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:- Pawan Kumar Pandey

UPSC Roll no:-

Mobile Number.

Attempted = 1, 3, 5, 6, 8
⇒ Please check if space management is fine.

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	32	⊘	32	⊘	27	35		35

Signature of invigilator

Very good

161

Signature of Examiner

1

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)

As per heisenberg uncertainity, uncertainity in position and momentum is given by $\boxed{\Delta x \cdot \Delta p \geq \dfrac{h}{4\pi}}$

For e^- moving through a potential difference of $\Delta \phi$,

Kinetic energy gained $\underset{(E)}{=} \underset{(\Delta\phi \text{ in } ev)}{e \Delta \phi} = \dfrac{p^2}{2m}$ $\left(\begin{array}{l} p = \text{momentum} \\ m = \text{mass} \end{array}\right)$

$\Rightarrow \cancel{p}\, E = \dfrac{p^2}{2m}$

differentiating both sides,

$\Delta E = \dfrac{1}{2m} \times 2p \cdot \Delta p$

$\Rightarrow \Delta E = \dfrac{p}{m} \Delta p$

$\Rightarrow \boxed{\Delta p = \dfrac{m \, \Delta E}{p}}$ — eq(i)

using given values

$\Delta E = 0.01 \times 10^3 \text{ volt}$

$m_e = 9.109 \times 10^{-31} \text{ kg}$

$\Rightarrow p = \sqrt{2m\, e \Delta\phi} \qquad \Delta\phi = 1 \times 10^3 V$

$p = \sqrt{2 \times 9.109 \times 10^{-31} \times \cancel{1.6 \times 10^{-19}} \times 10^3}$

$\Rightarrow \cancel{p = 1.71 \times 10^{-23} \text{ m/s}}$

$\Rightarrow p = 4.27 \times 10^{-14} \text{ m/s}$

using these values in eq (i)

$\Rightarrow \Delta p = \dfrac{9.1 \times 10^{-31} \text{ kg} \times 0.01 \times 10^3 \, V}{2 \times 4.27 \times 10^{-14} \text{ m/s}}$

$\Rightarrow \Delta p = 2.13 \times 10^{-16} \text{ m/s}$

$\Rightarrow \Delta x = \dfrac{h}{4\pi \, \Delta p}$

$\Rightarrow \Delta x = \dfrac{6.626 \times 10^{-34}}{4\pi \times 2.13 \times 10^{-16} \text{ m/s}}$

$\boxed{\Delta x = 2.47 \times 10^{-19} \text{ m}}$

This value is very low as e^- is accelerated through very high potential.

(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)

Mercury is a non-wetting liquid in which there is depression in its level due to capillary action as adhesive force is lower than cohesive force.

As we can see $\theta > 180°$ ⟹ Assuming

$$\boxed{\theta = 180°}$$

Force balance on the mercury :-

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

$$\boxed{h \, (\text{drop in level}) = \frac{2\gamma \cos\theta}{\rho g r_c}}$$

Given values: —

$r_c = 0.40 \, mm = 0.4 \times 10^{-3} \, m$

$\gamma = 0.90 \, N$

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

$\theta = 180°$
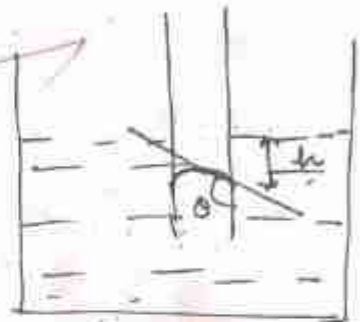
$g = 9.8 \, m/s^2$

$$h = \frac{2 \times 0.90 \times \cos 180°}{13.6 \times 10^3 \times 9.8 \times 0.4 \times 10^{-3}}$$

⟹ $h = -0.03376 \, m$

⟹ $\boxed{h = -33.76 \, mm}$

Negative sign shows drop in mercury level.

(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)

$$\boxed{\text{Density of a metal} = \frac{\text{Mass of unit cell}}{\text{Volume of a unit cell}}}$$

$$\text{Mass of a unit cell} = \frac{Z \times M}{N_0}$$

$$\text{Volume of a unit cell} = a^3$$

$$\Rightarrow \boxed{\rho = \frac{ZM}{N_0 a^3}} \quad\quad \text{—①}$$

$Z =$ effective no. of atoms present in a unit cell

$M =$ Molar Mass.

$a =$ length of side of a unit cell.

For a cubic unit cell, $\dfrac{1}{d^2_{h,k,l}} = \dfrac{h^2 + k^2 + l^2}{a}$ where

$d =$ interplanar distance and h, k, l are miller indices.
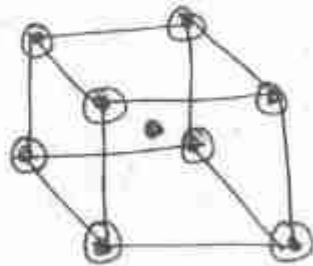
For $\boxed{d_{100} = a}$ From eq ① $\boxed{Z = \dfrac{\rho N_0 a^3}{M}}$

Putting values $\quad Z = \dfrac{0.53 \text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times (350 \times 10^{-10} \text{ cm})^3}{6.941 \text{ g mol}^{-1}}$

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

For Z=2 value, we can say Li crystallizes in a $\boxed{\text{BCC lattice}}$.

Li 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 σ = 0.36 nm². (10)

(λ) <u>Mean free path</u> is defined as the distance a molecule has to travel before a collision takes place with another molecule. $\boxed{\lambda = \dfrac{\bar{c}}{Z_1}}$

For Argon, Z_1 (collission number) $= \sqrt{2}\, \pi d^2 \bar{c}\, N^*$

where $\bar{c} = $ avergage velocity

$N^* = $ Number density

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

<u>we know</u> N^* (Number density) $= \dfrac{P}{KT}$

$P = $ Pressure

$K = $ Boltzmal Constant

$T = $ Temperature.

