

DIAS

All India TEST – SERIES CSE – 2024

Test-3

Syllabus -: Photochemistry, Surface chemistry & Inorganic Chemistry.

Instructions:-

1. Attempt five questions selecting at least 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.

Date:- 16-07-2024

Official use. Attempted Q 1, 3, 5, 6, 7

Q.NO.	1	2	3	4	5	6	7	8
MARKS	34		34	17	17	34	33	X

Signature of invigilator

V. Grodi
But & Revise
Bioinorganic

152

250

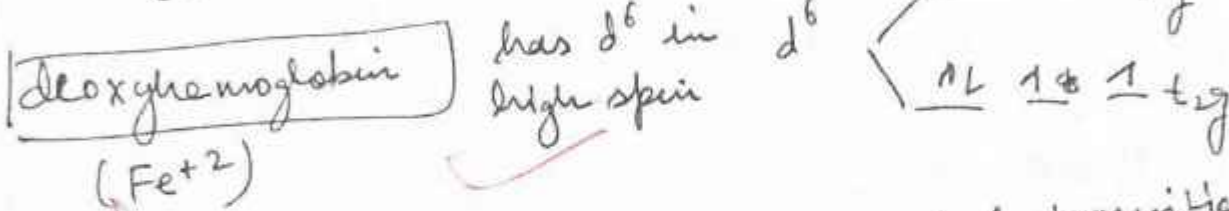
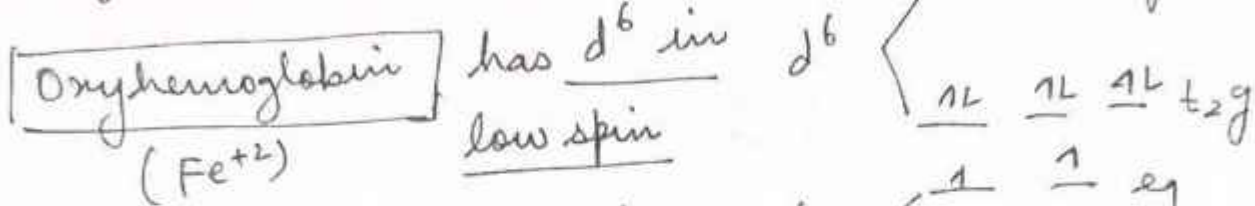
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Examiner

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SECTION - A

1. (a) Oxyhemoglobin is bright red, whereas deoxyhemoglobin is purple. Explain the difference in colour qualitatively. (10)

Oxyhemoglobin and deoxyhemoglobin differ in colour because of difference in configuration of d^6 state.



In deoxyhemoglobin \rightarrow high energy d-d transition takes place leading to emission of lower wavelength i.e. purple colour.

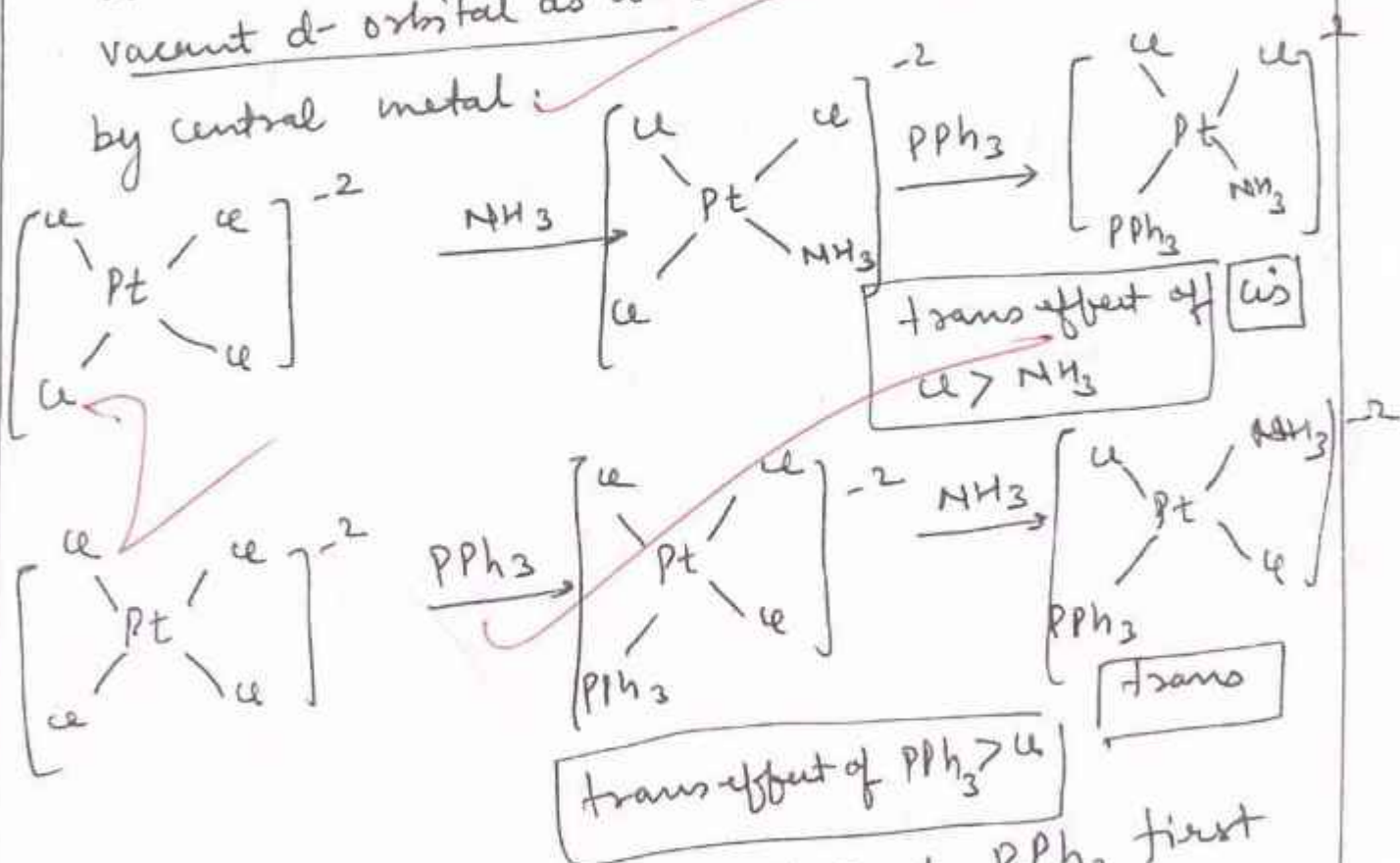
In oxyhaemoglobin \rightarrow no unpaired e^- is present in Fe^{+2} and thus colour shifts toward longer wavelength like Red.

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- (b) Given the reactants PPh_3 , NH_3 and $[\text{PtCl}_4]^{2-}$, propose efficient routes to both cis and trans $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$. (10)

cis and trans isomers of $[\text{PtCl}_2(\text{NH}_3)(\text{PPh}_3)]$ can be prepared using PPh_3 , NH_3 and $[\text{PtCl}_4]^{2-}$ as reactants via ligand substitution reaction (trans effect). It has to be noted that trans effect of PPh_3 is greater than NH_3 as PPh_3 has vacant d-orbital as well to accommodate e^- donated

by central metal:

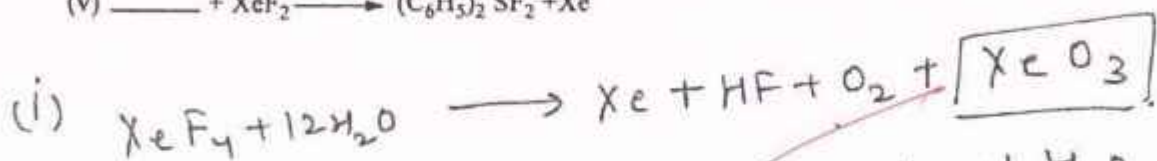
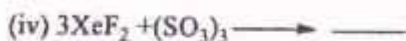


Thus, introducing NH_3 and PPh_3 first produces cis and trans isomers respectively.

