



ST. WILFRED'S P.G. COLLEGE

(Affiliated to the University of Rajasthan)

Sample Answer Sheets

Kapila

IQAC HEAD
ST. WILFRED'S P.G. COLLEGE
JAIPUR



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Where the mind is without fear! Where the head is held high!!

ST. WILFRED'S PG COLLEGE

SESSION - 2012 - 2013

Name/Roll No. Mahak Gami Patel Class MSc Bsc Section

Subject Inorganic Chemistry Paper I

Day Date Invigilator Signature

1	2	3	4	5	6	7	8	9	10	Total
12			10		15		13	06		62

Marks Obtained 62 Max Marks 100 Examiners Signature

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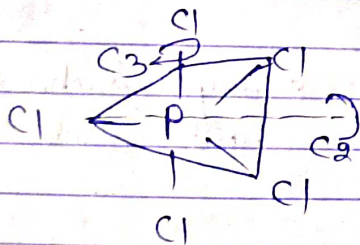
1. Symmetry Element:— It is a geometrical entity such as a point, a line or a plane about which a symmetry operation is performed. $(CO)_2$

Symmetry operation:— A symmetry operation is the movement of a molecule about the symmetry element in such a manner that the resulting configuration of the molecule is indistinguishable from the original.

There are five types of symmetry elements:-

- (i) Identity [E] - All molecules pass an identity elements which do not do any-thing to the molecule.
- (ii) proper axis of rotation (C_n)
- (iii) Plane of symmetry (σ)
- (iv) Improper axis of rotation (S_n)
- (v) Centre of symmetry (i)

Example :- PCl5 - Trigonal bi-pyramidal



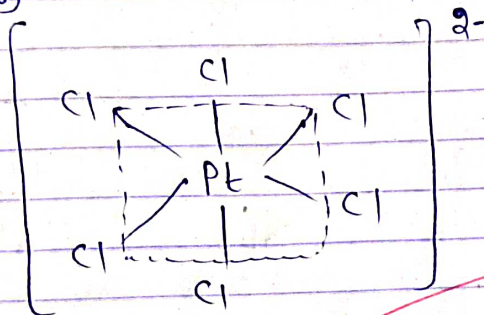
sp^3d hybridisation

- (i) Symmetry element - $E, C_3, 3C_2, 3\sigma_v, \sigma_h, 2S_6$
 Point group - D_{3h}
 $C_3, C_3^2, C_3 = E = 2$
 $C_2, C_2^2, C_2 = E = 3$
 $3\sigma_v = 3$

$$\sigma_h = 1$$

$$S_3^1, S_3^2, S_3^3 = E = 2$$

(ii) $[PtCl_6]^{2-} \rightarrow$ Octahedral



Point group :- O_h

Symmetry Element - $E, 3C_4, 4C_3, 3S_4, 3C_2$

Both Coincident with the C_4 axis, $6C_2, 5S_6, 3\sigma_h, 6\sigma_d$

Symmetry operation $E = 1$

$$C_4^1, C_4^2 = C_4^3, C_4^4 = E = 3 \times 3 = 9$$

$$C_3^1, C_3^2, C_3^3 = E = 8$$

$$C_2^1, C_2^2 = E = 6$$

$$3\sigma_h = 3$$

$$S_4^1, S_4^3 = C_2^1, S_4^2, S_4^4 = E = 2 \times 3 = 6$$

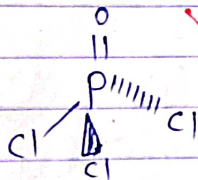
$$S_6^1, S_6^2 = C_3^1, S_6^3 = C_2^1, S_6^4 = C_3^2, S_6^5 = E = 2 \times 4 = 8$$

$$6 \text{ ord} = 6$$

$$i = 1$$

(iii) $\text{POCl}_3 \rightarrow$ trigonal pyramidal

Point group - C_{3v}
 Symmetry element $E, C_3, 3\sigma_v$
 operation $= E = 1$
 $C_3^1, C_3^2, C_2^3 = E = 2$
 $3\sigma_v = 3$



(iv) m-dinitrobenzene :-

Point group = C_{2v}
 element = $E, C_2, 2\sigma_v$
 operation $E = 1$
 $C_2 = 1$
 $2\sigma_v = 2$

2

84. Structure and Synthesis of metal Carbonyls :- ^{(CO)₃} The complex formed by the combination of CO molecules with transition metal atoms in low oxidation states are called metal carbonyls.