<u>Putting this N^* in λ</u>

$\boxed{\lambda = \dfrac{KT}{\sqrt{2}\, \pi d^2\, P}}$

Given $\pi d^2 (\sigma) = 0.36\ nm^2$

$\Rightarrow d^2 = \dfrac{0.36\ nm^2}{\pi}$

$\Rightarrow \boxed{d = 0.338\ nm}$

since $\lambda = d$ (given)

$\Rightarrow \sqrt{2}\, \pi d^3\, P = KT$

$\Rightarrow \boxed{P = \dfrac{KT}{\sqrt{2}\,(\pi d^2)\cdot d}}$

$\Rightarrow P = \dfrac{1.38\times 10^{-23} \times 298}{\sqrt{2}\times (0.36\times 10^{-18})\times 0.338\times 10^{-9}}$

$\Rightarrow \boxed{\begin{array}{l} P = 2.39\times 10^7\ Pascal \\ = 235.85\ atm \end{array}}$

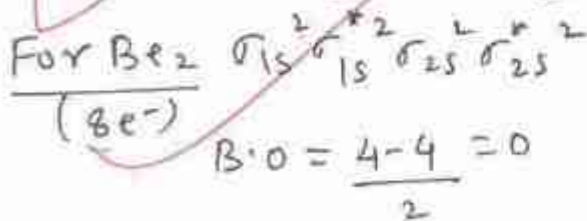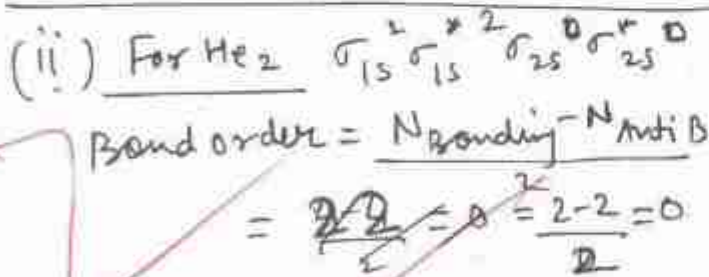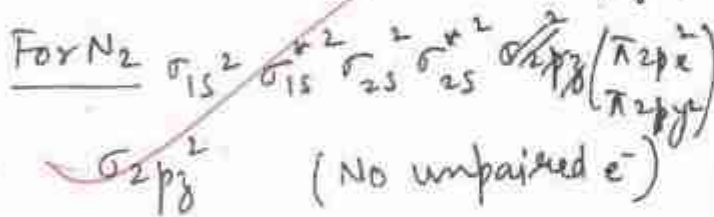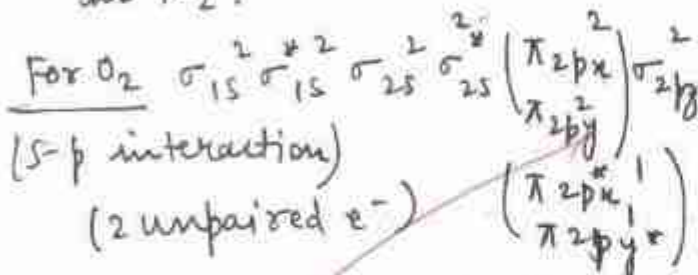<u>This is very high P</u> indicating at high P intermolecular distance decreases.

(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) This can be explained on the basis of **paramagnetism** in O_2 while **diamagnetism** in N_2.

For O_2 $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left(\begin{array}{c}\pi_{2px}^2 \\ \pi_{2py}^2\end{array}\right) \sigma_{2pz}^2$ (S-p interaction)

(2 unpaired e^-) $\left(\begin{array}{c}\pi_{2px}^{*1} \\ \pi_{2py}^{*1}\end{array}\right)$

For N_2 $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left(\begin{array}{c}\pi_{2px}^2 \\ \pi_{2py}^2\end{array}\right)$

σ_{2pz}^2 (No unpaired e^-)

(ii) For He_2 $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^0 \sigma_{2s}^{*0}$

Bond order $= \dfrac{N_{Bonding} - N_{Anti B}}{2}$

$= \dfrac{2-2}{2} = 0 = \dfrac{2-2}{2} = 0$

For Be_2 $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2}$

($8e^-$)

$B.O = \dfrac{4-4}{2} = 0$

Since Bond order $= 0$, they don't exist

(iii) For MO level given in part (i)

O_2 $B.O = \dfrac{10-6}{2} = 2$

N_2 $B.O = \dfrac{10-4}{2} = 3$

(iv) For H_2: $\sigma_{1s}^2 \sigma_{1s}^{*0}$

$B.O = \dfrac{2-0}{2} = 1$

For H_2^+ Ion: $\sigma_{1s}^1 \sigma_{1s}^{*0}$

$B.O = \dfrac{1-0}{2} = 0.5$

Since $B.O_{H_2^+} < B.O_{H_2}$

$\Rightarrow$ Bond Energy $H_2^+ < B.E_{H_2}$

$\Rightarrow$ H_2 is more stable

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

Virial equation of state is a power series in volume.

