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:- Utkarsh Patel

UPSC Roll no:-

Mobile Number.

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	34	28	31	30	23	33		

Signature of invigilator

Signature of Examiner

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)

Uncertainty of position can be found out utilising uncertainty principle which mathematically is given as,

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

$\left| p^2 = \frac{\hbar}{2m} \right.$

Now we have to found out Δp_x

we know, $\frac{p^2}{2m} = E$ or $\frac{2p\,\Delta p}{2m} = e\Delta V$

$\Rightarrow e\Delta V = \frac{p\Delta p}{m}$ further $p^2 = 2mE$

$p = \sqrt{2mE}$

$e\Delta V = \frac{\sqrt{2mE}}{m} \cdot \Delta p$

So $\Delta p = \frac{e\Delta V \cdot m}{\sqrt{2mE}} = \frac{e\Delta V\, m}{\sqrt{2meV}} = \frac{\sqrt{me}\cdot\Delta V}{\sqrt{2V}}$

Now,

$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$

So, $\Delta x = \frac{\hbar}{2\Delta p_x} = \frac{\hbar \cdot \sqrt{2V}}{2\pi \cdot 2\sqrt{me}\,\Delta V}$

$\Delta V = \pm 0.01$

$= 0.01 - (-0.01)$

$= 0.02$ KV

$= 0.02 \times 1000$

$= 20$ V

putting values, $\frac{6.626\times10^{-34} \cdot \sqrt{2\times1000}}{4\times3.14\times\sqrt{9.1\times10^{-31}\times1.6\times10^{-19}}\times20}$

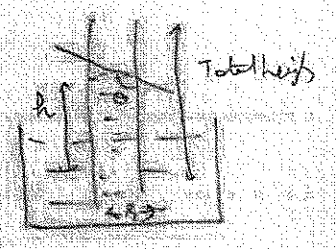
$= \frac{5.275\times10^{-35}\times44.72}{3.81\times10^{-25}\times20}$

$= 3.09\times10^{-10} = 3.09\ \text{Å}$

(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)

Ans- Mercury level in the capillary will change based on capillary action and wetting & drying nature of liquid.

Considering a capillary of radius 'r', liquid of density ρ.



1. Upward force acting on column will be = $2\pi r \cos\theta (2\pi r)$

2. downward force due to column = $(\pi r^2) h \rho g$

Equating both,

$$2\pi r \cos\theta \, 2\pi r = \pi r^2 h \rho g$$

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

Putting values,

$r = 0.40\ mm = 0.04 \times 10^{-2}\ m$.

$\gamma = 0.90\ N m^{-1}$, $\rho = 13.6 \times 10^3\ kg\ m^{-3}$.

$$h = \frac{2 \times 0.90 \times 13.6 \times 10^3 \cos\theta}{10^{-2} \times 0.04 \times 13.6 \times 10^3 \times 9.8\ m s^{-2}}$$

here $\cos\theta = 1$, $\theta = 180^\circ$

$$h = 2 \times 0.168\ m = 0.336\ m$$

liquid level be depressed by ~~0.168 m~~ ~~16.8 cm~~ 0.336 m

(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)

$\rho = 0.53$

$d = 100$

$d = 350$

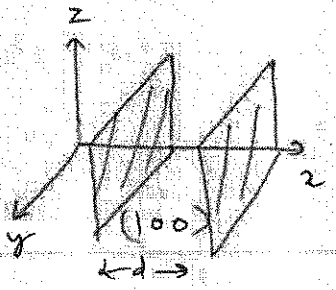
$M = 6.941$

$\rho = \frac{Z \times M}{N_A \times a^3}$

$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$

In this problem lattice type can be determined by finding the number of atoms present in a unit cell.

1) finding unit cell length 'a' -



Given, miller indices = 100

and interplanar distance, d = 350 pm

we know $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ so, $a = d\sqrt{h^2+k^2+l^2}$

$\Rightarrow a = 350\sqrt{1^2+0^2+0^2} = \boxed{350 \text{ pm}}$

Now, Given: $M(Li) = 6.941 \text{ g mol}^{-1}$, $\rho = 0.53 \text{ g cm}^{-3}$

we know $\rho = \frac{Z \times M}{N_A \times a^3} \Rightarrow Z = \frac{\rho \times N_A \times a^3}{M}$

putting values, $Z = \frac{0.53 \text{ g cm}^{-3} \times 6.022\times10^{23} \text{ mol}^{-1} \times (350\times10^{-10} \text{ cm})^3}{6.941 \text{ g mol}^{-1}}$

$\boxed{Z = 1.97 \approx 2}$

Since, value of Z is 2, lattice is B.C.C

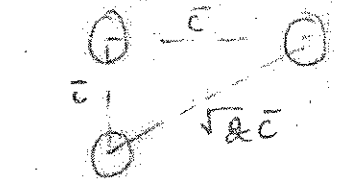
(e) Explain

(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 defined as distance travelled between two successive collisions.

Mathematically – $\lambda = \frac{\bar{c}}{z_1}$ $\quad \bar{c}$ = speed of molecule, z_1 = collision frequency

Calculating z_1 –



here, $z_1 = \pi d^2 \sqrt{2}\, \bar{c}\, N^*$ (N^* = no of molecule per unit volume)

So, $\lambda = \frac{\bar{c}}{\pi d^2 \sqrt{2}\, \bar{c}\, N^*} = \frac{1}{\pi d^2 \sqrt{2}\, N^*}$ ①

$N^* \Rightarrow \quad PV = nRT \Rightarrow P = \frac{N}{N_0 V} RT$

$\Rightarrow \frac{P N_0}{RT} = N^*$

$\Rightarrow \frac{P}{KT} = N^*$ ①'

from ① & ①' –

$\lambda = \frac{1}{\pi d^2 \sqrt{2}} \frac{KT}{P}$

given $\lambda = d$ and $\pi d^2 = \sigma = 0.36\ nm^2 \Rightarrow d = \sqrt{\frac{0.36}{\pi}}\ nm.$

So, $P = \frac{KT}{d\lambda(\pi d^2)\sqrt{2}} = \frac{KT}{d(\sigma)\sqrt{2}} = \frac{K \times 298K}{\left(\frac{0.36 \times 10^{-18}}{\pi}\right)^{1/2} \times 0.36 \times 10^{-18} \times \sqrt{2}}$

$= \frac{1.254 \times 10^{-23} \times 298 \times \pi^{1/2}}{(0.36 \times 10^{-18})^{1/2} \times 0.36 \times 10^{-18} \times \sqrt{2}}$

$P = \frac{7.29}{3.05} \times 10^{23+21} = 2.39 \times 10^{+7}\ Bar$

2.39×10^7 ✓ 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)**

(i) The magnetic behaviour of O_2, N_2 (liq) can be found as-

MO configuration of N_2 (14 e^-) $= (\sigma 1s)^2(\sigma 1s^*)^2(\sigma 2s)^2(\sigma 2s^*)^2(\pi 2p_x^2 = \pi 2p_y^2)(\sigma 2p_z^2)$ $(\pi 2p_x^* = \pi 2p_y^*)(\sigma 2p_z^0)$

= electrons are paired So, diamagnetic in nature, hence repel pole

MO configuration of O_2 (16 e^-) $= (\sigma 1s)^2(\sigma 1s^*)^2(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)(\pi 2p_x^{*1} = \pi 2p_y^{*1})$ $(\sigma 2p_z^{*0})$

= electrons are not paired So, paramagnetic hence, stick to (attracted in magnetic field). pole

(ii) He_2 & Be_2.

