CHEMICAL KINETICS

It is the branch of physical chemistry which deals with the rate of chemical reactions and also factors affecting the rate of the chemical reaction.
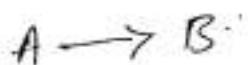
Rate of a chemical reaction :-

Rate, speed or velocity of a reaction has the same meaning in chemical kinetics.

Rate of a reaction is defined as "the rate of change of concentration of reactants or products in unit time."

$$Rate = -\frac{dx}{dt}$$ where dx = change in conc^n of Reactants or products with time. dt.

Let us consider the reaction of the type.

$$A \longrightarrow B$$

Rate of reaction with respect to $A = \dfrac{-d[A]}{dt}$

–ve sign indicates conc of a A decreases with time dt

Rate of reaction w.r.t to time B $= \dfrac{+d[B]}{dt}$

+ve sign indicates conc^n of B increases with time dt.

Thus over all rate of reaction $\dfrac{dx}{dt} = \dfrac{-d[A]}{dt} = \dfrac{+d[B]}{dt}$

factors influencing rate of reaction :-

① concentration of reactant's :- The rate of reaction increases with increase in concen of reactant. This is due to increase in number of collisions between reactant molecules per second.

② Effect of catalyst :-
The catalyst is a substance which alters the rate of reaction without undergoing chemical change.
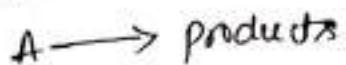
In presence of catalyst the rate of a reaction increases because the catalyst provides an alternative path with lower energy of activation hence more numb of reactant molecules can become product

③ effect of Temperature :-
As temperation of a reaction increases the rate of the reaction also increases, because as temperature increases the kinetics energy of molecules increases this increases the number of effective collision per unit volume per second increases as collision increases rate of reaction also increases.

Velocity constant:

Rate of a reaction depends on conⁿ of reactants consider the reaction.

A ⟶ products

Rate ∝ [A]

Rate = k[A] where k = velocity constant;
─ this is called rate law

when [A] = unity
Then | rate = k | ⊙ | Rate = Rate constant |
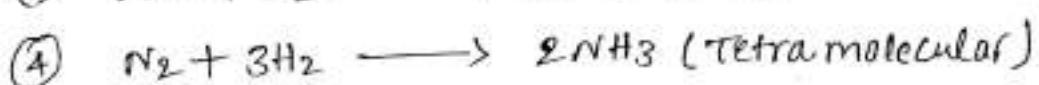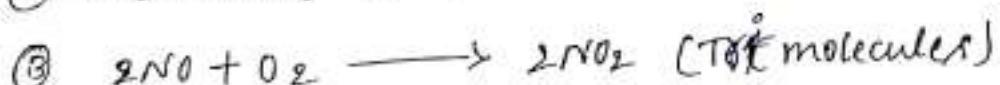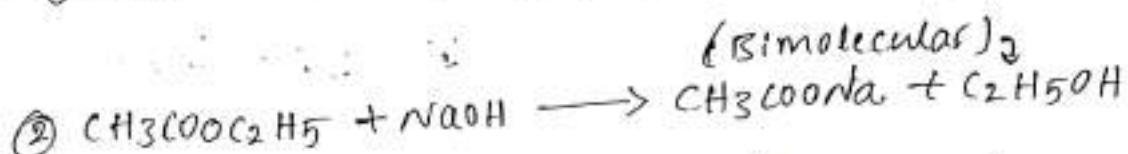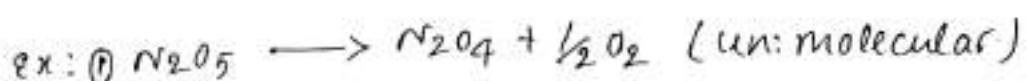
Molecularity of a reaction:-

The molecularity of a reaction is defined as the number of reactant molecules which take part in an elementary reaction:

⊕ molecularity is defined as " total number of reactant molecules taking part in a balanced chemical equation"

ex: ① $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ (unimolecular)

② $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ (Bimolecular)₂

③ $2NO + O_2 \longrightarrow 2NO_2$ (Tri molecules)

④ $N_2 + 3H_2 \longrightarrow 2NH_3$ (Tetra molecular)

order of a reaction :-

order of a reaction is defined as " sum of the powers of concentration terms appearing in an experimentaly determined rate eqn "

To understant the concept order of a reaction

$A + B \longrightarrow$ product.

According to law of mass action

$$rate \propto [A]^a \times [B]^b$$

$$rate = k [A]^a [B]^b$$

where $k \longrightarrow$ rate constant ⊕ velocity constant.

$$\boxed{order = a+b}$$

$a \longrightarrow$ order of ren" wrt 'A'
$b \longrightarrow$ order of ren". wrt 'B'
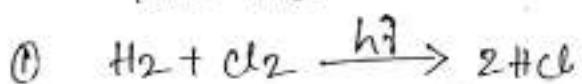
Zero order reaction :-

Reaction whose rate is independent of concentration of the reactants is called zero order reactions.

⑳
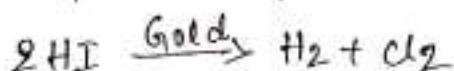
change in concentration of the reactants does not changes the rate of reaction.

Ex :- photo chemical combination of H_2 and Cl_2 to form HCl

① $H_2 + Cl_2 \xrightarrow{h\gamma} 2HCl$
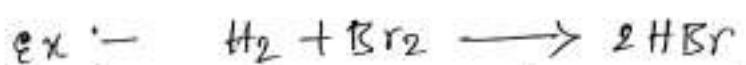
$$Rate. \propto [H_2]^0 [Cl_2]^0$$

② Decomposition of HI on gold surface

$$2HI \xrightarrow{Gold} H_2 + Cl_2$$

Fraction order reaction :-

A reaction in which sum of the powers of the concentration terms is a fraction is called 'fraction order reaction'.

ex :- $H_2 + Br_2 \longrightarrow 2HBr$

$$rate. \propto [H_2]^1 \times (Br_2)^{1/2}$$

$$\therefore order = 3/2$$

Mathematical characterstics of zero order reactions :-

consider a reaction $A \longrightarrow products$

$$\frac{dx}{dt} = K[A]^0 \quad \text{⑳} \quad \frac{dx}{dt} = K \qquad \because ([A]^0 = 1)$$

⑳ $\frac{dx}{dt} = K(a-x)^0$

$$\frac{dx}{dt} = k(a-x)^0$$

on Intigration

$x = kt + C$ C = integration constant.

when $t = 0$ $x = 0$ $\therefore$ $C = 0$

$x = kt + 0$

$$\boxed{k = \frac{x}{t}}$$ This is general eq^n for zero order reaction.

k has the unit concentration/time.
@ mol/dm^3 . s^{-1}
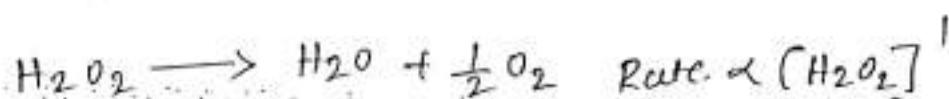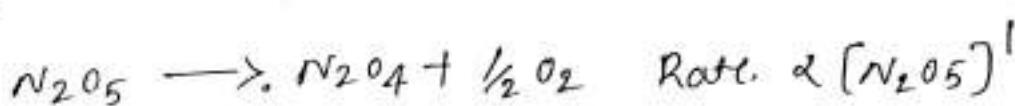
Difference. b/w order and molecularity.

order	Molecularity
1. order is the sum of the powers of conc^n terms in an. experimentaly. determined rate. equation	1. Total no of reactant molecu involved in. balanced chemical equation
2. order is an emphirical quantity @ determined. exptly	2. Molecularity is a. theoritica quantity
3. It can be a positive @ negative integer @ fractional number including zero	3. it is always a whole. number. and can not be zer0
4. It applies to the reaction as a whole.	4. it applies to each and individual step (elimentary reaction).