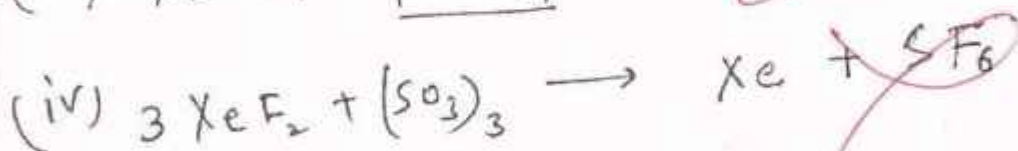
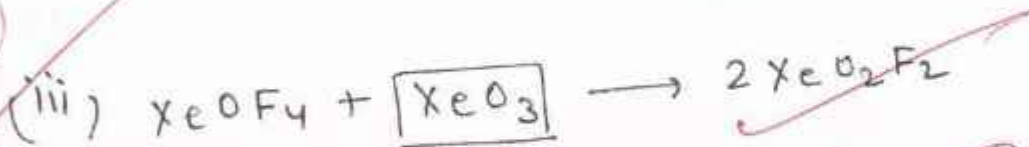
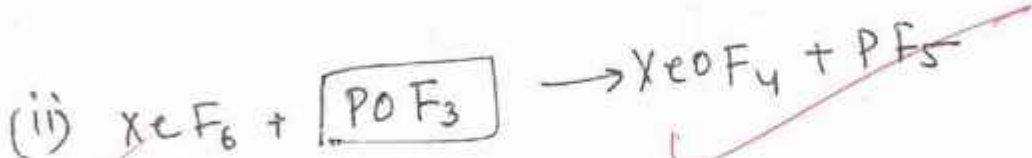
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(c) (Complete the following reaction:

(10)



Hydrolysis of $\text{XeF}_4 \Rightarrow$ Fluorination of H_2O
Oxidation of $\text{Xe}^{+4} \rightarrow \text{Xe}$.



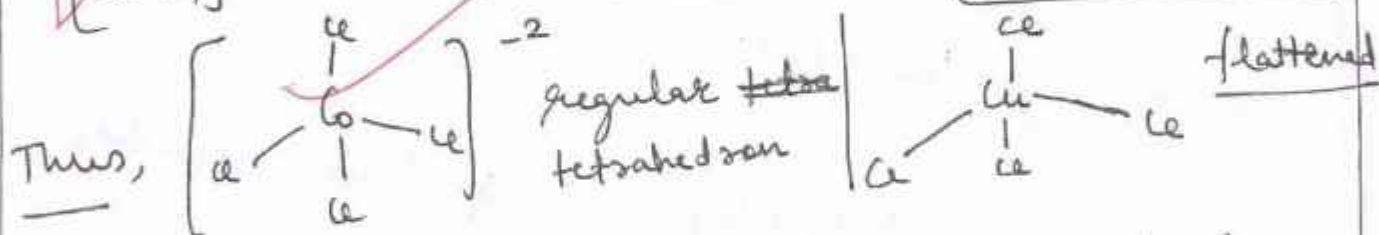
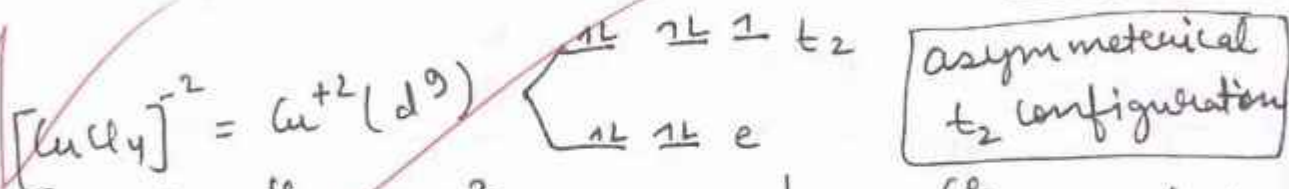
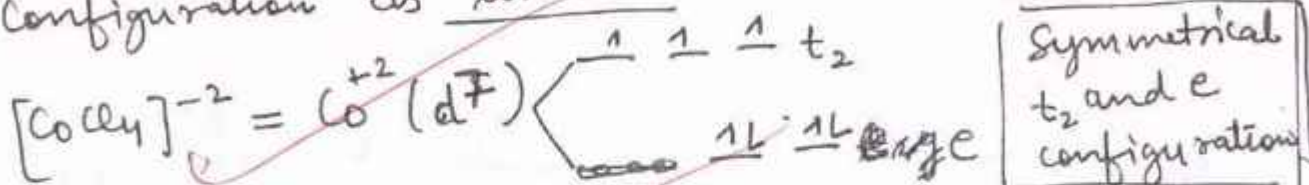
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(d) Discuss each of the following observations: (5+5)

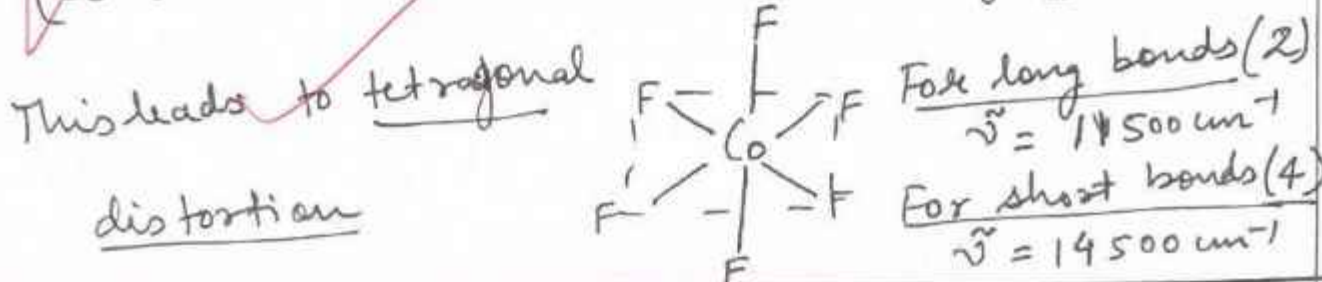
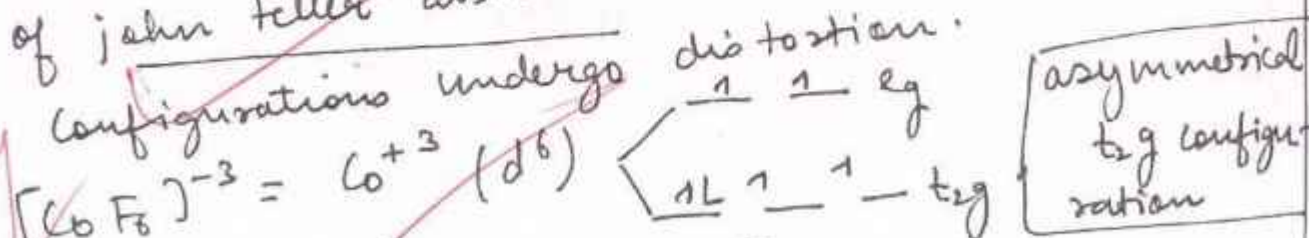
(i) the $[\text{CoCl}_4]^{2-}$ ion is a regular tetrahedron but $[\text{CuCl}_4]^{2-}$ has a flattened tetrahedral structure.

(ii) The electronic spectrum of $[\text{CoF}_6]^{3-}$ contains two bands with maxima at 11500 cm^{-1} and 14500 cm^{-1} .

(i) This can be explained on the basis of Jahn Teller distortion where asymmetrical degenerate configuration is unstable and undergoes distortion.



(ii) This also can be explained on the basis of Jahn Teller distortion where asymmetrical configurations undergo distortion.



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(e) Explain the structure and bonding in.

(10)

(i) Iodine pentafluoride and

(ii) Polythiazyl.

(i) $\boxed{IF_5}$ as per VSEPR's rule

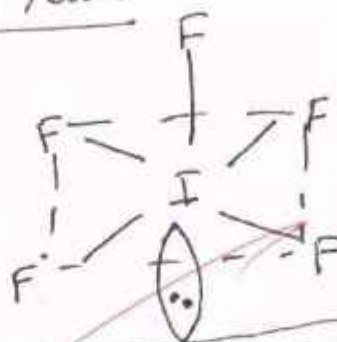
$$\begin{aligned} \text{No. of } e^- \text{ pairs} \\ = \frac{1}{2} [7 + 5] = 6 \end{aligned}$$

$$\text{No. of bond pairs} = 5$$

$$\text{No. of lone pairs} = 1$$

d-orbitals involved in hybridization are

$$= d_{x^2-y^2} \text{ and } d_{z^2}$$

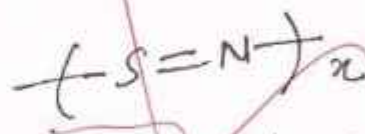


Hybridization = sp^3d^2
 Geometry = ~~Base~~ Octahedral
 Shape = Square Pyramidal

(ii) $(SN)_x$ polythiazyl

has linear structure

polymer like structure



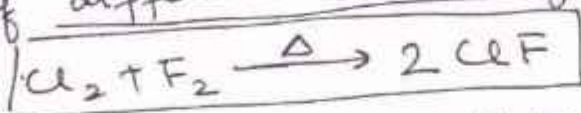
which results

in very high conductance.