MO configuration of He_2 = $(\sigma 1s)^2(\sigma 1s^*)^2$ & So, Bond order = $\frac{BMO - ABMO}{2} = 0$

Since Bond order is zero, hence not exist

$Be_2 \rightarrow (\sigma 1s)^2(\sigma 1s^*)^2(\sigma 2s)^2(\sigma 2s^*)^2$ = BO = $\frac{BMO - ABMO}{2} = \frac{4-4}{2} = 0$ (Not exist)

(iii) from part 1, Bond order (O_2) = $\frac{BMO - ABMO}{2} = \frac{6-2}{2} = 2$ (B.O.)

(1 in outer shell)

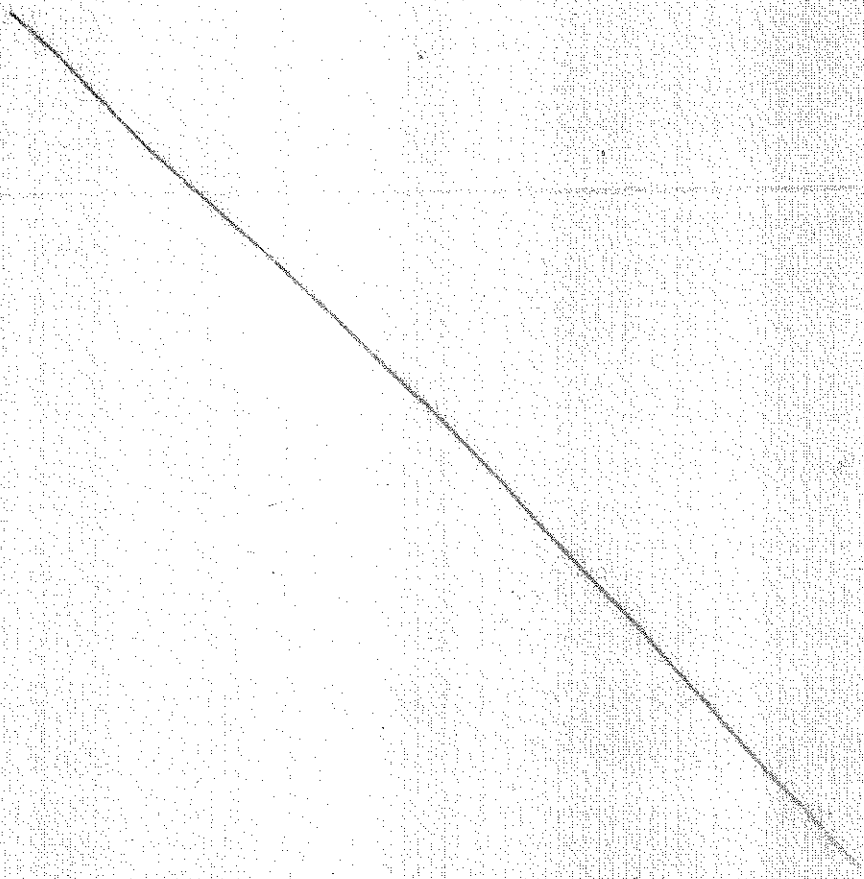
Bond order (N_2) = $\frac{BMO - ABMO}{2} = \frac{6-0}{2} = 3$ (B.O)

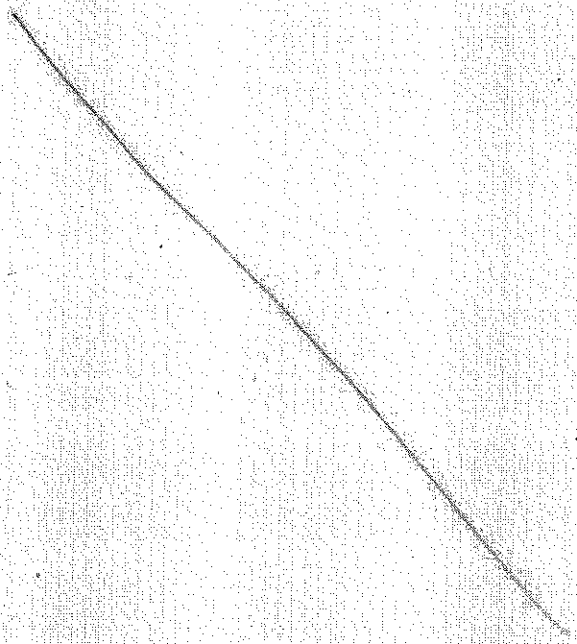
(iv) H_2 (MO configuration) = $(\sigma 1s)^2(\sigma 1s^*)$ = B.O = $\frac{2-0}{2} = 1$

H_2^+ (MO configuration) = $(\sigma 1s)^1(\sigma 1s^*)$ = $\frac{1-0}{2} = 0.5$

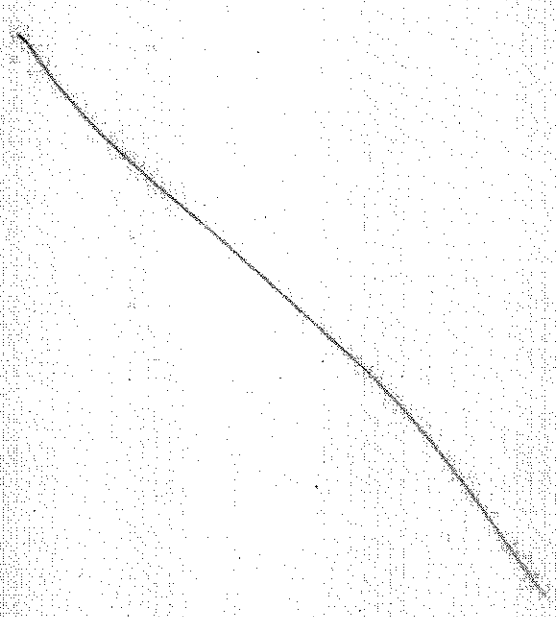
Since H_2 (BO) > H_2^+ (BO) Hence, H_2 is more stable

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)





(b) Calculate the temperature at which the root mean square velocity, the average velocity and the most probable velocity of oxygen gas are all equal to 1,500 m s^{-1}. (20)



(c) A certain closed cell from used as an insulating material is initially filled with polyatomic gas of molecular weight ~ 60. Letter, the gas diffuses out of the foam and is replaced by dry air (mean molecular weight r~30). Assuming that insulating property arises largely from the thermal conductivity of the gas, explain the factors which influence the thermal conductivity of the gas for each factor, make an argument whether insulating ability increases or decreases. What is the effect upon the insulating ability? **(10)**

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

Virial equation of gaseous state is derived from Vanderwall equation by arranging the terms in vanderwall equation and getting a form

$$Z = 1 + \frac{A}{V_m} + \frac{B}{V_m^2} + \cdots$$

where, Z = compressibility factor

A, B = first, 2nd virial constant

V_m = molar volume.

