

DIAS

All India TEST – SERIES CSE – 2023

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:- ANANYA RANA

Date - 23rd June 2023

UPSC Roll no:-

Mobile Number. 9588155398

Official use.

Q.NO.	1	2	3	4	5	6	7	8
MARKS	31	✓	30	30	26	✓	37	✓

Signature of invigilator

Signature of
Examiner

DIAS
SECTION-A

1.(a) The electron in H-atom may be thought of as confined to a nucleus of radius $0.5 \text{ \AA}$ calculate minimum uncertainty in momentum & kinetic energy. (10)

(mass of electron = $9.1 \times 10^{-31} \text{ kg}$, $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$)

According to Heisenberg Uncertainty Principle, position and momentum of a sub-atomic particle can't be determined accurately simultaneously.

Thus, $\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}$

According to given question, $\Delta x = 0.5 \text{ \AA} = 0.5 \times 10^{-10} \text{ m}$

$\therefore \Delta p_x \geq \frac{h}{4\pi \Delta x}$

$\therefore$ Minimum uncertainty in determining momentum is

$$\frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.14 \times 10^{-10} \text{ m}}$$

$\Delta p_x = 0.527 \times 10^{-24} \text{ kg m/s}$

Kinetic Energy = $\frac{p^2}{2m} \Rightarrow \Delta KE = \frac{p \Delta p}{m}$

$p = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = \frac{1}{2} m \frac{(\Delta x)^2}{(\Delta t)^2}$

$\Rightarrow \Delta KE = \frac{1}{2} m \frac{(\Delta x)^2}{(\Delta t)^2} \Delta p = \frac{(\Delta x)^2 \times \Delta p}{2 (\Delta t)^2} = \frac{(10^{-10})^2 \times (0.527 \times 10^{-24})}{2}$

$\Delta KE = 0.2635 \times 10^{-44} \text{ J}$

DIAS

b) Determine the activation Energy of flow of diethyl ether if its viscosity is 2.84 milli-poise at 273K and 2.33 milli-poise at 293 K. (10)

Viscosity of any liquid is defined as the amount of force required to maintain a unit gradient between 2 layers of contact having unit area.

$$\ln \frac{\eta_2}{\eta_1} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{2.33}{2.84} = \frac{E_a}{8314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(-\frac{1}{273} + \frac{1}{293} \right)$$

$$\ln \frac{2.84}{2.33} = \frac{E_a \times 20}{293 \times 273 \times 8314 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Rightarrow E_a = \frac{293 \times 273 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{20} \times \ln \frac{2.84}{2.33}$$

$$= 33251.427 \times 0.1979$$

$$= 6581.647 \text{ J mol}^{-1}$$

Thus, activation energy = 6.581 KJ : mol⁻¹

DIAS

c) The angle between the planes having miller indices (110) and (111) in a Simple cubic lattice. (10)

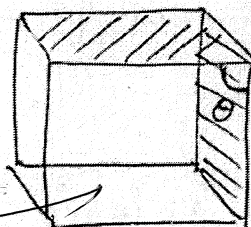
The simple cubic lattice is a primitive type of unit cell having atoms/ions/molecules only at the corners.

The angle between the planes of a lattice is determined using the miller indices of the planes.

According to definition of dot product.

$$\vec{A} \cdot \vec{B} = |\vec{A}| |\vec{B}| \cos \theta$$

$$\Rightarrow \cos \theta = \frac{\vec{A} \cdot \vec{B}}{|\vec{A}| \cdot |\vec{B}|} \quad (1)$$



θ = angle between 2 shaded planes

In the given question, $(110) = 1\hat{i} + 1\hat{j} + 0\hat{k}$
and $(111) = 1\hat{i} + 1\hat{j} + 1\hat{k}$.

Putting values in (1) we get

$$\cos \theta = \frac{(1\hat{i} + 1\hat{j} + 0\hat{k}) \cdot (1\hat{i} + 1\hat{j} + 1\hat{k})}{\sqrt{1^2 + 1^2 + 0^2} \sqrt{1^2 + 1^2 + 1^2}}$$

$$= \frac{(1+1)}{\sqrt{2} \times \sqrt{3}} = \frac{2}{\sqrt{2} \times \sqrt{3}} = \frac{\sqrt{2}}{\sqrt{3}} = 0.8164$$

$$\Rightarrow \cos \theta = 0.8164$$

$$\text{Thus } \theta = \cos^{-1}(0.8164) = 35.31^\circ$$

Thus, angle between both the planes is 35.31° is an acute angle.

DIAS

(d) The critical temperature (T_c) for CO_2 is 300K and its critical density is 0.45 g/cm. Calculate critical pressure and Vanderwall's constant 'a' & 'b'. (10)

The critical constants of a gas i.e. T_c , P_c and V_c are those unique values that help in determining the conditions required for its liquefaction.

