Nisha Sisodia 13.5 250

Submit copy with Name & Roll no.

Q.1

i) **Black Body Radiation**: is a type of radiation where all the energy absorbed by the body. It is given by Planck's whose theory of quantisation of energy depends on the black body radiation.

How it leads to quantisation:-

According to Planck, Black body absorb quanta of energy which he calls a "packet of energy".

Mathematically, he represented the absorption as

$$E = Nh\nu$$

where E = energy absorbed by body

N = No. of quanta of energy absorbed

h = planck's constant = 6.636×10^{-34} Js

ν = frequency of the molecule.

The term 'N' in the formula has discrete value such as 1, 2, 3 ... etc. It not have any fraction like 1.5, 1.25 — so this leads to the quantisation.

b) Angular wave function - helps to determine the shape of the molecule. Shroedinger wave equation solution for this function gives information about l (azimuthal quantum no.) & m (magnetic quantum no.)

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2 \quad (\Theta \text{ dependent term})$$

$$\frac{1}{\Phi^2}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2 \quad (\Phi_m \text{ dependent term})$$

for p- orbital, $l=1$, $m=0,\pm1$

l	m	$\Theta_{l,m}$
1	0	$\sqrt{\frac{3}{2}}\cos\theta$
1	±1	$\sqrt{\frac{3}{4}}\sin\theta$

m	Φ
0	$1/\sqrt{2\pi}$
+1	$\cos\phi/\sqrt{\pi}$ or $\frac{1}{\sqrt{2\pi}}e^{i\phi}$
−1	$\sin\phi/\sqrt{\pi}$ or $\frac{1}{\sqrt{2\pi}}e^{-i\phi}$

then take linear combination

∴ for p_z ($l=1, m=0$)

$$\Theta\Phi = \sqrt{\frac{3}{2}}\cos\theta \times \frac{1}{\sqrt{2\pi}}$$

$$\boxed{\psi_{p_z} = \sqrt{\frac{3}{4\pi}}\cos\theta} \quad ; \quad \boxed{p_x = \sqrt{\frac{3}{4}}\sin\theta \times \frac{\cos\phi}{\sqrt{\pi}} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi}$$

similarly $\boxed{p_y = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi}$

show $p_x^2 + p_y^2 + p_z^2 = \text{constant}$

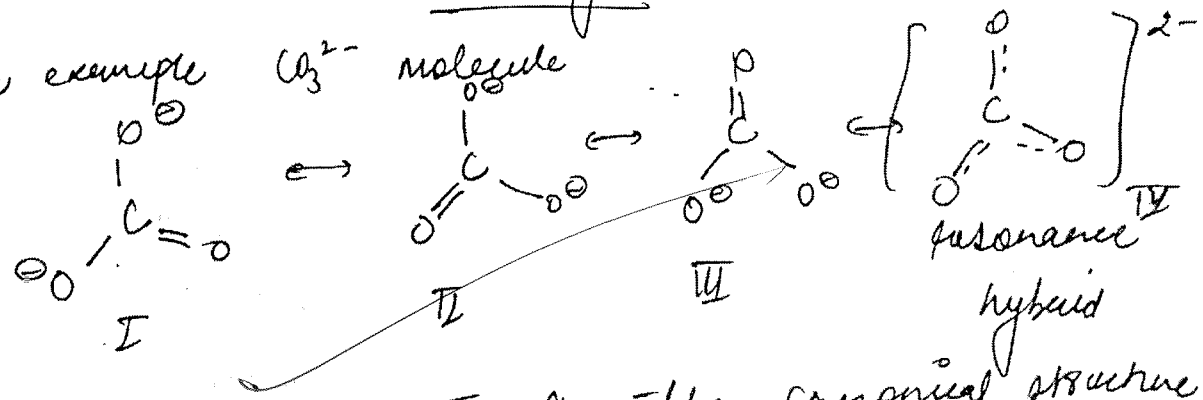
$$\frac{3}{4\pi}\sin^2\theta\cos^2\phi + \frac{3}{4\pi}\sin^2\theta\sin^2\phi + \frac{3}{4\pi}\cos^2\theta \Rightarrow \frac{3}{4\pi}\sin^2\theta\left(\cos^2\phi + \sin^2\phi\right) + \frac{3}{4\pi}\cos^2\theta$$

$$= \frac{3}{4\pi}\sin^2\theta + \frac{3}{4\pi}\cos^2\theta \quad \left(\because \cos^2\phi + \sin^2\phi = 1\right)$$

$$= \boxed{\frac{3}{4\pi}}$$ which is a constant. Hence the sum of square of p-orbital gives a constant which does not depend on θ & ϕ.

4) Resonance energy: is the stabilisation energy. it arises when the individual atom/molecule not able to show the complete property of atom. It is the average of all the structure contributing to the stability. The individual molecule known as the "canonical structures" & the average structure is known as "Resonance hybrid"

for example CO_3^{2-} molecule



where I, II, III are the canonical structure & IV is the resonance hybrid. The structure IV will help in explaining the stabilisation energy & all the properties of carbonate.

Calculation: Resonance energy is calculated by taking difference of estimated energy of a compound & the actual energy.

$$E_{res} = E_{estimate} - E_{act}$$

⇒ it leads to the lowering of energy of the molecule & hence the stabilization.