From Vanderwall equation, $P = \cancel{\dfrac{V_m}{RT}} \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$

$\Rightarrow \dfrac{PV_m}{RT} = \dfrac{V_m}{V_m - b} - \dfrac{a}{V_m RT}$ taking $\boxed{\dfrac{PV_m}{RT} = Z}$

(compressibility factor)

$\Rightarrow Z = \dfrac{1}{1 - \dfrac{b}{V_m}} - \dfrac{a}{V_m RT}$

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

$= 1 + \dfrac{b}{V_m} + \dfrac{b^2}{V_m^2} + \dfrac{b^3}{V_m^3} - \dfrac{a}{V_m RT}$

$\boxed{Z = 1 + \left(b - \dfrac{a}{RT}\right)\dfrac{1}{V_m} + \dfrac{b^2}{V_m^2} + \dfrac{b^3}{V_m^3} + \cdots}$

2nd virial coefficient :- $b - \dfrac{a}{RT} = 0$ when T= boyle's temperature

$\Rightarrow \boxed{T_B = \dfrac{a}{Rb}}$

From $3^{rd}, 4^{th} \cdots$ virial coefficients, ~~whole~~ molar Volume and radius of atom can be determined.

(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)

$\boxed{\text{For Cartesian Coordinates}}$ $\hat{H}\psi = E\psi$

$\hat{H}\,(\text{Hamaltonian operator}) = \left[-\dfrac{h^2}{2m}\nabla^2 + V \right]$

$\nabla^2 = \left(\dfrac{d^2}{dx^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2} \right)$ $V = \dfrac{-Z_1 e^2}{4\pi \varepsilon_0\, r_0}$

$\Rightarrow \quad \dfrac{-h^2}{2m}\left[\left(\dfrac{d^2\psi}{dx^2}\right) + \left(\dfrac{d^2\psi}{dy^2}\right) + \left(\dfrac{d^2\psi}{dz^2}\right) \right]\psi + \left(\dfrac{-Ze^2}{4\pi\varepsilon_0 r} \right) = E\psi$

$[Z=1 \text{ for H})$

$\Rightarrow \boxed{ \left(\dfrac{d^2\psi}{dx^2} + \dfrac{d^2\psi}{dy^2} + \dfrac{d^2\psi}{dz^2} \right) + \dfrac{8\pi^2 m (E-V)}{h^2} = 0 }$

$\boxed{\text{In Polar Coordinates}}$

$\nabla^2 = \dfrac{1}{r^2}\dfrac{d}{dr}\left(r\dfrac{d}{dr} \right) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta} \right)$

$\qquad + \dfrac{\partial^2}{r^2\sin^2\theta\, \partial\phi^2}$

$\dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial\psi}{\partial r} \right) + \dfrac{1}{r^2\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\dfrac{\partial\psi}{\partial\theta} \right)$

$\qquad + \dfrac{1}{r^2\sin\theta}\left(\dfrac{\partial^2\psi}{\partial\phi^2} \right) + \dfrac{8\pi^2 m}{h^2}\left(E + \dfrac{Ze^2}{4\pi\varepsilon_0 r} \right) = 0$

schrodinger wave equation .

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

$\boxed{\text{Relation between polar and cartesian}}$

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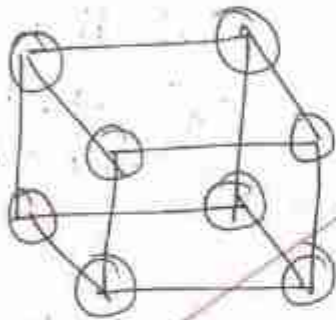
$$n\lambda = 2d \sin\theta$$

$$(1) \frac{(1.541 \text{ Å})}{2 \sin(24.88°)} = d$$

$$\Rightarrow \boxed{d = 1.832 \text{ Å}}$$

For simple cubic,
$$d = a$$
$a = $ unit cell length
$$= 1.832 \text{ Å}$$

$$2R = \frac{\sqrt{3}\, a}{2} \qquad R = \text{radius}$$

$$2R = a$$
$$R + r = \frac{\sqrt{3}\, a}{2} \qquad (r = \text{radius of void})$$

$$\frac{R + r}{2R} = \frac{\sqrt{3}\, a}{2 \times a} \Rightarrow \left(1 + \frac{r}{R}\right) = \sqrt{3} \Rightarrow \frac{r}{R} = \sqrt{3} - 1$$

$$\Rightarrow r = R(\sqrt{3} - 1)$$

$$\Rightarrow r = \frac{a}{2}(\sqrt{3} - 1) = 0.67 \text{ Å}$$

Max allowed value is 0.67 Å. Thus, it can't accomodate atom of 1.68 Å in void.

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

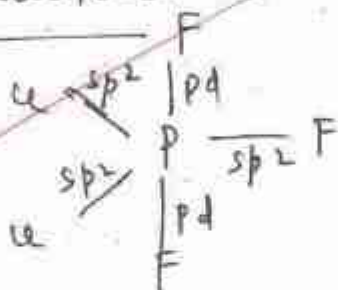$\boxed{PCl_2F_3}$ using drago's rule $\boxed{\begin{array}{l} e^- pair = \frac{1}{2}[5+5] = 5 \\ bond\ pair = 5 \\ lone\ pair = 0 \end{array}}$

As per VSEPR theory, more electronegative atom occupy axial position first to minimise bond-pair, bond-pair repulsion.

$Sp^3 d^2$ hybridization with trigonal bypyramidal shape geometry.