Critical constants can be determined using isotherm method.
Van der waal equation is written as:

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

where $a, b =$
vander waal
constants

$$\Rightarrow \boxed{P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}} \quad \text{--- (1) Differentiating equation (1) w.r.t } V_m \text{ at constant temperature } T$$

twice we get,

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} \quad \text{--- (2)}$$

$$\text{and } \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} \quad \text{--- (3)}$$

At critical point, $\left(\frac{\partial P}{\partial V_m}\right)_T = \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = 0$

Thus, we get. $\frac{RT_c}{(V_{m,c} - b)^2} = \frac{2a}{V_{m,c}^3}$ and $\frac{2RT_c}{(V_{m,c} - b)^3} = \frac{6a}{V_{m,c}^4}$

Dividing we get, $\boxed{T_c = \frac{8a}{27Rb}}$, $\boxed{V_c = 3b}$, $\boxed{P_c = \frac{a}{27b^2}}$

Given: Critical density $= \rho_c = \frac{m}{V_c} = 0.45 \text{ g cm}^{-3} \Rightarrow V_c = \frac{m}{0.45 \text{ g cm}^{-3}}$
 $\Rightarrow V_c = \frac{44 \text{ g mol}^{-1} \times 1000}{45 \text{ g cm}^{-3}} = 97.77 \text{ cm}^3 \text{ mol}^{-1} = 97.77 \times 10^{-3} \text{ L mol}^{-1}$

$\Rightarrow V_c = 3b = 97.77 \times 10^{-3} \text{ L mol}^{-1} \Rightarrow \boxed{b = 32.59 \times 10^{-3} \text{ L mol}^{-1}}$

Putting value of T_c and b we get $300 \text{ K} = \frac{8a}{27 \times 0.03259 \text{ L mol}^{-1} \times 0.03259 \text{ L mol}^{-1} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}$
 $\Rightarrow a = \frac{300 \times 27 \times 0.03259 \times 0.03259 \times 8.314}{8} \text{ L}^2 \text{ atm mol}^{-2} = 2.709 \text{ L}^2 \text{ atm mol}^{-2}$

Putting values of a, b in P_c we get $P_c = \frac{2.709 \text{ L}^2 \text{ atm mol}^{-2}}{27 \times (0.03259)^2 \text{ L}^2 \text{ mol}^{-2}} = 3.078 \text{ atm}$

Thus, $\boxed{P_c = 3.078 \text{ atm}}$

$\boxed{a = 2.709 \text{ L}^2 \text{ atm mol}^{-2}}$

$\boxed{b = 32.59 \times 10^{-3} \text{ L mol}^{-1}}$

DIAS INDIA EDUTECH (P) LTD.

18, Pusa Road Karol Bagh, New Delhi - 110005

PH: 011-40079000, 9350934622

DIAS

Briefly explain the following statement:

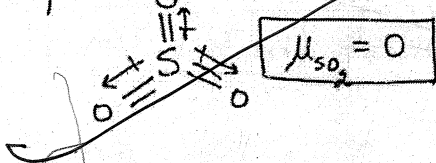
(10)

- (i) SO_3 is non-polar while SO_2 is polar
 (ii) O_2^+ is less stable than O_2

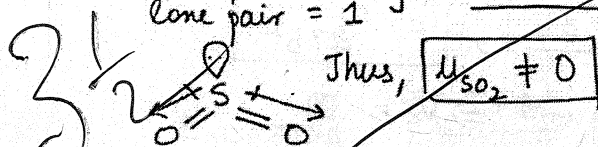
i) The polar and non-polar character of a molecule is dependent on the Shape of the molecule and the resulting dipole moment

(a) SO_3 Using drago formula,
 electron pair = $\frac{6}{2} = 3 \therefore sp^2$
hybridisation

lone pair = 0
 bond pair = 3 $\Rightarrow$ trigonal shape

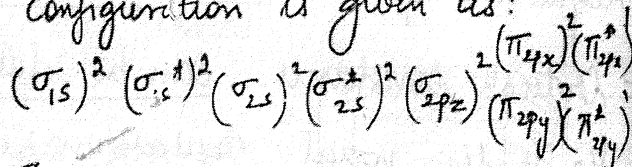


(b) SO_2 electron formula = $\frac{6}{2} = 3$
 bond pair = 2
 lone pair = 1 $\Rightarrow$ Bent shape



Hence, SO_3 is non-polar
 while SO_2 is polar

(ii) O_2 has 16 e^- . Its MO configuration is given as:

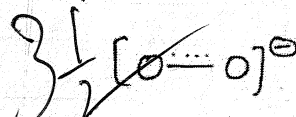


Thus, Bond order = $\frac{e_{\text{bonding}} - e_{\text{anti}}}{2}$

$$= \frac{10 - 6}{2} = 2 \quad \boxed{O = O}$$

for O_2^+ 1 e^- is added to antibonding π orbital
 (either $\pi_{2p_x}^*$ or $\pi_{2p_y}^*$)

Thus, Bond order = $\frac{10 - 7}{2} = \frac{3}{2} = 1.5$



Hence, bond order decreases on addition of 1 more e^- .
 Since, bond order depicts the strength of bond and hence the stability, thus a decrease in bond order means decrease of stability. Hence, O_2^+ is less stable than O_2

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

Reduced equation of state is defined as the equation which consists of atleast 2 constants other than the universal gas constant. The gases in such state are said to be following law of corresponding states.