1) Vander Wall equation shows the deviation of behaviour of gas from ideal gas equation. It gives the equation for real gases by removing 2 assumption taken in ideal gas i.e. considering the force of attraction correction & excluded volume correction.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where P is pressure of gas
a = force of attraction between the molecule.
V is the volume of the gas
b represents the excluded volume $= 4N_0\left(\frac{4}{3}\pi r^3\right)$

R = Universal gas constant = 8.314 $JK^{-1}mol^{-1}$
T = Temperature of the gas in Kelvin

Isotherm of real gases: As discussed earlier, he gave the isotherm of real gases by removing 2 unnecessary assumption from ideal gas

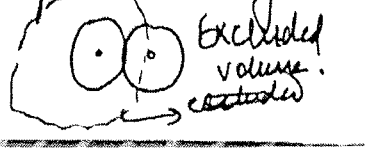
1) force of attraction correction: Not all the gas molecule have equal force. Molecule in the bulk have net balanced force & have same impact. But molecule near the wall faces the net drag force which reduces its speed & hence the impact, $\therefore P_{real} < P_{ideal}$

$$P_{ideal} = P_{real} + \frac{n^2a}{V^2}$$

$P < \frac{n}{V} \propto \frac{n}{V}$ ↳ due to net drag force near wall towards bulk
↳ due to collision with wall

2) Volume correction:

Kinetic theory of gases considers that volume of gas is negligible but this is not true, molecule can't be compressed beyond a certain limit. Consider 2 gas molecule of radius r, for this excluded radius will be 2r. Gas can't penetrate beyond this limit $\therefore$ Volume = $\frac{4}{3}\pi(2r)^3$ · volume = $4 \times \frac{4}{3}\pi r^3$
of molecule per mol



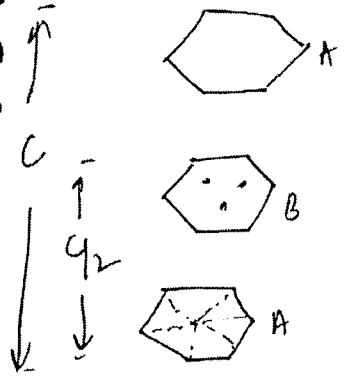
Relationship of HCP cubic packing :-

Packing efficiency tells about the volume of atom occupied in the total volume of the unit cell.

$$\phi = \frac{V_{atom}}{V_{total}} = \frac{n \times V_{occupied}}{V_{unit\,cell}}$$

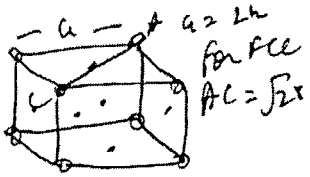
(Packing efficiency)

HCP follows AB-AB type packing



For AB AB type $\frac{c}{2} = d_{111}$ → interplanar distancing $= \frac{a}{\sqrt{h^2+k^2+l^2}}$

$$\frac{c}{2} = \frac{a}{\sqrt{3}}$$



For FCC type packing

$4r = \sqrt{2}a \quad \therefore a = \frac{4r}{\sqrt{2}}$

Hence $\frac{c}{2} = \frac{4r}{\sqrt{2}\times\sqrt{3}}$

$\Rightarrow c = \frac{8r}{\sqrt{6}}$

There are 6 equilateral triangle in the packing :-

Area of triangle $= \frac{1}{2} \times base \times height$

$$\text{Area} = 6 \times \left(\frac{1}{2} \times 2r \times 2r \sin 60^\circ\right)$$

$$\text{area} = 6\left(2r^2 \times \frac{\sqrt{3}}{2}\right) = 6\sqrt{3}r^2$$

$\therefore$ volume of atom $=$ area $\times c = 6\sqrt{3}r^2 \times \frac{8r}{\sqrt{6}} = \frac{48r^3}{\sqrt{2}}$

No. of atoms in the unit cell :- 12 atoms present @ corner shared by 6 unit cell, 3 atom shared by 1 unit cell. 2 atoms present at face shared by 2 unit cell

$$= 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6$$

$$\therefore \phi = \frac{6 \times 48r^3/\sqrt{2}}{\frac{4}{3}\pi r^3} = 74.6\%$$

which is equivalent of FCC type of packing.

Ans 2 Ideal gas equation is a hypothetical concept on time at very low pressure & high temperature. Real gas is the fact. various scientist gives their equation for the behaviour of the ideal gas. vanderwall & Dieterici are some of them.

Virial equation - used when more than 2 constant are involved in the equation other than universal gas constant.

$$P = \frac{RT}{V_m - b} \exp\left(-\frac{a}{V_m RT}\right) \longrightarrow (1)$$

Multiply the equation with $\frac{V_m}{RT}$

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} \exp\left(-\frac{a}{V_m RT}\right)$$

$$Z = \frac{V_m}{V_m - b} \exp\left(-\frac{a}{V_m RT}\right) \quad \left(\text{since } Z \text{ is compressibility factor} = \frac{PV_m}{RT}\right)$$

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

Expanding the equation:-

$$\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \cdots$$

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

Putting both the terms in the equation (2).