First order reactions :-
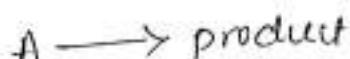
A reaction in which rate is proportional to first power of the concentration of the reactants.

ex:

$$N_2O_5 \longrightarrow N_2O_4 + \tfrac{1}{2}O_2 \quad Rate \propto [N_2O_5]^1$$

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \quad Rate \propto [H_2O_2]^1$$

Rate equation for I order reaction

consider a reaction.

$$A \longrightarrow product$$

Let a mol dm^{-3} be the initial concentration of A. If after time t, x mol dm^{-3} of A decompose, the remaining concentration of A is $(a-x)$. The rate of formation of the product at any instant is $\dfrac{dx}{dt}$.

$$\therefore \quad \dfrac{dx}{dt} \propto (a-x)$$

$$\dfrac{dx}{dt} = k(a-x)$$

$$\dfrac{dx}{a-x} = k \cdot dt$$

on integration.

$$\int \dfrac{dx}{a-x} = k \int dt$$

$$\ln \dfrac{a}{a-x} = kt$$

$$k = \dfrac{1}{t} \ln \dfrac{a}{a-x}$$

Inte.

$$\int \dfrac{dx}{a-x} = k \int dt$$

$$-\ln(a-x) = kt + C$$

To find C
$$t = 0 \quad x = 0$$

$$-\ln a = C$$

$$-\ln(a-x) = kt - \ln a$$

$$\ln a - \ln(a-x) = kt$$

$$\ln \left(\dfrac{a}{a-x}\right) = kt$$

on converting to common log
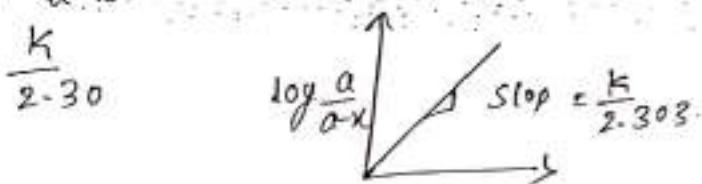
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$ unit of K is time^{-1} ⓐ s^{-1} ⓑ

min^{-1}

some characteristics of the first order reaction.

1. A plot of $\log \frac{a}{a-x}$ vls time is a straight line
with slope $\frac{K}{2.30}$

$\log \frac{a}{a-x}$ / slope $= \frac{K}{2.303}$

Time $\longrightarrow$
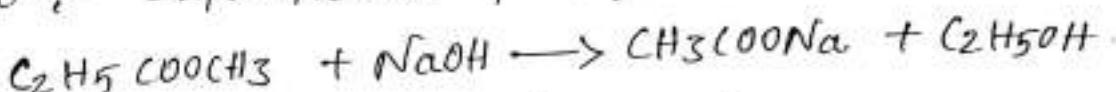
2. The value of "K" in a first order reaction is
independent of concentration
(Because. In 1 order rate eq^n both denominator &
numerator gets cancelled)

SECOND ORDER REACTION :-

Reactions whose rate is directly proportional
to second power of the concentration of reactants.

ex :- saponification of ethyl acetate

$$C_2H_5COOCH_3 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$
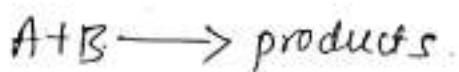
Rate $\propto [CH_3COOCH_3]^1 [NaOH]^1$

order $= 1+1 = 2$

<u>Expression for rate constant of a second order</u>
<u>reaction when a=b</u> [when initial con^n of both reactants are same.]

Let us consider a second order reaction. of the type.

$$A + B \longrightarrow products$$

where a mole dm^3 and b mole/dm^3 are the initial concentration of 'A' and 'B' respectively. x mole/dm^3 is the decrease in concentrations of reactant molecules in time t secs.

(a-x) mole/dm^3 and (b-x) mol./dm^3 are the remaining concentrations of A & B at any time t secs.

Rate α [A] [B]

$$\frac{dx}{dt} = k(a-x)(b-x)$$

when the con^n are equal. a=b

$$\frac{dx}{dt} = k(a-x)(a-x)$$

$$\frac{dx}{dt} = k(a-x)^2$$

$$\frac{dx}{(a-x)^2} = k \cdot dt$$

on integration.

$$\int \frac{1}{(a-x)^2} dx = k \cdot \int dt$$

NOTE

$$\int (a \pm bx)^n dn$$

$$= \frac{(a+bx)^{n+1}}{n+1 \cdot b}$$

$$= \int (a-x)^{-2}$$

$$= \frac{(a-x)^{-2+1}}{[-2+1](-1)}$$

$$= \frac{(a-x)^{-1}}{-1}$$

$$= \frac{1}{a-x}$$

$$\frac{1}{a-x} = kt + c \longrightarrow ①$$

Where c = integration const.

When $t = 0$ $x = 0$

$$\frac{1}{a} = k(0) + c \qquad \therefore c = \frac{1}{a}$$

substituting the value of c in ①

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$kt = \frac{a - (a-x)}{a(a-x)}$$

$$kt = \frac{a - a + x}{a(a-x)}$$

$$kt = \frac{x}{a(a-x)}$$

$$\boxed{k = \frac{1}{t} \frac{x}{a(a-x)}}$$

Expression for rate const of 2nd order reaction when $a = b$

unit of k is

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$= \frac{1}{s} \cdot \frac{conc}{conc \times conc}$$

$$= \frac{1}{s} \cdot \frac{1}{mol \cdot dm^{-3}}$$

$$\boxed{k = sec^{-1} mol^{-1} dm^3}$$
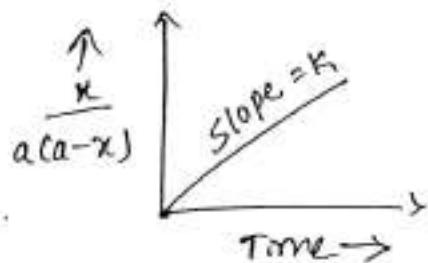
characteristics of II order reactions:-

① All II order reactions should obey II order rate eqⁿ when concentration of reactants initially and at different intervals of time are substituted in respective eqⁿ gives constant K.

② K depends on conⁿ in case of IInd order reaction

In II order rate eqⁿ $K = \dfrac{1}{t} \cdot \dfrac{x}{a(a-x)} = \dfrac{1}{s} \dfrac{conⁿ}{(conⁿ \times conⁿ)}$

two conc terms in denominator and one conc term in numerator ∴ it depends on conc

③ A graph of $\dfrac{x}{a(a-x)}$ against time. is a straight line with slope K.

Expression for rate constant of a second order reaction. when concentration of the reactants are not equal $(a \neq b)$:-

Let us consider a second order reaction of the type. $A + B \longrightarrow$ products.