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3. (a) What are interhalogen compounds? How are they classified? Give structures of IF_5 and IF_7 . (10)

Interhalogen compounds are those compounds obtained by reaction of two halogens ~~of~~ containing one halogen as anion (more electronegative) two halogens of different electronegativity.



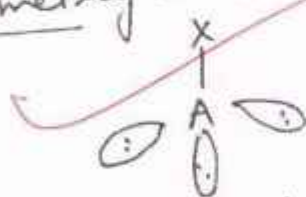
Stability of interhalogen compounds

More stable than halogens as electronegativity difference is high

Stability \propto electronegativity difference
Eg $ClF_5 < IF_5$ in stability

Classification of Interhalogen compounds

① AX type tetrahedral geometry and linear.



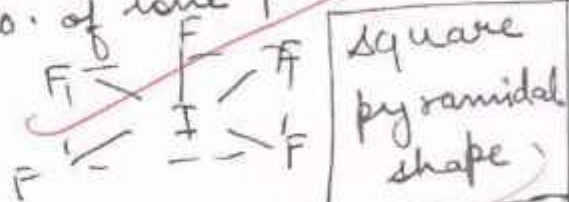
② AX₃ type

tetragonal bipyramidal geometry, T-shaped



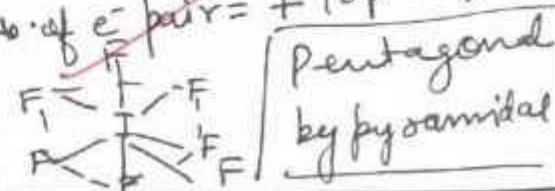
③ AX₅ type Eg IF_5

No. of e⁻ pair = 6 (sp^3d^2)
No. of bond pair = 5
No. of lone pair = 1



④ AX₇ type Eg IF_7

No. of e⁻ pair = 7 (sp^3d^3)

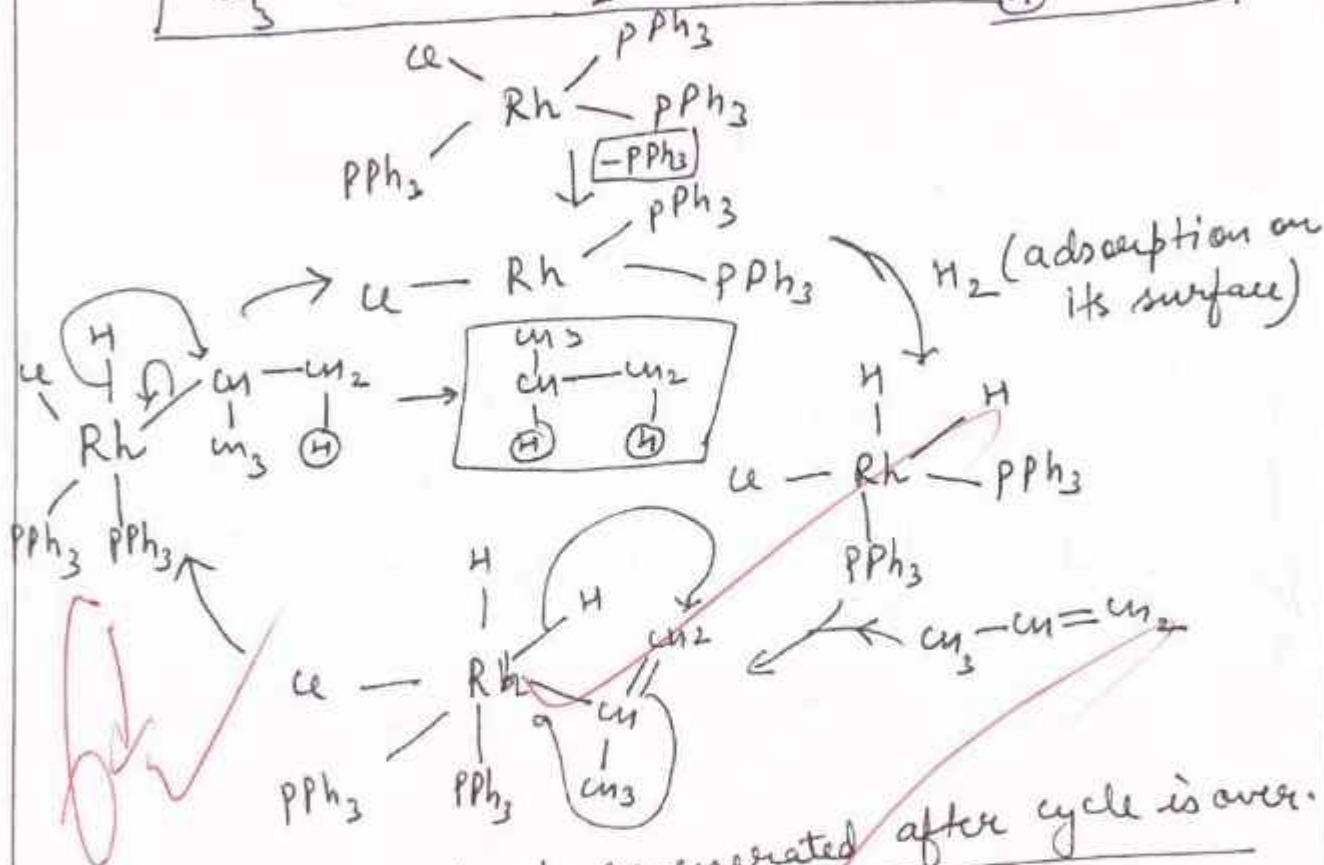
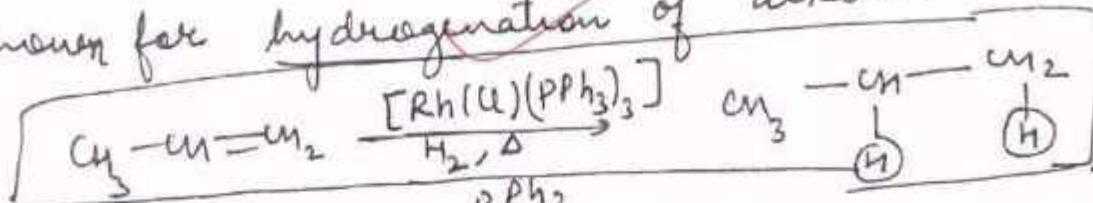


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(b) Write the catalytic cycle for the hydrogenation of propene by $[RhCl(PPh_3)_3]$. Write the drawback of this catalyst. (10)

$[RhCl(PPh_3)_3]$ is Willkinson catalyst

known for hydrogenation of alkenes.



Again catalyst is regenerated after cycle is over.