Depending on the number of metal atoms in a given carbonyl, carbonyls have been classified into the following two types -

(1) Mono nuclear Carbonyls :- These complex contain only one metal atom per molecule and are of type $M_x(CO)_y$, Here $x=1$

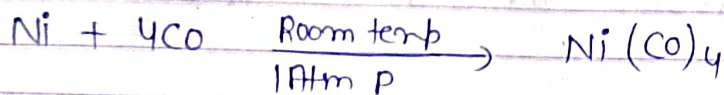
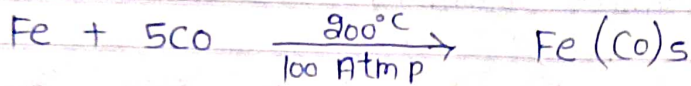
Ex $V(CO)_5$, $Cr(CO)_6$ etc

(2) Poly nuclear Carbonyls :- These contain two or more metals per molecule and are of the type $M_x(CO)_y$. These carbonyl contain two metal atoms as bridged carbonyls.

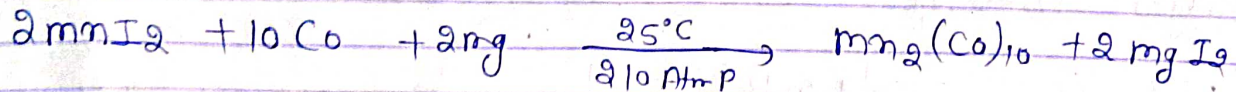
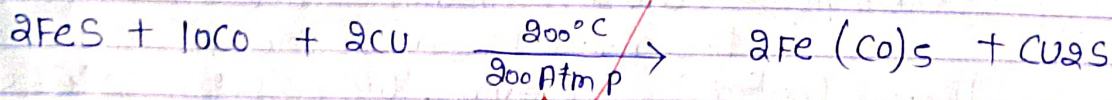
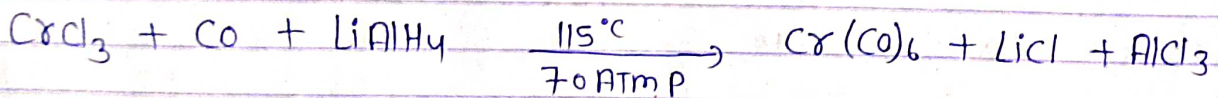
Ex $[Fe(CO)_12]$, $[MnRe(CO)_{10}]$

General methods of preparation :-

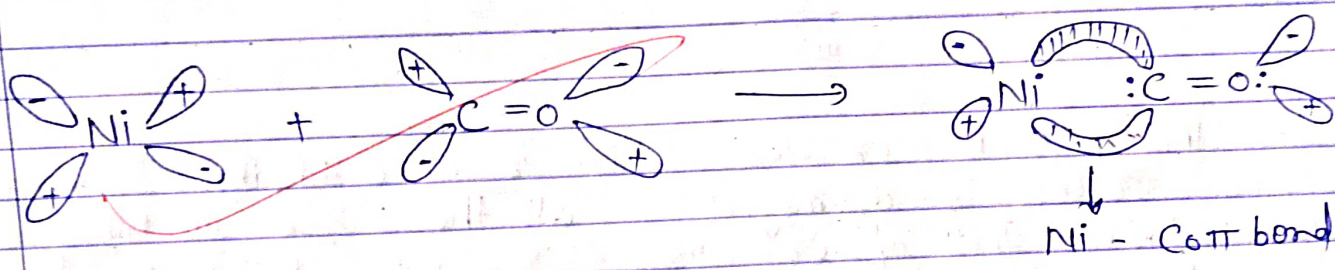
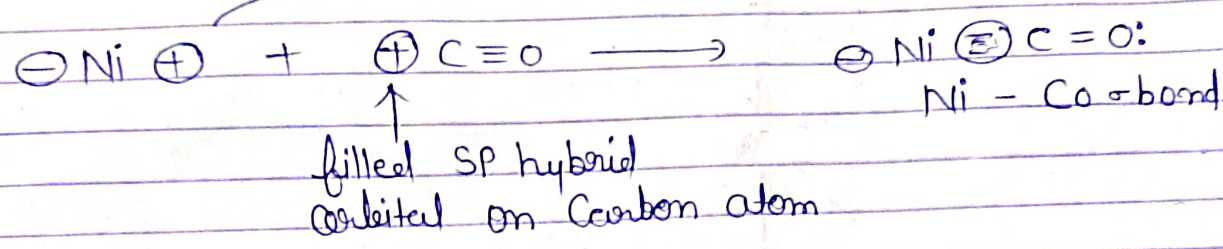
(i) By direct synthesis :-