When "a" mole/dm³ and "b" mol/dm³ are the initial concentration of reactants A & B respectively x mole/dm³ is the decrease in concentration of reactant A and B in time 't' secs $(a-x)$ mol/dm³ and $(b-x)$ mole/dm³ be the

remaining concentration of A & B in time t seconds.

$$\text{Rate} = K[A][B]$$

$$\frac{dx}{dt} = K(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = K \cdot dt$$

when the concentration of both reactants are not equal $(a \neq b)$

then $\dfrac{dx}{(a-x)(b-x)} = k \cdot \int dt$

using partial fraction.

$$\frac{1}{(a-x)(b-x)} = \frac{P}{(a-x)} + \frac{Q}{(b-x)} \quad - \text{①}$$

$$\frac{1}{(a-x)(b-x)} = \frac{P(b-x) + Q(a-x)}{(a-x)(b-x)}$$

$$1 = P(b-x) + Q(a-x)$$

put $x = b$ $\therefore 1 = Q(a-b)$ ⓐ

put $x = a$ $\therefore 1 = P(b-a)$ ⓐ

$$\boxed{\begin{array}{l} Q = \dfrac{1}{(a-b)} \\[2mm] P = \dfrac{1}{(b-a)} \end{array}}$$

substitute the value of 'P' and Q in eqⁿ①

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-x)(b-a)} + \frac{1}{(b-x)(a-b)}$$

$$\therefore \int \frac{dx}{(a-x)(b-x)} = k \cdot \int dt$$

$$\therefore \int \frac{dx}{(a-x)(b-x)} = k \int dt$$

$$\int \left[\frac{1}{(a-x)(b-a)} + \frac{1}{(b-x)(a-b)} \right] dx = k \int dt$$

$$\frac{1}{(b-a)} \int \frac{1}{a-x} dx + \frac{1}{a-b} \int \frac{1}{(b-x)} \cdot dx = k \cdot \int dt$$

on integration.

$$\frac{1}{(b-a)} (- \ln (a-x)) + \frac{1}{a-b} [-\ln (b-x)) = kt + C$$

$$\frac{1}{a-b} \left[\ln (a-x) - \ln (b-x) \right] = kt + C$$

$$\frac{1}{a-b} \ln \frac{(a-x)}{(b-x)} = kt + C \quad \text{——②} \quad C = \text{integration const.}$$

put $x=0 \quad t=0$

$$\frac{1}{a-b} \ln \frac{a}{b} = 0 + C \quad \text{⓪} \quad C = \frac{1}{a-b} \ln \frac{a}{b}.$$

Substitute in eqn ②

$$\frac{1}{a-b} \ln \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \ln \frac{a}{b}$$

$$\frac{1}{a-b} \left[\ln \frac{(a-x)}{(b-x)} - \ln \frac{a}{b} \right] = kt$$

$$\frac{1}{a-b} = \ln \left[\frac{(a-x)}{(b-x)} \Big/ \frac{a}{b} \right] = kt$$

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

$\ln a - \ln b = \ln \frac{a}{b}$

on converting to common log.

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

is an expression for second order rate. eq^n when the initial con^n of reactants are different.

Pseudo unimolecular reactions:—

For some reactions molecularity is two and order is one. (the reactions nohose molecularity and order are not same) such reactions are called pseudo unimolecular reactions.

ex: Acid hydrolysis of methyl acetate

$$CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH$$

Rate $\alpha [CH_3COOCH_3]^1 [H_2O]^0$

In above reaction large quantity of water is taken when compared to quantity of ester

∴ change in $conc^n$ of water during reaction is neglected and Rate of reaction depends only on concn of ester, hence it is a first order reaction

Half life period :– ($t_{1/2}$ or $t_{0.5}$)

Half life period :- It is the time required to complete the reaction by 50% (or)

It is the time required to reduce the initial concentration of reactant to half of it's original value.

* **Relationship between HLP and I order reaction:-**

W.K.t I^{st} order rate eqn $k = \dfrac{2.303}{t_{1/2}} \log \dfrac{a}{a-x}$

when $t = t_{1/2}$ $x = \dfrac{a}{2}$

∴ $k = 9.\dfrac{303}{t_{1/2}} \log \dfrac{a}{a-\frac{a}{2}}$ (or) $k = \dfrac{2.303}{t_{1/2}} \log 2$

$k = \dfrac{2.303}{t_{1/2}} \times 0.3010$

$$\boxed{t_{1/2} = \dfrac{0.693}{k}}$$

∴ HLP of a 1st order reaction.
is independant of initial
concentration

* **Relationship b/w HLP and IInd order reaction:-**

consider rate eqn for IInd order reaction.

$k = \dfrac{1}{t} \dfrac{x}{a(a-x)}$ when $x = \dfrac{a}{2}$ $t = t_{1/2}$

$k = \dfrac{1}{t_{1/2}} \dfrac{a/2}{a(a-\frac{a}{2})}$

$k = \dfrac{1}{t_{1/2}} \dfrac{a/2}{a \times \frac{a}{2}}$ ∴ $k = \dfrac{1}{t_{1/2} \cdot a}$

$t_{1/2} = \dfrac{1}{k \cdot a}$ (or) $\boxed{t_{1/2} \propto \dfrac{1}{a}}$

from above eqn it is known that half life
period of a II order reaction is inversly proportion
to initial concentration of reactants

In general. HLP and order of reaction are related by the equation

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where a = initial concn

n = order of the reaction

If n = 1 then $$t_{1/2} \propto \frac{1}{a^0}$$ I order

If n = 2 then $$t_{1/2} \propto \frac{1}{a}$$ II order

Mean life period or Average life (l) :-

this is defined as the reciprocal of rate constant.

mean life $$l = \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$ I order reah.

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

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

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

NOTE :- Mean life period is more use ful for radio active series. parent isotope. disintegrates to give daughter nucleus. daughter is also radioactive and disintigrates this will continuous. with different life periods here the term mean life is usefull

Rate of disintegration @ Radio active decay:-

Radio active decay fallows I order kinetics

$\therefore$ Rate of disintegration depends on single species

A radio active element is unstable, it emits (disinteg -rates) α @ β - particle, a daughter element is formed; which may be stable @ radio active

The rate of disintegration of a radio active element at any instant is directly proportional to number of atoms present in parent radio active element at that instant. this is known as law of radio active decay. According to this concept

Rate of disintegration $\dfrac{-dN}{dt} \propto N$

$- dN$ is decrease in concn of radio active element in time dt. N is concn of parent radio active element.

$\dfrac{-dN}{dt} = \lambda N \qquad \lambda = $ decay cayst

integrating $\dfrac{-dN}{N} = \lambda\, dt$

$\qquad\qquad \ln N = -\lambda t + C \qquad C = $ integration constant

$\qquad\qquad N = N_0 \qquad t = 0$

$\qquad\qquad C = \ln N_0$

$\therefore \ln N = -\lambda t + \ln N_0$

$\left| \lambda t = \ln \dfrac{N_0}{N} \right.$

$\boxed{\lambda = \dfrac{1}{t} \ln \dfrac{N_0}{N}} \quad @ \quad \boxed{\lambda = \dfrac{2.303}{t} \log \dfrac{N_0}{N}}$

HLP of radio active element :-

HLP of radio active element is time required to reduce the radio active element to half of its original value.

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

$$t = t_{1/2} \quad N = \frac{N_0}{2}$$

$$\lambda = \frac{2.303}{t_{1/2}} \times \log 2 \quad \textcircled{or} \quad \boxed{t_{1/2} = \frac{0.693}{\lambda}}$$

Methods of determination of order of reaction :-

① Integration method. ② Trial and error method.