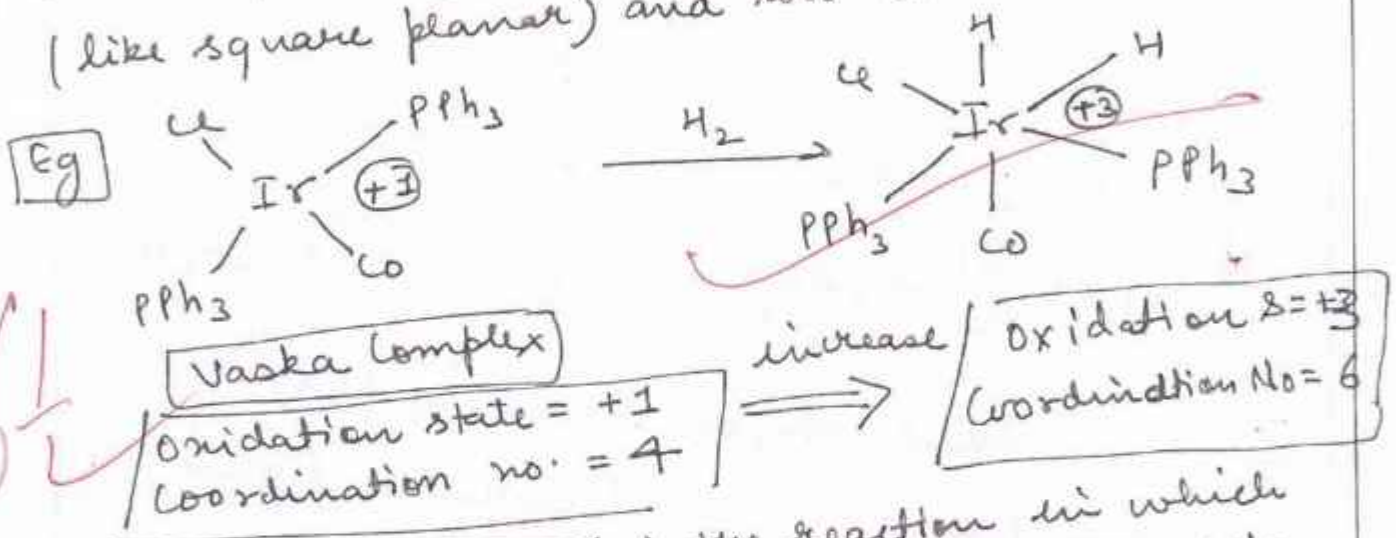
Drawback of Catalyst

Rhodium complex is difficult to obtain in normal condition. Not stable generally \Rightarrow require high temperature for reaction.

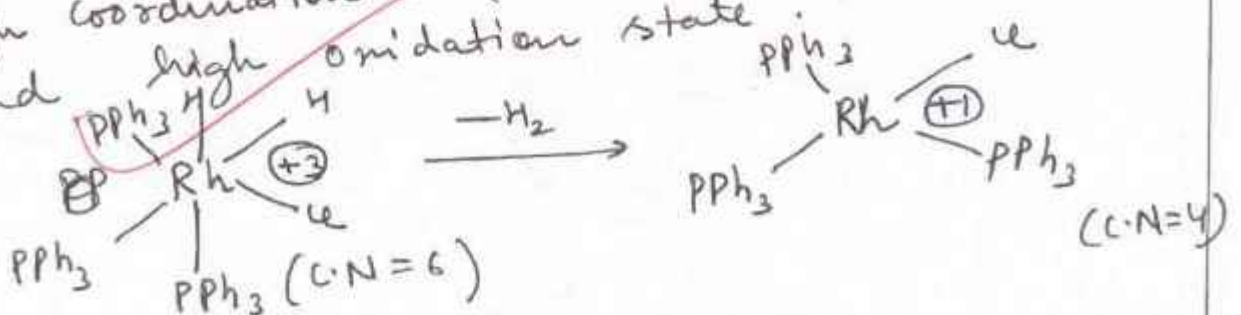
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- (c) Explain the terms oxidative addition and reductive elimination in the hydrogenation reactions and how the coordination numbers of the metal atom alter with an example. (10)

Oxidative addition is a reaction in which both coordination number and oxidation state of central metal increase. It is generally found in complexes of lower coordination number (like square planar) and low oxidation state.



Reductive elimination is the reaction in which coordination number as well as oxidation state decreases. Generally found in complexes with high coordination no. (like square bipyramidal) and high oxidation state.



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(d) Write the following ligand-exchange reaction: (20)



(ii) Which of the reactions should have a larger ΔS° ?

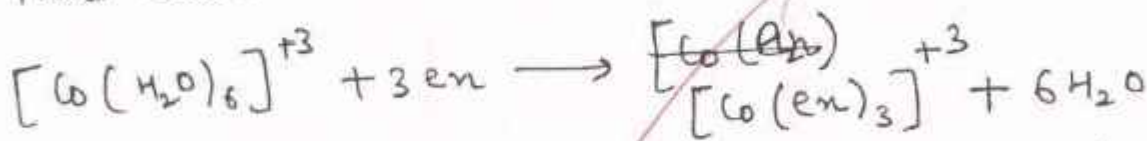
(iii) Given that Co-N bond length is approximately same in both complexes. Which reaction will have a larger equilibrium constant? Example your choice.

Ligand exchange reaction takes place as per e^- donating capacity of incoming ligand.

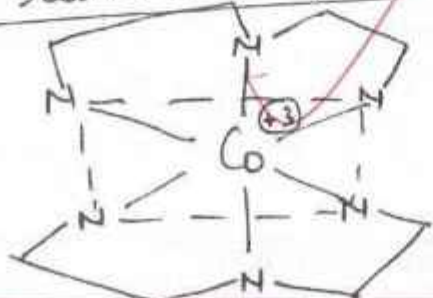
① Since, each NH_3 can donate $2e^-$, thus, each NH_3 replaces one H_2O molecule.



② Since, each ethylene diamine (en) has donating capacity of $4e^-$ (bidentate ligand), thus each en will replace 2 H_2O molecule.



This results in formation of chelate ring.



4-chelated rings

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(ii) ΔS° (entropy change) measures change in randomness in overall reaction.

In ① randomness of 6NH_3 is replaced by randomness of $6 \text{H}_2\text{O}$ molecules. As both of them have similar randomness, thus net change in randomness is 0 $\Rightarrow \Delta S^\circ \approx 0$

In ② randomness of 3 ethylene diamine is replaced by $6 \text{H}_2\text{O}$ water molecules. Since, No. of molecules in product is more, thus, product has more randomness

$$\Delta S^\circ = S_{\text{product}} - S_{\text{reactant}} > 0$$

Thus, reaction ② has larger and positive ΔS°

(iii) As per Gibbs equation $\Delta G_1^\circ = \Delta H^\circ - T\Delta S^\circ$

For reaction 1 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ (0)$
 $\Delta G^\circ = \Delta H^\circ$

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For reaction ② $\Delta G_2^\circ = \Delta H^\circ - T\Delta S^\circ$

since, Co-N bond length is same for both the complexes, thus ΔH° for both the reactions are almost similar.

Since, reaction ② has $+$ ve ΔS° thus,

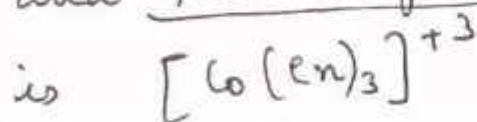
$$|\Delta G_2^\circ| > |\Delta G_1^\circ|$$

We know $\Delta G^\circ = -RT \ln K_{eq}$

since $|\Delta G_2^\circ| > |\Delta G_1^\circ|$

$$\Rightarrow |K_{eq,2}| > |K_{eq,1}|$$

\Rightarrow Reaction ② (formation of chelate rings in product) has larger equilibrium constant and thermodynamically more stable product



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SECTION - B

5(a) Give the kurnakov method to differentiate cis and trans square planar complex. (10)

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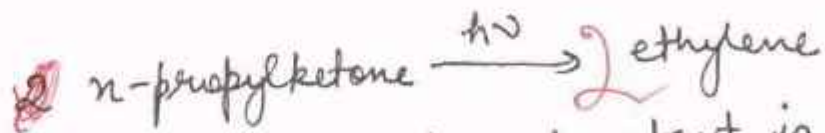
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(b) For the photochemical formation of ethylene from di-n-propylketone using a radiation of wave length 313 nm, the quantum yield is 0.21. calculate the number of moles of ethylene formed when the sample is irradiated with 50 watt of this radiation assuming that all the radiation is absorbed by the sample. (10)

As per Einstein's photo chemical equivalence, each absorbing material absorb only one quanta of energy.



