomic structure, chemical bonding, liquid state, solid state, gaseous state

Instructions:-

1. Attempt five questions selecting atleast one question each section. apart from question 1&5 which is compulsory.
2. Write answer in space provided for this purpose only.
3. Total time allowed is 3hr and Marks is 250.

Information:

Name of student:- AAYUSH SAINI

UPSC Roll no:- 0841601

Mobile Number. [redacted]

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	21	6	36	31	34	6	32	33

Signature of invigilator

V. Gupta

156/250

Signature of Examiner

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Physical – I

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MARKS	21	16	35	28	37	16	32	23

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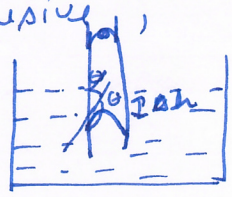
SECTION- A

1.(a) When an electron was accelerated through a potential difference of 1.00 ± 0.01 kilovolt, what is the uncertainty of position of the electron along its line of projection? **(10)**

(b) . How far will the mercury level be depressed when a glass capillary with 0.40 mm. radius is placed in a dish of mercury? Given the surface tension of liquid mercury is 0.90 N m and its density is 13.6×10^3 kg m^{-1}. **(10)**

When a capillary is dipped in Mercury, two forces $F_{cohesion}$, $F_{adhesion}$ acts.

Since in mercury $F_{cohesive} > F_{adhesive}$, Mercury level falls in capillary



Considering, h = height mercury falls

r = radius of capillary = 0.4 mm

γ = surface tension = 0.9 N/m

ρ = density = 13.6×10^3 Kg/m^3

θ = Angle of contact

Equating – Upward force due to surface tension = weight of the column gone down

$$\gamma(2\pi r)\cos\theta = \pi r^2 h \rho g$$

$$h = \frac{2\gamma\cos\theta}{\rho g r}$$

~~Sin~~ Considering $\theta = 180°$ (as mercury level falls)

$$h = -\frac{2\gamma}{\rho g r}$$

7/8

$$h = \frac{-2(0.90\ N/m)}{(13.6\times10^3\ kg/m^3)(9\ m/s^2)(0.4\times10^{-3}\ m)}$$

$$= -3.37\times10^{-2}\ m = -3.37\ cm$$

Thus the mercury level drops by $\boxed{3.37\ cm}$

(c) The density of Li metal is 0.53 g cm^{-3} and the separation of the (100) plans of the metal is 350 pm. Determine whether the lattice is f.c.c or b.c.c M(Li) = 6.941 g mol-1 **(10)**

Since, wavelength of X-ray lies in range $10^{-10} - 10^{-12}$ cm, which is equivalent to size of an atom, it is used to determine the position of atoms.

given that $(hkl) = (100)$

d (separation of planes) = 350 pm

Let a = side of a unit cell

$$\frac{1}{d^2_{hkl}} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

where h, k, l = miller indices

a = b = c (for cube)

$\therefore d_{hkl} = a = 350$ pm —(i)

given that $\rho = 0.53 g/cm^3$ (density)

M = 6.941 g/mol (molar mass)

Z = number of atoms per unit cell

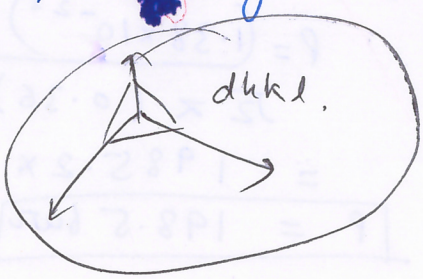
we know, $\rho = \frac{ZM}{N_0 a^3}$ where $N_0 = 6.022 \times 10^{23}/mol$

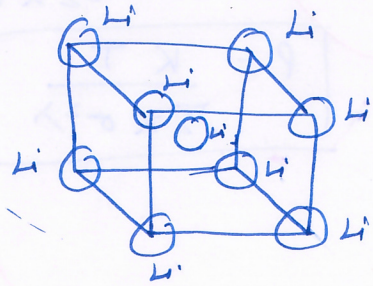
$$(0.53 g/cm^3) = \frac{Z\,(6.941 g/mol)}{(6.022 \times 10^{23}/mol)\,(350 \times 10^{-10} cm^3)}$$

$Z \simeq 1.97$

$\boxed{Z \simeq 2}$

Thus, Li is arranged in $\boxed{BCC}$ lattice

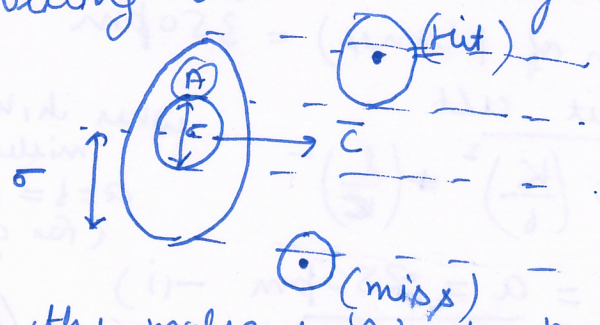




(d) At what pressure does the mean free path of argon at 25° C become comparable to the diameter of the atoms themselves? Given $\sigma = 0.36\ nm^2$. **(10)**

Mean free path is the total distance travelled by the molecule in motion between two subsequent collisions

Let us take a molecule of diameter σ, travelling with a average velocity $\bar{c}$.



Thus the molecule 'A', to prevent collision draws a cylinder of radius 'σ'.

volume swept/sec $= \pi \sigma^2 \bar{c}$

No. of molecules undergoing collision $= \pi \sigma^2 \bar{c} N_A^*$

Taking relative motion consideration $\boxed{\text{where } N_A^* = \frac{N_A}{\text{Volume}}}$

Z_1 (collision number) $= \sqrt{2} \pi r^2 \bar{c} N_A^*$

Since λ (mean free path) $= \frac{\bar{c}}{Z_1} = \frac{1}{\sqrt{2} \pi \sigma^2 N_A^*}$ —(i)

Assuming ideal gas behaviour

$PV = \frac{N}{N_A} RT \Rightarrow P = N_A^* KT$ —(ii)

$N_A^* = \frac{P}{KT}$ —(iii)

Using equation (iii) in (i)

$\lambda = \frac{KT}{\sqrt{2} \pi \sigma^2 P}$

$\boxed{P = \frac{KT}{\sqrt{2} \pi \sigma^2 \lambda}}$

given $\lambda = \sigma = 0.36\ nm$

$P = \frac{(1.38 \times 10^{-23})(298\ K)}{\sqrt{2} \pi (0.36)^2 (10^{-18})(0.36)(10^{-9})}$

$= 1985.2 \times 10^4$ Pascals

$\boxed{P = 198.5\ bar}$

(e) Explain on the basis of MO theory, why:

i) Liquid oxygen sticks to the poles of a magnet while liquid nitrogen does not do so.

ii) He_2 and Be_2 molecules do not exist.