In this method the reaction whose order is to be determined is experimentelly carried out by ordinary titration method. The initial conch. of reactants and concentration of reactants converted to products are determined at different intervals of time [a and (a-x)]. Then the value obtained are substituted in I, II order rate equation. which rate equation gives constant 'K' values is the order of the reaction.

② Half life period method :-

The reaction whose order is to be determined is carried out in two different vessels at same temp^r with different initial concentrations.

Let the concentrations are a_1 and a_2. The half lifes of reactants are determined separately and, half lifes are T_1 and T_2

We know that $T_1 \propto \dfrac{1}{a_1^{n-1}}$ and $T_2 \propto \dfrac{1}{a_2^{n-1}}$

$$\frac{T_1}{T_2} = \frac{a_2^{n-1}}{a_1^{n-1}} \quad @ \quad \frac{T_1}{T_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on B.S $\log \dfrac{T_1}{T_2} = (n-1) \log \dfrac{a_2}{a_1}$

$$\boxed{n = 1 + \frac{\log T_1 - \log T_2}{\log a_2 - \log a_1}}$$

By knowing Half lifes T_1 T_2 & initial conn. a_1 a_2 order of rean. can be calculated.

③ **Ostwald's Isolation method.** :-

This method is suitable to determine the order of the reaction having (having) more than two reactants

Let us consider a reaction of the type.

$$A + B + C + D \longrightarrow products$$

$$Rate \propto [A]^{n_1} [B]^{n_2} [C]^{n_3} [D]^{n_4}$$

n_1, n_2, n_3 and n_4 are the order with respect to reactants A B C and D respectively.
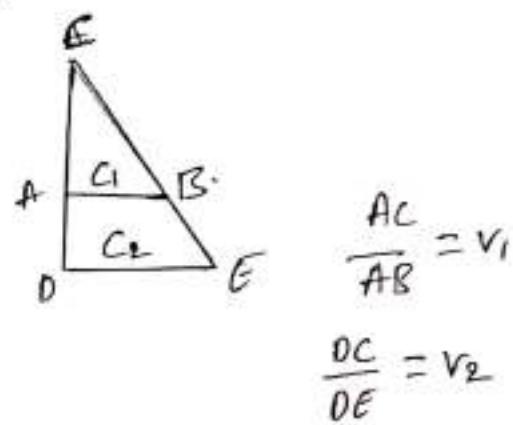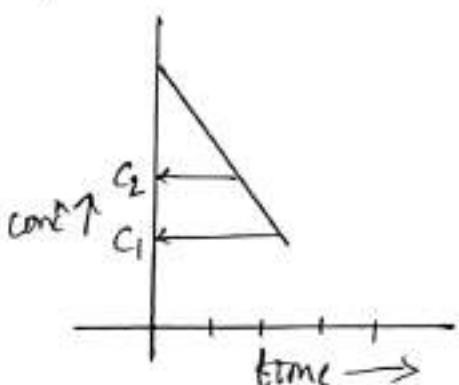
To determine the order of the reaction for above reaction. one of the reactant say "A" is taken in small quantity and the quantity of

other reactants B C and D are taken in excess.
The order with respect to A is determined by ordinary titration method. order is n_1
Similarly the quantity of B is small. order with respect to B is determined. (n_2)
In same way C and D are determined. $(n_3 \& n_4)$

then order $\boxed{n = n_1 + n_2 + n_3 + n_4}$

Differential method @ vant Hoff's method :-

In this method the reaction whose order is to be determined is carried out experimentaly. The decrease in conn of reactant with time is determined. Then a graph of conn of reactant against time is plotted.

$$\frac{AC}{AB} = V_1$$

$$\frac{DC}{DE} = V_2$$

from the graph the slopes at two different conn's C_1 and C_2 are determined.
The slopes gives the valocities $V_1 \& V_2$ of the reaction

If 'n' is the order of the reaction then rate eqn. can be written as
$$V_1 = k C_1^n \quad —① \qquad V_2 = k \cdot C_2^n \quad —②$$

$$\therefore \frac{V_1}{V_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking log on B.S

$$\log \frac{V_1}{V_2} = n \log \frac{C_1}{C_2}$$

@ $$\boxed{n = \frac{\log V_1 - \log V_2}{\log C_1 - \log C_2}}$$

By knowing V_1, V_2 and C_1, C_2 order 'n' can be determined.

Theories of reaction rates :-

In general the rate of chemical reactions have been determined at constant temperature. experimentally it was confirmed that the rate of chemical reaction increases to a large extent with increase in temperature. To account for the increase in rate with increase in temperature no of theories have been put forward.

they are

1) Arrhenius theory.

2) collision theory

3) Lindaman's hypothesis @ Lindamanix theory.

4) Activated complex theory @ Transition state theory.

Arrhenius theory :-

Arrhenious proved that the rate of rea^n increases exponantially with increase in temperature, He derived an emperical equation which gives the relation b/w rate constant (k) and absolute temperature. The eq^n is

$$k = A \cdot e^{-Ea/RT}$$

where
- $k \longrightarrow$ rate constant
- $A \longrightarrow$ Arrhenius factor @ frequency factor.
- $Ea \longrightarrow$ Activation energy
- $R \longrightarrow$ universal gas constant
- $T \longrightarrow$ Absolute temperature.
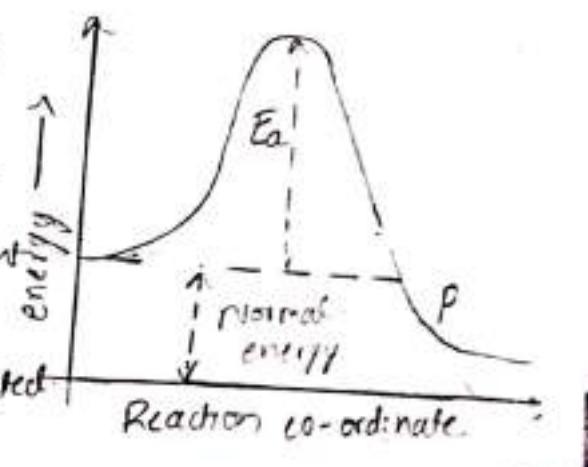
Activation energy (Ea)

It is defined as "The minimum excess energy compared to normal energy required by the reactant molecule to acquire threshold energy to participate in chemical reactions is called Activation energy"

$$Ea = Threshold \ energy - Normal \ energy$$

The increase in temperature supplies 'Ea' to the reactant molecule and helps the reactant molecule to aquire threshold energy. As a result, at higher temp^r more no of reactant molecule can participate in the reaction and can be get converted into product.

Reaction co-ordinate.

Determination of energy of activation from Arrhenius equation:-

$$K = A \cdot e^{-\frac{Ea}{RT}}$$

K = Rate constant.

A = Arrhenius factor

$e^{-Ea/RT}$ = fraction of the total molecules which are active

Taking log on B.S

$$\ln K = \ln A - \frac{Ea}{RT}$$

$\div$ by 2.303

$$\frac{\ln K}{2.303} = \frac{\ln A}{2.303} - \frac{Ea}{2.303RT}$$

converted to common log

$$\log K = \log A - \frac{Ea}{2.303RT} \qquad —①$$

at two temp's T_1 and T_2 at two rate const k_1 and k_2 eqn① can be written as

$$\log k_1 = \log A - \frac{Ea}{2.303RT_1} \longrightarrow ②$$

$$\log k_2 = \log A - \frac{Ea}{2.303RT_2} \longrightarrow ③$$

substract eqn② from eqn ③

$$\log k_2 - \log k_1 = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{where } R = \text{Gas constants}$$

By knowing k_1 k_2 and $T_1 T_2$ energy of activation E_a can be determin

2) Collision theory :-

According to this theory a chemical reaction to occur the collision b/w the reactant molecules is must. During collision, there is redistribution of energy (amongst the molecules) takes place. consequently. a small fraction of mole acquire energy which is equal to @ greater than the threshold energy. These molecules are termed as activated molecules. which can take part in reaction.