Let the time for which reaction reactant is irradiated is 1 hour (3600 sec).

$$\text{Energy supplied by source} = P \times t = 50 \times 3600 = 180000 \text{ J}$$

$$\text{Energy of absorbed by 1 mole absorb reactant} = \frac{N_0 h c}{\lambda} = \frac{6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8}{313 \times 10^{-9}} = 382445.1 \text{ J}$$

$$\text{No. of einstein of energy absorbed} = \frac{180000}{382445.1} = 0.471$$

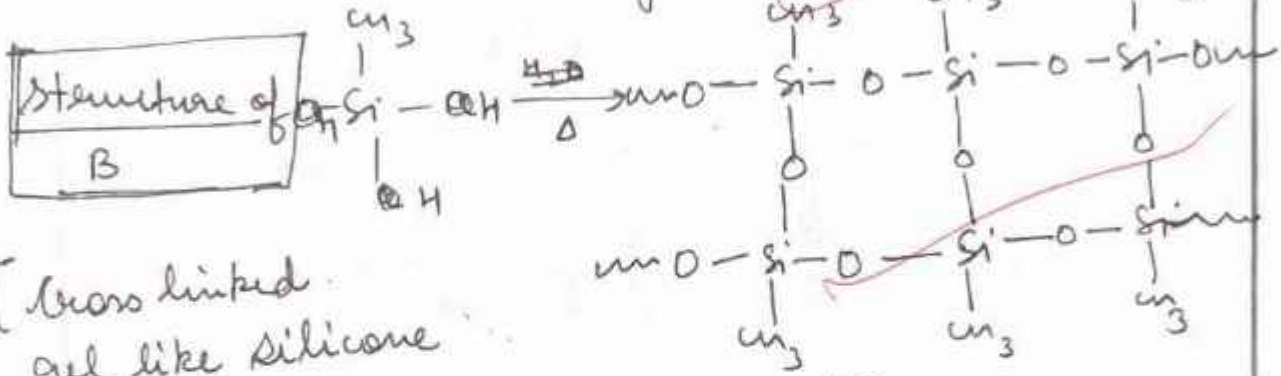
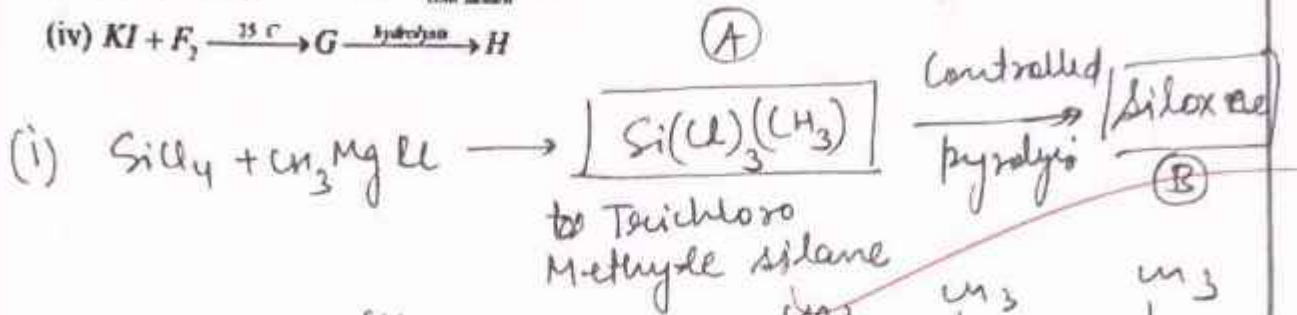
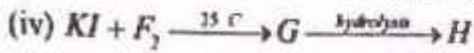
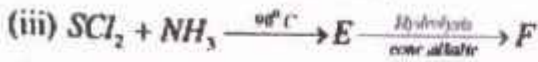
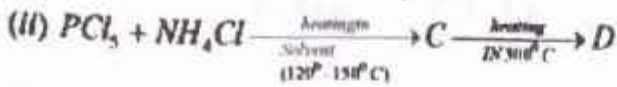
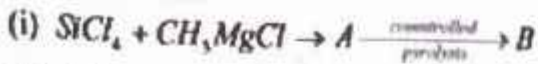
$$\phi = \frac{\text{No. of moles of reactants decomposed}}{\text{No. of einstein of energy}} \Rightarrow 0.21 = \frac{\text{moles of reactants decomposed}}{0.471}$$

$$\Rightarrow \text{mole of n-propylketone decomposed (per hour)} = 0.09891 \text{ hr}^{-1}$$

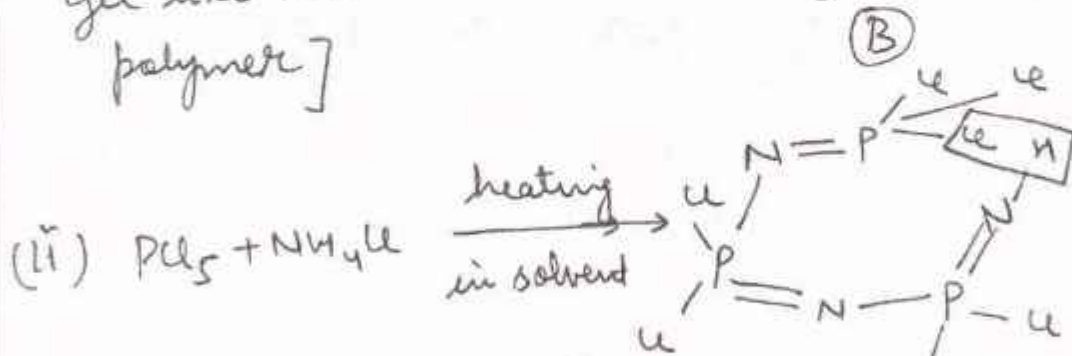
$$\Rightarrow \text{mole of ethylene formed (per hour)} = \frac{0.09891}{2} = 0.0494 \text{ hr}^{-1}$$

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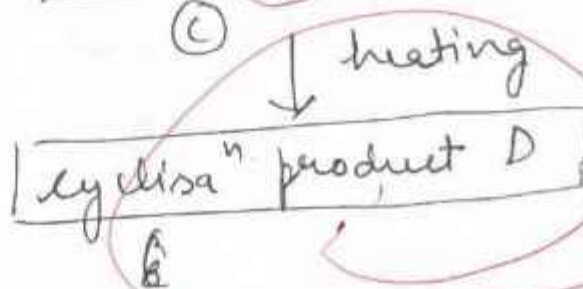
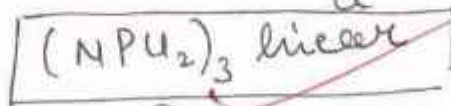
(c) In the following sequence of reactions, identify the product (A-H). (20)



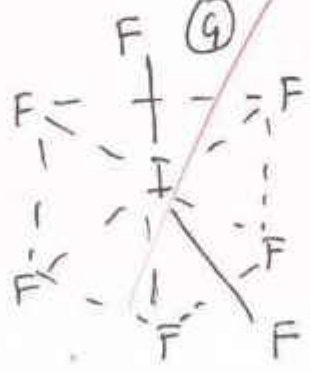
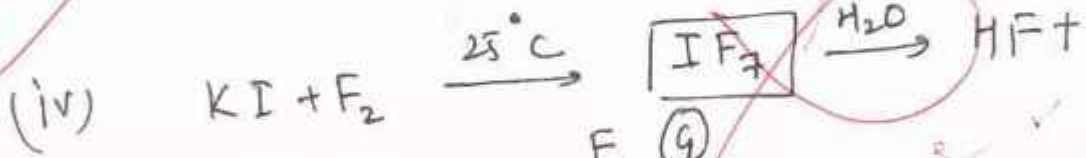
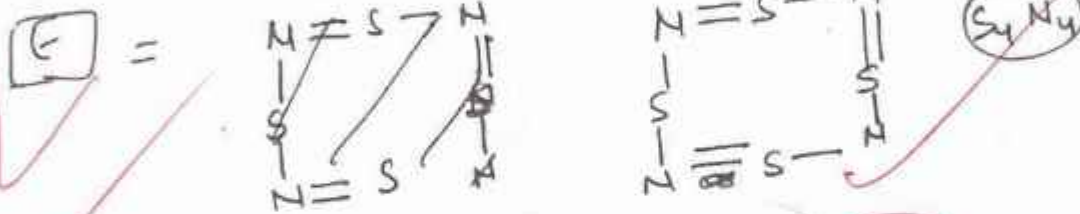
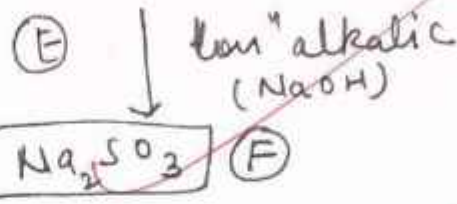
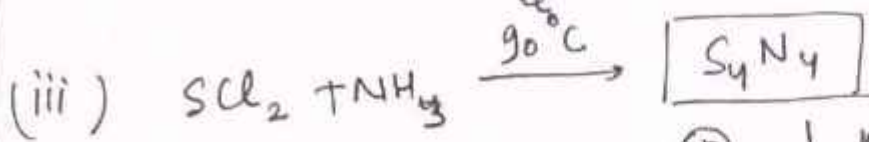
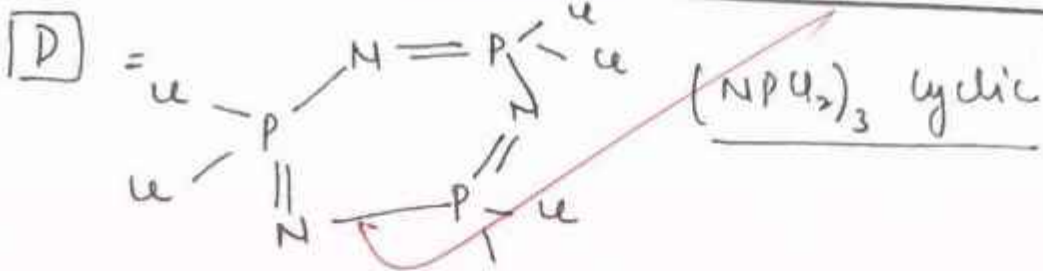
[Cross linked gel like silicone polymer]