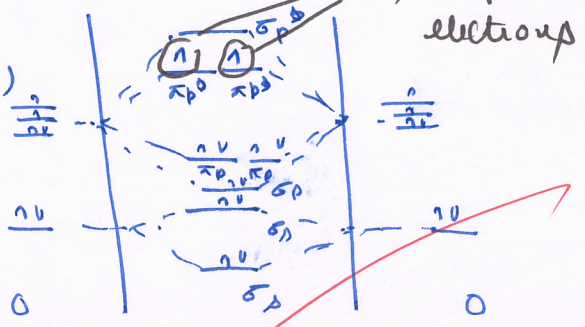
iii) The bond order in oxygen is 2, while that of nitrogne is 3.

iv) Hydronge molecule is more stable than H_2^+ ion. **(10)**

MO Theory is based on mixture of all the orbitals of atoms to form equal number of Bonding and Antibonding orbital. The theory is provided by $\boxed{\text{Pauling}}$

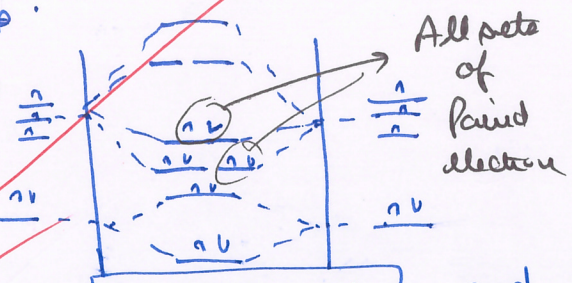
(i) Magnetic property depends on number of unpaired electrons using $\boxed{\text{MOT}}$.

O_2 (MOT)



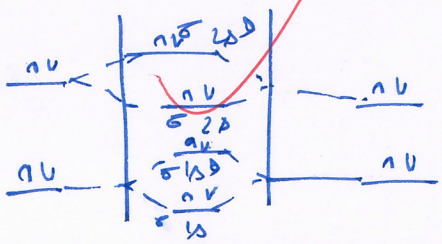
~~Since tab~~

N_2 (MOT)



Thus O_2 is $\boxed{\text{Paramagnetic}}$ and sticks to poles and N_2 is $\boxed{\text{Diamagnetic}}$, does not do so

(ii) Be_2 ($Be = 1s^2\ 2s^2$)

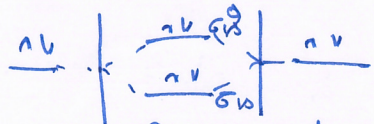


Bond Order $= \boxed{\left(\frac{N_{BMO} - N_{ABMO}}{2}\right)}$

$= \frac{4-4}{2} = \boxed{0}$

For Be_2

$Be = 1s^2$



Bond order $= \frac{2-2}{2} = \boxed{0}$

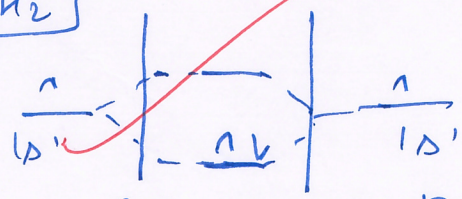
$\therefore$ Both have Bond order $= 0$

(iii) From MOT diagram of ~~part~~ (i)

$B.O_{(O_2)} = \frac{8-4}{2} = 2$

$B.O_{(N_2)} = \frac{8-2}{2} = 3$

(iv) H_2 $\quad H = 1s^1$



$B.O_{(H_2)} = \frac{2-0}{2} = 1$

For H_2^+ $\quad B.O = \frac{1-0}{1} = 0.5$

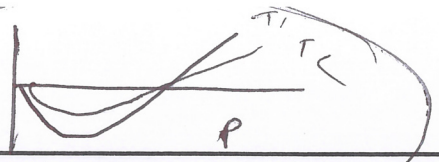
Thus $\boxed{B.O\ H_2 > B.O\ H_2^+}$

H_2 is more stable

2.(a) An atom makes a transition from an excited state with lifetime of 1 ns to the ground state by emitting a photon of wave length 600 nm. Calculate the uncertainty in the energy of the excited state. Also calculate the percentage uncertainty if the energy is measured from the ground state. **(20)**

Define

Provide for require of virial eqn



3(a) Derive virial equation of state starting from Vanderwall equation of state. **(10)**

Vanderwaal equation is given by (for real gases)

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad -(i)$$

where,
P = Pressure
a = Pressure correction factor
V_m = Molar volume
b = Volume correction factor
R = gas Constant
T = Temperature.

$$\left(P + \frac{a}{V_m^2}\right) = \left(\frac{RT}{V_m - b}\right)$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\frac{PV_m}{RT} = Z = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

where Z = Compressibility factor

$$Z = \left(\frac{1}{1 - b/V_m}\right) - \frac{a}{V_m RT}$$

Since $b << V_m$

$$\therefore Z = \left(1 - b/V_m\right)^{-1} - \frac{a}{V_m RT}$$

$$= \left[1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 - - -\right] - \frac{a}{V_m RT}$$

$$= \cancel{1 + b} \quad 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + - - -$$

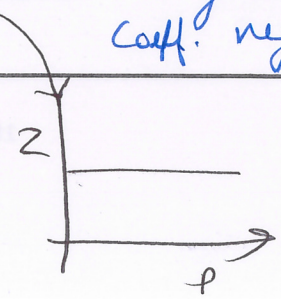
$$\boxed{Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} - - -}$$

where $B, C, D - -$ are virial coefficients

where $B = b - \frac{a}{RT}$, $C = b^2$, $D = b^3$ and so on

Further, virial equation can be utilized to derive Boyle's Temp.
(Temp. at which Real gas behaves as ideal)

With $B = 0 = b - \frac{a}{RT} \Rightarrow \boxed{T = \frac{a}{Rb}}$, Considering higher order coeff. negligible.