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

$$Z = 1 + \frac{b}{V_m} - \frac{a}{V_m RT} + \frac{b^2}{V_m^2} - \frac{ba}{V_m V_m RT} + \cdots$$

• Neglecting the higher terms because their contribution to the equation is very less.

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

very small contribution

$b - \frac{a}{RT}$ = 2nd virial coefficient, $\frac{a^2}{RT^2} - \frac{ab}{RT}$ = 3rd virial coefficient.

Boyle's temperature - is the temperature at which real gas behaves ideally.

For this, 2nd virial coefficient = 0.

$$b - \frac{a}{RT_B} = 0$$

$$\therefore b = \frac{a}{RT_B}$$

$$T_B = \frac{a}{Rb}$$ is the Boyle's temperature

//

b) No. of collision of gases are not given by the individual speed of the molecule, But it is the average speed of the gas molecule which gives the contribution for the speed.

Collision frequency $Z_{AB} = \frac{1}{\sqrt{2}} \sqrt{2}\, \pi \sigma^2 \bar{c}\, N_A^* N_B^*$

where σ is the radius of the molecule, $\bar{c}$ is the average speed $= \sqrt{\frac{8RT}{\pi M}}$; N_A^* N_B^* are No. of molecule per unit volume.

Maxwell distribution also helpful in determining the no. of collision per square meter per second.

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

↳ fraction of gas molecule, M = Molar mass, c is the speed.

Average speed is used to calculate the number of collision per square meter per second.

$$c_{av} = \sqrt{\frac{8RT}{\pi M}} \Rightarrow$$

Given: P = 1 atm, T = 298K, M = 32×10^{-3} kg, R = 8.314 J K^{-1} mol^{-1}

$$c_{av} = \sqrt{\frac{8 \times 8.314 \times 298}{3.14 \times 32 \times 10^{-3}}} = \sqrt{\frac{19820.57}{0.10048}}$$

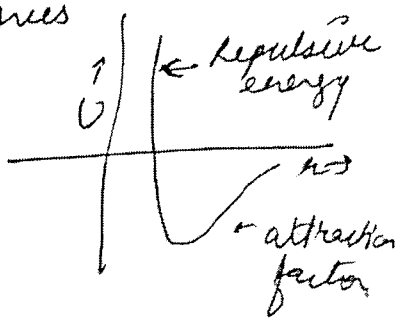
$$\boxed{c_{av} = 444.13 \text{ m/s}}$$

1) Lattice energy is the energy release when 2 ionic gases are come closer to lattice site from infinity to form the crystalline solid structure.

Born Lande is the theoretical aspect of Lattice energy & give the expression for it.

According to Born Lande - Lattice energy is the net balance of attractive + repulsive forces

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



Repulsive force $U_{rep} = \frac{B}{r^n}$

$\therefore$ Lattice energy, $U = \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$

Calculating the value of B, first derivative of lattice energy with respect to radius is minimum. so $\frac{\partial U}{\partial r} = 0$

$\frac{\partial U}{\partial r} = \frac{-Z_+ Z_- e^2}{4\pi\varepsilon_0 r^2} - \frac{nB}{r^{n+1}} = 0 \quad \therefore \frac{-Z_+ Z_- e^2}{4\pi\varepsilon_0 r^2} = \frac{nB}{r^{n+1}}$

$\therefore B = \frac{-Z_+ Z_- e^2 r^n}{n\, 4\pi\varepsilon_0 r}$ $\quad \therefore U = \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0 r} + \left(\frac{-Z_+ Z_- e^2}{n\, 4\pi\varepsilon_0 r} \times r^n\right)\frac{1}{r^n}$

n is born exponent,

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

The above lattice energy is for the molecule & not considered other structure feature of the molecule. To consider them, it has to be multiplied by 'A' (Madelung constant for coordination No. factor) & No. for the the number of molecule. $\therefore$

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

where $Z_+ Z_-$ - product of cation & anion Charges

A = Madelung constant depend on the coordination number only, irrespective of nature

where n = Born exponent
ε_0 = permittivity in space
No = number of molecule
e = electronic charge
r = radius of the molecule

Factors on which Lattice energy depends :

1) From the Born Lande formula, we can say that lattice energy depends on the Madelung constant. As the value of madelung constant increases, lattice energy increases.

2) Lattice energy also depends on the radius. It is inversely proportional to it. As the radius increases lattice energy decreases.

3) It also depends on the product of charges of cation & anion ($Z_+ Z_-$). Higher the product higher will be the value of lattice energy.

$\therefore U \propto Z_+ Z_-$, $U \propto \frac{1}{r_+ + r_-}$; $U \propto A$

For ex. Lattice energy of $MgBr_2 > LiBr$ because of higher $Z_+ Z_-$ value.

Also, n value is greater than 1, & product of charges $(Z_+ Z_-) <$ ∴, Lattice energy will always be negative hence stable.

Madelung constant is the structural property of the molecule, it depends only on the geometry & coordination number of the molecule & donot depend on the nature of molecule. Higher the value of madelung constant stablizes the molecule by increasing the lattice energy.

d) Hybridisation is the theoretical concept where the atomic orbital of equal energy & symmetry come to form hybrid orbital. The number of atomic orbital come together is same the number of hybrid orbital formed.