(Phosphonitric halide)



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Pentagonal pyramidal

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(d) Which metals is involve in photosynthesis. Give reaction. (10)

Magnesium is involved in photosynthesis

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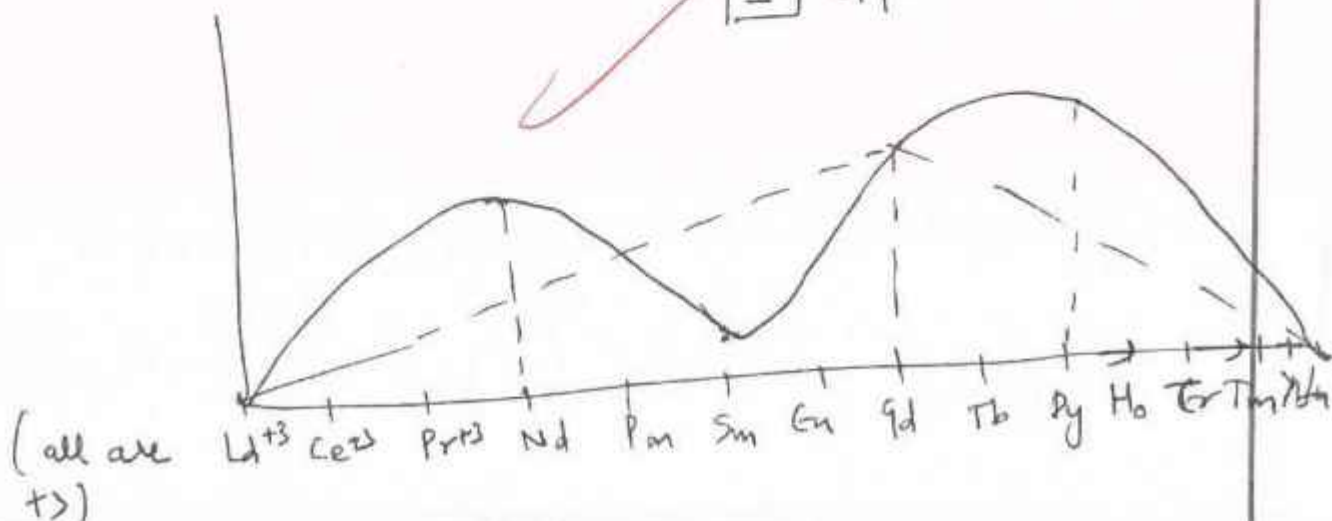
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6.(a) Magnetic susceptibility measurements are of little use in the structural elucidation of lanthanide complexes. Justify the statement. (10)

Magnetic susceptibility measurement are of little use in structural elucidation of lanthanide complexes because of difference in theoretical and experimental magnetic moment of lanthanids.

e^- in lanthanids are deep seated and thus, ~~or~~ in 4f orbital due to which orbital motion of e^- are not quenched which results in L-S coupling and theoretical magnetic moment ~~can~~ differ from experimental ~~but~~ except for f^0 and f^7, f^{14} configuration.

theoretical
 experimental.



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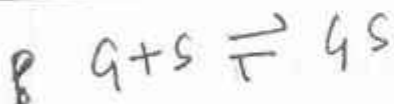
(b) Derive BET adsorption isotherm expression. for the process. (20)

BET adsorption isotherm relates the adsorbed fraction of a gas to its pressure.

Assumption for B.E.T. isotherm

- All surface active sites are identical in size, shape etc.
- surface active sites are limited
- there is interaction among adsorbed gas molecules
- ~~chemisorption~~ Multi-layer formation takes place

Consider following multi-layer adsorption -

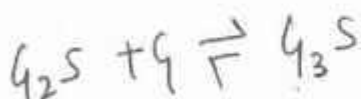


$$K_1 = \frac{[G_1 S]}{[G][S]} = \frac{\theta_1}{\theta_0 P}$$

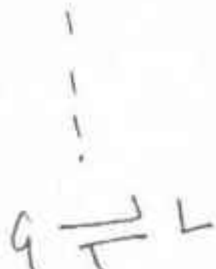
$\theta_0 =$ Vacant surface active sites



$$K_2 = \frac{[G_2 S]}{[G_1 S][G]} = \frac{\theta_2}{\theta_1 P}$$



$$K_3 = \frac{[G_3 S]}{[G][G_2 S]} = \frac{\theta_3}{\theta_2 P}$$



(Hill liquefaction)

$$K_L = \frac{1}{P_0}$$

$P_0 =$ saturation vapour pressure.

$$K_1 \gg K_2 \approx K_3 \approx \dots \approx K_L = \frac{1}{P_0}$$

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This is because ~~the~~ first adsorption takes place on solid surface and subsequent adsorptions on gas molecule.

Now $\theta_1 = K_1 P \theta_0$ $\theta_2 = K_2 \theta_1 P = \left(\frac{P}{P_0}\right) K_1 P \theta_0$

$$\theta_3 = K_3 \theta_2 P = \left(\frac{P}{P_0}\right)^2 K_1 P \theta_0$$

since, $\theta_0 + \theta_1 + \theta_2 + \dots = 1$

$$\Rightarrow \theta_0 + K_1 P \theta_0 \left(1 + \left(\frac{P}{P_0}\right) + \left(\frac{P}{P_0}\right)^2 + \dots\right) = 1$$

$$\Rightarrow \theta_0 + \frac{K_1 P \theta_0}{1 - \frac{P}{P_0}} = 1 \Rightarrow \theta_0 \left(1 + \frac{K_1 P}{1 - \frac{P}{P_0}}\right) = 1$$

$$\Rightarrow \theta_0 = \frac{(1 - P/P_0)}{K_1 P + (1 - P/P_0)} \quad \text{B.E.T isotherm}$$

Now $\theta_1 = \frac{V_1}{V_{\text{mono}}}$ $\theta_2 = \frac{V_2}{2V_{\text{mono}}}$ $\theta_3 = \frac{V_3}{3V_{\text{mono}}}$

(V_{mono} = Volume of mono-layer formation)

$$V_{\text{Total}} = V_1 + V_2 + V_3 + \dots$$

$$V = V_{\text{mono}} (\theta_1 + 2\theta_2 + 3\theta_3 + \dots)$$

$$V = V_{\text{mono}} (K_1 P \theta_0) \left[1 + 2\left(\frac{P}{P_0}\right) + 3\left(\frac{P}{P_0}\right)^2 + \dots\right]$$

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$$V = V_{mon} K_1 P_0 \times \frac{1}{\left(1 - \frac{P}{P_0}\right)^2}$$

using expression for $\theta_0 \Rightarrow V = \frac{K_1 P}{V_{mon}}$

$$V = (K_1 P V_{mon}) \times \frac{1}{\left(1 - \frac{P}{P_0}\right) \left[K_1 P + \left(1 - \frac{P}{P_0}\right) \right]}$$

taking comprehensive constant $(c) = \frac{K_1}{K_L} = K_1 P_0$

$$\Rightarrow \frac{V}{V_{mon}} = P \times \frac{c}{P_0} \times \frac{1}{\left(1 - \frac{P}{P_0}\right)} \times \frac{1}{cP + P_0 - P}$$