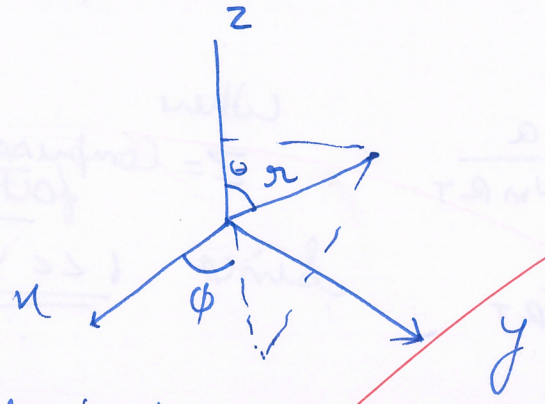


(b) Give the schrodinger's wave equation for H-atoms in cartesian and polar co – ordinates. With the helps of a diagram show the relation between the two coordinates. **(10)**

In ~~Polar~~ Cartesian Coordinates

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

where
- ψ = wave function
- m = mass of molecule
- E = Total Energy
- V = Potential Energy



Coordinates:

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

{Provide range}
$0 < r < \infty$
$0 < \theta < \pi$
$0 < \phi < 2\pi$

$\tan\phi = y/x$

Shrodinger Equation in Polar coordinates

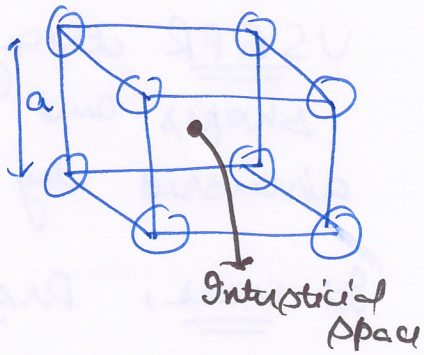
$$\psi = R\Theta\Phi$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta\sin\theta}\frac{\partial(\Theta\sin\theta)}{\partial\theta} + \frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} + \frac{8\pi^2 r^2 m}{h^2}(E-V) = 0$$

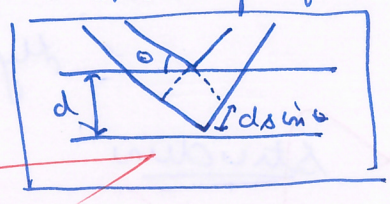
From this ψ can be derived which is used to ~~get~~ determine the position of wave function.

(c) In a certain material of simple cubic structure, (100) diffraction is obtained at $\Theta = 24.88^0$ with radiation of $\lambda = 1.541$ Å. Can this material accommodate an atom of 1.68 Å radius interstitially in void space without lattice distortion? **(10)**

Since, X-ray wavelength lies in range $10^{-10} - 10^{-12}$ m, it is utilized to determine lattice structure. Formula for which is provided by Bragg's equation



$$\boxed{n\lambda = 2d\sin\theta}$$, where λ = wavelength, d = distance between planes, θ = Angle of reflection, n = order of reflection



determining d_{hkl},

$$\lambda = 2\left(\frac{d}{n}\right)\sin\theta$$

$$\lambda = 2d_{hkl}\sin\theta$$

$$d_{hkl} = \frac{\lambda}{2\sin\theta} = \frac{(1.541)\text{ Å}}{2(\sin 24.88^\circ)}$$

$$\boxed{d_{hkl} = 1.83\text{ Å}}$$

Since $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ a = side of a unit cell, h, k, l = miller indices.

$$d_{hkl} = \frac{a}{\sqrt{1+0+0}} \Rightarrow \boxed{a = 1.83\text{ Å}}$$

Finding size of Interstitial void

Since $\cancel{\frac{\sqrt{3}a}{2}}$ $2r_a = a$

$$r_a = \frac{a}{2} = 0.915\text{ Å}$$

Also, $\frac{\sqrt{3}}{2}a = r_a + r_v \Rightarrow r_v = \frac{\sqrt{3}}{2}(1.83) - (0.915)$

$$\boxed{r_v = 0.67\text{ Å}}$$ = radius of void

Since $r_v < 1.68$ Å (It cannot be accomodated)

{ Provide for radius ratio also }

(d) Using VSEPR theory, predict the shapes of pCl_2F_3 and SF_4. Indicate the state of hybridization in each case. **(10)**

VSEPR theory helps in determining the shapes and geometry of the hybrid orbitals discussed by Valence bond theory (VBT)

It uses, Drago's Formula $= \frac{1}{2}(V + M - A + C)$
(Bond Pair)
(B.P.)

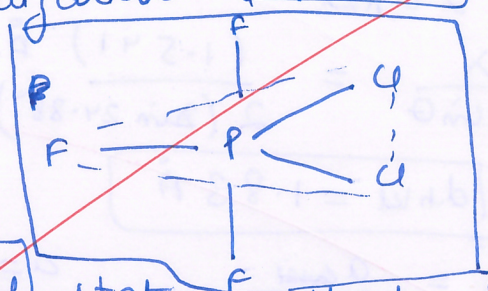
where V = Valency of Central atom
M = Number of monoatomic atoms
A = Anionic Charge
C = Cationic Charge

(i) PCl_2F_3

$B.P. = \frac{1}{2}(5+5) = 5$

$\therefore$ Hybridization $= \boxed{sp^3d^2}$

Structure



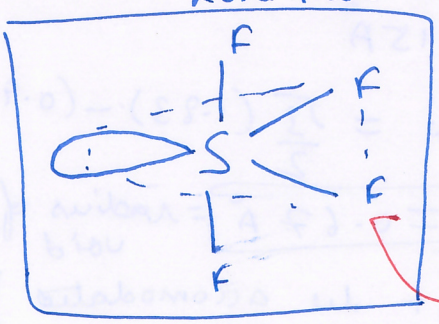
Trigonal Bi-Pyramidal
($\mu \neq 0$)

Since, Bent Rule states that electronegative atom goes to position of less % s-character. 2-F atoms become axial

(ii) SF_4

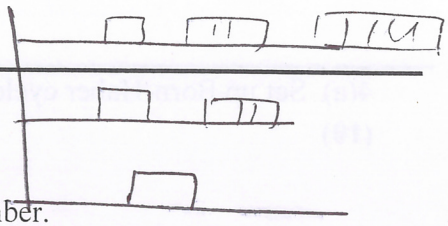
$B.P. = \frac{1}{2}(6+4) = 5$ $\boxed{sp^3d^2}$ ⇒ Hybridization

Lone Pair $= B.P. - 4 = 1$



Shape = Sea-Saw
Geometry = Trigonal Bi-Pyramidal

Since, lone pair occupies more volume, it remains at equitorial position, where angle is 120°



(e) The energy levels of the electron in hydrogen atoms are given by

$$E_n = -R_H / n^2, n = 1, 2, 3, ...$$

Where R_H is the Rydherg constant and n is the principal quantum number.