Van der Waal equation of state is given as:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad \text{where } P = \text{Pressure of the gas}$$

$$V_m = \text{molar volume of the gas}$$

$$T = \text{Temperature in K}$$

$$R = \text{Universal gas constant}$$

$$a, b = \text{van der Waal state constants}$$

$$-(1)$$

Defining new constants as

$$\boxed{\pi = \frac{P}{P_c}}, \quad \boxed{\theta = \frac{T}{T_c}} \quad \text{and} \quad \boxed{\phi = \frac{V}{V_c}}$$

where P_c, V_c, T_c are critical constants.

Hence equation (1) becomes, $\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R(\theta T_c)$

Putting values of $\boxed{T_c = \frac{8a}{27Rb}}$, $\boxed{V_c = 3b}$, $\boxed{P_c = \frac{a}{27b^2}}$ we get

$$\left[\pi \left(\frac{a}{27b^2}\right) + \frac{a}{\phi^2 (9b^2)}\right] [3b\phi - b] = R\theta \left(\frac{8a}{27Rb}\right)$$

$$\Rightarrow \left(\frac{\pi}{27} + \frac{1}{9\phi^2}\right) [3\phi - 1] = \frac{8R\theta}{27R}$$

$$\Rightarrow \boxed{\left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) = 8\theta} \quad \rightarrow \text{Reduced equation of state}$$

This equation contains 3 constants π, ϕ and θ and can be utilised to determine the values of P, T and Volume of a gas.

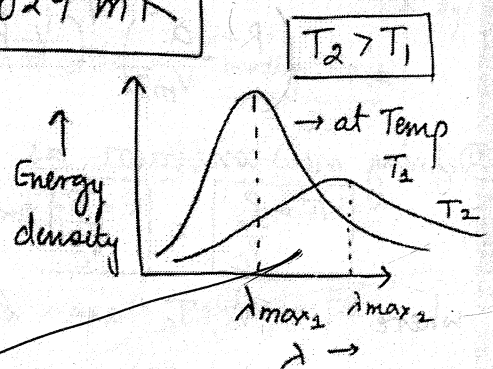
DIAS

(b) What is Wien-displacement law? Using this determine $\lambda_{\max}$ of energy distribution of black body at 1300 K Temperature. (10)

Wien-displacement law states that for a black body the product of the wavelength of emission and its temperature is always constant.

Mathematically, $\lambda_{\max} T = 0.029 \text{ m K}$

$\lambda_{\max}$ = wavelength for a given temperature at which the energy density of emission is maximum.



According to statement, Temperature = 1300 K

Thus, $\lambda_{\max} \times 1300 \text{ K} = 0.029 \text{ m K}$

$$\Rightarrow \lambda_{\max} = \frac{0.029 \text{ m}}{1300} = 2.23 \times 10^{-5} \text{ m}$$

The value of maximum $\lambda = 2.23 \times 10^{-5} \text{ m}$ lies in the infrared region.

According to this law, it is also clear that as Temperature increases the wavelength for maximum emission decreases.

(c) KNO_3 crystallizes in orthorhombic system with unit cell dimension $a = 542 \text{ pm}$, $b = 917 \text{ pm}$ and $c = 645 \text{ pm}$. Calculate diffraction angle for first order reflection from (100) (010) & (111) plane using radiation with wave length 154.1 pm . (10)

Orthorhombic system is defined with the cell parameters a, b, c and α, β, γ having following properties:

$$a \neq b \neq c \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ$$

According to Bragg's law, $2d \sin \theta = n\lambda$ where

d : interplanar distance

n : order of diffraction

θ : angle of reflection

λ : wavelength of light used.

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

Given: $a = 542 \text{ pm}$ $n = 1$

$b = 917 \text{ pm}$

$c = 645 \text{ pm}$

$\lambda = 154.1 \text{ pm}$

(i) $\therefore \frac{1}{d_{100}^2} = \left(\frac{1}{542}\right)^2 \Rightarrow d_{100} = 542 \text{ pm}$

$\therefore 2 \times d_{100} \sin \theta = 154.1$

$\Rightarrow \sin \theta = \frac{154.1}{2 \times 542} = 0.142 \Rightarrow \theta_{100} = 8.16^\circ$

(ii) $\frac{1}{d_{010}^2} = \frac{1}{917^2} \Rightarrow d_{010} = 917 \text{ pm}$

$\therefore \sin \theta = \frac{154.1}{2 \times 917} = 0.084$

$\theta_{010} = 4.81^\circ$

(iii) $\frac{1}{d_{111}^2} = \frac{1}{(542)^2} + \frac{1}{(917)^2} + \frac{1}{(645)^2} = \frac{10^{-6}}{6.98} \times (3.4 + 1.19 + 2.40)$

$= 6.98 \times 10^{-6}$

$\Rightarrow d_{111}^2 = \frac{10^6}{6.98} \Rightarrow d_{111} = 0.3785 \times 10^3 = 3785 \text{ pm}$

$\Rightarrow 2 \sin \theta_{111} = \frac{154.1}{2 \times 3785} = 0.203 \Rightarrow \theta_{111} = 11.71^\circ$

Thus, $\theta_{100} = 8.16^\circ$, $\theta_{010} = 4.81^\circ$ and $\theta_{111} = 11.71^\circ$

DIAS INDIA EDUTECH (P) LTD.