$\boxed{Regular\ shape}$ (as no lone pair)

$\boxed{combination\ of\ sp^2\ and\ pd\ hybrid\ orbitals}$ Bent Rule

$\boxed{SF_4}$ $e^- pair = \frac{1}{2}[6+4] = 6$

bond pair = 4
lone pair = 2

$\boxed{Geometry}$ = square pyramidal

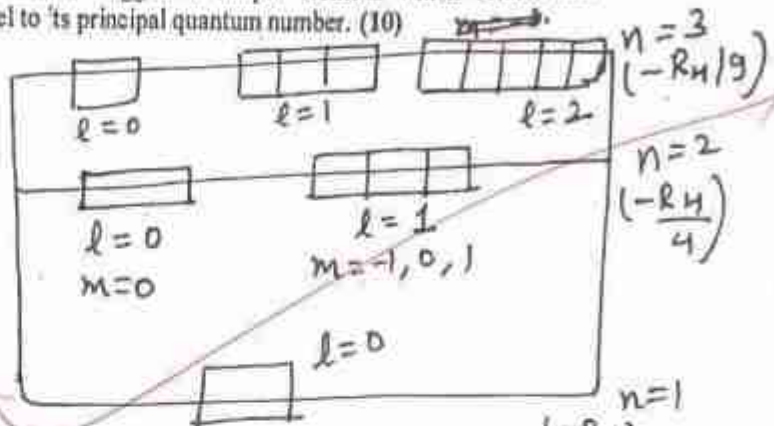$\boxed{Shape}$ square planar (presence of 2 lone pairs)

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

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

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 'ts principal quantum number. (10)

(i) $E_1 = -\dfrac{R_H}{1} = -R_H$

$E_2 = \dfrac{-R_H}{4}$

$E_3 = \dfrac{-R_H}{9}$

$n = 3 \ (-R_H/9)$

$\ell = 0 \qquad \ell = 1 \qquad \ell = 2$

$n = 2 \ \left(-\dfrac{R_H}{4}\right)$

$\ell = 0 \qquad \ell = 1$
$m = 0 \qquad m = -1, 0, 1$

$\ell = 0$

$n = 1 \ (-R_H)$

(ii)

For $\ell = 0 \quad m = 0$

For $\ell = 1 \quad m = -1, 0, 1$

For $\ell = 2 \quad m = -3, \theta 1, 0, 1, 2, 3$

$\left(\ell = 0 \text{ to } n-1 \rightarrow \text{azimuthal quantum number} \right)$

degeneracy of the energy level $= \displaystyle\sum_{\ell=0}^{\ell=n-1} (2\ell+1)$

$\boxed{\text{degeneracy of energy level} = n^2}$

(ii)

For $n = 1 \qquad$ degeneracy $= 1$

$n = 2 \qquad$ degeneracy $= 4 \quad \left(\begin{array}{cc} \ell = 0 & ; \ \ell = 1 \\ m = 0 & ; \ m = -1, 0, 1 \end{array} \right)$

$n = 3 \qquad$ degeneracy $= 9 \quad \left(\begin{array}{ccc} \ell = 0, & \ell = 1 & , \ \ell = 2 \\ m = 0 & ; \ m = -1, 0, 1 & ; \ m = -3, -1, \\ & & 0, 1, 2\theta \end{array} \right)$

SECTION – B

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

__Arrangement of atoms :-__

12 at corners $= \frac{1}{6} \times 6 + \frac{1}{6} \times 6 = 2$

2 at face centre $= \frac{1}{2} \times 1 + \frac{1}{2} \times 1 = 1$
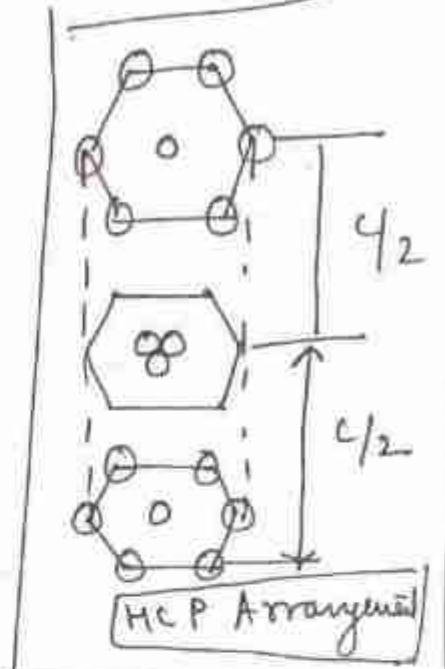
3 at centre of Hexagon $= 3$

$$\boxed{Z_{total} = 6}$$

$\boxed{\text{Volume of a unit cell}} = \text{Area} \times \text{height}$

Area cross section $= 6 \times \frac{\sqrt{3}}{4} a^2$

$V_{unit\,cell} = \frac{3}{2} \times \sqrt{3}\, a^2 \times C$

$\boxed{\text{Volume occupied by atoms}} = Z \times \frac{4}{3} \pi r^3 = 8 \pi r^3$

$\boxed{\text{Relation between } r, a, c}$

($r = $ radius of atom)

(ii)

$4r^2 = \frac{c^2}{4} + \frac{a^2}{3}$

$4 \times \frac{a^2}{4} = \frac{c^2}{4} + \frac{a^2}{3}$

$\Rightarrow \frac{2a^2}{3} = \frac{c^2}{4} \Rightarrow \boxed{c = \frac{2\sqrt{2}\, a}{\sqrt{3}}}$ ②

HCP Arrangement

$a = $ sides of hexagon
$c = $ height of HCP

(i) __along side of hexagon__

$\boxed{2a = 4r}$ ——①
$2r = a$

$\phi = \dfrac{\text{Volume of occupied atoms}}{\text{Volume of unit cell}}$

$= \dfrac{8 \pi \left(\frac{a}{2}\right)^3}{\frac{6\sqrt{3}}{4} a^2 \times \frac{2\sqrt{2}\, a}{\sqrt{3}}}$

$\boxed{\phi = \dfrac{\pi}{3\sqrt{2}} = 0.74 \mid = 74\%}$

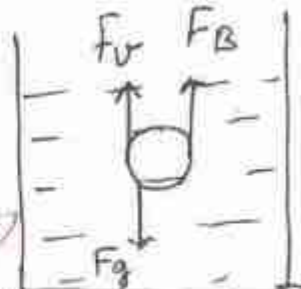(b) What is Stroke's law. How it is utilized to determine viscosity of liquid?   (10)