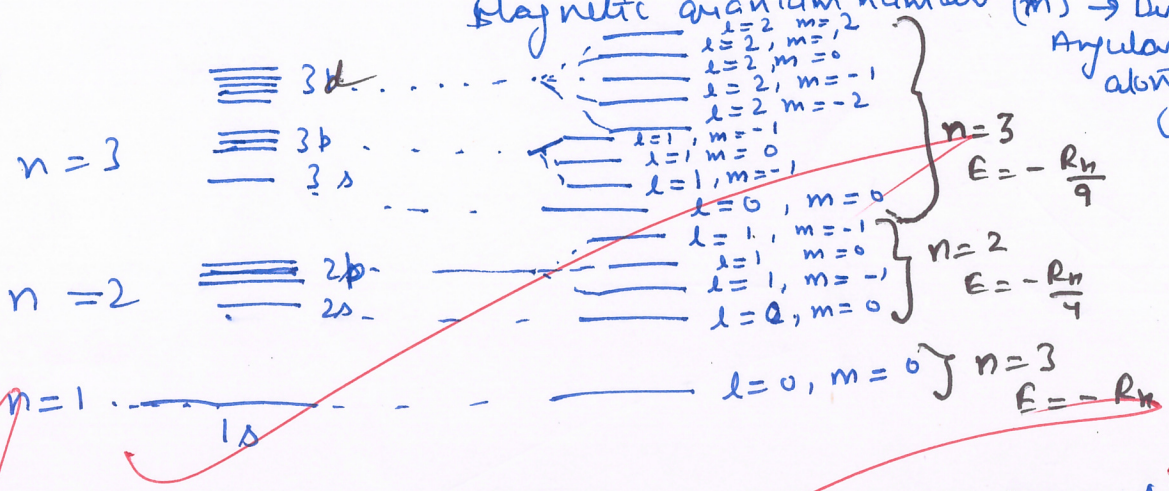
i) Draw a clearly labelled energy level diagram showing the first three energy levels of the electron and all of the quantum states helonging to each energy level.

ii) Give the degeneracies of the first three energy levels, giving the allowed l and m_l values and the orbitals rotations. Suggest a simple formula which relates the degeneracy of an energy level to its principal quantum number. **(10)**

Quantum numbers are provided by schrodinger wave equation solutions.

Such that Principal quantum number (n) → Determines energy
Azimuthal quantum number (l) → Angular momentum
Magnetic quantum number (m) → Directions of Angular momentum along z-direction

(i)



(ii) Degeneracies are the energy equivalent states

Since, energy depends only on 'n', and is independent of 'l' an 'm', Different l and m positions have same energy belonging to particular shell (n)

Since, $l = n - 1$ (maximum value)
and $m = 2l + 1$ (no. of values)

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

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

$$\boxed{D = n^2}$$

$\therefore$ No. of degeneracy of an energy level is $\boxed{n^2}$

4(a) Set up Born-Haber cycle for determining the enthalpy of solvation of Mg^{2+} ions from $MgCl_2$ by water. **(10)**

(d) Which of the following pairs is expected to have the larger bond angle and why? **(10)**

(1) H_2O *and* NH_3 (2) SF_2 *and* BeF_2

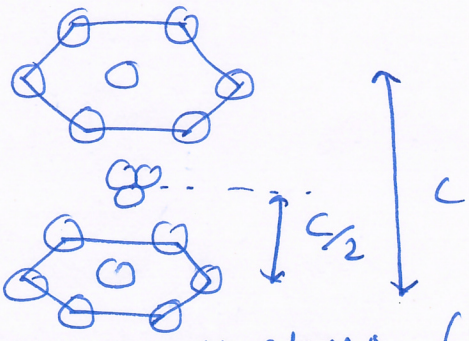
(3) BF_3 *and* BF_4^- (4) PH_3 *and* NH_3

(5) NH_3 *and* NF_3

SECTION – B

5(a)Derive the packing fraction for HCP. **(10)**

HCP is a specific form of FCC (face centred cubic) such that :-



Packing fraction (η) – $\frac{\text{Volume of all atoms } (V_a)}{\text{Volume of the trapezium } (V_t)}$ —(X)

$V_a = 6 \times V_{atom} = 6 \times \frac{4}{3}\pi r^3$ where r = radius of atom

$V_t \Rightarrow$ Assuming, most compact form (111) of FCC is equivalent in HCP.

$\therefore \boxed{\frac{c}{2} = \frac{a}{\sqrt{3}}} \Rightarrow c = \frac{2a}{\sqrt{3}}$ —(i) {a = Interplane distance}

Also, for FCC, $4r = \sqrt{2}a$ —(ii)

$\therefore$ Using (i) and (ii) $\boxed{r = \frac{\sqrt{6}}{8}c}$

$\therefore V_t = 6 \times A_{eq.} \times c$ (where A_{eq} = Area of equilateral triangle $\Rightarrow \sqrt{3}r^2$)

$V_t = 6 \times \sqrt{3}r^2 \times \frac{8r}{\sqrt{6}}$ —(iv)

Putting Va and Vt in eq (X).

$$\eta = \frac{\cancel{6} \times \frac{\cancel{4}}{3}\cancel{\pi}\cancel{r^3}}{\cancel{6} \times \frac{\sqrt{3}}{\sqrt{6}} \times \cancel{8}_2 \cancel{r^3}} = \frac{\pi}{\sqrt{18}} = 0.7401$$

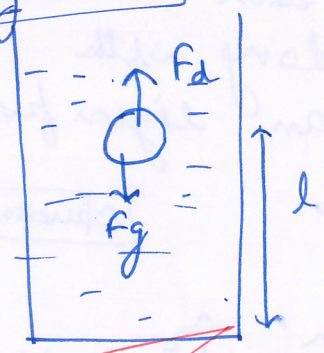
$\therefore \boxed{\eta = 74.01\%}$

Eg. of such Paking are Hg and Cd

(b) What is Stroke's law. How it is utilized to determine viscosity of liquid? **(10)**

Stoke's law is based on equalization of forces, such that terminal velocity is achieved of a solid steel ball falling through a liquid column. It states drag force to be

$$F_d = 6\pi\eta r v \quad -(i)$$



For terminal velocity,

$$F_d = F_g$$

F_d = Force of Drag.

F_g = gravitational force

$$\cancel{F_d = \frac{4}{3}\pi r^3(\rho_l)\, g}$$

$$\cancel{F_g = \frac{4}{3}\pi}$$

$$F_g = \frac{4}{3}\pi r^3(\rho_s - \rho_l)\, g \quad -(ii)$$

where η = coeff. of viscosity
r = radius of ball
v = Terminal velocity
ρ_l = density of liquid
ρ_s = density of ball
$g = 9.81\, m/s^2$.

Equating (i) = (ii)

$$\cancel{6}^{3}\pi\eta v = \frac{\cancel{4}^{2}}{3}\pi r^3(\rho_s - \rho_l)\, g$$

$$\eta = \frac{2}{9}\frac{r^2(\rho_s - \rho_l)\, g}{v}$$

$$v = \frac{l}{t} \Rightarrow \eta = \frac{2}{9}\frac{r^2(\rho_s - \rho_l)\, g\, t}{l}$$

where l = length
t = time

It can be utilized as,

$$\frac{\eta_l}{\eta_w} = \frac{(\rho_s - \rho_l)\, t_l}{(\rho_s - \rho_w)\, t_w}$$

to determine unkown viscosity using known one.