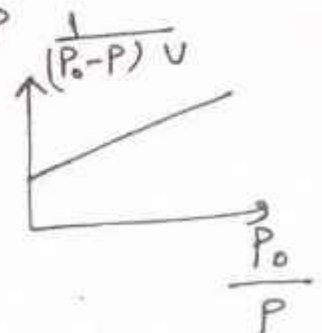
$$\Rightarrow \frac{V}{V_{mon}} = \frac{cP}{P_0} \times \frac{1}{\left(1 - \frac{P}{P_0}\right) \left[(c-1)P + P_0 \right]}$$

$$\Rightarrow \frac{V_{mon}}{V} = \frac{\left[(c-1)P + P_0 \right] \left[P_0 - P \right]}{cP}$$

$$\Rightarrow \frac{(P_0 - P)}{V} \times \frac{P}{(P_0 - P)} \times \frac{1}{V_{mon}} = (c-1)$$

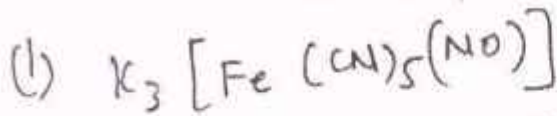
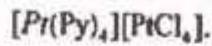
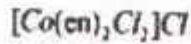
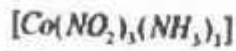
$$\Rightarrow \frac{V_{mon}}{V} \times \frac{1}{(P_0 - P)} = (c-1) + \frac{P_0}{cP}$$

$$\Rightarrow \frac{1}{(P_0 - P) V} = \frac{c-1}{V_{mon}} + \frac{P_0}{cP V_{mon}}$$



DIAS

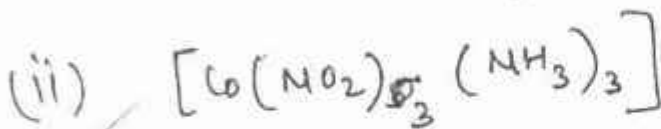
(c) Write IUPAC nomenclatures of (10)



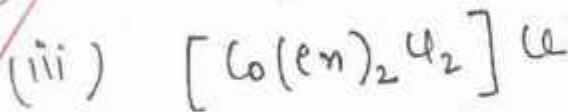
$$x - 5 = -3 \Rightarrow x = +2$$

~~Pentacyanido nitrosyl~~

Potassium Pentacyanidonitrosyl ferrate (II)



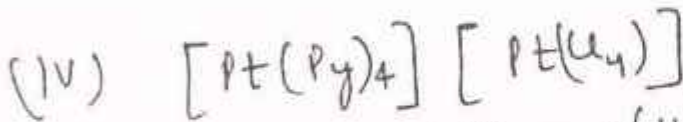
~~Triammine trinitro~~ Cobalt (III)



$$x - 2 = +1$$

$$x = +3$$

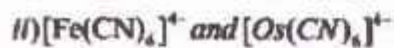
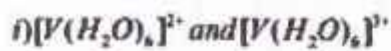
~~Dichloro bis-(ethylenediamine)~~ Cobalt (III) chloride



~~Tetrapyridine~~ platinum (II) tetrachloro platinate (II)

DIAS

- (d) Compare the $10 Dq$ values of the following ions with proper justification (At. No. of V, Fe and Os are 23, 26 and 76 respectively) (10)



$10 Dq$ is equivalent to octahedral splitting (Δ_o) energy.

- (i) Δ_o depend on oxidation state of central atom. As V^{+3} has higher charge, attraction between ligand and V^{+3} is more than attraction between V^{+2} and ligand causing more splitting.

Thus, $[V(H_2O)_6]^{3+} > [V(H_2O)_6]^{2+}$ in Δ_o or $10 Dq$.

- (ii) As we move down the group (from $3d \rightarrow 4d \rightarrow 5d$) size increases and thus charge density decrease (for same oxidation state in Fe^{+2} , Os^{+2}). Due to less charge density in Os^{+2} , repulsion between ligand and charge density is less and attraction is more. Thus,

$10 Dq$ value of $[Os(CN)_6]^{4-} > [Fe(CN)_6]^{4-}$

DIAS

- 7(a) Explain homogeneous and heterogeneous catalysis with a suitable example for each. Derive the expression for the rate of a surface catalysis reaction. (10)

Catalysis is the process of increase of rate of reaction by involving catalyst in a reaction.

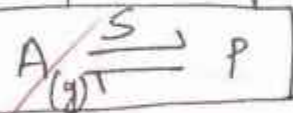
Homogeneous Catalysis

When catalyst and reactants are in the same phase, it is called homogeneous catalysis.

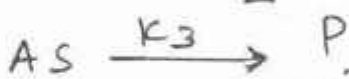
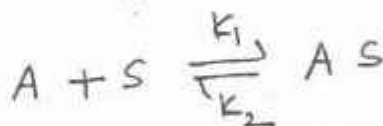
Heterogeneous Catalysis

When catalyst and reactants are present in different phases.

Eg Surface Catalysis reaction where gases get adsorbed on solid (s) catalyst surface to form products.



Mechanism



$$\frac{d[AS]}{dt} = k_1[A][S] - k_2[AS] - k_3[AS]$$

Let $[A] = P$; $[S] = C_s(1-\theta)$; $[AS] = \theta \cdot C_s$
 (θ = fraction of surface active sites C_s occupied by gas A) and Steady state approximation on $[AS]$

$$\Rightarrow k_1 \cdot P \cdot (1-\theta) - k_2 \theta - k_3 \theta = 0 \Rightarrow \theta = \frac{k_1 P}{k_1 P + k_2 + k_3}$$

As per inselwood theory, rate $\propto \theta$.

$$\Rightarrow \text{rate} = k_3 \theta \Rightarrow \text{rate} = \frac{k_1 k_3 P}{k_1 P + k_2 + k_3}$$

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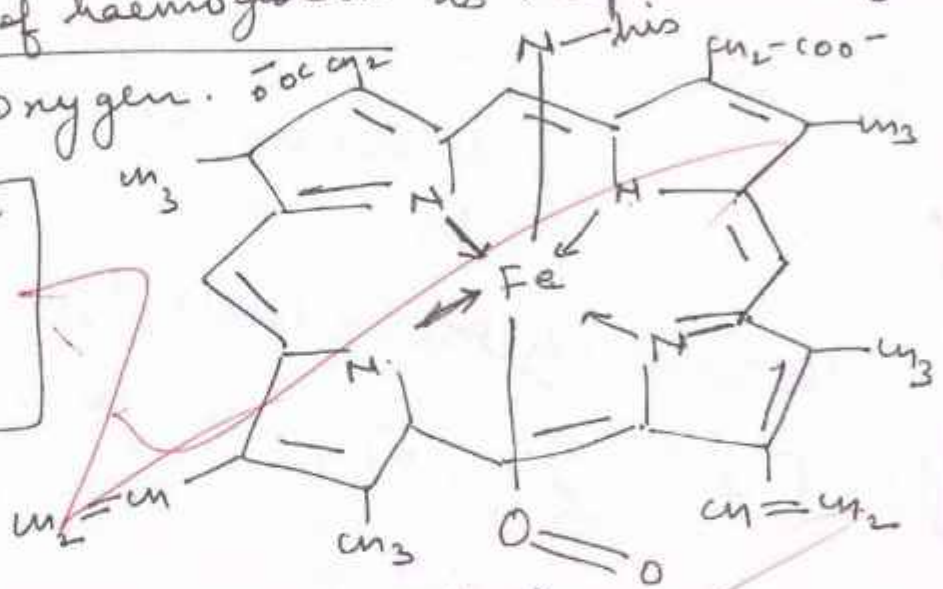
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(b) Heme acts as carrier of O_2 in the system whereas toxic effects of CO can be explained by replacement reaction. Explain. (10)