Recall, Vanderwall equation of gas is given by -

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

P = Pressure

a, b = are constants for pressure & volume correction

R = gas constant

T = Temperature

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

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

$$\frac{PV_m}{RT} = \frac{RV_m}{V_m - b} - \frac{a^2}{V_m RT}$$ Ans.

$$Z = \frac{1}{1 - \frac{b}{V_m}} - \frac{a^2}{V_m RT} \Rightarrow \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a^2}{V_m RT}$$

$$Z \Rightarrow \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \cdots\right) - \frac{a^2}{V_m RT}$$

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \frac{b^2}{V_m^2} + \cdots$$

Here $A = b - \frac{a}{RT}$

$B = b^2$ and so, on

We generally neglect 'B' onwards

$$\Leftarrow \boxed{Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \frac{b^2}{V_m^2} + \cdots}$$

derived

(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)

Schrodinger wave equation for H-atoms in caretsian coordinate can be obtained using Hamiltonian opeator on Hydrogen wave function ψ

So, $\hat{H}\psi = E\psi$.

So, $\frac{-\hbar^2}{2m}\left(\nabla_e^2 + \nabla_p^2\right)\psi = E\psi$

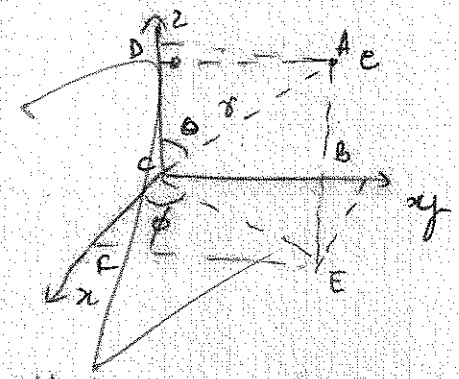
here, $m_e << m_p$ So, proton is static & electron revolve

So, $\frac{-\hbar^2}{2m}\nabla_e^2\psi_e = E\psi$

or cartesian: $\boxed{\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_e = E_e\psi_e}$ — (1)

Now. It can't be solved in cartesian so, converting to polar coordinate. Assume proton is static & electron revolve at distance 'r' from nucleus. here, θ varies from 0 to π

& ϕ varies from 0 to 2π (projection of r in xy plain)



So, Δ DAC –

$AD = r\sin\theta$ and $CD = r\cos\theta$

So, $CE = AD = r\sin\theta$

Now in Δ FCE = $FC = CE\cos\phi$

$= r\sin\theta\cos\phi$

and $BC = FE\sin\phi$

$= r\sin\theta\sin\phi$

So, $Z = r\cos\theta$

$X = r\sin\theta\cos\phi$

$Y = r\sin\theta\sin\phi$

putting these values in equation 1 –

$$\frac{-\hbar^2}{2m}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi_e = E_e$$

(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)

Simple cubic packing will lead to formation of a cubic void which will accomodate atom in this void space.

From, Bragg's equation we know,

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

λ = Radiation wavelength
d = inter planar distance
n = order of reflection

considering $n = 1$

$$d = \frac{\lambda}{\sin\theta} = \frac{1.541\ \text{Å}}{2\sin(24.88)}$$

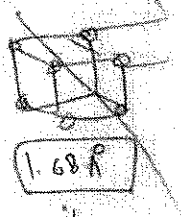
$$d = 3.66\ \text{Å}/2$$

$\theta = 24.88$

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

$d = \frac{a}{\sqrt{h+k+l}}$

$a =$

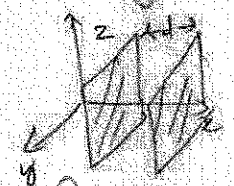


1.68 Å

void

$\frac{2r}{2} =$

Now, calculating unit cell length, a.



So, $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ hence $= a = d\sqrt{h^2+k^2+l^2}$

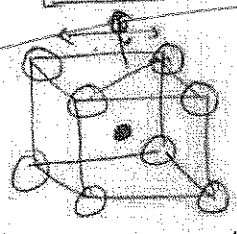
given $(h, k, l) = (1\,0\,0)$

So, $a = 3.66\sqrt{1^2+0^2+0^2} = 3.66\text{Å}/2 = 1.83$

Now, for a cubic void,

we know $\frac{r}{R} \Rightarrow 0.732 \leq \frac{r}{R} < 1$

$a = 2R$



here, calculating $\frac{r}{R} \Rightarrow$ r, given $= 1.68$ Å

Now $R = \frac{a}{2} = \frac{3.66}{2} = \frac{1.83\ \text{Å}}{2} = 0.915$

So, $\frac{r}{R} = \frac{1.68}{0.915} = \frac{1.83}{0.91}$ which is outside of range

$0.732 - 1.00$

So, lattice distortion will happen

(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 is based on concept of hybridisation which orients that hybridised orbitals in such a ways to minimise repulsion of electrons and lowest energy of molecule.