Some conditions for hybridisation :-

1) principal quantum number should be equal for the atomic orbital. eg 2s, 2p

2) Energy & atomic orbital should be nearly equal, also symmetry of atomic orbital matter for eg. if 2- is the internuclear axis then 1 will hybridise with 2 more effectively & form sigma bond.

Hybrid orbitals are better for Bonding than pure-orbital :-

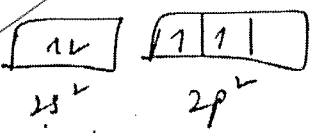
1) same environment around the hybrid orbital facilitate the bonding formation.

2) effective bonding takes place as the hybrid orbital contain all the available orbital for the bonding.

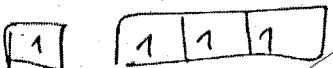
3) Lower energy orbital will form the bond first which is more stable than pt.

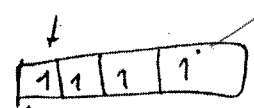
The above 4 points for sigma bond formation can be understand by taking example of CH_4.

$C(6) = 1s^2\ 2s^2\ 2p^2$

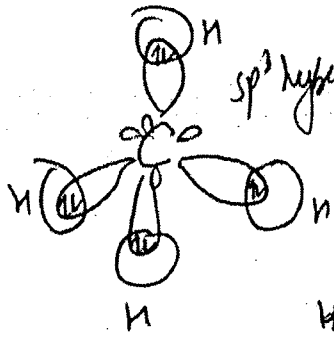


↓ excited





effective bonding formation achieved via sp^3 hybridisation



sp^3 hybrid orbital

H's form hydrogen similarly form the bond

Ans. 39) According to Born interpretation, it is necessary for a wave function to be normalized to get the probability of finding the e⁻ in space = 1.

Normalisation means when the wave function multiply with its conjugate wave function & integrate over limit, it will give the maximum probability of finding the electron & that is equal to one.

For example for particle in 1-D, $\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

$\sqrt{\frac{2}{L}}$ is the normalisation constant

$$\text{probability} = \int_0^L \psi^2 d\tau = \int_0^L \psi\psi^* d\tau = 1$$

$$\frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx \Rightarrow \frac{2}{L} \times \frac{L}{2} \left(\because \int_0^L \sin^2 \frac{n\pi x}{L} = \frac{L}{2}\right)$$

probability = 1

In Quantum Mechanical Study: it is necessary to use the normalised wave function:-

1) probability of finding the electron will be maximum
2) orthogonality of the factor can be enforced.
3) Average value of any quantity can be easily found for ex. $\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

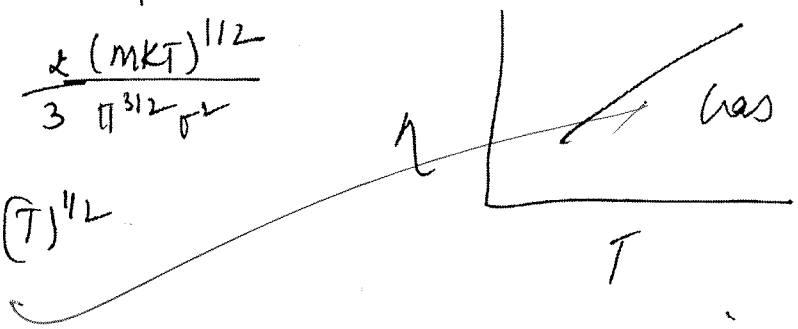
average value $\langle x \rangle = \frac{\langle \psi | x | \psi^* \rangle}{\langle \psi | \psi^* \rangle}$, if wave function is normalized then the denominator will be equal to 1 & we can easily get the average value (concept of Variation theorem).

b) Viscosity is the resistance to flow.

For Gas: Viscosity increases with increase in the temperature This is because of the increase in the transfer of momentum from one layer to another with increase in temperature. As the momentum transfer increases, the speed of collision of the molecule with the other reduces & hence viscosity increases.

$$\eta = \frac{\alpha (MKT)^{1/2}}{3\pi^{3/2}\sigma^2}$$

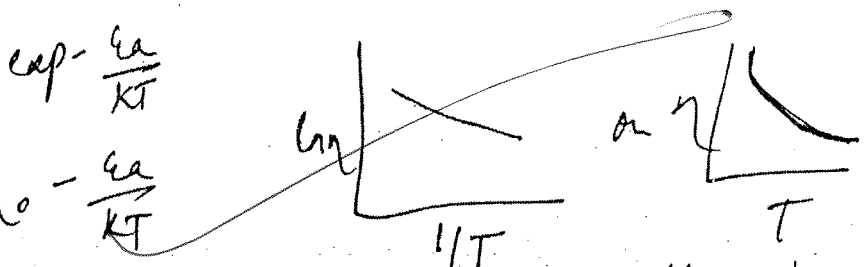
$$\eta \propto (T)^{1/2}$$



For liquid: Viscosity decreases with increase in temperature because, certain minimum energy required for the flow of liquid. With increase in temperature, thermal energy of the liquid increases which will increase their flow & reduce the activation energy & hence the viscosity also reduces.

$$\eta = \eta_0 \exp^{-\frac{E_a}{KT}}$$

$$\ln\eta = \ln\eta_0 - \frac{E_a}{KT}$$



∴ with increase in the temperature, the viscosity of gases increase & viscosity of liquid decreases.