18, Pusa Road Karol Bagh, New Delhi - 110005

PH: 011-40079000, 9350934622

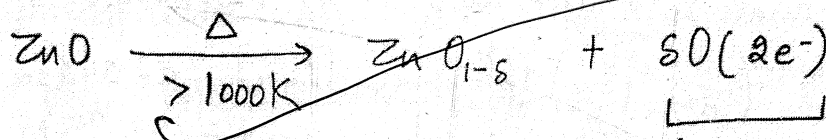
DIAS

(d) Some solids generally oxide are insulator and white at room temperature but upon heating at high temperature above 1000K show colour property and start conducting electricity explain phenomenon.

(10)

Solids which are generally perfect in structure often show defects when heated to higher temperatures. One of the most common effect is metal excess defect which causes solid oxides to appear coloured and show conducting properties.

example - Zinc oxide. (ZnO)



$2e^-$ move into
interstitial positions

(i) Appearance of colour

The $2e^-$ which have now become free can get themselves involved in transition and when these electrons relax back to original state, they emit radiation which if present in visible region appears as colour.

$\begin{matrix} e^- \\ \downarrow \\ e^- \end{matrix} \rightarrow \begin{matrix} e^- \\ \downarrow \\ e^- \end{matrix} \rightarrow \lambda$
excitation relaxation

(ii) Conduction property

The $2e^-$ are free to move inside the lattice thus causing an overall movement of charge and thus showing conduction property.

DIAS

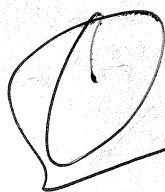
(e) Calculate the Fermi energy of Ag-metal, given that atomic mass of Ag is 107.8 g mol^{-1} the density of metal is 10.5 g cm^{-3} (10)

Fermi energy is defined as the highest level of energy upto which levels are filled by the electrons. It is represented by E_f .

- density of metal = 10.5 g cm^{-3}
- atomic mass = 107.8 g mol^{-1}

$$\Rightarrow \text{volume of metal} = \frac{\text{mass}}{\text{density}} = \frac{107.8 \text{ g mol}^{-1}}{10.5 \text{ g cm}^{-3}} = 10.26 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{Energy } E_f = \frac{KT}{2}$$



4(a) Describe the crystal structures of ZnO & HgI_2 .

(10)

Crystal structures are the arrangement of cation and anion based on their sizes and charges to give rise to a stable configuration.

(1) Crystal structure of ZnO

anions: as face-centred cubic arrangement
cation: alternate tetrahedral voids

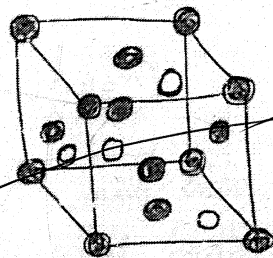
Coordination No: Cation : Anion

4 : 4

No. of atoms: Cation : Anion

4 : 4

formula unit = ZnO (1 unit)



● $\rightarrow \text{O}^{2-}$
 ○ $\rightarrow \text{Zn}$

(2) Crystal structure of HgI_2

DIAS

(b) Explain the following using molecular orbital theory.

(i) The bond length of H_2 is smaller than that of H_2^+ .

(ii) The dissociation energy decreases in going from N_2 to N_2^+ whereas it increases in going from O_2 to O_2^+ .

(iii) The dissociation energy of N_2 is maximum amongst the homonuclear di-atomic molecules. (5+10+5)

(i) Molecular orbital diagram of H_2 having $2e^-$

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

$$\text{Bond order of } H_2 = \frac{2-0}{2} = 1 \quad [H-H]$$

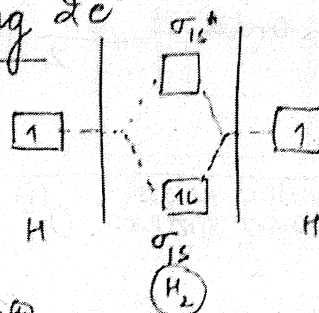
$$H_2^+ : (\sigma_{1s})^1 (\sigma_{1s}^*)^0$$

$$\text{Bond order of } H_2^+ = \frac{1-0}{2} = 0.5 \quad [H \cdots H]^+ \text{ weaker bond}$$

Since, Bond order $\propto \frac{1}{\text{bond length}}$

$\therefore$ as bond order decrease, bond length increase.

Bond order: $H_2 > H_2^+$
 Bond length: $H_2^+ > H_2$



(ii) Molecular orbital diagram of N_2 having $14e^-$ which involves s-p mixing

$$N_2 : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^2 ; N_2^+ : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^1 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^1$$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

$$\text{Bond order} = \frac{9-4}{2} = 2.5$$

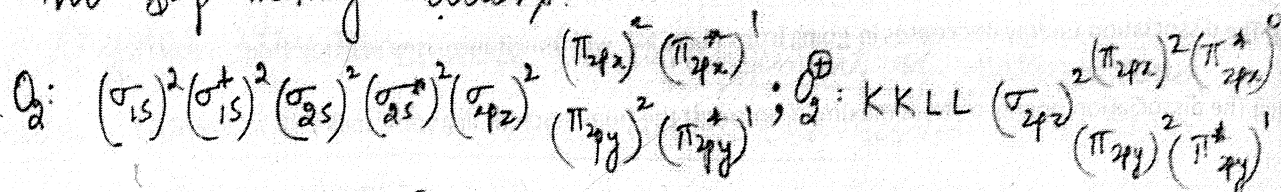
Thus, Bond order: $N_2 > N_2^+$

Since Bond order $\propto$ Bond dissociation energy

$\therefore$ Bond dissociation energy: $N_2 > N_2^+$

DIAS

(i) Molecular Orbital Configuration for O_2 with 16e⁻ where no s-p mixing occurs.