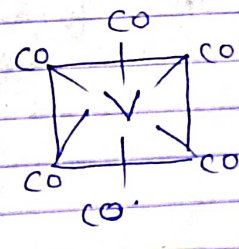
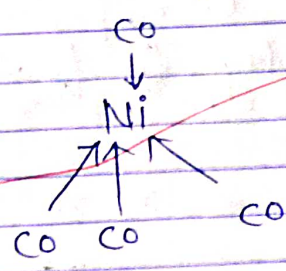
(ii) By Carbonylating the metallic salts with CO in presence of a reducing agent



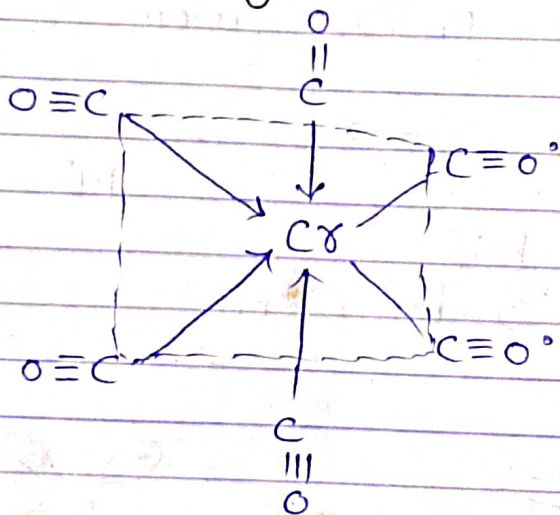
Bonding and Structure — empty sp^3 hybrid orbitals on Ni-atom.



formation of one Ni \rightarrow Co π bond



Structure and bonding in $\text{Cr}(\text{CO})_6$:-



In this molecule, Cr atom is in zero oxidation state and since $\text{Cr}(\text{CO})_6$ is diamagnetic, all the six electrons in the valance shell of Cr-atom ($\text{Cr} = 3d^5, 4s^1$) get paired in $3d$ -orbitals. Thus the valance shell configuration of Cr-atom in $\text{Cr}(\text{CO})_6$ becomes $3d^6, 4s^0$. σ -bond results from the overlap b/w an empty $d^2 sp^3$ hybrid orbital on Cr-atom and doubly filled sp hybrid orbital on C-atom in CO molecule.

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Name/Roll No..... Mahak. Sani. Patil..... Class. MSc (Phy)..... Section.....

Subject..... Inorganic..... Paper..... I.....

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Marks Obtained..... Max Marks..... Examiners Signature.....

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UNIT-V

Q.4.

law of radio active decay:- Radio activity was discovered in

1886 by the French Scientist Henry

Becquerel while working with Phosphorescent materials.

A substance ~~is~~ which possessed the

property of emitting such active rays was called radio active substance and the property was called radio activity.