Case I – PCl_2F_3 – we know,

$$EP = \frac{1}{2}(V + E + A - C)$$

where, EP = electron pair
V = valence shell electron } on central atom
E = monatom number
A = negative charge
C = positive charge

So, for PCl_2F_3

$$EP = \frac{1}{2}(5 + 5 + 0 - 0) \leftarrow$$

$EP. = 5$

Now, BP = 5 (BP = Bond pair)

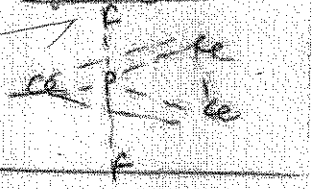
LP = 5 − 5 = 0 (lone pair)

Since No, lone pair so, shape will be like geometry defined by hybridisation sp^3d i.e. Trigonal bypyramidal. but as per Bent's Rule more electron egative will opt more 'p' character hybridised orbital so,

2) SF_4 = $EP = \frac{1}{2}(6 + 4 + 0 + 0) = 5$

BP = 4 so, LP = 1

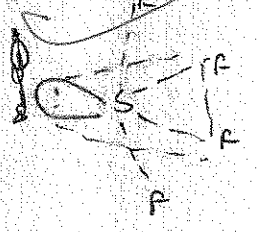
Shape = Trigonal bypyramidal



So, geometry ≠ shape here, lone pair occupies equatorial plane to minimise repulsion so,

Shape = Stag

hybridisation is sp^3d



Shape is distorted seesaw

geometry trigonal pyramidal

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

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

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

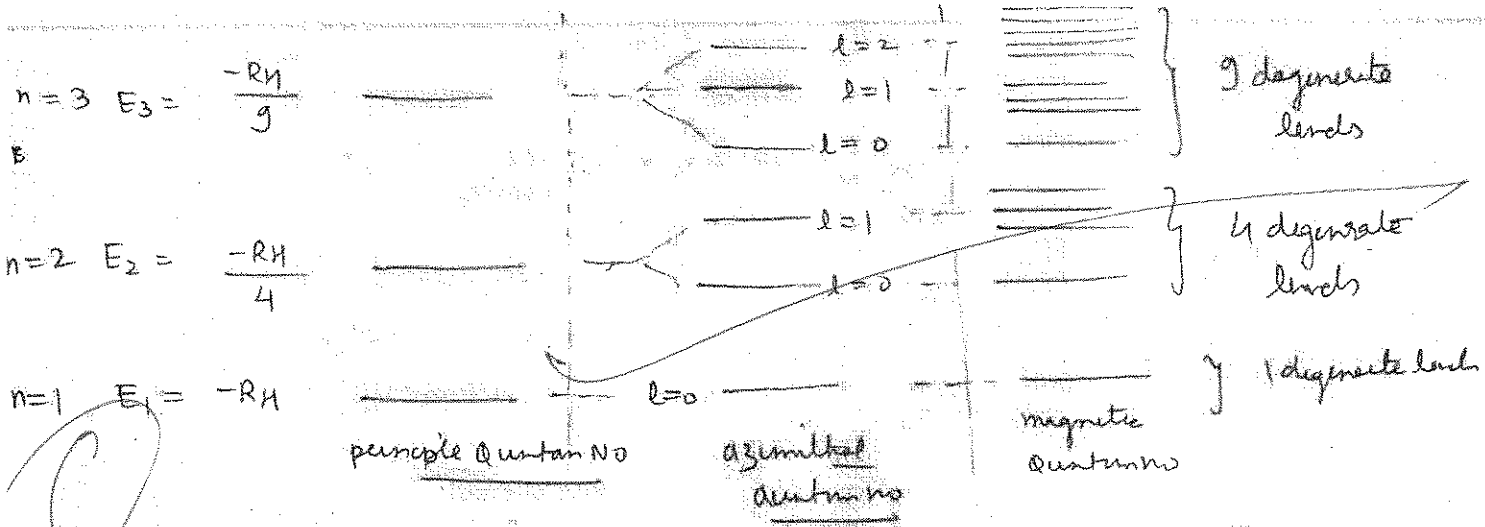
i) Draw a clearly labelled energy level diagram showing the first three energy levels of the electron and all of the quantum states belonging to each energy level.

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)**

$m = 2l+1$
$l = n-1$
$n = 2$
l 0, 1
$m = 2l+1$
$= 2(1)+1$
$= 3$
$2l+1$

Energy level of 'H' atom varies as per principle Quantum no. 'n'. which is given as- $E_n = \frac{-R_H}{n^2}$

For first three energy levels diagram of energy variation is -



n	l = (n-1)	m = 2l+1
0	0	0
1	0, 1	0, +1, 0, -1
2	0, 1, 2	0, +1, 0, -1, +2, +1, 0, -1, -2

A simple formula based on energy diagram is $= n^2$ where n is principle quantum no.

for n = 1 = degeneracy = 1
n = 2 = degeneracy = $2^2 = 4$
n = 3 = degeneracy = $3^2 = 9$

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

Born-Haber cycle is useful in theoretical calculation of Lattice energy, enthalpy of formation etc. It gives a good idea about stability of a ionic molecule. It is based on 1st law of thermodynamics & Hess law of Heat summation.

1st cycle -

$MgCl_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2Cl^-(aq)$ ($\Delta H_{solution}$)

$MgCl_2(s) \xrightarrow{\Delta U} Mg^{+} + 2Cl^-$

$Mg^{+} + 2Cl^- \xrightarrow{\Delta H_{Hydration}} Mg^{2+}(aq) + 2Cl^-(aq)$

So, $\Delta H_{solution} = \Delta H_{(Mg^{2+})_{solution}} + 2\Delta H_{(Cl^-)_{solution}} = \Delta U_{MgCl_2} + \Delta H_{Hyd.}$

So, $\Delta H_{(Mg^{2+})} = \Delta U_{MgCl_2} + \Delta H_{Hyd} - 2\Delta H_{(Cl^-)_{solution}}$ — (1)

Now, calculating ΔU_{MgCl_2}

$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$; ΔH_f

$Mg(s) \xrightarrow{\Delta H_{IE_1}} Mg^{+} \xrightarrow{\Delta H_{IE_2}} Mg^{2+}$

$Cl_2(g) \xrightarrow{\Delta H_{DE}} 2Cl \xrightarrow{2 \times \Delta H \text{ electron gain enthalpy}} 2Cl^-$

$Mg^{2+} + 2Cl^- \xrightarrow{\Delta U} MgCl_2(s)$

So, $\Delta H_f = \Delta U + \Delta H_{IE_1} + \Delta H_{IE_2} + \Delta H_{DE} + 2\Delta H_{EA}$ — (2)

from (1) & (2)

$\Delta H_{(Mg^{2+})_{solution}} = \Delta H_f + \Delta H_{IE_1} + \Delta H_{IE_2} + \Delta H_{DE} - 2\Delta H_{EA} + \Delta H_{Hyd} - 2\Delta H_{(Cl^-)_{solution}}$

(b) A drop of water, 0.6 mm in radius, is split up into 1250 tiny drops. Find the increase in surface energy. [γ_{water} (surface tension of water)=72 dynes/cm]. **(10)**

Surface energy is defined as amount of work done to increase the surface area by unit value.