$$\text{Bond order} = \frac{10 - 6}{2} = 2$$

$$\text{Bond order} = \frac{10 - 5}{2} = 2.5$$

Bond order: $O_2^+ > O_2$

as electron removed from anti-bonding orbital.

Bond dissociation energy: $O_2^+ > O_2$

(ii) Bond dissociation energy of N_2 is maximum among all diatomic homonuclear molecules because it has the maximum bond order among them all.

	H_2	He_2	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
B.O.	1	0	1	0	1	2	3	2	1	0

maximum bond order

$N \equiv N \rightarrow 1 \sigma\text{-bond}$
 $\rightarrow 2 \pi\text{-bond}$

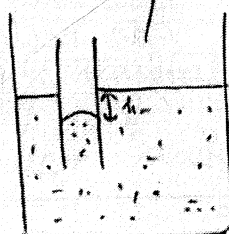
Thus, it is very difficult to break these bonds giving rise to bond dissociation energy of 1300 kJ mol⁻¹

DIAS

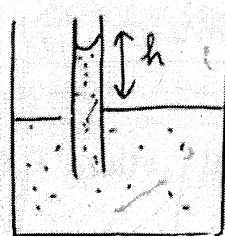
(c) The surface tension of Hg at 0°C is 480.3 dyne/cm while the density is 13.60 g/cm^3 . If it is desired to obtain a full of 10.0 cm height in what capillary radius of capillary tube will have to be used? The angle of contact is 140° . (10)

Capillary action for any liquid is a direct consequence of the surface tension of the liquid.

In case of capillary action, 2 forces i.e. force due to weight of liquid must balance force of buoyancy.



falling liquid
eg - Hg



rising liquid
eg - H_2O

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

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

r = radius of capillary
 γ = surface tension
 θ = angle of contact
 ρ = density of liquid
 g = gravity

According to given question

$$\gamma = 480.3 \text{ dyne/cm}$$

$$\theta = 140^\circ$$

$$h = 10 \text{ cm}$$

$$\rho = 1360 \text{ g cm}^{-3}$$

$$\therefore r = \frac{2\gamma \cos \theta}{h \rho g} = \frac{2 \times 480.3 \text{ dyne cm}^{-1} \times \cos 140^\circ}{10 \text{ cm} \times 1360 \text{ g cm}^{-3} \times 980 \text{ cm s}^{-2}}$$

$$= \frac{-735.862 \text{ g cm s}^{-2}}{13328000 \text{ g s}^{-2}}$$

$$\boxed{r = 5.52 \times 10^{-5} \text{ cm}}$$

$\therefore$ radius of capillary should be $5.52 \times 10^{-5} \text{ cm}$

DIAS

d) Determine the atomic radii of Xenon Vanderwall constant 'a' & 'b' 0.05156 liter/mol.

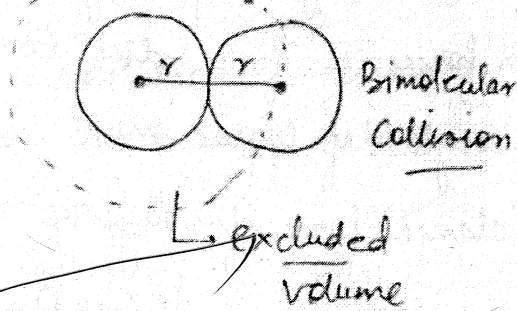
(10)

The van der Waal constant 'b' denotes the excluded volume that is not part of the free movement of the gas molecules in the gas volume.

Thus, the excluded volume per pair

$$= \frac{4}{3} \pi (2r)^3$$

$$= 8 \left[\frac{4}{3} \pi r^3 \right]$$



Thus, excluded volume per molecule = $4 \left[\frac{4}{3} \pi r^3 \right] = \frac{4}{3} b$

where $b = 4 \times \text{volume of 1 molecule}$

Given: $b = 0.05156 \text{ L mol}^{-1} = 4 \times \frac{4}{3} \pi r^3$

$$\Rightarrow r^3 = \frac{3b}{16\pi}$$

$$\Rightarrow r = \left(\frac{3b}{16\pi} \right)^{1/3}$$

Putting all values, we get

$$r = \left(\frac{3 \times 0.05156 \text{ L mol}^{-1}}{16 \times 3.14 \times 6.022 \times 10^{23} \text{ mol}^{-1}} \right)^{1/3}$$

$$= (0.0005112623 \times 10^{-23} \text{ L})^{1/3}$$

$$1 \text{ L} = 10^3 \text{ cm}^3$$

$$= (0.0005112623 \times 10^{-20} \text{ cm}^3)^{1/3}$$

$$= (5.1126 \times 10^{-24} \text{ cm}^3)^{1/3}$$

$$\text{radius} = 1.7227 \times 10^{-8} \text{ cm} = 1.7227 \text{ \AA}$$

DIAS INDIA EDUTECH (P) LTD.