Derivation of rate constant of a bimolecular reaction from collision theory. :- consider a gaseous bimolecular reaction.

$$A + B \longrightarrow product$$

Let z be the number of molecules colliding per c.c per second. in a bimolecular reaction. Let q be the fraction. of molecules which are in activated state. According to collision theory

$$\boxed{k = zq} \quad -①$$

According to maxwell's laws of distribution of molecular velocities that in a gas containing 'n' no. of molecules. 'n' be the fraction. of molecules gained activation energy & it is given. by

$$n' = ne^{-Ea/RT}$$

$$q = \frac{\text{number of activated molecules}}{\text{Total number of molecules}} = \frac{n'}{n}$$

$$= e^{-Ea/RT}$$

$$\boxed{k = ze^{-Ea/RT}}$$

The value of z can be evaluated by kinetic theory of gases.

Case(i): when both the reactant are of the same kind then.

$$\boxed{Z_{AA} = \sqrt{2}\,\pi\, v\sigma^2 n^2}$$

$V \longrightarrow$ Average velocity

$\sigma \longrightarrow$ collision diameter

$n \longrightarrow$ total no of molecules

Case (ii):- when the reactant molecules are of different kind

$$\boxed{Z_{AB} = \sqrt{2}\,\pi\, v\left(\frac{\sigma_A + \sigma_B}{2}\right) n_A n_B}$$

where

$\sigma_A \longrightarrow$ collision diameter of A

$\sigma_B \longrightarrow$ collision diameter of B

$n_A \longrightarrow$ no of molecules of A

$n_B \longrightarrow$ no of molecules of B
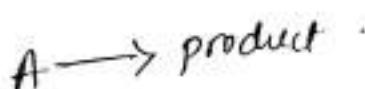
limitation of collision theory:-

1) The theory is applicable only for gaseous bimolecular reactions involving simple molecules like H_2, O_2, N_2 etc

2) According to the collision theory all activated molecules can take part in the reaction but it is not true practically.

In addition to 'Ea' the reactant molecules must possess proper orientation at the time of collision

3) The theory fails to explain unimolecular reaction
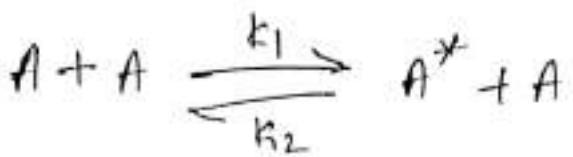
3) Lindemann's Hypothesis:-

According to this hypothesis even in unimolecular reactions bimolecular collisions take place. during this collision a activated molecule is formed. Lindamann said that there is a time gap b/w activation and reaction. during this time gap the activated molecule either loose energy to give back the reactant (or) decompose to give the product.

consider a unimolecular reaction of type

$$A \longrightarrow product$$

-the According to Lindamann's hypothesis unimolecular reaction undergoes bimolecular collision.

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A$$
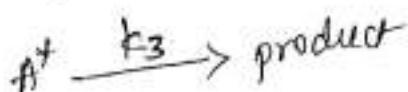
Where A^* = Activated molecule

A = molecule with less energy

k_1 = rate constant for activation process

k_2 = rate constant for deactivation process

the activated molecule (A^*) may also decompose into product

$$A^* \xrightarrow{k_3} product$$

Where k_3 = rate constant for decomposition.

(a) formation of product :

The rate of disapperance of A (reactant) to form products is directly proportional to the concentration of A^*

∴ $$\dfrac{-d\,[A]}{dt} = k_3\,[A^*] \longleftarrow \text{①}$$

Rate of formation of A^* = $k_1\,[A]^2 \longleftarrow \text{②}$

Rate of disappearance of A^* = $k_2\,[A]\,[A^*] + k_3\,[A^*]$
$$\longleftarrow \text{③}$$

[∵ Rate of disappearence of A^* take place in 2 ways deactivate to give original reactant molecule

(a) activated molecules decompose to give products]

According to steady state principle.. when an activated molecule @ activated complex with a short life span is formed in a reaction. then it's rate of formation is equal to rate of disappearance.

$\therefore$ eqn ② = eqn ③

$$k_1[A]^2 = k_2[A][A^*] + k_3[A^*]$$

$$k_1[A]^2 = [A^*](k_2[A] + k_3)$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3}$$

Substitute the value of $[A^*]$ in eqn ①

$$\therefore -\frac{d[A]}{dt} = \frac{k_3 k_1[A]^2}{k_2[A] + k_3} \qquad ④$$

Two possibalities have been considered at this stage

<u>case - 1</u> :- when $k_2[A] >> k_3$ means rate of deactivation of the activated molecule to give back reactant (k_2) is very much greater than the activated molecule to give product (k_3)

then eqn ④ becomes

$$-\frac{d[A]}{dt} = \frac{k_3.k_1[A]^2}{k_2[A]}$$

$$=$$

$$-\frac{d[A]}{dt} = k[A] \qquad \text{where } \frac{k_3 k_1}{k_2} = k \text{ (constant)}$$

this shows that the reaction is first order

Case 2:- when $k_2[A] \lll k_3$ means rate of deactivation of the activated molecules to give back reactant (k_2) is very much smaller than the activated molecule to give product (k_3)

then eqⁿ ④ becomes

$$-\frac{d[A]}{dt} = \frac{k_3 \cdot k_1 [A]^2}{k_3}$$
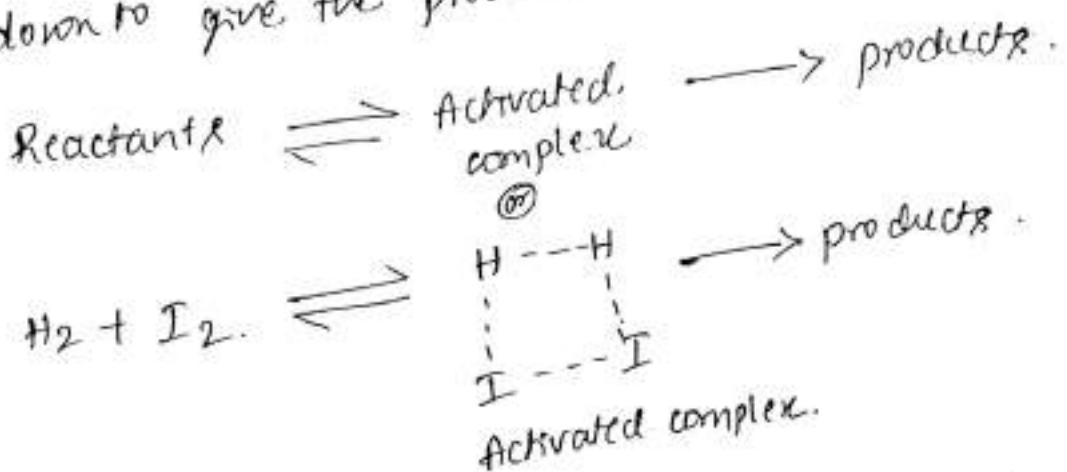
$$-\frac{d[A]}{dt} = k_1 [A]^2$$

this shows that the reaction is second order. unimolecular reaction follows I order kinetics when the conⁿ of reactant 'A' is high and it follows II order when the conⁿ of reactant A is low.
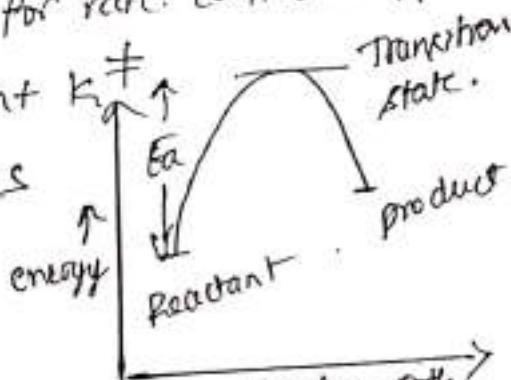
Activated complex theory ⓞⓡ Transition state theory :—
[Rate constant based on equilibrium constant and Thermodynamic aspects]