Theory of radioactive disintegration:- Rutherford and Soddy formulated the theory of radioactive disintegration, according to this theory -

- (i) Radioactive ~~elements~~ elements are constantly emitting α , β & γ rays and produce new radioactive products.
- (ii) The rate of disintegration is not affected by external factors as temp, pressure but it depends upon the number of atoms.



$$-\frac{dN}{dt} \propto N \Rightarrow -\frac{dN}{dt} = \lambda N$$

$$-\lambda dt = \frac{dN}{N}$$

$$\int_0^t dt = 1, \lambda = -\frac{dN}{N}$$

$$\int \frac{dN}{N} = -\int \lambda dt$$

$$\ln N = -\lambda t + C$$

$$\text{At } t=0 \quad N=N_0 \quad N=N_0$$

$$C = \ln N_0$$

($\lambda = \text{Velocity Constant}$)

$$\ln\left(\frac{N}{N_0}\right) = -\lambda t$$

$$N = N_0 e^{-\lambda t}$$

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

Half life period :-

$$\lambda = \frac{2.303}{t_{1/2}} \log \frac{1}{2}$$

$$t_{1/2} = \frac{\ln 0.5}{\lambda}$$

$$t_{1/2} = \frac{0.693}{\lambda}$$

The time $t_{1/2}$ required for disintegration of one half of the original amount of the radio active substance is called its half-life period.

Ans 9(b) Geiger-Nuttall rule :- Geiger and Nuttall found that those
isotopes which decay slowly emit α -particles
short range while those which disintegrate rapidly:

A relationship b/w the decay const λ and the range R , was discovered by Geiger, Nuttall in 1921.

$$\log \lambda = A + B \log R \quad \text{--- (1)}$$

(A & B = Const)

A plot of $\log \lambda$ against $\log R$ will give a straight line. Where R is the range in standard air.

$\log^n (1)$ is known as Geiger - Nuttall law. It is only approximation.

The range of R is related to the energy of α -particles in the form

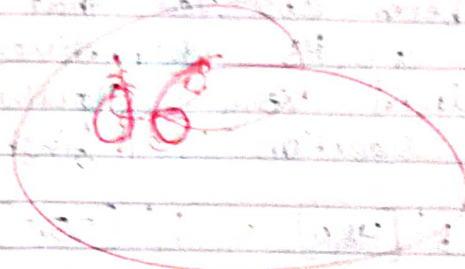
$$R = a v^3$$

$$E = \frac{1}{2} m v^2 = \frac{1}{2} m \frac{R^{2/3}}{a^{2/3}} = \boxed{g R^{2/3}}$$

there must be a similar connection b/w the half-life and the disintegration energy $E \Rightarrow$

$$T_{1/2} R^B = 1$$

$$\frac{3}{2} B \log E + B' = \log t$$



UNIT - IV

(CO₂)

Acid Hydrolysis :- These are the substitution reaction in which a ligand is replaced by a water or by OH⁻ group.

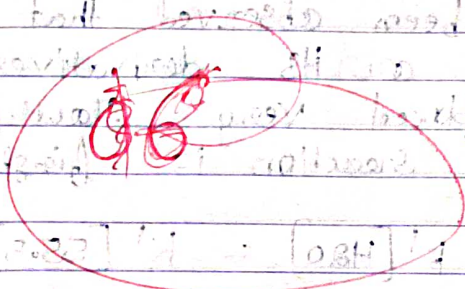
The reaction in which an aqua complex is formed as a result of the replacement of a ligand by H₂O molecules are called Acid Hydrolysis.

Acid hydrolysis reactions occur in neutral and acidic solution ($Mn < 3$).

there must be a similar connection b/w the half-life and the disintegration energy $E \Rightarrow$

$$T_{1/2} R^B = \lambda$$

$$\boxed{\frac{3}{2} B \log E + B' = \log \lambda}$$



UNIT - IV

(CO2)

Acid Hydrolysis:- These are the substitution reaction in which a ligand is replaced by a water or by OH^- group.

The reaction in which an aqua complex is formed as a result of the replacement of a ligand by H_2O molecules are called Acid Hydrolysis.

Acid hydrolysis reactions occur in neutral and acidic solution ($pH < 3$).