(c) Verify that the wave function $\psi(x) = x\, e^{-ax^2}$ is an eigenfunction of the operator $d^2/dx^2 - 4a^2x^2$. What is the corresponding eigenvalue? **(10)**

Wave function when operates over an operator and the function gets regenerated along with a constant value, is called as an eigen function of that operator.

$$\hat{H}\psi = E\psi$$

Operator, Eigen function, Eigen value

$$\hat{A} = \frac{\hat{d}^2}{dx^2} - 4a^2\hat{x}^2$$

$$\hat{A}\psi = \left(\frac{\hat{d}^2}{dx^2} - 4a^2\hat{x}^2\right)\left(x\, e^{-ax^2}\right)$$

$$= \frac{\hat{d}^2}{dx^2}\left(x\, e^{-ax^2}\right) - 4a^2x^3 e^{-ax^2}$$

$$= \cancel{\frac{\hat{d}}{dx}\left(e^{-2ax} - 2axe^{-2ax}\right) - 4a^2x^3e^{-2ax}}$$

$$= \cancel{-2a\, e^{-2ax} - 2a\, e^{-2ax}}$$

$$\hat{A}\psi = \frac{\hat{d}}{dx^2}\left(e^{-ax^2} - (ax)(2x)\, e^{-ax^2}\right) - 4a^2x^3 e^{-ax^2}$$

$$\hat{A}\psi = (-a)(2x)\, e^{-ax^2} - \cancel{(2ax^2)(-a2x)\, e^{-ax^2}} - 4axe^{-ax^2} \cancel{- 4a^2x^3e^{-ax^2}}$$

$$= -6ax\, e^{-ax^2}$$

$$\boxed{\hat{A}\psi = -6\psi}$$

Thus ψ is a eigen function of operator $\frac{\hat{d}^2}{dx^2} - 4a^2x^2$ with Eigen value $\boxed{-6}$

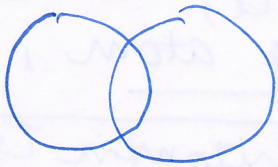
(d) ((i) Construct a trial LCAO – MO wavefunction for the H_2 molecule. **(10)**

ii) The trial VB wavefunction used by Heitler and london to dscrible the H_2 molecule in terms of hydrogne – like wavefunction is

$$\phi = c_1\psi_a(1)\psi_b(2) + c_2\psi_a(2)\psi_b(1)$$

Compare with the wavefunction you written in (i) and comment on the differences, if any.

(i) For H_2



$H_A = C_A \psi_A$

$H_B = C_B \psi_B$

$H_A - H_B \Rightarrow \boxed{\psi = C_A \psi_A \pm C_B \psi_B}$

Bonding M.O $\Rightarrow \psi = C_A \psi_A + C_B \psi_B$

Antibonding M.O. $\Rightarrow \psi = C_A \psi_A - C_B \psi_B$

(ii) $\Phi = C_1 \psi_a(1) \psi_b(2) + C_2 \psi_a(2) \psi_b(1)$

~~This considers NAONONCE~~

~~i.e. $H_a - H_B \longleftrightarrow \overset{+}{H_a} - \overset{-}{H_1} \longleftrightarrow \overset{-}{H_a} - \overset{+}{H_1}$~~

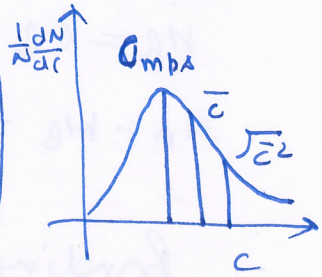
This considers exchange of e^- between the two hydrogens while above one donot.

(e) Write down equation for distribution of molecular speed on the basis of this explains the temperature dependance of distribution. **(10)**

Since, gaseous molecules are under continuous elastic collision, continuous kinetic exchange takes place, ~~it~~ thus, rather than speed of individual atom, distribution is studied

Maxwell-Boltzman Equation of molecular speed distribution

$$\frac{1}{N}\frac{dN}{dc} = 4\pi c^2 \left(\frac{m}{2\pi KT}\right)^{3/2} \exp\left(-\frac{mc^2}{2KT}\right)$$

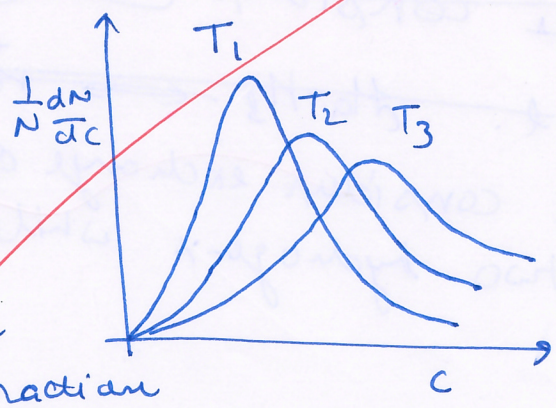


where, m = mass of molecule
K = 1.38×10^{-23} (Boltzman Constant)
C = speed of molecule
$\frac{dN}{N}$ = fraction of molecule at particular speed.
T = Temperature (in K)

Dependence of Temperature ⇒

$$c \propto \sqrt{\frac{1}{T}}$$

$T_1 < T_2 < T_3$



As temperature increase, fraction of molecules associated with higher speed increases, while fraction of molecules with ~~we~~ more probable speed decreases. (Since total no. of molecules remain const. & dist. becomes more broader.)

7(a) the density of ethyl acetate at 30^0C is 0.9850 g $m L^{-1}$. Calculate the surface tension of ethyl acetate, given the parachor values of C, H, O and the double bond are 8.2, 16.3, 19.5 and 21.5 respectively. **(10)**

Eotvos gave Temperature dependence of surface tension

$$\frac{M_m}{\rho}\gamma^{2/3} = a + bt$$

Further Ramsay's modification $\frac{M_m}{\rho}\gamma^{2/3} = b(t - t_c + 6)$

Further Mchod gave the concept of Parachor

Such that,

$$\boxed{\frac{M_m}{\rho}\gamma^{1/4} = P} \quad \text{—(i)}$$

where
M_m = molar mass
ρ = density
γ = surface tension
P = Parachor values

(Parachor is additive property)