This theory was proposed by Eyring and Polany.
According to this theory reactant molecules in a reaction are first transformed into an energy rich intermediate compound called activated complex. This activated complex is highly unstable and it breaks down to give the products.

$$Reactants \rightleftharpoons \underset{\substack{Activated \\ complex}}{} \longrightarrow products.$$

ⓞⓡ

$$H_2 + I_2 \rightleftharpoons \underset{Activated\ complex.}{\begin{array}{c} H---H \\ \vdots \quad \vdots \\ I---I \end{array}} \longrightarrow products.$$

Eyring derived an expression for rate constant k in terms of equilibrium constant $k^{\ddagger}$ by using statistical mechanics. According to that

$$k = \frac{RT}{Nh} \cdot k^{\ddagger} \quad —①$$

where: k = rate constant for reaction. $A + B \longrightarrow$ product

$k^{\ddagger}$ = equilibrium constant for formation of activated complex.

N = Avagadro number

h = plank's constant T = Absolute temp.

from thermodynamics.

$$\Delta G^0 = -RT \ln k \quad \text{---②}$$

where. $k = $ equn constant.

$\Delta G^0 = $ standard free energy change during the reaction

$$\therefore k = e^{-\frac{\Delta G^0}{RT}} \quad \text{---③}$$

for activated. complex equilibrium constant $(k^{\ddagger})$

can be written as

$$k^{\ddagger} = e^{-\frac{\Delta G^{\ddagger}}{RT}} \quad \text{---④}$$

where. $\Delta G^{\ddagger} = $ free energy change for activated. complex

But $\Delta G = \Delta H - T.\Delta S$ (from Gibbs - Helmoltz equation)

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T.\Delta S^{\ddagger} \quad \text{---⑤}$$

where. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy change and entropy change for the formation of activated complex

substituting the value of $\Delta G^{\ddagger}$ in equ ④

$$k^{\ddagger} = e^{-\frac{(\Delta H^{\ddagger} - T.\Delta S^{\ddagger})}{RT}}$$

$$k^{\ddagger} = e^{-\Delta H^{\ddagger}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \quad \text{---⑥}$$

substituting the value of $k^{\ddagger}$ in eq^{n}①

$$k = \frac{RT}{Nh} \cdot e^{\frac{-\Delta H^{\ddagger}}{RT}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \longrightarrow ⑦$$

an eq^n ⑦ the value of $\frac{RT}{Nh}$ is constant. at a particular temperature and $\Delta H^{\ddagger}$ is equal to energy of activation Ea then eq^n ⑦ can be written as

$$\boxed{k = \frac{RT}{Nh} \cdot e^{\frac{-Ea}{RT}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}}}$$

This is the expression for k based on transition state theory.

coordination chemistry

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IV semester

① Valence bond theory.

Linus Pauling proposed a theory in 1931 to explain the shucta and magnetic properties of complex compounds. He was awarded Nobel prize in chemistry in 1954.

The important assumptions of VBT are,

*. A coordinate covalent bond is formed by the overlapping of suitable empty orbitals of a transition metal ion with filled orbitals of Ligand.

*. The central metal ion in the complex makes available a set of empty orbitals for hybridization by rearrangement of electrons. The numbe of empty orbitals thus made available correspond to the coordina -tion number of the central metal ion.

*. the transition metal atom ⓐ an ion may used inner (n-1)d orbitals ⓑ outer 'nd' orbital for hybridization.

→ If inner (n-1)d orbital is involved in hybridization, they are resulting complex called "Inner orbital ⓐ Spin pair ⓑ Lowspin complex

→ If outer 'nd' orbital is involved in hybridization, the resulting complex is "outer orbital complex ⓐ spin free ⓑ High spin complex".

*. The formed coordinate covalent bond have fixed directional property as a result they orient in a definite direction. Hence, the resulting complex acquires a definite geometrical shape with definite bond angle, type of hybridization decides geometry of complexes

*. The formed complex compound exhibits different magnetic properties such as Diamagnetic and paramagnetic.

→ The complex compound contains one ⓐ more unpaired electrons is paramagnetic and hence, attracted towards magnet.

→ A complex compound which doesnot contains any unpaired electrons is diamagnetic. and is repell by the magnet.

Merits of valence bond theory.

⇒ VBT satisfactorily explains geometrical shape and magnetic properties of complex compounds.

⇒ This theory explains the formation of inner orbital complex and outer orbital complex.

## Demerits of valence bond theory.

Limitations of VBT are,

1. It can not be extended quantitatively.

2. This theory does not explain characterstic absorption spectra of the co-ordination compounds and their colour.

3. VBT fails to explain thermodynamic stability of complexes.

4. VBT does not provide any satisfactory explanation for existance of inner orbital and outer orbital complex.

5. VBT fails to explain the shape and magnetic properties of some of metal complexes.
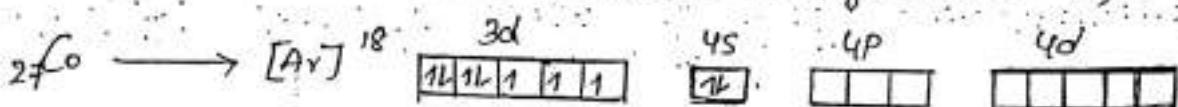
example: $[Cu(NH_3)_4]^{2+}$ Cuprammonium cation should be tetrahedral in shape and paramagnetic in nature. But, practically it is square planar and Diamagnetic in nature. Deviation in structure and magnetic property can not be explained by VBT.