18, Pusa Road Karol Bagh, New Delhi - 110005

PH: 011-40079000, 9350934622

DIAS

SECTION - B

5(a) (i) What are Miller indices what are its significance. (5)

(ii) Calculate inter Planar distance of orthorhombic crystal having Miller indices (1, 2, 3) unit cell dimension are 50, 100, 300 Picometer. (5)

(a) (i) Miller indices are the numerical values corresponding to the intercepts made by crystal planes on the three mutually perpendicular axes. They are represented as (h, k, l) corresponding to intercepts at x-, y- and z-axis respectively.

→ They are calculated by taking reciprocals of the intercepts and finally converting to integral values.

→ **Significance** → (1) helpful in determining the value of intercepts on each axis
(2) don't have '∞' value ∴ ease calculation of determination of angle.

(b) Orthorhombic cell : $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

$(h, k, l) = (1, 2, 3)$ and $a = 50 \text{ pm}$, $b = 100 \text{ pm}$, $c = 300 \text{ pm}$

let $a = 50 \text{ pm} = x$ ⇒ $b = 2x$ and $c = 6x$

$$\text{Thus, } \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{1}{x^2} + \frac{(2)^2}{(2x)^2} + \frac{(3)^2}{(6x)^2} = \frac{1}{x^2} + \frac{1}{x^2} + \frac{1}{4x^2} = \frac{9}{4x^2}$$

$$\Rightarrow d_{hkl}^2 = \frac{4x^2}{9} \Rightarrow d_{hkl} = \frac{2x}{3}$$

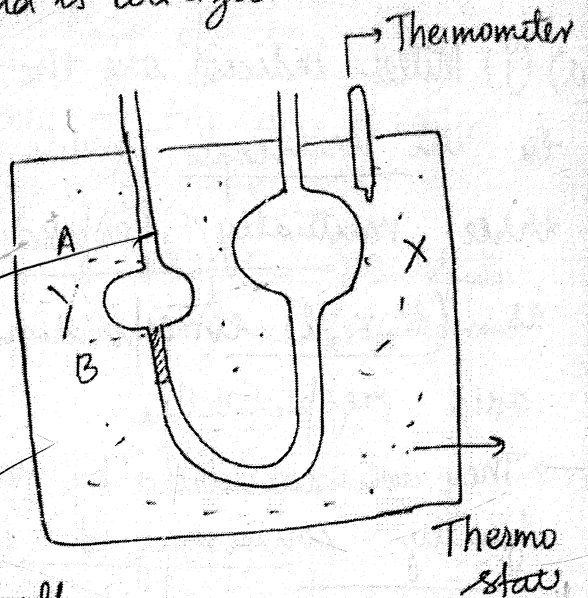
Putting value of x, we get $d_{hkl} = \frac{2}{3} \times 50 \text{ pm} = 33.33 \text{ pm}$

(b) What is stalagmometer how surface tension can be determined by using this?

(10)

Stalagmometer is an instrument with 2 bulbs connected via U-shaped tube and is utilized to measure surface tension.

Diagram:

~~How~~ Working:

- ① Liquid is first sucked into bulb Y from X.
- ② The liquid is then allowed to move from A to B via small capillary (shaded) in bulb Y.
- ③ Time for its flow is noted.

(c) The angular wave function for $l=2, m=0$ is given as

$$Y(00) = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

And that for $l=1, m=1$ is

$$Y(11) = \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$$

Show that both are orthogonal.

(10)

Orthogonality is the property of wavefunctions which states that no two different wavefunctions can exist in space of each other or are perpendicular to each other. Mathematically,

$$\int_{\text{space}} \Psi_m \Psi_n dz = 0 \quad [m \neq n]$$

Putting given values we get,

$$\begin{aligned} \int_{\text{space}} \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1) \times \left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi dz &= K \int_0^\pi \int_0^{2\pi} (3 \cos^2 \theta - 1) \sin \theta \cos \phi \sin \theta d\theta d\phi \\ &\Rightarrow K \int_0^\pi (3 \cos^2 \theta - 1) \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi \quad \left(\text{as } dz = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi\right) \\ &\Rightarrow K \int_0^\pi (3 \cos^2 \theta - 1) d\theta \int_0^\pi \sin^2 \theta d\theta \left[\sin \phi\right]_0^{2\pi} \quad \text{and } [K = \text{constant}] \\ &= 0 \quad \text{as } (\sin \phi)_0^{2\pi} = 0 \end{aligned}$$