It has been observed that NH_3 or amines like ethylenediamine or its derivatives co-ordinated to $\text{Co}(\text{III})$ are replaced very slowly by H_2O and hydrolysis of the reaction is first order.

$$k = k' [\text{H}_2\text{O}] = k' [55.5]$$

$$\text{Rate} = k [\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$$

$$k' [\text{Co}(\text{NH}_3)_5\text{X}]^{2+} [\text{H}_2\text{O}]$$

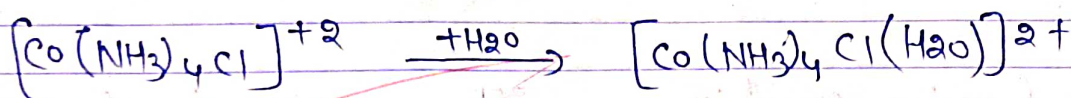
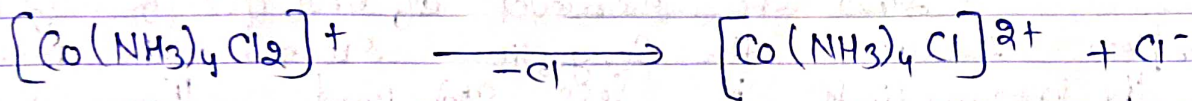
$$k' [\text{Co}(\text{NH}_3)_5\text{X}]^{2+} [55.5]$$

Factors affecting: Acid hydrolysis :-

(i) Effect of Charge on the Complex :- (1) Lim. rate as the charge of the complex

① in Cl dissociation S_N1 process seems to be operative.

The acid hydrolysis of divalent complex like $[Co(NH_3)_4(H_2O)Cl]^{2+}$ also takes place in two steps.



Effect of Chelation:— rate of aquation of the complex is \uparrow as chelation \uparrow . The rates of aquation is slowed down by chelation because of \downarrow stability of the transition state due to less efficient solvation.

does not distinguish between S_N1 and S_N2 mechanism.

(iii) Effect of substitution on ethylenediamine steric hindrance:—

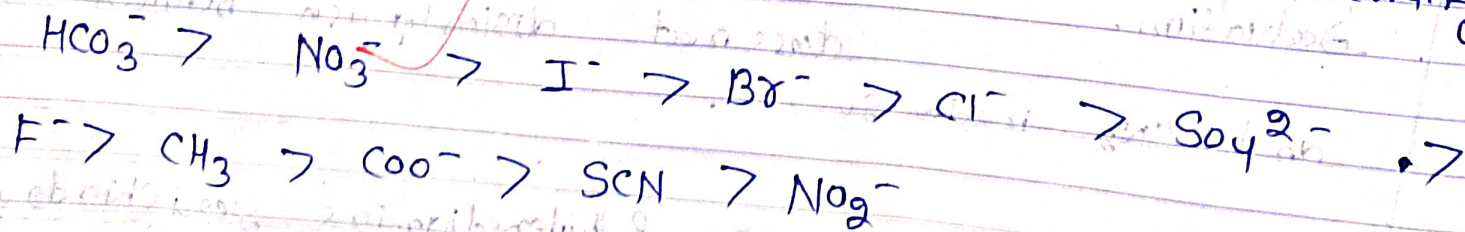
When H atom on C atom or on N atom of en group of trans $[\text{Co(en)}_2\text{Cl}_2]^+$ are replaced by the alkyl group like CH_3 the ligand become more bulky.

Since the removal of one Cl^- ion from the complex reduces the congestion around the metal. Thus the intermediate is less strained than the complex.

v) Effect of leaving group:-

The rate of reaction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ depends on the nature of X^- which reacts with H_2O molecules.

Bond breaking step is important in rate determining step because the



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Marks Obtained..... Max Marks..... Examiners Signature.....

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UNIT-3

(COS)

Q.6. When the term stability is used without qualification it means that the complex exists and under suitable condition it may be stored for a long time.