Applications of VBT : ②
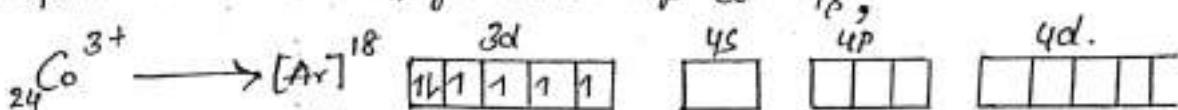
VBT can be used to explain the formation, type of hybridisatio electronic configuaration (arrangement) geometrical shape and magnetic properties of complex compounds.

ex: ① $[Co(F)_6]^{3-}$ (Hexa fluro cobaltate(III))

In the given complex anion the transition metal is cobalt with atomic number 27. It's electronic configuaration is,

$_{27}Co \longrightarrow [Ar]^{18}$ 3d 4s 4p 4d
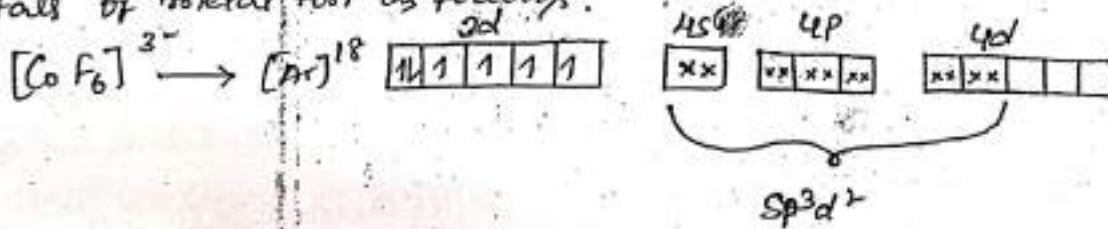
In given complex anion. Cobalt is in +3 oxidation state Therfore electronic configuaration of Co^{3+} is,

$_{24}Co^{3+} \longrightarrow [Ar]^{18}$ 3d 4s 4p 4d.

When transition metal atom is approached by 6 F ligands the transition metal undergoes sp^3d^2 hybridisation. This metal ion provides outer d-orbital for hybridisation because flouride ligands are the weak field ligands. It is incapable to force the electrons to pair up in the inner 3d-orbital due to sp^3d^2 hybridisation the formed six hybrid orbitals posses same shape and same energy they differ in their orientation. The six hybrid orbitals orient corners of the regular octahedron
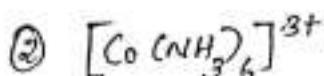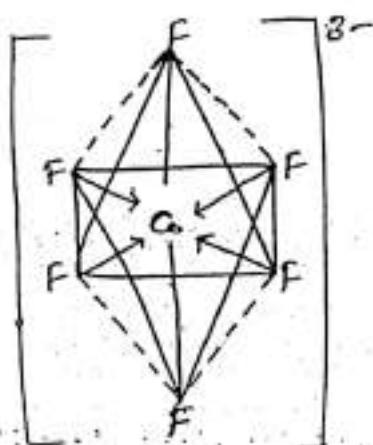
The electrons of ligands are accomodated in the hybrid orbitals of metal ion as follows.

$[Co F_6]^{3-} \longrightarrow [Ar]^{18}$ 3d 4s 4p 4d
sp^3d^2
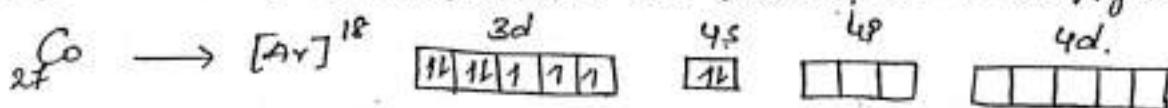
Due to sp^3d^2 hybridisation the complex anion is octahedra in shape which as fallows. (figure)

It is an outer orbital complex. ⊕ spin free complex ⊕ High spin complex. Due to presence of 4 unpaired electrons the complex anion is paramagnetic.

② $[Co(NH_3)_6]^{3+}$
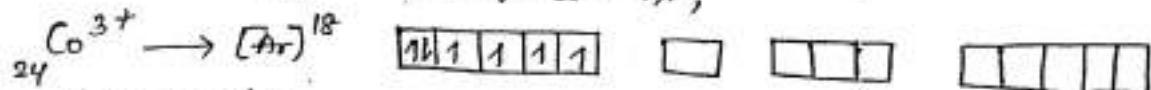
In the given complex cation the transition metal is Cobalt with atomic number 27. It's electronic configuaration,

$_{27}Co \longrightarrow [Ar]^{18}$

3d					4s	4p	4d
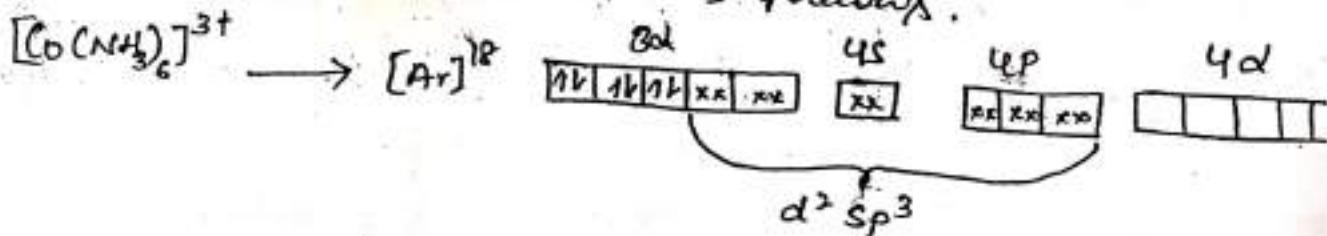
In given complex cation Cobalt is in +3 oxidation state. Therefore electronic configuaration of Co^{3+} is,

$_{24}Co^{3+} \longrightarrow [Ar]^{18}$
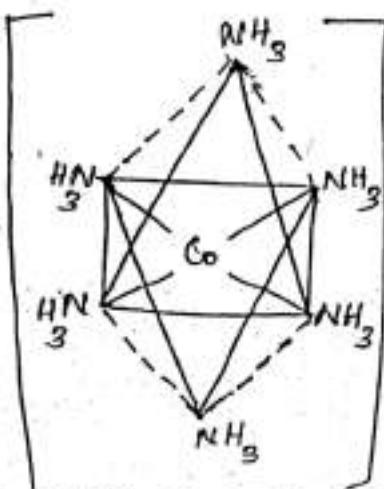
when Co^{3+} is approached by six ammine ligands. the transition metal ion undergoes d^2sp^3 hybridisation. the metal ion provides inner 3d-orbital for hybridisation. because, NH_3 ligands are strong field ligands. It is capable to force the electrons to pair up in the inner 3-d orbital. due to d^2sp^3 hybridisation, the formed six hybrid orbitals posses same shape and same energy. The six ligands orient toward the corners of a regular octahedron.

The electrons of ligand will accomodate in the hybrid orbitals of metal ion as fallows.

$[Co(NH_3)_6]^{3+} \longrightarrow [Ar]^{18}$

3d   4s   4p   4d

d^2sp^3

Octahedral in shape.

It is an inner orbital complex or low spin complex. Due to presence of paired electrons the complex cation is Diamagnetic in nature.

③ $[Fe(CN)_6]^{4-}$

In Hexacyano ferrate (II) the transition metal is Iron. It's electronic configuaration is,

$_{26}Fe \longrightarrow [Ar]^{18}$

		3d				4s		4p		

In give complex anion Iron is in +2 oxidation state Therefore electronic configuaration is,
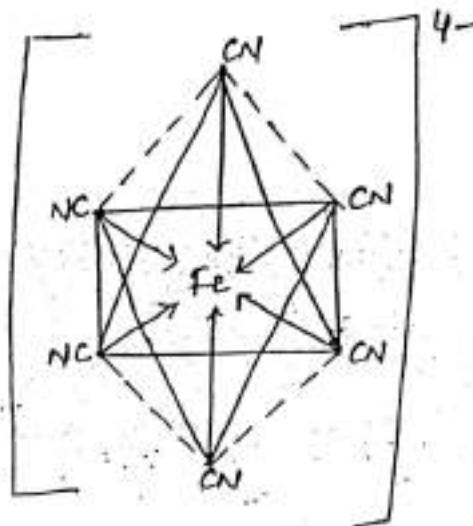
$_{24}Fe^{2+} \longrightarrow [Ar]^{18}$

with 3d, 4s, 4p

when metal ion is approached by 6 cyanide ligands which are strong field ligands, the 6 electrons the 3d-orbitals are forced to pair up in some 3d-orbital. Hence, the metal undergoes d^2sp^3 hybridisation.