As per sterokes law, viscous force experienced by an object falling through a liquid is directly propostion to it's velocity and radius.

$$F_{viscous} = 6\pi \eta \, r v$$

F_g = gravitational force

F_B = Buoyancy Force

F_v = Viscous force

From Mass balance

$$F_g = F_v + F_B$$

$$\Rightarrow f_B \times \frac{4}{3}\pi r^3 g = 6\pi \eta \, r v + f_l \times \frac{4}{3}\pi r^3 g$$

$$\Rightarrow 6\pi \eta \, r v = (f_B - f_l) \times \frac{4\pi r^3}{3} g$$

$$\Rightarrow \boxed{\eta = \frac{2}{9}(f_B - f_l)\frac{r^2 g}{v}}$$

Ball falling through liquid

f_l = density of liquid

f_B = density of ball

r = radius of ball

η = viscosity coefficient of liquid

v = velocity of ball

For water $\eta_{water} = \frac{2}{9}(f_B - f_w)\frac{r^2 g}{v_1}$

For unknown liquid (x) $\eta_x = \frac{2}{9}(f_B - f_x)\frac{r^2 g}{v_2}$

$$\frac{\eta_{water}}{\eta_x} = \frac{(f_B - f_w)}{v_1} \times \frac{v_2}{(f_B - f_x)}$$

For falling through same distance $\frac{v_2}{v_1} = \frac{t_1}{t_2}$

$$\Rightarrow \boxed{\frac{\eta_{water}}{\eta_x} = \frac{f_B - f_w}{f_B - f_x} \times \frac{t_1}{t_2}}$$

t = time taken to fall a distance 'l' in liquid.

(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)

A function is said to be an eigenfunction of a operator If it reproduces the function with a constant value, when operated over an operator

$$\boxed{\hat{A}\,\psi = A\,\psi}$$

$\hat{A}$ = operator $\quad \psi$ = eigen function

A = Eigen Value.

Now $\left(\dfrac{d^2}{dx^2} - 4a^2x^2\right)\psi(x) = \dfrac{d^2}{dx^2}\left(x e^{-ax^2}\right) - 4a^2x^2\left(x e^{-ax^2}\right)$

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

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

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

$$= -2ax e^{-ax^2}$$

$\Rightarrow \left(\dfrac{d^2}{dx^2} - 4a^2x^2\right)\left(x e^{-ax^2}\right) = (-2a)\left(x e^{-ax^2}\right)$

$\Rightarrow x e^{-ax^2}$ is an eigen function with eigen value of $(-2a)$.

(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 dscribe 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 LCAO-MO , consider ψ_a = wave function of H_A
($H_A - H_B$) ψ_b = wave function of H_B

$$\Rightarrow \boxed{\psi_{LCAO} = C_a \psi_a \pm C_b \psi_b}$$

C_a, C_b = e^- carrying capacity of A and B.

$\boxed{\text{For Bonding}}$

$\psi_{LCAO} = C_a \psi_a + C_b \psi_b$

$\boxed{\text{For anti bonding}}$

$\psi_{LCAO} = C_a \psi_a - C_b \psi_b$

For H_2 molecule $C_a = C_b$ and after normalizing

① — $\boxed{\psi_{H_2} = \dfrac{\psi_a \pm \psi_b}{\sqrt{2}}}$

for bonding $\psi_{H_2} = \dfrac{\psi_a + \psi_b}{\sqrt{2}}$

(ii) As compared to eq(i), there are following difference in eq (2) $\phi = c_1 \psi_a(1)\psi_b(2) + c_2 \psi_a(2)\psi_b(1)$

① eq ① is normalised while eq (2) is not

② eq ① corresponds to combination of entire orbitals to form molecular orbitals while eq ② corresponds only to valence orbitals

③ Exchange energy is taken in eq ② that is exchange of e_1 and e_2 between two atoms of Hydrogen.

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

(i) <u>For Maxwell distribution</u>

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

$\frac{dN}{N}$ = fraction of molecules with speed between c and $c+dc$

N = total no. of molecules.
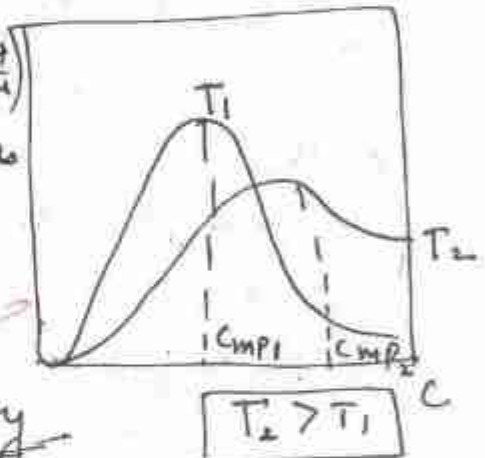
m = mass of 1 atom T = temperature

c = speed of atom K = boltzman constant

(ii) <u>Temperature dependence</u> : $\frac{1}{dc}\left(\frac{dN}{N}\right)$

(a) <u>as T increases</u>; C_{mp} increases

as $C_{mp} = \sqrt{\frac{2RT}{M}}$

(b) <u>More fraction</u> of molecules associated with <u>large velocity</u> as kinetic energy of molecules increase.

$\boxed{T_2 > T_1}$

$\boxed{\text{Net result} = \text{distribution becomes flatter and broader}}$

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

Born lande equation relates theoratical lattice energy to various factors.