① First we will calculate radius of new drops

$\frac{4}{3}\pi r_1^3 = 1250 \times \frac{4}{3}\pi r_2^3$

$r_2 =$

$\gamma \times$ change in $4\pi r^2$

r_1 = large drop radius

r_2 = small drop radius

forthis,

Volume of large droplet = 1250 × volume of tiny drop

$\frac{4}{3}\pi r_1^3 = 1250 \times \frac{4}{3}\pi r_2^3$

Now $\frac{r_1^3}{1250} = r_2^3$

$r_2 = \left(\frac{0.06^3\ cm^3}{1250}\right)^{1/3} = \frac{.06}{10.77} = 5.569 \times 10^{-3}\ cm$

$= .005569\ cm$

② change in area for new drop formation

Change in area $= 4\pi r_1^2 - 1250 \times 4\pi r_2^2$

$= 4\pi(r_1^2 - 1250 \times r_2^2)$

$= 4 \times 3.14\,(.06^2 - 1250 \times (5.569 \times 10^{-3})^2]$

$= 4 \times 3.14 \times .03517$

$= 0.44\ cm^2$

③ Surface energy = change in area × surface tension

$= 0.44\ cm^2 \times 72$ dyne/cm

$= 31.81$ dyne cm

(c) The X-ray diffraction pattern of silver, known to crystallize in the cubic system, was obtained using X-ray's with wave length 154.1 pm. The first six lines occurred at the following angles : 19.08°, 22.17° 32.26°, 38.74°, 40.82° and 49.00°. (a) Determine the type of the cubic system, (b) Calculate the length of the edge of the cube, (c) Calculate the interplanar distance of the plane (111). (20)

The diffraction pattern using Bragg equation is calculated as follows

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

$\lambda = 2d\sin\theta$ | for first order $n=1$

now, $\frac{\lambda}{2d} = \sin\theta$

$\sin^2\theta = \frac{\lambda^2}{(2d)^2}$, putting value of d $\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2)$

$\sin^2\theta = K(h^2+k^2+l^2)$

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

$n\lambda^2 = 4d^2\sin^2\theta$

$\sin^2\theta = \frac{\lambda^2}{4d^2}$

here,

θ	19.08°	22.17°	32.26°	38.74°	40.82°	49.00°
$\sin\theta$	0.3268	0.377	0.533	0.625	0.6536	0.75
$\sin^2\theta$	0.1068	0.142	0.2849	0.3916	0.427	0.5695
	3K	4K	8K	9K	12K	

Now, we will one by assume different cubic system and calculate pattern of K –

1) for at to be premitive cubic system (diffraction pattern)

'K' order will be K, 2K, 3K, 4K, 5K 6K

So, $\frac{2K}{K} = \frac{0.142}{.1068} = 1.32 \neq 2$

So, not premitive structure.

For it to be BCC., diffraction pattern will be –

2K, 4K, 6K; 8K, 10K, 12K for first 6 lines

So, $\frac{4K}{2K} = 2$ for first two lines.

Checking in our case = $\frac{0.142}{0.1068} = 1.32 \neq 2$

So, not BCC

3) For it to be FCC, diffraction pattern will be

3K, 4K, 8K, 11K, 12K - - - -

So, for first two lines

$$\frac{4K}{3K} = \frac{4}{3} = 1.33$$

Checking in our case,

$$\frac{0.142}{0.1068} = 1.33 \text{ (it matches)}.$$

all odd, even
100 ×
110 ×
111 ✓ 3K
200 × 4K
210 ×
211 ×
220 ✓ 8K
221 ×
310 ×
311 ✓ 11K
222 ✓ 12K

So, type of cubic system will be FCC

(b) Calculation of length of edge, a.

from Bragg equation – $n\lambda = 2d\sin\theta$

$$\lambda = 2\frac{a}{\sqrt{h^2+k^2+l^2}}\sin\theta$$

So, $a = \frac{\lambda \cdot \sqrt{h^2+k^2+l^2}}{2 \cdot \sin\theta}$

putting values in equation

$$a = \frac{154.1\ pm \times (1^2+1^2+1^2)^{1/2}}{2 \times \sin(\text{~~0.3268~~} 19.08)}$$

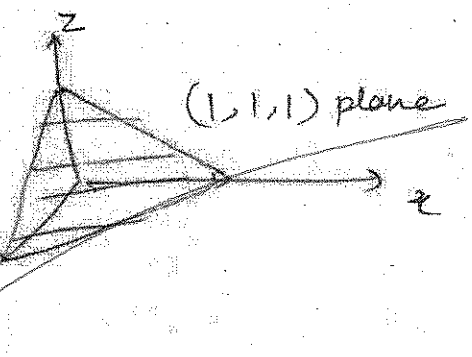
$$= \frac{154.1 \times \sqrt{3}}{2 \times 0.3268}$$

$$\boxed{a = 408.36\ pm}$$ edge length

(E) Interplanar distance calculation.

we know.

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$



putting values.

$$d_{hkl} = \frac{408.36}{\sqrt{1^2+1^2+1^2}}$$

$$\boxed{d_{hkl} = 235.77\ pm}$$ distance between (1 1 1) planes.

(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

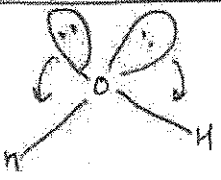
(3) BF_3 and BF_4^- (4) PH_3 and NH_3

(5) NH_3 and NF_3

Bond angle is angle formed between central atom and bond pairs

(1) H_2O & NH_3 –

Shape of H_2O & NH_3 –



Hybridisation – sp^3

Shape – Bent V

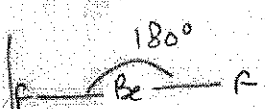
Hybridisation sp^3

Trigonal pyramidal

Here, NH_3 have large bond angle as one lone pair while in H_2O we have 2 lone pair repulsion.

(2) SF_2 & BeF_2

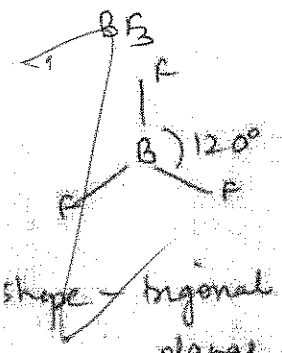
Shape – Bent V shape



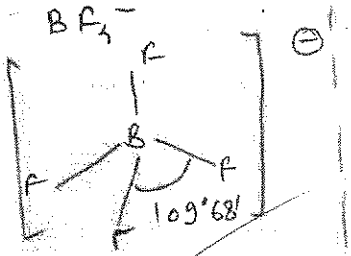
shape linear

BeF_2 has large bond angle as linear

(3) BF_3 and BF_4^-



Shape – trigonal planar

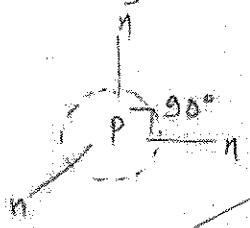


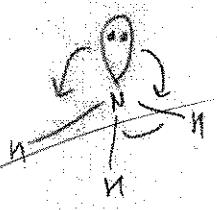
tetrahedral

Here – BF_3 has large bond angle as trigonal planar

(4)