For $CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

Calculating P

$$4P_C + 2P_O + 8P_H + 1P_{D.B}$$

$$= (4)(8.2) + 2(19.5) + 8(16.3) + 21.5$$

$$\boxed{P = 223.7}$$

$M_m = 88\ g/mol$ $\quad \rho = 0.9850\ g/cm^3$

Putting in (i)

$$\frac{88}{0.9850}\gamma^{1/4} = 223.7$$

$$\boxed{\gamma = 39.307\ dyne/cm}$$

(b) Show that Hermitian operator always gives real eigen value whenever applied to normalized wave function. (10)

Hermitian operator $\Rightarrow$

$$\langle \psi_n^* | A | \psi_n^* \rangle = \langle \psi_n^* | A^* | \psi_n \rangle$$

such that $A =$ ~~eigen~~ operator

$\psi_n =$ wave function

We know,

~~$\psi_n A$~~ $\hat{A}\psi_n = a_n \psi_n$ —(i) where

$\hat{A}^* \psi_n^* = a_n^* \psi_n^*$ —(ii) $\psi_n^* =$ complex conjugate of ψ_n

$a_n =$ Eigen values

$a_n^* =$

Multiplying eq. (i) by ψ_n^*

and eq. (ii) by ψ_n

$$\psi_n^* \hat{A} \psi_n = a_n \psi_n^* \psi_n \quad \text{—(i)}$$

$$\psi_n \hat{A}^* \psi_n^* = a_n^* \psi_n \psi_n^* \quad \text{—(ii)}$$

Subtracting and integrating over space.

$$\underbrace{\int_{space} (\psi_n^* \hat{A} \psi_n - \psi_n \hat{A}^* \psi_n^*) dz}_{\text{As } \hat{A} \text{ is hermitian operator}} = \int_{space} (a_n - a_n^*) \psi_n \psi_n^* \, dz$$

$\boxed{LHS = 0}$

$$\int_{space} (a_n - a_n^*) \psi_n \psi_n^* \, dz = 0$$

Since $\int_{space} \psi_n \psi_n^* \, dz = 1$

$$\boxed{a_n = a_n^*}$$

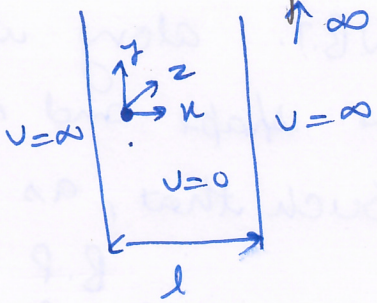
Thus, both real and complex eigen values are equal iff $(a_n = a_n^*) \Rightarrow$ both are $\boxed{\text{real}}$.

Deviation from mean position

Remember expectation values

(c) Derive Heisenberg uncertainty principle for particle in 1-D box . **(10)**

Assuming, a box of length l and particle moving along only the x-direction, $V=0$ (Inside box), $V=\infty$ (outside)



As per schrodinger wave eqn

$$\boxed{\psi = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)}$$

Heisenberg uncertainity principle $\boxed{\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}}$

$$\boxed{\Delta v = \sqrt{\langle v^2\rangle - \langle v\rangle^2}}$$

$$\therefore \langle \psi | \hat{p}_x | \psi \rangle = \int_0^l \left(\frac{2}{l}\right)\sin\left(\frac{n\pi x}{l}\right)(-i\hbar)\frac{\partial}{\partial x}\left(\sin\left(\frac{n\pi x}{l}\right)\right) dx$$

$$= \int_0^l \left(\frac{2}{l}\right)(-i\hbar)\left(\frac{n\pi}{l}\right)\sin\left(\frac{n\pi x}{l}\right)\cos\left(\frac{n\pi x}{l}\right) dx$$

$$\boxed{\langle \hat{p}_x \rangle = 0}$$

$$\langle \psi | \hat{p}_x^2 | \psi \rangle = \int_0^l \left(\frac{2}{l}\right)(-\hbar^2)\left(\frac{n\pi}{l}\right)^2 \sin^2\left(\frac{n\pi x}{l}\right) dx$$

$$\boxed{\langle \hat{p}_x^2 \rangle = \frac{n^2 h^2}{4l^2}}$$

$$\langle \psi | \hat{x} | \psi \rangle = \int_0^l \left(\frac{2}{l}\right) x \sin^2\left(\frac{n\pi x}{l}\right) dx = \boxed{\frac{l}{2}}$$

$$\boxed{\langle \hat{x} \rangle = \frac{l}{2}}$$

$$\langle \psi | \hat{x}^2 | \psi \rangle = \int_0^l \left(\frac{2}{l}\right) x^2 \sin^2\left(\frac{n\pi x}{l}\right) dx = *$$

$$\langle \hat{x}^2 \rangle =$$

$$\Delta \hat{p}_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2} = \frac{nh}{2l}$$

$$\Delta \hat{x} = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

Not VESPR

(d) Discuss the structure of IF_7 and $POCl_3$ on the basis of hybridization. (10)

V.B.T. along with VSEPR theory explains the shape and structure of covalent molecules. Such that, as per Drago's formula

$$B.P = \frac{1}{2}(V + M - A + C)$$

(Bond Pair)

V = Valency of central atom

M = number of monovalent atoms

A = Anionic Charge

C = Cationic charge.

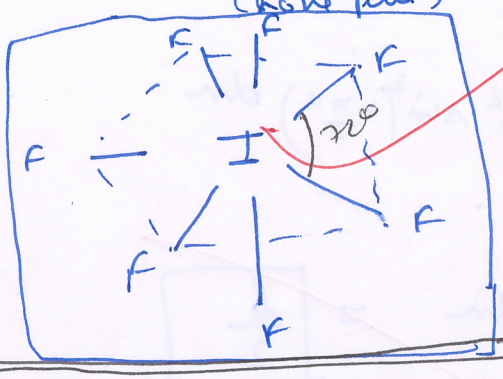
For,

IF_7

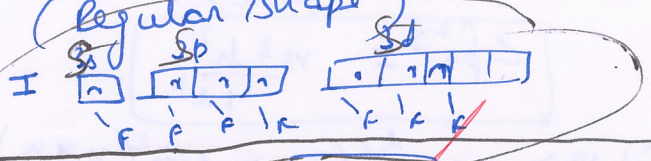
$B.P. = \frac{1}{2}(7+7) = 7$

$L.P. = 0$ (Lone pair)

Hybridization $= sp^3d^3$



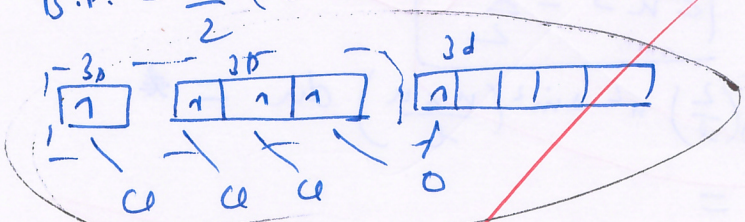
Pentagonal bi-Pyramidal (Regular shape)