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

$Z_+ Z_-$ = charge of cation and anion
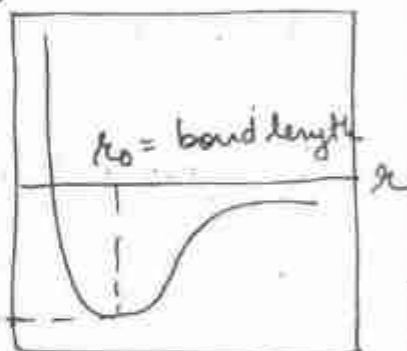r_0 = bond length
A = Madelum constant
n = born exponent

Derivation Let two ion Z_+ and Z_- come close to each other such that potential varies as below.

$$U_{attractive}\binom{attractive}{potential} = \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0 r}$$

$$U_{repulsive}\binom{repulsive}{potential} = \frac{B}{r^n}$$

$(B = constant)$

r_0 = bond length

$$U_T = U_{att} + U_{rep} = \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0 r} + \frac{B}{r^n}$$

$$\boxed{\frac{dU}{dr} = 0 \quad at \quad U_{min} = U_0 \quad and \quad r = r_0}$$

$$\Rightarrow \frac{dU}{dr} = \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0}\left(\frac{-1}{r^2}\right) + \frac{B(r^{-n+1})}{1-n} = 0$$

$$\Rightarrow \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0} \left(\frac{1}{r_0^2}\right) = \left(\frac{1}{1-n}\right)(B)\left(\frac{1}{r^{1-n}}\right)$$

$$\Rightarrow B = \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0 r_0^2}(1-n)(r_0^{1-n})$$

Putting this in U_+ $\Rightarrow$ $U = \frac{Z_+ Z_- e^2}{4\pi \varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$

But in lattice, there are infinit repeation of a unit cell involving many interactions between anion and cation. To check this Madlung constant is introduce.

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

$\boxed{\text{A depend only on crystal property not on ions)}}$

(ii) $\boxed{\text{Modifications imposed on } U_c}$

(a) U_c is calculated only for ionic compounds. But as per fajan's rule, no compound is purely ionic. Thus, factor of covalency has to be included as U_c give higher value of lattic energy.

(b) atoms vibrate continuously. Even at $T=0\,K$ they have zero point vibrational energy $= \frac{1}{2}h\nu$

(c) specific heat capacity $\boxed{C = a + bT + cT^2}$ is not 0 at even 0 K.

$\boxed{\text{despite all 3 factor, } U_c \text{ is good formula to estimate lattice energy}}$

(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

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

<u>Most probable</u> distance is that distance where there is <u>highest possibility</u> of finding e^-.

$$\boxed{\begin{array}{l}\text{Probability of finding } e^- \\ (\text{Probability density}) \ (R)\end{array} = r^2 \Psi_{XS}^2 = \frac{1}{\sqrt{\pi a_0^{3/2}}} r^2 \exp\left(\frac{2r}{a_0}\right)}$$

Now $\boxed{\dfrac{dR}{dr} = 0 \quad \text{at} \quad r = r_{mp}}$

$\dfrac{dR}{dr} = \dfrac{d}{dr}\left[\dfrac{1}{\sqrt{\pi a_0^{3/2}}} r^2 \exp\left(\dfrac{-2r}{a_0}\right)\right]$

$= \dfrac{1}{\sqrt{\pi a_0^{3/2}}}\left[r^2\left(\dfrac{-2}{a_0}\right)\exp\left(\dfrac{-2r}{a_0}\right) + \exp\left(-\dfrac{2r}{a_0}\right)(2r)\right]$

Now $\dfrac{dR}{dr} = 0$

$\Rightarrow) \quad \dfrac{2r^2}{a_0} = 2r$

$\Rightarrow) \quad \boxed{r_{mp} = a_0}$

$r^2 \Psi_{XS}^2$

$\boxed{r_{mp} = a_0}$

(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)

Frankel and Schottky defects are stoichiometric defects where formula of compound does not change.

(i)

Schottky defect	Frankel defect
① equal no. of cation and anion are missing from lattice points.	① one of the ions occupy interstial space (void space) in Lattice. Since, cation is small, it only occupies void
② Density of compound changes as ions are missing	② Density of compound does not change as they occupy void only
③ observed in compounds where $r_+ \approx r_-$	③ observed where $r_+ << r_-$
④ generally in large coordination no. = 6, 8 eg. $CsCl$	④ in low coordination no. = 6, 4 eg. $AgCl$

(ii) In non stiochiometric defects, formula of compound changes. $ZnO \xrightarrow{heat} ZnO_{1-\delta}(2\delta e^-) + \delta O$ where as formula does not change in schottky and frankel defect.

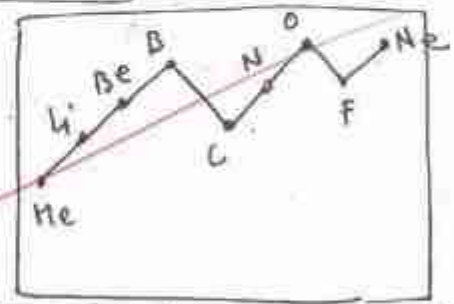(d) Draw and explain curves showing the variation of first and second ionization energies for the elements from H to Ne. (10)

Z

	M^+	M^{+2}
1 H = $1s^1$	$1s^0$	—
2 He = $1s^2$	$1s^1$	$1s^0$
3 Li = $1s^2 2s^1$	$1s^2 2s^0$	$1s^1$
4 Be = $1s^2 2s^2$	$1s^2 2s^1$	$1s^2 2s^0$
5 B = $1s^2 2s^2 2p^1$	$1s^2 2s^2$	$1s^2 2s^1$
6 C = $1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2$
7 N = $1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^1$
8 O = $1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^2$
9 F = $1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^4$	$1s^2 2p^2 2p^3$
10 Ne = $1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^4$

General trend → Ionization energy increase from moving left to right in a period as Z_{eff} increase.