4) Band theory is the Molecular orbital theory concept of determining the conductance of the atom/element. There are 2 Band for an atom.

One is Valance Band - which is filled band or lower energy band.

Other is Conductance Band - which may be empty or partially filled.

The energy difference between the valance Band & Conductance band determines the conductivity. i.e. known as fermi energy.

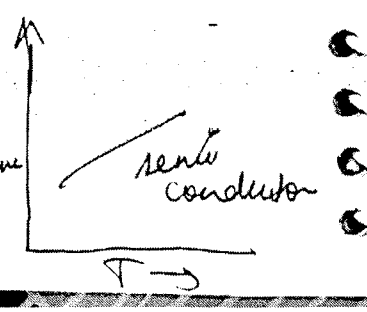
For Conductor : The fermi energy (E_f) is very less for the conductor sometimes the conductance band overlap with valance Band & electron transition is very easy, even at room temperature. For example alkali metal - conductance band overlap with valance band.

No E_f.

For semiconductor : The energy difference between valance & conductance band is significant. so the electron transition can't take place at room temperature. But as the temperature increases, electron in valance Band gain the thermal energy & can easily move to the conductance Band. i.e., with increase in the temperature there conductivity increases.

$$\rho = \rho_0 \exp\left(\frac{-E_f}{KT}\right)$$

$$\ln \rho = \ln \rho_0 - \frac{E_f}{KT}$$



d) i) Miller Indices are the inverse of weiss indices, they are the reciprocal of the intercepts, which then multiplied with a factor to make that number a integer.

significance ii) It represents the particular set of parallel planes (111) (222) (333) - -

2) parallel planes are represented by zero miller indices for example (110) diagonal plane parallel to z-axis.

3) negative value of ~~miller~~ intercept represented by bar in miller indices for eg (11-1) ⇒ (11$\bar{1}$)

4) higher the intercept lower will be the miller indices

(3 2 1) ⟹ (2 3 6)
Intercept Miller indices

5) interplanar distance can be calculated by using following formula $\boxed{\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$

ii) Using above formula, a = 50pm, b = 100pm, c = 300pm
h = 1, k = 2, l = 3 consider x = 50pm ∴ a = x, b = 2x, c = 6x

$$\frac{1}{d_{hkl}^2} = \frac{1}{x^2} + \frac{4}{4x^2} + \frac{9}{36x^2} \Rightarrow \frac{1}{d_{hkl}^2} = \frac{12+12+3}{12x^2}$$

$$d_{hkl}^2 = \frac{12x^2}{27} = \frac{12 \times 50 \times 50}{27} = 1111.11$$

$$\therefore \boxed{d_{hkl} = 33.33\ pm}$$

c) Given: $\eta_{water} = 1.002 \times 10^{-3}\ Nm^{-2}s$, $t_w = 102.2s$, $\rho_w = 0.998 gcc$

$\eta_{toulene} = ?$, $t_{toulene} = 68.9s$; $\rho_t = 0.866 gcc$

Ostwald viscometer used to calculate the viscosity of liquid; $V = \frac{\pi r^4 \Delta P t}{8 l \eta}$ ΔP = pressure head, t = time, l = length of tube, η = viscosity, V = volume

rearranges $\boxed{\eta = \frac{\pi r^4 \Delta P t}{8 l V}}$

For a liquid, all other things are constant than time.

$\therefore \frac{\eta_1}{\eta_2} = \frac{t_1}{t_2}$

$\therefore$ to calculate the $\eta_{toulene}$ —

$$\frac{\eta_{toulene}}{\eta_{water}} = \frac{t_{toulene}}{t_{water}}$$

$$\frac{\eta_t}{1.002 \times 10^{-3}} = \frac{68.9s}{102.2s}$$

$$\therefore \eta_t = \frac{68.9 \times 1.002 \times 10^{-3}}{102.2} = 6.755 \times 10^{-4}\ Nm^{-2}s$$

$\therefore$ viscosity of toulene comes out to be $6.755 \times 10^{-4}\ Nm^{-2}s$

other formula $\frac{\eta_t}{\eta_w} = \frac{\rho_t t_t}{\rho_w t_w} = \frac{0.866 \times 68.9}{0.998 \times 102.2}$ (density)

$\eta = \frac{1.002 \times 10^{-3} \times 68.9 \times 0.866}{102.2 \times 0.998} = 5.86 \times 10^{-4}\ Nm^{-2}s$

from this $\eta_{toulene}$ is $5.86 \times 10^{-4}\ Nm^{-2}s$

4a) VSEPR theory is used to determine the shape & structure of the molecule.

According to this theory, hybridisation = $\frac{1}{2}(V+M-C+A)$

V = No. of valance e⁻, M = No. of monovalent atom,

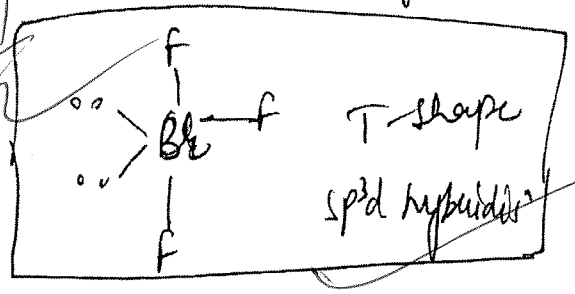
C = cation charge, A = anion charge.