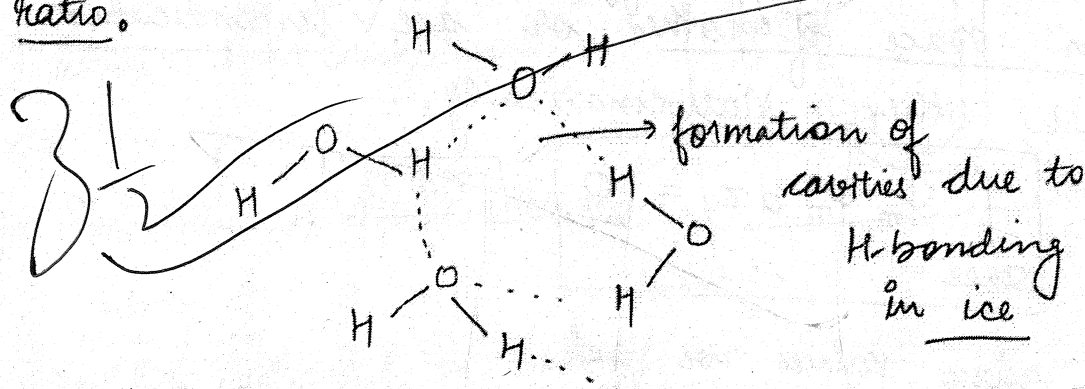
Thus, both the functions are orthogonal

(d) (i) Density ice is lower than liquid water explain.

(5+5)

(ii) Find the percentage covalent character in HCl molecule having bond length $1.275 \text{ \AA}$ dipole 1.03 Debye .

(d) (i) Density of ice is lower than that of liquid water because in ice, there is a tetrahedral arrangement of H_2O molecules leading to formation of cavities which cause a decrease in overall mass to volume ratio.



(ii) Each covalent bond is found to have some polar character (except for homonuclear diatomic molecules). This polar or ionic character is calculated as follows:

$$\% \text{ ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{calculated}}} \times 100 = \frac{1.275 \times 10^{-10} \text{ m} \times 1.6 \times 10^{-19} \text{ C}}{1.03 \times 3.31 \times 10^{-30} \text{ Cm}}$$

$$= 0.5983 \times 10^{-1} \times 100$$

$$= 0.059\%$$

$$\approx 0.06\%$$

$\therefore$ % covalent character

$$= 100 - 0.06\% \approx 99.94\%$$

Thus, HCl is predominantly covalent in character.

DIAS INDIA EDUTECH (P) LTD.

18, Pusa Road Karol Bagh, New Delhi - 110005

PH: 011-40079000, 9350934622

(c) Write down BORN-LANDE equation for lattice energy on the basis of this explains the factor on which lattice energy depends. (10)

Born-Lande equation is the mathematical method to explain the dependence of lattice energy on various factors.

$$\text{Mathematically, } U_c = - \frac{N_A N_B e^2 A}{4\pi \epsilon_0 r} \left(1 - \frac{1}{n}\right)$$

where N_A, N_B = Nuclear charges of atom A & B
or ions

A = Madelung constant

n = Born-Lande factor

r = distance of separation between ions

ϵ_0 = permissivity of the air.

e = electronic charge.

Thus, according to this equation, lattice energy depends on following factors:

(1) $U_c \propto A$ Madelung constant defines the structural arrangement of various ions in the crystal. It is determined by geometry of the crystal.

(2) $U_c \propto \frac{1}{n}$ 'n' represents the compressibility of the crystal. Larger ions have larger value of 'n'.

(3) $U_c \propto \frac{1}{r}$ more the separation, less will be the packing $\therefore$ less the U_c .

(4) $U_c \propto N_A N_B$ more the product of charges, greater the U_c
eg. $(U_c)_{MgCl_2} > (U_c)_{NaCl}$

7(a) Show that value of linear momentum of particle moving in 1-D box of length 'a' is zero.

(10)

The particle in a 1-D box can travel freely in both the directions and thus the net linear momentum sums out to be zero. Mathematically, it can be found by finding the expectation value of linear momentum.

The wavefunction for particle moving in 1-D box of length 'a' is given by $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$.

while the linear momentum operator is given is

$$-\frac{i\hbar}{\partial x}$$

$$\text{expectation value} = \int_{\text{space}} \psi | \hat{A} | \psi dx$$

Thus, operating the operator on the ψ gives

$$\begin{aligned} \int_0^a \left(\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) - \frac{i\hbar}{\partial x} \left(\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) dx &= -\frac{i\hbar}{a} \int_0^a \sin \frac{n\pi x}{a} \frac{\partial}{\partial x} \left(\sin \frac{n\pi x}{a} \right) dx \\ &= -\frac{i\hbar}{a} \int_0^a \sin \frac{n\pi x}{a} \cos \frac{n\pi x}{a} \left(\frac{n\pi}{a} \right) dx \\ &= -\frac{i\hbar}{a} \int_0^a \sin \frac{2n\pi x}{a} \times \frac{n\pi}{a} dx \\ &= 0 \end{aligned}$$

Thus value of linear momentum of a particle in a 1-D box of length 'a' = 0.

(b) Position and momentum operator does not commute. Justify and its physical significance. (10)

Commutation of operators signify that both operators when simultaneously operated on a function give a certain value. However, the position and momentum operator don't commute.