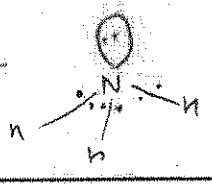
PH_3 & NH_3

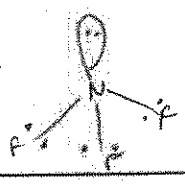




Here, PH_3 is a deago molecule where bond angle $\approx 90°$ while in NH_3 is tetrahedral with one lone pair repulsion so, $NH_3 > PH_3$

(5) NH_3 & NF_3



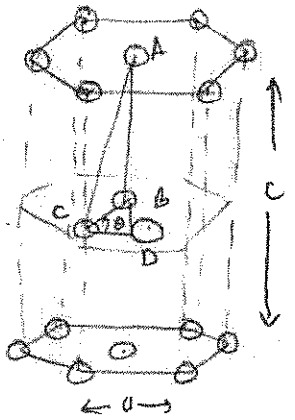


Here, Bond electrons are near more electronegative atom so, in NF_3 less bond pair repulsion & hence less angle so, $NH_3 > NF_3$

SECTION – B

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

'H CP' packing occurs ABAB type of packing of atoms. The unit cell comes out to be.



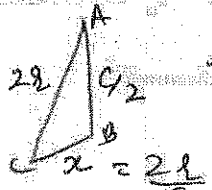
To find packing fraction –

No. of atoms in unit cell, Z =

$Z = \frac{1}{2} \times 2$ (face centre) + $\frac{1}{6} \times 12$ (corner) + 3 (in middle layer)

$Z = 6$

Now, in ΔABC –



in ΔCBD –

$BC = \frac{BD}{\cos 30^\circ} = \frac{2r \times 2}{\sqrt{3}} = \frac{2r}{\sqrt{3}}$

Now, packing fraction = $\frac{2 \times \frac{4}{3}\pi r^3}{\text{volume}}$ – (1)

$= \frac{2 \times \frac{4}{3}\pi r^3}{6 \times \frac{\sqrt{3}}{4} a^3 \times c} = \frac{2 \times \frac{4}{3}\pi r^3}{6 \times \frac{\sqrt{3}}{4} a^3 \times c}$

from ΔABC –

$\left(\frac{c}{2}\right)^2 = (2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2 = 4r^2 - \frac{4r^2}{3} = \frac{8r^2}{3}$ $\Rightarrow c = \sqrt{\frac{8}{3}} \times 2$

putting in (1), values of c & $a = 2r$, $Z = 6$

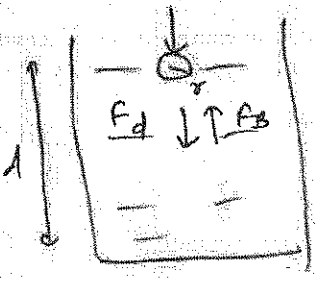
packing fraction = $\frac{6 \times \frac{4}{3}\pi r^3}{6 \times \sqrt{\frac{3}{4}} \times (2r)^3 \times \sqrt{\frac{8}{3}} \times 2} = 74\%$ ✓

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

1) Stroke's law - whenever a solid flows through a liquid two forces are acting on it - force of buoyancy and viscous drag force. when both the forces become equal solid acquires a constant velocity.

2) Determination of viscosity of liquid

Assume a solid steel ball of radius 'r' flows through liquid and complete distance 'd'. Viscosity of liquid is η_l



Now, as per stroke law.

$F_D = F_B$ (both forces equal).

$\Rightarrow 6\pi\eta r v = mg$

$3 \cancel{6}\cancel{\pi}\eta r v = \left(\frac{4}{3}\cancel{\pi} r^3 \rho_s - \frac{4}{3}\cancel{\pi} r^3 \rho_L\right) g$

where,
ρ_s = density of solid
ρ_L = density of liquid

So, $\eta_l = \frac{2(\rho_s - \rho_L) r^2 g}{9 \times v_l}$ — (I)

Now, finding $\eta_w = \frac{2(\rho_s - \rho_w) r^2 g}{9 \times v_s}$ — (II)

Now, η_l / η_w $\frac{\eta_l}{\eta_w} = \frac{(\rho_s - \rho_l) v_s}{v_l (\rho_s - \rho_w)}$

we know $v = \frac{d}{t}$

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

we find viscosity of liquid by once making ball fall from water & pulley values.

(d) (i)

(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)**

When an operator is operated on a function and we get the same function back multiplied by a constant value. function is called as eigen function.

i.e. $\hat{A}\,\psi_n = a\,\psi_n$ $\quad \hat{A}$ = operator, a = eigen value, ψ_n = eigen function

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

Given in the question, $\hat{A} = d^2/dx^2 - 4a^2x^2$, $\psi(x) = x\, e^{-ax^2}$

So,

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

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

$$= \left[x\frac{d^2}{dx^2}e^{-ax^2} + e^{-ax^2}\frac{d^2}{dx^2}x\right] - 4a^2x^2\, x\, e^{-ax^2}$$

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

$$= x\,\frac{d}{dx}\left[e^{-ax^2}\cdot\frac{d}{dx}(-ax^2)\right] + e^{-ax^2}\frac{d}{dx}(1) - 4a^2x^3 e^{-ax^2}$$

$$= x\,\frac{d}{dx}\left[e^{-ax^2}\,d(-2ax)\right] + 0 - 4a^2x^3 e^{-ax^2}$$

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

$$= x(-2a)\left[e^{-ax^2} + x\, e^{-ax^2}(-2ax)\right] + \left(-4a^2x^3 e^{-ax^2}\right)$$

$$= -2ax\, e^{-ax^2} + 2ax^3 e^{-ax^2} - 4a^2x^3 e^{-ax^2}$$

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

eigen value $(-2a)$

Verified

(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) construction of LCAO - MO wavefunction for H_2 molecule.

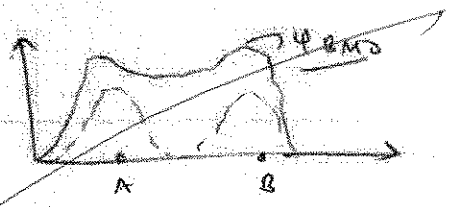
consider wavefunctions associated with H_A & H_A are ψ_A & ψ_B respectively.

So, as per LCAO $\psi = C_A\psi_A \pm C_B\psi_B$ — (1) trial wavefunction

Now for BMO (Bonding Molecular orbital)

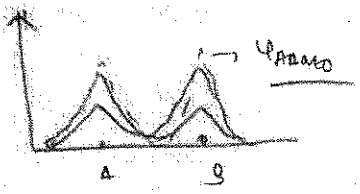
$$\psi_{BMO} = C_A\psi_A + C_B\psi_B$$

$$\text{or } \psi^2_{BMO} = C_A^2\psi_A^2 + C_B^2\psi_B^2 + 2C_AC_B\psi_A\psi_B$$



for ABMO – $\psi_{ABMO} = C_A\psi_A - C_B\psi_B$

$$\psi^2_{ABMO} = C_A^2\psi_A^2 + C_B^2\psi_B^2 - 2C_AC_B\psi_A\psi_B$$



(ii) Trial wave function for VBT gives as.

$$\phi = C_1\psi_a(1)\psi_b(2) + C_2\psi_a(2)\psi_b(1) \quad \text{— (1)}$$

comparison and differences – 1) In MOT trial wavefunction atomic orbitals loose their character to form molecular orbital while in VBT trial function atomic orbital retain their character.