For BrF_3 Hybridisation = $\frac{1}{2}(7+3) = 5$

sp^3d

Total electrons pair = 5; Bond pair = 3, lone pair = 2

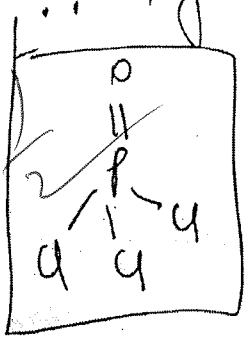
According to above information structure will be T-shape & geometry will be Trigonal bipyramidal



For $POCl_3$ Hybridisation = $\frac{1}{2}(5+3) = 4$ sp^3 hybridised

total electron pair = 4, Bond pair = 4, lone pair = 0,

∴ regular geometry, tetrahedral shape.

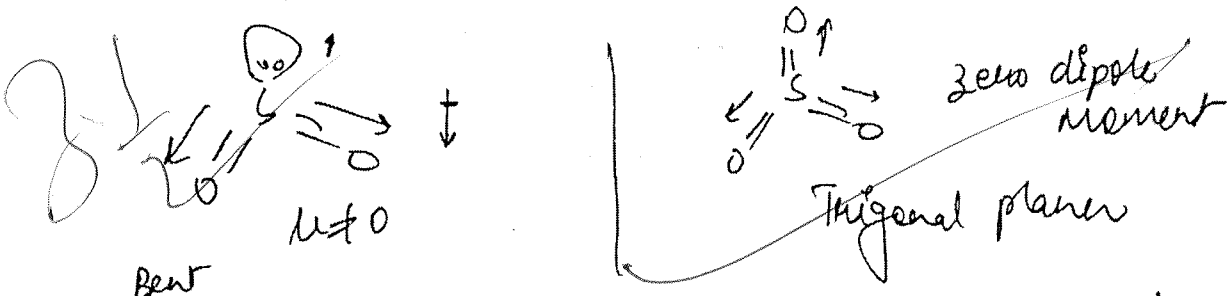


Hybridisation = sp^3

Tetrahedral shape

Molecule	Hybridisation	Shape	Geometry
BrF_3	sp^3d	T-shape	Trigonal bipyramid
$POCl_3$	sp^3	Tetrahedral regular	regular Tetrahedral

b) i) SO_2 is polar. Because according to VESPR theory, shape is bent (2 Bond pairs & 1 lone pair) & hence the molecule has net dipole moment & hence polar while in SO_3, shape is trigonal planar (3 BP & 0 LP) hence there is no net dipole moment & non polar molecule



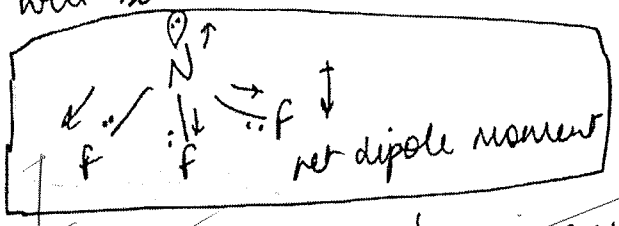
ii) Covalent Bond is formed by sharing of electron of outermost shell of one atom to the outermost shell of the another atom. It forms a strong bond. For example: Diamond if we apply any force on it, it will not break because of the presence of covalent bond - Non brittle bond is the characteristic of covalent bond.

Ionic bond is formed by the complete transfer of electron from one atom to another & leads to a Noble gas configuration of each atom. For example NaCl, Na^+ gives its electron to Cl ⊖ & hence both completed their noble gas configuration. With the application of force NaCl crystal will break because of the brittle nature of ionic bond, which will break while applying pressure. Hence diamond is covalent much harder than NaCl which is ionic.

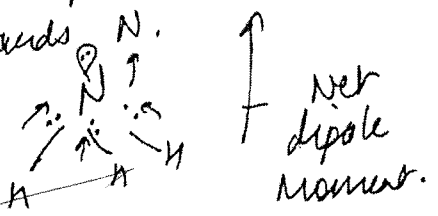
4) i) Dipole moment is defined as the product of charge & the separation between different charges

$\mu = q \times d$ q = charge, d = separation of charge.

For NF_3, F is more electronegative than nitrogen F = 4.1, N = 3.1 in electronegative value, ∴ the electron pair will be attracted towards F.



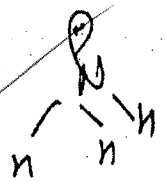
NH_3 → N is more electronegative than hydrogen. H = 2.1, N = 3.1 ∴ electron pair will be attracted towards N.

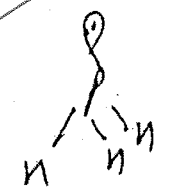


Hence the dipole moment of $NF_3 < NH_3$.

ii) Bond angle of $NH_3 > PH_3$

For NH_3 → electronegativity of N > P ∴ the lone pair is more attracted by N & hence lp-bp repulsion will be less & Bond angle will be more. Also BP-BP repulsion is more in NH_3 because of smaller size of N, but in PH_3 large size of P also reduces the bond-bond pair repulsion & hence less angle.