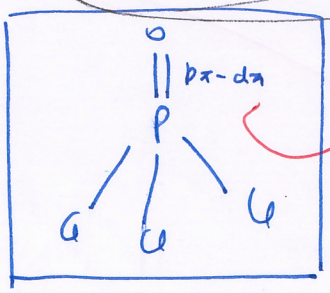


$POCl_3$

$B.P. = \frac{1}{2}(5+3) = 4$

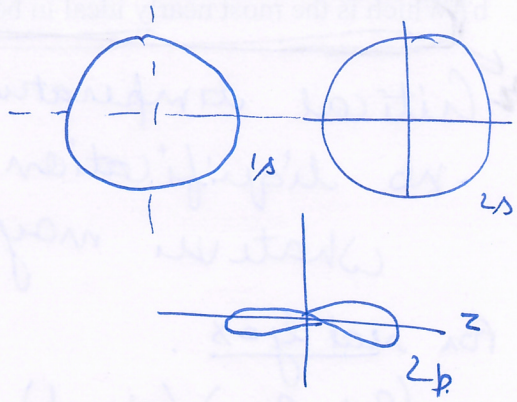
sp^3





Tetrahedral shape

(e) Draw the radial part of the wave function and radial probability distribution for hydrogen atoms for 1s, 2s and 2p orbitals. **(10)**

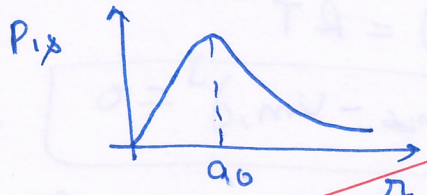


1s

$$R_{1s} = 2\left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)$$

$$P_{1s} = 4\pi r^2 R_{1s}^2$$

$$4\pi r^2 \left[\frac{4}{a_0^3} \exp\left(-\frac{2r}{a_0}\right)\right]$$

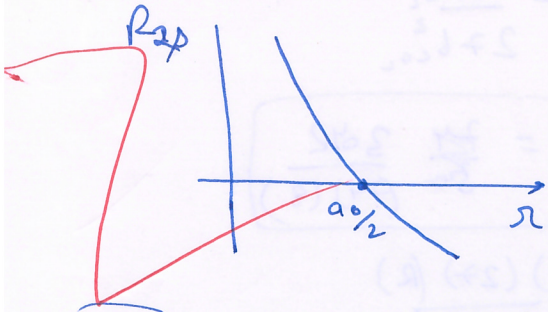


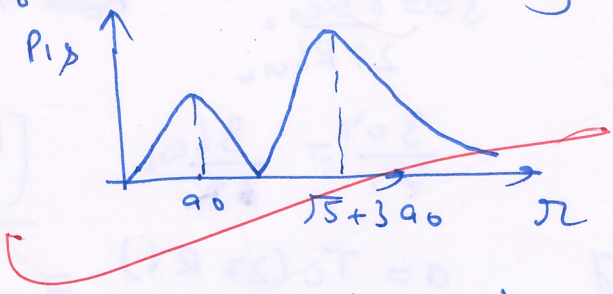
where $a_0 = 0.53$ Å

2s

$$R_{2s} = \left(\frac{1}{2a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$$

$$P_{2s} = 4\pi r^2 \left[\frac{1}{8a_0^3}\left(2 - \frac{2}{a_0}\right)^2 \exp\left(-\frac{2r}{a_0}\right)\right]$$

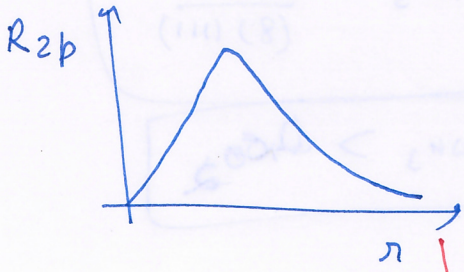




2p

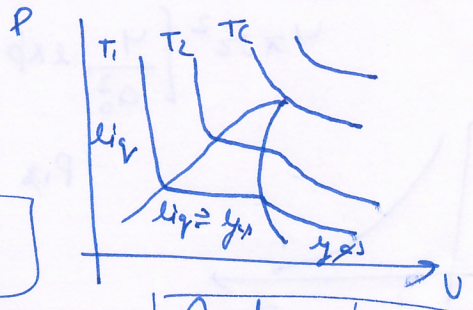
$$R_{2p} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{a_0}\right) \exp\left(-\frac{2r}{2a_0}\right)$$

$$P_{2p} = 4\pi r^2 \left[\frac{1}{3}\left(\frac{1}{8a_0^3}\right)\left(\frac{r^2}{a_0^2}\right) \exp\left(\frac{-r}{a_0}\right)\right]$$



8(a). The critical temperature and pressure for CO_2 gas are 304 K and 74 atm, respectively, and for NH_3 are 405 K and 111 atm, respectively. Which gas has the smaller values of the van der Waals' constants, a and b? Which is the most nearly ideal in behavior at 300 K and 10 atm?. **(10)**

CO_2 Critical temperature is the temp above which no liquification of gas is possible, whatever may be the pressure applied.



Andrew's plot

For real gas.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

solving Eq. $\boxed{(V_{m,c} - V_{m,c})^3 = 0}$

It gives, $V_{m,c} = 3b$ $\quad P_c = \frac{a}{27b^2}$ $\quad T_c = \frac{8a}{27Rb}$.

For CO_2 $\quad T_c = 304K$ $\quad P_c = 74$ atm

$$304 = \frac{8a_{CO_2}}{27Rb_{CO_2}} \qquad 74 = \frac{a_{CO_2}}{27b_{CO_2}^2}$$

$$\frac{304}{74} = \frac{8b_{CO_2}}{R} \qquad \boxed{b_{CO_2} = \frac{304R}{(74)(8)}}$$

Similarly $\quad a = \frac{T_c(27Rb)}{8} = \frac{(T_c)(27)(R)}{8}$

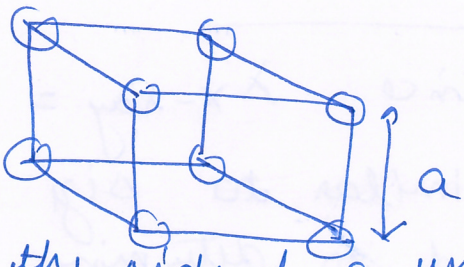
For NH_3 $\quad 405 = \frac{8a}{27Rb}$ $\quad 111 = \frac{a}{27b^2}$

$$\frac{405}{111} = \frac{8b}{R} \qquad \boxed{b_{NH_3} = \frac{405R}{(8)(111)}}$$

$\boxed{b_{CO_2} > b_{NH_3}}$ and $\boxed{a_{NH_3} > a_{CO_2}}$

(b) What is atomic radius of a cubic lattice? Find the atomic packing factor in , body- centrad cubic system and face-centred cubic system. **(10)**

(i) In Cubic lattice

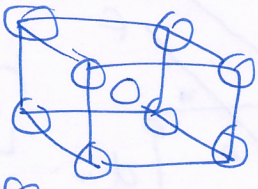


r = radius

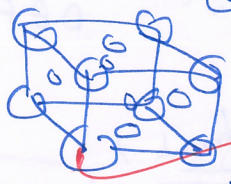
$2r = a$

So, atomic radius is half the side of a unit cell in simple cubic lattic.