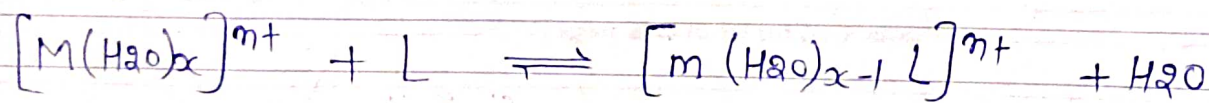
Two kinds of stability of complexes has shown which are as follows:-

(i) Thermodynamic stability :- This is measure of the extent to which the complex will form or will be

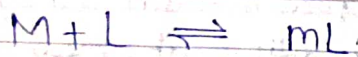
transformed into another species.

Kinetic stability - This refers to the speed with which the formations leading to the attainment of equilibrium will occur.

Formation constant :- When a metal ion in aqueous solution interacts with a neutral and monodentate ligand.



We may write the equilibrium reaction simplified.



$$K_f = \frac{[ML]}{[M][L]}$$

K_f is called the formation constant of the complex.

Experimental determination of formation constant -

Spectrophotometric Method: - The relationship b/w the absorbance or optical density at a particular wavelength concentration is expressed by Beer's law which is given as

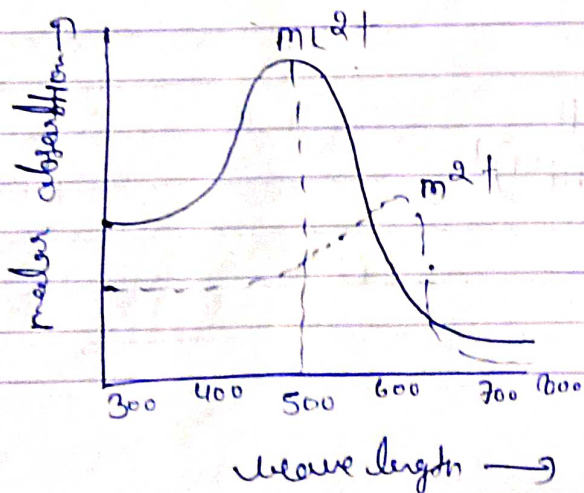
$$A = \epsilon \cdot l \cdot c$$

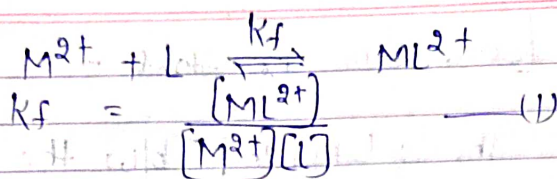
ϵ = molar extinction coefficient

l = length of the absorption cell

c = concentration of the complex

How the spectrum of a metal ion M^{2+} , changes on coordination with ligand, L has been shown in figure.





We know that -

$$C_m = [M^{2+}] + [ML^{2+}] \quad (2)$$

$$C_L = [L] + [ML^{2+}] \quad (3)$$

$$A = \epsilon [ML^{2+}]^L [M^{2+}] \quad (4)$$

$$[ML^{2+}] = \frac{A}{\epsilon [M^{2+}]^L} \quad (5)$$

C_m = total concentration of the metal ion

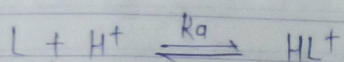
C_L = total concentration of the ligand

Thus:-

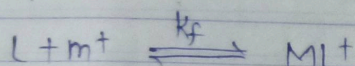
$$[M^{2+}] = C_m - \frac{A}{\epsilon [M^{2+}]^L}$$

$$[L] = C_L - \frac{A}{\epsilon [M^{2+}]^L} \quad (6)$$

Potentiometric method:- When the ligand is a weak base or acid
 Competition b/w hydrogen ions and metal ions
 for the ligand can be used for the determination of the formation
 const.



$$K_a = \frac{[HL^+]}{[L][H^+]}$$



$$K_f = \frac{[ML^+]}{[L][M^+]}$$

$$C_H = [H^+] + [HL^+]$$

$$C_M = [M^+] + [ML^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

$$K_f = \frac{[ML^+]}{[M^+][L]}$$

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