Also lone pair is present in nearly pure s-orbital, ∴ Bond pair formed with p-orbital of phosphine.

d) expectation value can be calculated by the following formula $\langle r \rangle = \frac{\langle \psi | \hat{r} | \psi' \rangle}{\langle \psi | \psi' \rangle}$ → (1)

which gives the criteria of Variation theory which says that the average / expectation value found is greater than or equal to the actual value.

i) for $\langle r \rangle$, using formula (1). $\psi = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0)$

$$\langle r \rangle = \frac{\int_0^\infty \frac{1}{\pi a_0^3} r \exp^{-2r/a_0} d\tau}{\int_0^\infty \frac{1}{\pi a_0^3} e^{-2r/a_0} d\tau}$$

$d\tau = r^2 dr \sin\theta d\theta d\phi = 4\pi r^2 dr$

since the wave function is normalised, denominator = 1.

$$\langle r \rangle = \int_0^\infty \frac{1}{\pi a_0^3} \times 4\pi r^2 \times r e^{-\frac{2r}{a_0}} dr$$

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr \qquad \int_0^\infty r^n e^{-ar} = \frac{n!}{(a)^{n+1}}$$

$$= \frac{4}{a_0^3} \times \frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{4 \times 6}{a_0^3} \times \frac{a_0^4}{4 \times 4} = \frac{3}{2} a_0$$

$$\therefore \boxed{\langle r \rangle = \frac{3}{2} a_0}$$

Similarly $\langle r^2 \rangle = \frac{4}{a_0^3} \int_0^\infty r^4 e^{-2r/a_0} dr$

$$= \frac{4}{a_0^3} \times \frac{4!}{\left(\frac{2}{a_0}\right)^5} = \frac{4 \times 4 \times 3 \times 2 \times a_0^5}{a_0^3 \times 4 \times 4 \times 2}$$

$$\boxed{\langle r^2 \rangle = 3 a_0^2}$$

• Uncertainity in the position of e^-

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

$$= \sqrt{3a_0^2 - \frac{9}{4}a_0^2}$$

$$= \sqrt{\frac{12-9}{4}(a_0^2)}$$

$$\boxed{\Delta r = \sqrt{\frac{3}{4}}\, a_0}$$

Hence $\boxed{\langle r \rangle = \frac{3}{2} a_0, \quad \langle r^2 \rangle = 3a_0^2, \quad \Delta r = \sqrt{\frac{3}{4}}\, a_0}$

5q) $d = 154.05\ pm$

θ	21.65°	25.21°	37.06°	44.96°	47.58°
$\sin\theta$	0.3689	0.4259	0.6026	0.7066	0.7382
$\sin^2\theta$	0.1361	0.1813	0.3631	0.4992	0.5449

$\boxed{K = 0.04536}$

According to Bragg's equation $n\lambda = 2d\sin\theta$

$\lambda = 2d_{h,k,l}\sin\theta \quad \left(\because d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}\right)$

$\lambda = \frac{2a}{\sqrt{h^2+k^2+l^2}}\sin\theta \rightarrow (1) \quad \therefore \sin\theta = \frac{\lambda}{2a}\times\sqrt{h^2+k^2+l^2}$

$\therefore \sin^2\theta = \frac{\lambda^2}{4a^2}\times(h^2+k^2+l^2) \Rightarrow \boxed{\sin^2\theta = K(h^2+k^2+l^2)}$

where $K = \frac{\lambda^2}{4a^2}$

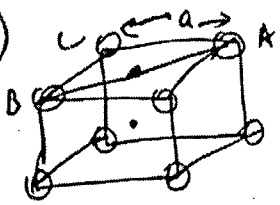
Here the common factor from above row, $K = 0.04536$

$\therefore \sin^2\theta$: 3K 4K 8K 11K 12K

can be written as

i) This sequence follows FCC type of lattice

ii)



$AB = 4r$

For FCC $AB^2 = AC^2 + BC^2$

$\therefore AB^2 = 2a^2$

$AB = \sqrt{2}a$

$\therefore 4r = \sqrt{2}a$

$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$

Calculating 'a' using eq. 1.

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

consider, $\theta = 21.65$
for this $(h,k,l) = (1,1,1)$

$$154.05\text{pm} = \frac{2a}{\sqrt{3}} \times 0.3689$$

$$a = \frac{154.05\text{pm} \times \sqrt{3}}{2 \times 0.3689} = 361.63\text{pm}.$$

iii) $\boxed{\rho = \frac{Z \times M}{N_A \times a^3}}$ given $\rho = 8.812\,\text{g cm}^{-3}$, $M = 63.5\,\text{g}$.
$a = 361.63\text{pm} = 361.63 \times 10^{-10}\,\text{cm}$
Z (for FCC) $= 4$

$$\therefore N_A = \frac{4 \times 63.5}{8.812 \times (361.63 \times 10^{-10})^3}$$

$$= \frac{4 \times 63.5}{8.812 \times (361.63)^3} \times 10^{30} = \frac{254 \times 10^{30}}{4.167 \times 10^8}$$

$$\boxed{N_A = 6.095 \times 10^{23}\ \text{mol}^{-1}}$$

iv) Radius $r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2}}{4} \times 361.63\text{pm}$

$$\boxed{r = 127.855\text{pm}}$$

| 1 | 4 |

∴ type of crystal is FCC, length of side of the cube is 361.63 pm, value of avogadro constant is $6.095 \times 10^{23}\ \text{mol}^{-1}$; & radius of copper atom is 127.855pm.