In B.C.C $\quad 2r = \frac{\sqrt{3}}{2} a$



In FCC $\quad 2r = \frac{\sqrt{2}}{2} a$



Atomic Packing $\Rightarrow \eta = \frac{\text{Volume occupied by atoms}}{\text{Volume of lattice}}$

For BCC $\quad \boxed{Z=2}$

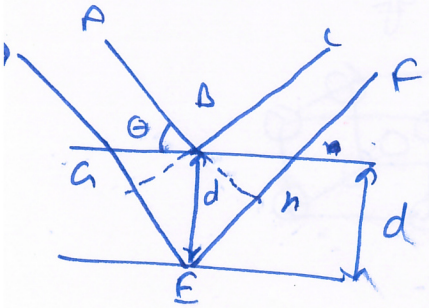
$$\Rightarrow \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4}{\sqrt{3}}\right)^3 r^3} = \boxed{68\%} \quad \boxed{Z=2}$$

For FCC $\Rightarrow \boxed{Z=4}$

$$= \frac{2 \times \frac{4}{3} \pi r^3}{(2\sqrt{2}) r^3} = \boxed{74.01\%}$$

(c) Drive bragge's equation. Using X-ray powder pattern of a compounds describe how do you calcuate the spacing between the planes. **(10)**

Since $\lambda_{x\text{-ray}} = 10^{-10} - 10^{-12}$ m which is similar to size of atom. It can be used to determine structure of lattice.



For constructive Interference

$[DEF - ABC] = n\lambda$

$DEF - ABC = GE + EH$

$= 2d\sin\theta$

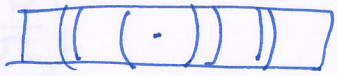
where n = order of reflection

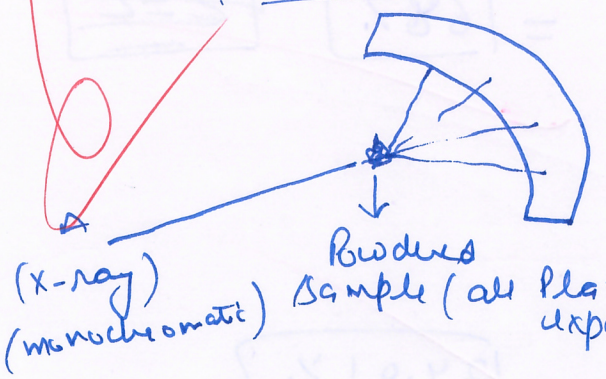
Therefore,

$$n\lambda = 2d\sin\theta$$

Powder method to determine spacing

(Expain more)





Using ~~dac~~ Bragg's equation

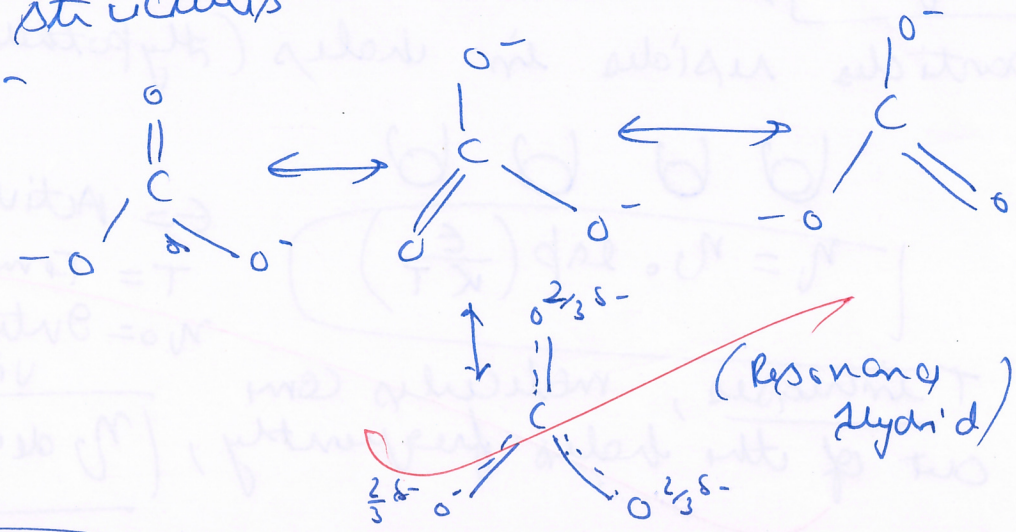
$$d = \frac{n\lambda}{2\sin\theta}$$

can be utilized to determine spacing.

(d) What do you understand by resonance energy? How it is calculated. **(10)**

Resonance is a phenomena ~~when~~ arising when no single structure represents complete picture of the molecule, such that a hybrid structure is made and the other structures are called canonical structures

CO_3^{2-}



(Resonance Hybrid)

Resonance Energy → It is the the energy difference between the ~~can~~ most stable canonical structure energy and hybrid structure energy

In can be calculated using: (Determined experimental)

→ Heat of hydrogenation method.

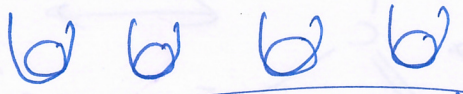
→ Bond dissociation energy method etc. (Thermodynamic method)

→ Spectroscopy.

(e) why viscosity of gas increases with increase in temperature while that of liquid decreases with temperature. **(10)**

Viscosity is the resistance offered by the slower layer of fluid to the faster one.

For liquid ⇒ Assumed that the fluid particles resides in holes (Hypothetical)



$$\eta = \eta_0 \exp\left(\frac{\epsilon}{kT}\right)$$

ϵ = Activation energy
T = Temp.
η_0 = Intrinsic viscosity

As T increases, molecules come out of the holes frequently, η decreases

For gases ⇒ As on temperature increasing Kinetic energy of the gas increases, frequent collision occur, viscosity increases

$$\eta = \frac{1}{3} m n \lambda \bar{c}$$

Since both λ and $\bar{c}$ (mean free path and average velocity) increases with increase in temperature.

η increases for gas.