1st I-E

2nd I-E

① dip in Li I-E → due to removal leading to filled $1s^2$.

② dip in 'O' I-E → removal leading to half filled p^3.

③ N very high — due to fully filled p3

dip in C → removal leads to fully filled stable $1s^2 2s^2$

dip in F → removal leading to $2p^3$.

34

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)

For vander wal gas critical constants are

$$T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3b$$

From these three eq^n $a = \frac{27 R^2}{64} \frac{T_c^2}{P_c} \Rightarrow a \propto \frac{T_c^2}{P_c}$

For CO_2 $\quad \frac{T_c^2}{P_c} = \frac{(304)^2}{74} = 1248.86$ For NH_3 $\quad \frac{T_c^2}{P_c} = \frac{(405)^2}{111}$
$$= 1477.7$$

∴ Since $\frac{T_c^2}{P_c}(NH_3) > \frac{T_c^2}{P_c}(CO_2) \Rightarrow \boxed{a_{NH_3} > a_{CO_2}}$ CO_2 has smaller 'a'

For CO_2 Now, $\frac{T_c}{P_c} = \frac{8b}{R} \Rightarrow b \propto \frac{T_c}{P_c}$

For CO_2 $\quad \frac{T_c}{P_c} = 4.108$ For NH_3 $\quad \frac{T_c}{P_c} = 3.64$

$\Rightarrow \boxed{b_{CO_2} > b_{NH_3}}$ NH_3 has smaller 'b'

$T = 300 K$ is less than T_c for CO_2 and more but near to $(T_c = 304 K)$. But $T = 300K$ is very less than T_c for NH_3 (405 K). Thus, CO_2 is most nearly ideal at 300 K.
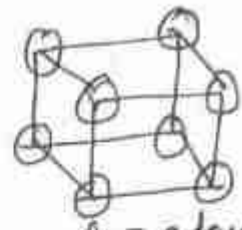
(b) What is atomic radius of a cubic lattice? Find the atomic packing factor in , body- centrad cubic system and face-centred cubic system.

(10)

In Cubic lattice (simple)

atoms are in contact along the edge $\Rightarrow$ $2r = a$ $\Rightarrow$ $r = \dfrac{a}{2}$

$r = $ atomic radius

In BCC   atomic packing $= \dfrac{V_{atom} \times Z}{V_{unit\,cell}}$

(ϕ)

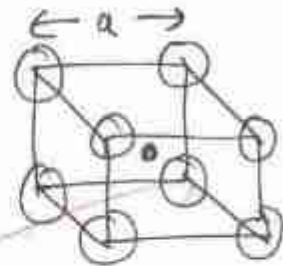$Z = \dfrac{1}{8} \times 8 + 1 = 2$

$V_{unitcell} = a^3$ $V_{atom} = \dfrac{4}{3}\pi r^3$

Along body diagonal $\dfrac{\sqrt{3}\,a}{2} = 2r \Rightarrow r = \dfrac{\sqrt{3}\,a}{4}$

$\phi_{(BCC)} = 2 \times \dfrac{4}{3}\pi \times \dfrac{3\sqrt{3}}{64} \dfrac{a^3}{a^3} = \dfrac{\sqrt{3}\,\pi}{8}$

$\boxed{\phi_{BCC} = \dfrac{\sqrt{3}\,\pi}{8} = 0.68}$

In FCC $Z = \dfrac{1}{8} \times 8 + \dfrac{1}{2} \times 6 = 4$

corners   Face center.

along face diagonal $\sqrt{2}\,a = 4r \Rightarrow r = \dfrac{\sqrt{2}\,a}{4}$

$\phi_{FCC} = 4 \times \dfrac{4}{3}\pi \times \dfrac{2\sqrt{2} \times a^3}{64 \times a^3} = \boxed{\dfrac{\sqrt{2}\,\pi}{6} = 0.74}$

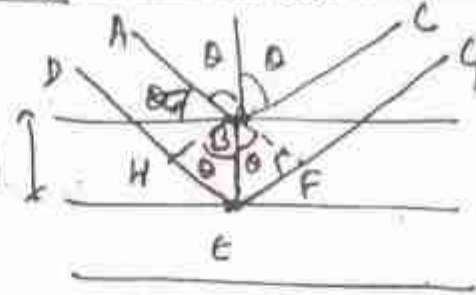(c) Drive bragge's equation. Using X-ray powder pattern of a compounds describe how do you calcuate the spacing between the planes.

(II)

<u>From the figure,</u>

$$\sin\theta = \frac{EF}{d} \Rightarrow EF = d\sin\theta$$

Similarly $EH = d\sin\theta$

<u>For constructive interference</u> of ABC and DEG rays
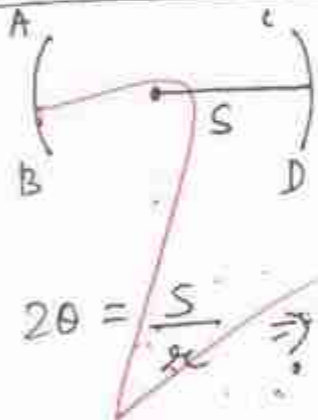
Path difference $= n\lambda$ — ①

n = order of reflection
λ = wavelength used

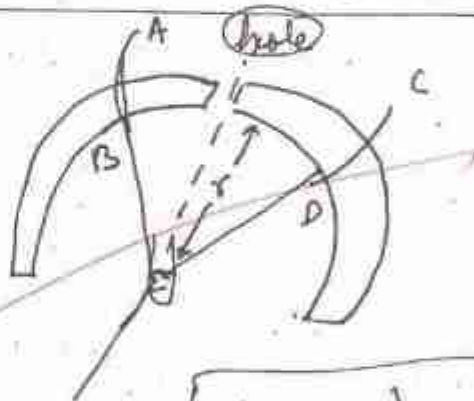Path difference $= EH + EF = 2d\sin\theta$ — ②

From eq ① and ②

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

θ = angle of diffraction
d = interplanar distance.