Mathematically, $[A B] = 0$ for A and B to commute
ie $AB - BA = 0$

Now position operator = x and momentum operator = $p_x = -i\hbar \frac{\partial}{\partial x}$

$$\therefore x \left(-i\hbar \frac{\partial}{\partial x} \right) \psi - \left(-i\hbar \frac{\partial}{\partial x} \right) (x\psi)$$

$$= -ix\hbar \frac{\partial \psi}{\partial x} + i\hbar \left[x \frac{\partial \psi}{\partial x} + \psi \right] = i\hbar \psi$$

$$\Rightarrow \boxed{[x p_x] = i\hbar \neq 0} \text{ Thus, they do not commute.}$$

Significance of non-commutation of position and momentum operator:

They follow Heisenberg Uncertainty Principle (HUP) which states that position and momentum of a sub-atomic particle can't be determined with accuracy simultaneously.

$$\begin{aligned} \Delta x \Delta p_x &\geq \frac{1}{2} [x p_x]_{\text{real}} \\ &= \frac{1}{2} [i\hbar]_{\text{real}} \\ &= \frac{\hbar}{2} \Rightarrow \boxed{\Delta x \cdot \Delta p \geq \frac{\hbar}{2}} \end{aligned}$$

(c) For the electron present in He^+ in 1s orbital determine the expectation value of position $\langle r \rangle$. (10)

The wavefunction of H-like atom for 1s orbital is given as $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$

Expectation value is defined as the average value of any physical quantity in quantum space.

Mathematically, it is given as. $\int \psi^* |A| \psi dz$

$$\langle r \rangle = \int_{\text{space}} \psi^* \langle r \rangle \psi dz$$

$$dz = 4\pi r^2 dr$$

$$= \frac{1}{\pi} \cdot \left(\frac{Z}{a_0} \right)^3 \cdot \int_0^\infty \exp\left(-\frac{Zr}{a_0}\right) r \exp\left(-\frac{Zr}{a_0}\right) r^2 dr \times 4\pi$$

$$= 4 \cdot \left(\frac{Z}{a_0} \right)^3 \int_0^\infty r^3 \exp\left(-\frac{2Zr}{a_0}\right) dr$$

$$= \frac{4 \left(\frac{Z}{a_0} \right)^3 \Gamma(4)}{2 \times \left(\frac{2Z}{a_0} \right)^4}$$

$$= \frac{4 \times \left(\frac{Z}{a_0} \right)^3 \times 24}{2 \times 16}$$

$$\begin{aligned} \text{r-function} &= \frac{\Gamma(n+1)}{2 a^{n+1}} \\ &= \frac{\Gamma(4)}{2 a^{4+1}} \end{aligned}$$

$$= \frac{3a_0}{2Z} = \frac{3a_0}{2(2)} = \frac{3a_0}{4} \text{ as } Z=2 \text{ for } \text{He}^+$$

DIAS

(d) Discuss the structure of BrF_5 and SOCl_2 on the basis of hybridisation. (10)

The structures of molecules can be discussed on the basis of hybridisation by using drago formula.

(i) Structure of BrF_5

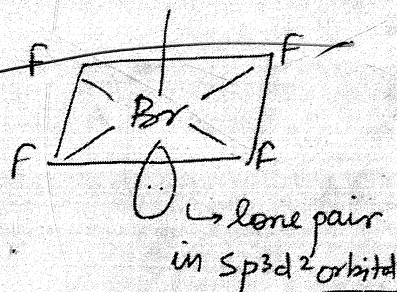
Electron pair = $\frac{V + M - C + A}{2}$

Br: $\begin{array}{|c|c|c|c|c|c|} \hline 1 & 1 & 1 & 1 & 1 & 1 \\ \hline \end{array}$ sp^3d^2

$= \frac{7 + 5}{2} = 6 \therefore \text{sp}^3\text{d}^2$

V = Valence e^- of central atom
 M = Monovalent atom
 C = cationic charge
 A = Anionic charge

Thus, geometry is octahedral
 but shape is square pyramidal



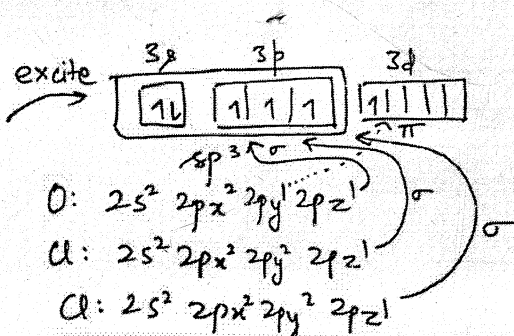
(ii) Structure of SOCl_2

Electron pair = $\frac{6 + 2}{2} = 4 \therefore \text{sp}^3$ hybridisation

3 bond pair $\oplus$ 1 lone pair $\therefore$ pyramidal shape

$\rightarrow$ lone pair in sp^3 orbital.

π -bond: $p\pi-d\pi$



(e) Derive Kelvin equation give its significance.

(10)

Kelvin equation gives the relationship between vapour pressure and surface tension and explains the effect of size of bubble on its vapour pressure.

Significance of Kelvin equation

① Vapour pressure $\propto \frac{1}{\text{radius of bubble}}$

ie smaller the bubble greater the vapour pressure, thus small sized bubbles are generated in aviation turbine fuel engine so as to achieve ignition temperature faster.

② Vapour Pressure $\propto$ Surface Tension

Thus, soap bubbles which have low surface tension need less vapour pressure to exist, hence are more easy to be sustained than pure water bubbles.