2) In MOT, two separate linear combination taken for Bonding & Non-bonding.

3) VBT trial wavefunction consider exchange of electrons not in MOT.

4) VBT trial wavefunction can be modified to consider contribution from ionic character and also consider hybridisation.

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

In case of gases there is frequent collisions among molecules, Hence role of individual speed of molecules diminishes as it keeps changing rather distribution of molecular speed becomes important.

Maxwell (4π²)(e^{-ax²})

Maxwell equation for Molecular speed

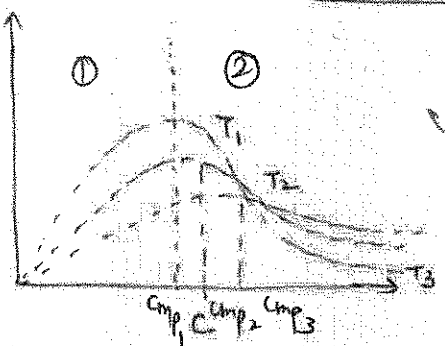
$$\frac{dN}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \; e^{\left(-\frac{Mc^2}{2RT}\right)} dc$$

Here, $\frac{dN}{N}$ = fraction of gas molecule, M = molar mass of gas

c = speed of gas molecules. , dc = fraction of speed, ±dc.

To plot fraction of Molecule vs ~~velo~~ speed range dc, plot has first relation as $\frac{1}{dc}\left(\frac{dN}{N}\right) \propto \frac{1}{T^{3/2}}$ ① and then $\frac{1}{dc}\left(\frac{dN}{N}\right) \propto e^{-Mc^2}$ ②

So,



$\frac{1}{N}\left(\frac{dN}{dc}\right)$

here, $T_3 > T_2 > T_1$

$c_{mp_3} > c_{mp_2} > c_{mp_1}$

here, we also know,

$$c_{mp} = \sqrt{\frac{2RT}{M}}$$

So, as Temperature increase, c_{mp} increases but fraction corresponding to dc_{mp} decreases.

c_{mp} = most probable speed

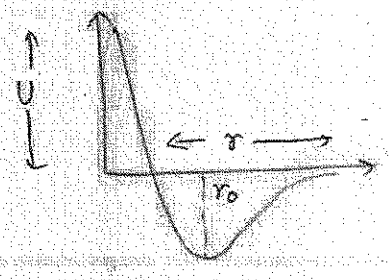
So, as temperature increase fraction of molecule for with c_{mp} increase but peak decrease as overall fraction remains 1.

6.(a) Deduce the Born –Landed equation for lattice energy. What modifications are imposed on this for better results? (15)

Born Lande equation is used for theoretical calculation of lattice energy. It is based on the principle that when one mole of ions are brought closer from infinite distance there is attraction as well repulsion at particular distance leading to energy minima

$$V_{att} = \frac{Z+Z-e^2}{4\pi\varepsilon_0 r}$$

$$V_{repulsion} = +\frac{B}{r^n}$$



So $V_{Total} = V_{att} + V_{rep}$

$$= \frac{Z+Z-e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \quad -(I)$$

at $r = r_0$ $\frac{dV}{dr} = 0$ So, $0 = \frac{-Z+Z-e^2}{4\pi\varepsilon_0 r^2} - \frac{nB}{r^{1+n}}$

$$B = \frac{-Z+Z-e^2 r_0^{1+n}}{n\,4\pi\varepsilon_0 r_0^2} = -\frac{Z+Z-e^2 r_0^{n-1}}{4\pi\varepsilon_0 n} \quad -(II)$$

$\frac{r^{-n+1}}{-n+1}$ $\quad -n r^{-n-1}$ $\quad -n r^{-n}$ $\quad -n r^{(1-n)}$

putting value of B from (II) to (I)

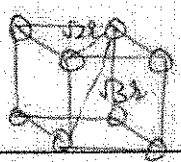
$$V_{Total} = \frac{Z+Z-e^2}{4\pi\varepsilon_0 r_0} - \frac{Z+Z-e^2 r_0^{n-1}}{4\pi\varepsilon_0 n r_0^n}$$

$$V_T = \frac{Z+Z-e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \quad -(III)$$

Now, this is for one ion pair, but in crystal unit cell there is particular arrangment of ions. considering NaCl-

1 Na^+ surrounded by 6 Cl^- at $\sqrt{1}r$

1 Na^+ surrounded by 12 Na^+ at $\sqrt{2}r$ and so on.



Accomodating this in equation - (III)

$$V_{Total} = \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0 r_0}\left[\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} \cdots\right]\left(1 - \frac{1}{n}\right)$$

here, we introduce Madelung constant, A which shows the contributions for a particular arrangment of ions in crystal

For 1 mole -

$$\boxed{V_{Total} = \frac{Z_+ Z_- e^2 N_0 A}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)}$$

Modifications imposed on it -

1. Considering correction for covalent character present in the ionic compound.
2. Introduction of zero point energy in the lattice energy calculation. Zero point energy = $\frac{1}{2} h\nu_0 N_0$
3. Considering Vanderwall intermolecular attraction in the molecule.
4. considering contribution of heat capacity of molecule

$$\boxed{C = a + bT + cT^2}$$

All these corrections further improve theoretical value of U_0 we get from Born-Landé equation.

(b) Calculate the most probable distance, r_{mp}, of the electron from the nucleus in the ground state of hydrogen atom, given that the normalized ground state wavefunction is

$$\Psi_{XS} = \frac{1}{\sqrt{\pi a_0^{3/2}}} \exp(-r/a_0) . \qquad (15)$$

$R_{1,0}$

$P(r) = \frac{dP}{dr}$

- Most probable distance r_{mp} is defined as the distance from nucleus where probability of finding electron has high probability.
- For this we define Probability function, $P(r)$ as -

$$P(r) = 4\pi r^2 \psi_{xs}^2$$

In our case -

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

at maxima, $\frac{dP_{xs}}{dr} = 0$

So,

$$\frac{dP_{xs}}{dr} = \frac{d}{dr} \left[4\pi r^2 \frac{1}{(\pi a_0^{3/2})^{1/2}} \exp(2r/a_0) \right]$$

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

$$= \frac{4\pi}{(\pi a_0^{3/2})^2} \left[r^2 \frac{d}{dr} \exp(2r/a_0) + \exp(2r/a_0) \frac{d}{dr} r^2 \right]$$

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

$$\frac{dP}{dr} = K\left[r\exp(-r/a_0)\left(-\frac{r}{a_0}+2\right)\right] \quad \text{where } K = \frac{4\pi}{(\pi a_0^3)^2}$$

putting $\frac{dP_{rs}}{dr} = 0$

we get values, $r = 0$ not possible

$\exp\left(-\frac{r}{a_0}\right) = 0 \Rightarrow \frac{1}{\exp(r/a_0)} = 0$

So, $r = \infty$ not possible

$\left(-\frac{r}{a_0}+2\right) = 0$

$r_{mp} = 2a_0$ acceptable

So, $r_{mp} = a_0$ Answer.