S = spacing between the arcs formed on the film and hole

$$2\theta = \frac{S}{r} \Rightarrow \boxed{\theta = \frac{S}{2r}}$$
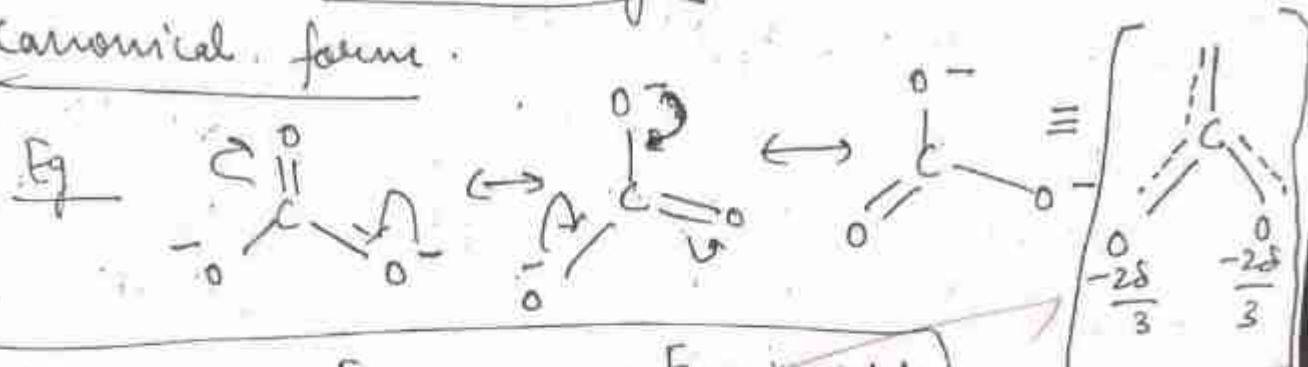
using this θ in braggs equation :- $\boxed{\dfrac{d}{n} = \dfrac{\lambda}{2\sin\theta}}$

$\dfrac{d}{n}$ = interplanar distance

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

Resonance energy is defined as the energy difference between the Resonance hybrid and the most stable canonical form.

Eg

$$E_{Resonance} = E_{Resonance\ Hybrid} - E_{Most\ stable\ resonating\ structure}$$

Resonance hybrid

⇒ Since Resonance hybrid is a hypothetical structure and does not exist in real form, Its energy can't be determined.

⇒ So, Resonance energy is indirectly calculated using heat of hydrogenation of the compound.

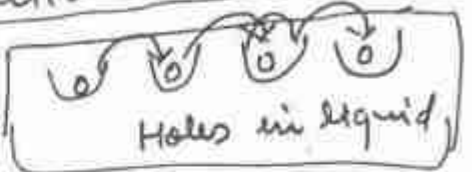Thus Resonance energy $= |\Delta E^{\circ}_{Theoretical} - \Delta E^{\circ}_{practical}|$

$\Delta E_{theoretical} =$ theoretical heat of hydrogenation (HoH)

$\Delta E_{practical} =$ practice (HoH)

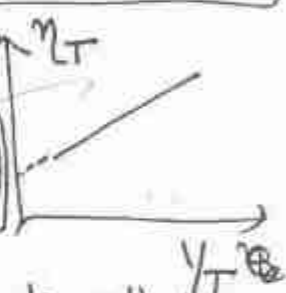(e) why viscosity of gas increases with increase in temperature while that of liquid decreases with temperature.
(10)

Viscosity of liquid arises due to activated flow (i.e laminar flow of liquid). As per hole theory, when temperature increase, more activation energy is available for liquid molecules to move in and out of liquid. Holes in liquid.
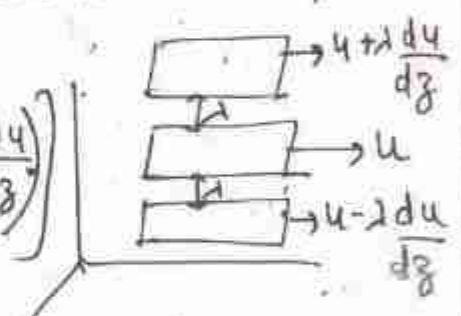
This, resistance to flow decrease and $\uparrow \eta_T$

Viscosity also decrease $\eta_T = \eta_0 \exp\left(\frac{\epsilon}{KT}\right)$

Viscosity of gas → this arises not due to activated flow but due to transfer of momentum from one layer to another.

Change in momentum $= \frac{1}{4} N^* \bar{c} \left[m \left(u - \lambda \frac{du}{dz} - u - \lambda \frac{du}{dz} \right) \right]$

$= \frac{1}{4} N^* \bar{c} \, m \times (2\lambda) \frac{du}{dz}$

$\boxed{\eta = \frac{N^* \bar{c} \, m \, \lambda}{2}}$ $\lambda \theta = \frac{1}{\sqrt{2} \, \pi d^2 N^*}$

$\eta = \frac{m}{2\sqrt{2} \pi d^2} \bar{c} = \frac{m}{2\sqrt{2} \pi d^2} \sqrt{\frac{8RT}{\pi M_0}}$

$\lambda = $ mean free path.

$\eta_T = \eta_0 \exp\left(-\frac{\epsilon}{2kT}\right)$

$\boxed{\eta \propto \sqrt{T}}$