b) According to the Bohr Model

$$E = \frac{-me^4Z^2}{8n^2h^2\varepsilon_0^2} \qquad E_2 - E_1 = \frac{me^4Z^2}{8h^2\varepsilon_0^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = \frac{me^4Z^2}{8h^2\varepsilon_0^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{since } \Delta E = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{me^4Z^2}{8h^3c\varepsilon_0^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \therefore \boxed{\frac{1}{\lambda} = (R_H)Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

$R_H = 1.09 \times 10^7\ m^{-1}$, $Z = 1$ for H-atom

$n_1 = 1$, $n_2 = 3$

$$\frac{1}{\lambda} = 1.09 \times 10^7 \times (1)^2\left(\frac{1}{1} - \frac{1}{9}\right)$$

$$= 1.09 \times 10^7\left(\frac{8}{9}\right)$$

$$\lambda = \frac{9}{1.09 \times 10^7 \times 8} = 1.032 \times 10^{-7}\ m$$

$$\boxed{\lambda = 103\ nm}$$

Lyman series: the calculated wavelength belongs to Lyman series as $n_1 = 1$, no other energy transition can take place from $n_2 \rightarrow 1$ only Lyman series which is observed in UV-region.

c) Molecular orbital theory can be use to draw the diagram of homonuclear as well as heteronuclear diatomic molecule. For molecule higher than Nitrogen no s-p interaction takes place because of higher energy difference in 2s & 2p.

F_2 is homonuclear diatomic molecule, its electronic configuration is $[F] = 1s^2 2s^2 2p_x^1 2p_y^2 2p_z^2$

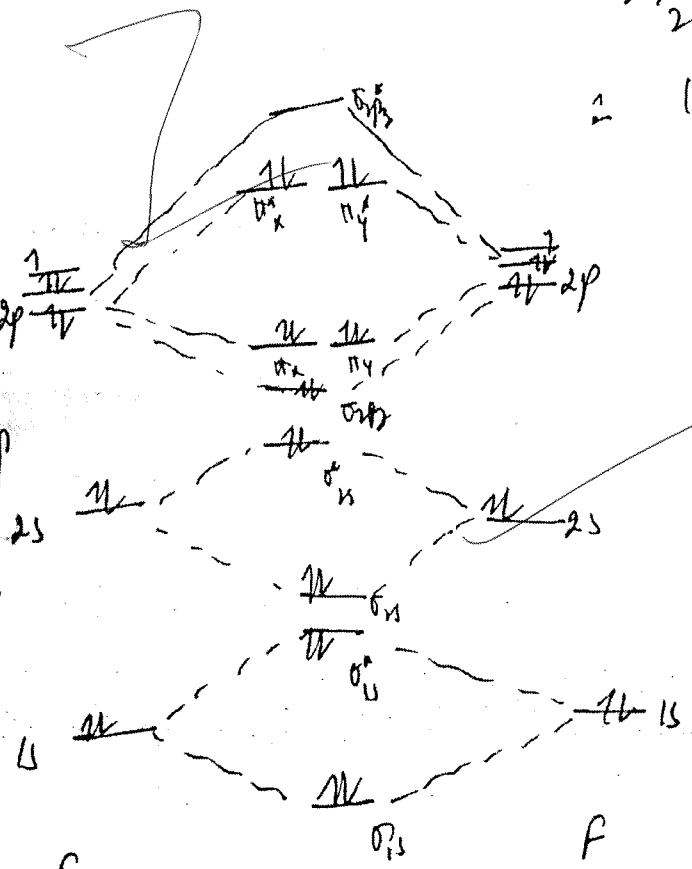
$(F) \Rightarrow 1s^2 2s^2 2p_z^2 2p_y^2 2p_x^1$

ii) 5 atomic orbitals are involved which led to formation of 10 molecular orbitals, 5 Bonding & 5 anti bonding.

iii) Bond order of a molecule $= \frac{1}{2}$ (No. of Bonding e^- − anti bond e^-)

$= \frac{1}{2}(6-4) = 1$

$\therefore$ 1 covalent Bond exist between 2 F atom.



Addition of electron goes to $\sigma^*_{2p_z}$ which is anti bonding & hence destablizes the molecule.

d) According to de-broglie, e^- associated with both wave as well as particle nature of the matter.

Wave-particle duality is showing the characteristic of both wave & particle. For particle - showing photoelectric effect & for wave - showing constructive or destructive interference. If both the characteristic shown then its said to be follows wave particle duality.

For wave nature $E = mc^2$

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

molecule following wave particle duality will have equal energy of both

$$mc^2 = \frac{hc}{\lambda} \quad \therefore \quad \lambda = \frac{h}{mc} \Rightarrow \lambda = \frac{h}{p}$$

where λ = wavelength, h = planck's constant,
m = mass of e^-, c = speed of light.

evidence - Heisenberg uncertainty principle, follows only for microscopic particle but for macroscopic particles particle character dominates & heisenberg uncertainty principle is not followed. But for microscopic particle → Heisenberg uncertainty principle is significant Hence shows wave-particle duality evidence.