$\exp(-r/a_0) = 0$

$e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty}$

$\frac{2r}{1s} = -2$

$r = 2a_0$

Plot of most probable distance

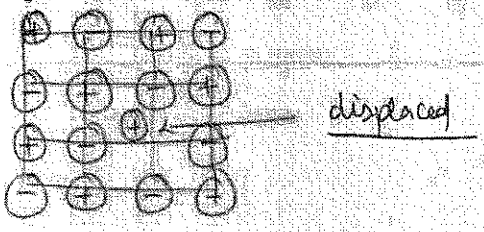
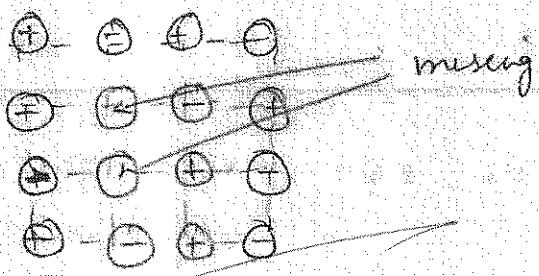
$4\pi r^2 \psi_{1s}^2$

a_0 r

(c) What is the basic difference between Schottky and Frenkel defects in ionic crystals? How do solids with such defect differ from non – stoichiometric compounds. (10)

Schottky and frenkel difect are both stoichiometry difect as unit formula doesn't change.

Difference between frenkel & shottky difect

Frenkel	Schottky
1. Here, one of constituent ion move into interstetial space.  displaced	1. Here, both cation & Anion constituent are missing  missing
2. Shown by compounds with low coordination no = 4,6	2. high coordinate no 6,8
3. density doesn't change conductivity improve	3. density decrease
	4. improve more in comparison

Difference from Nonstoichiometric compound –

Stoichiometric (Frenkel & Shottky)	Non-stoichiometric
I. Formula of compound doesn't change	I. formula change
II. Not impart colour	II. imparts colour to compound (Ex- Fabry centre)
III. conductivity improve by small amount	III) increase significantly
IV) density may or may not change	IV) density changes

(d) Draw and explain curves showing the variation of first and second ionization energies for the elements from H to Ne. **(10)**

Ionisation energy is defined as the amount of energy required to remove the outermost electron for an isolated gaseous atom.

1) First ionisation energy -

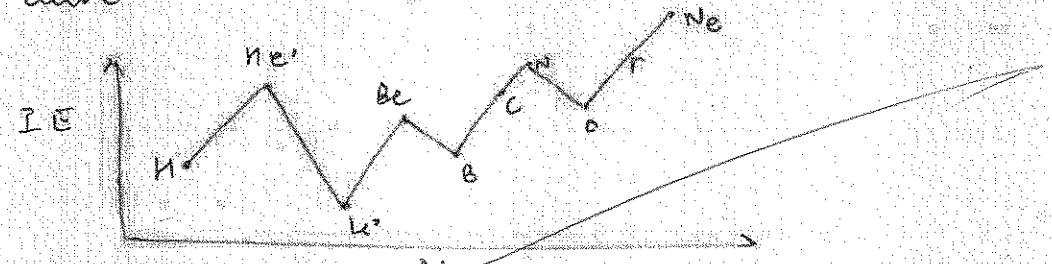
general expectation - is increase in IE from left to right as Zeff increases $H < Li < Be < B < C < N < O < F < Ne$

but 1. noble gas configuration has highest IE

2. IE (Be) > IE (B) as $^{\circ}Be$ has ns^2 electrons

3. IE (N) > IE (O) as p^3 configuration

So, curve

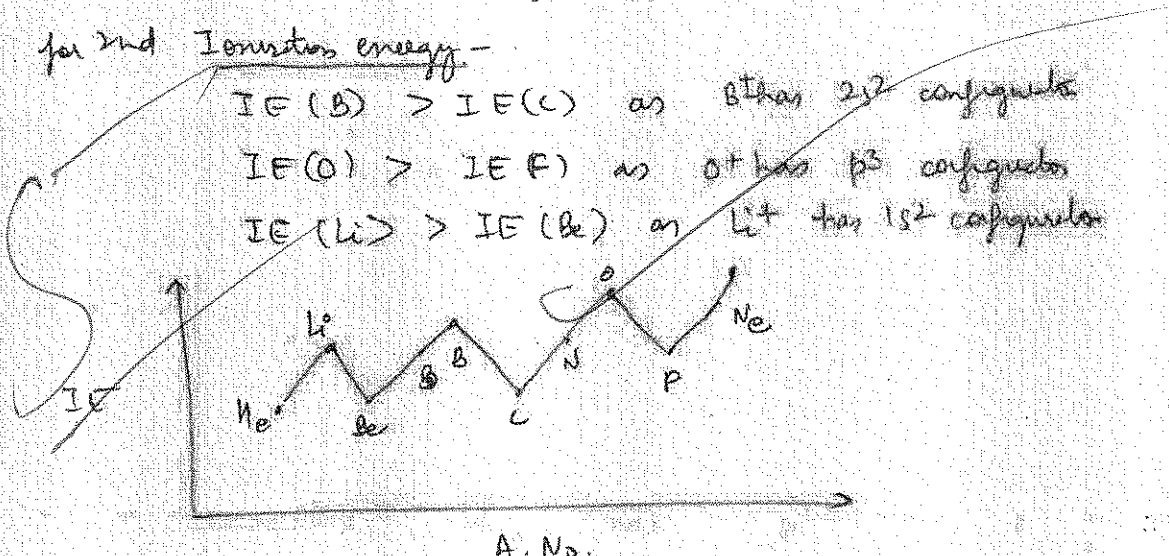


2) for 2nd Ionisation energy -

IE (B) > IE (C) as B^+ has $2s^2$ configuration

IE (O) > IE F) as O^+ has p^3 configuration

IE (Li^+) > IE (Be^+) as Li^+ has $1s^2$ configuration



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)**

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