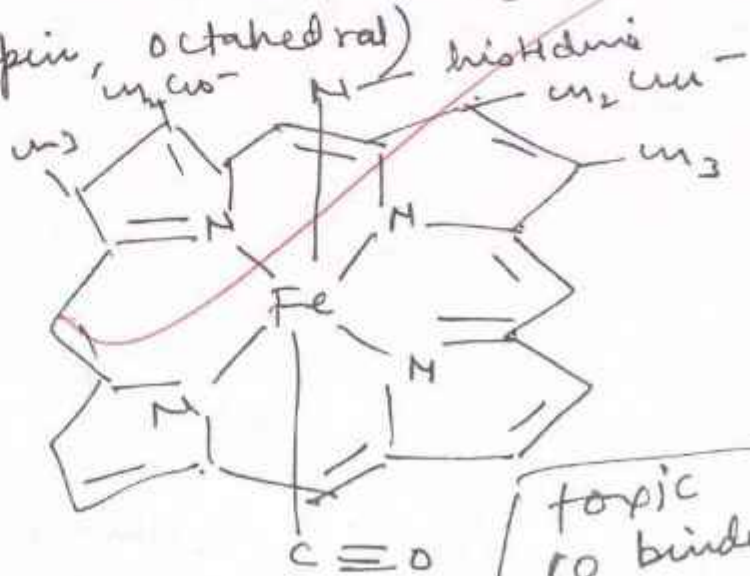
Heme group consists of iron porphyrin ring which is bonded to 'histidine - N' of the poly peptide chain and O_2 molecule in oxygenated form which act as carrier of O_2 . Heme group of haemoglobin is responsible for carrying oxygen.

Heme group in oxygenated haemoglobin



Fe^{+2} ($3d^6$ low spin, octahedral)

Toxicity of CO is introduced when $O=O$ in oxygenated heme group is replaced by carbon monoxide

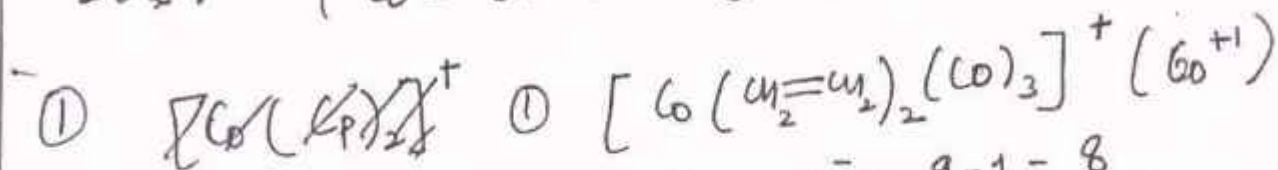


toxic CO binded

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(c) Write three complexes of Cobalt which follow 18 e rule, using at least two of cyclopentadienyl, CO, and ethylene as ligands. (10)

As per 18 e⁻ rule, total number of valence electron and e⁻ donated by ligand must be 18 e⁻. (Co = 3d⁷4s² = 9 valence electron)




Cp = cyclopentadiene

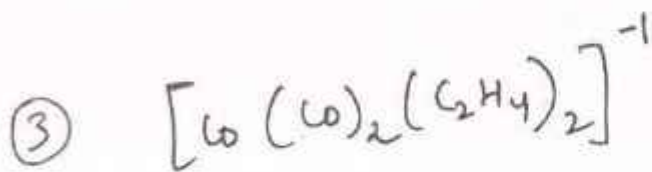
No. of valence e⁻ = 9 - 1 = 8
 e⁻ donated by CH₂=CH₂ = 4
 e⁻ donated by CO = $\frac{6}{18 e^-}$

Tricarbonyl diethylene Cobalt (I)



Dicarbonyl cyclopentadienyl Cobalt (I)

e⁻ donated by  = 6
 e⁻ in Co⁺ = 8
 e⁻ donated by CO = $\frac{4}{18}$



e⁻ in Co⁻¹ = 10
 e⁻ donated by CO = 4
 e⁻ donated by C₂H₄ = $\frac{4}{18}$

thus, Cobalt can attain negative charge as well.

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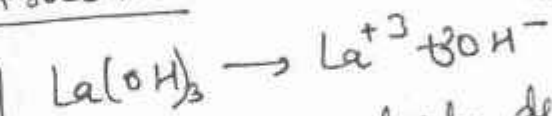
(d) (i) What is lanthanide contraction? How does it account for higher basicity of $\text{La}(\text{OH})_3$ compared to $\text{Lu}(\text{OH})_3$? (5)

(ii) How can lanthanides be separated by ion-exchange method? Explain the principle involved in it. (5)

(i) Lanthanide contraction refers to ~~higher~~ rapid and regular decrease in size of lanthanoids as we move from Lanthanum (La) to Lutetium (Lu).

Reason e^- in f -orbital has very poor shielding capacity which results in higher effective nuclear charge as one moves from La \rightarrow Lu due to high attraction between nucleus and e^- .

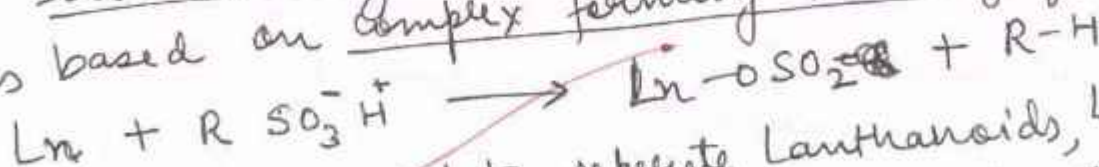
Basicity of $\text{La}(\text{OH})_3$ and $\text{Lu}(\text{OH})_3$



As size regularly decreases from La \rightarrow Lu, covalent character

of hydroxides increase from La \rightarrow Lu. Thus, $\text{Lu}(\text{OH})_3$ is precipitated while $\text{La}(\text{OH})_3$ remains ionic giving OH^- ions.

(ii) Ion-exchange method to separate lanthanides is based on complex forming tendency of lanthanide.



When resin is used to separate lanthanoids, Lanthanum (La) forms the complex first and separated as La-O SO_2^- from where La^{+3} can be extracted. Since, La has the highest complex tendency among all, it is separated rapidly.

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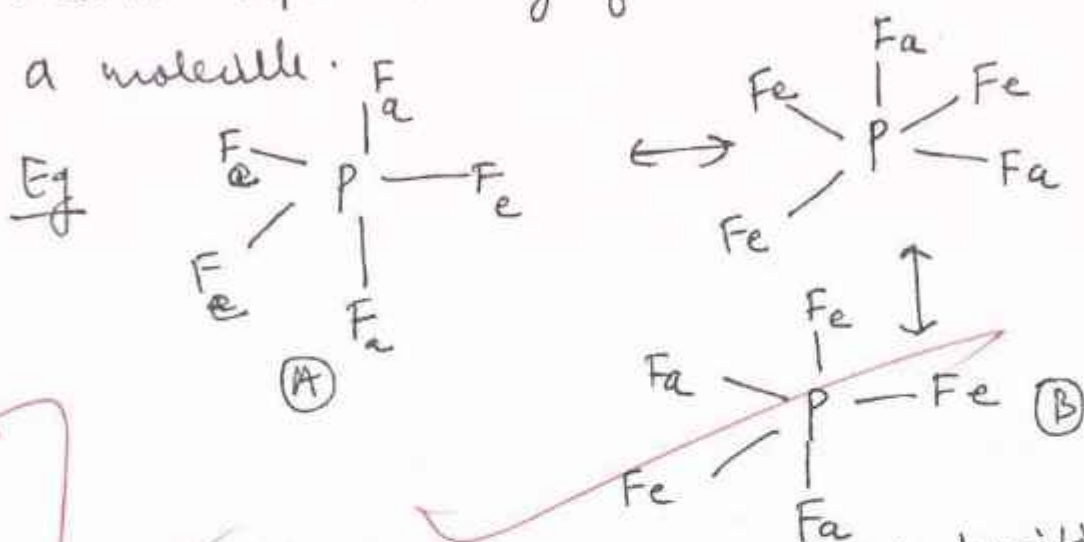
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(e) What are fluxional molecules? Discuss method of characterization. (10)

Fluxional molecules are those which exist in continuously changing structures due to rapid exchange of atoms arrangement within a molecule.



The fluorine at axial and equatorial positions continuously exchange their position thus two structures are indistinguishable at room temp. as enough energy is present at room temperature to overcome pseudo energy barrier energy barrier for its conversion. But at low temperatures, exchange of F molecules stop and 2 structures are distinguishable as shown in NMR (F-19) spectra.