The electronic arrangement of given complex.

$[Fe(CN)_6]^{4-} \longrightarrow [Ar]^{18}$
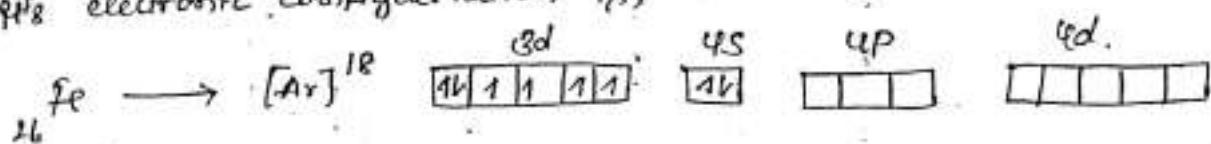
d^2sp^3

Since, there is no unpaired electrons the complex anion is Diamagnetic in nature. Due to d^2sp^3 hybridisation. It is octahedral in shape. which is as shown below.

$$\left[Fe(CN)_6 \right]^{4-}$$
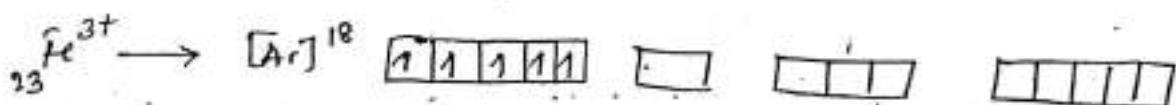
It is inner orbital complex and low spin complex.

① $\left[Fe(CN)_6 \right]^{3-}$

Hexa cyano ferrate (III) the transition metal is Iron. and it's electronic configuaration is,

$_{26}Fe \longrightarrow [Ar]^{18}$ 3d   4S   4p   4d.
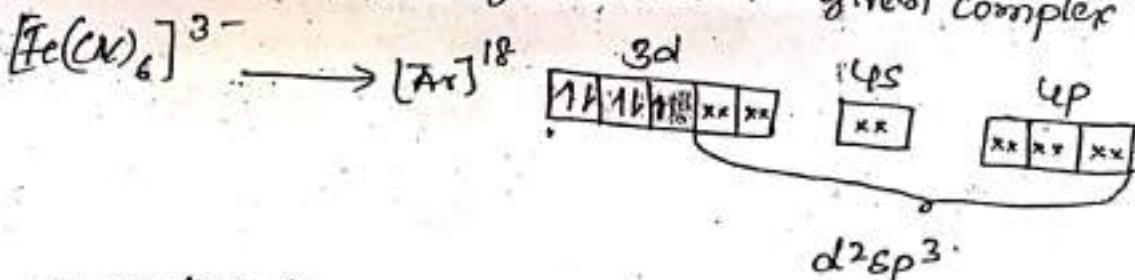
In the given Complex anion Iron is in +3 oxidation state therefore the electronic configuaration of Fe^{3+} is,

$_{23}Fe^{3+} \longrightarrow [Ar]^{18}$

when the metal ion Iron is approached by 6 cyanide ligands which are strong field ligands. the electrons of 3d orbitals are forced to pair up in 3d-orbital. Hence, the metal ion undergoes d^2sp^3 hybridization.
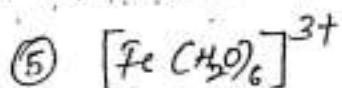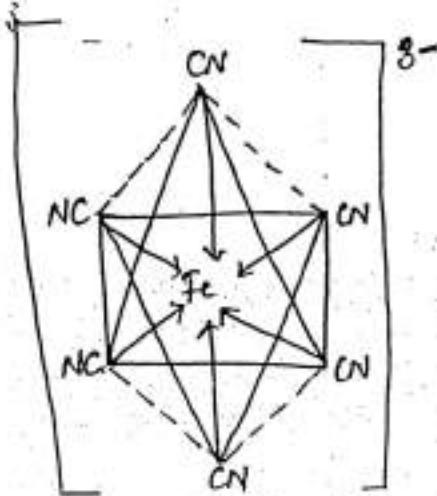
The electronic configuaration of given complex is,

$\left[Fe(CN)_6 \right]^{3-} \longrightarrow [Ar]^{18}$ 3d   4S   4p

d^2sp^3
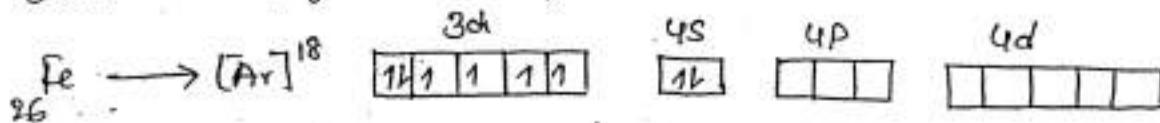
Since, there is on unpaired electrons .the complex is Paramagnetic in nature, octahedral is shape

$$[Fe(CN)_6]^{3-}$$

⑤ $[Fe(H_2O)_6]^{3+}$
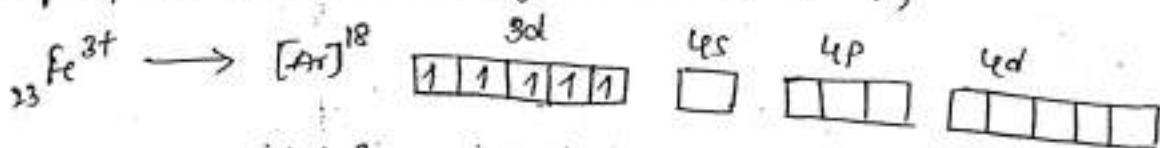
Hexa aqua Iron(III). the transition metal is Iron. and it's electronic configuaration is,
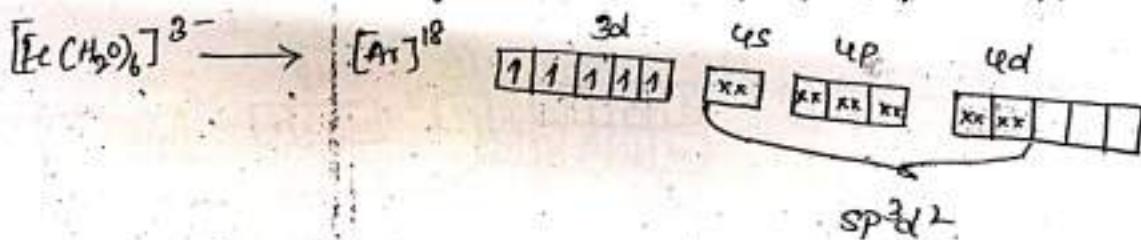
$_{26}Fe \longrightarrow [Ar]^{18}$

	3d					4s	4p			4d				
	↿⇂	↑	↑	↑	↑		↿⇂								

In given complex ion the Iron is ion +3 oxidation state Therefore, the electronic configuaration of Fe^{3+} is,

$_{23}Fe^{3+} \longrightarrow [Ar]^{18}$

|	3d					4s	4p			4d				
	↑	↑	↑	↑	↑										
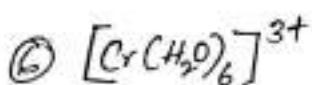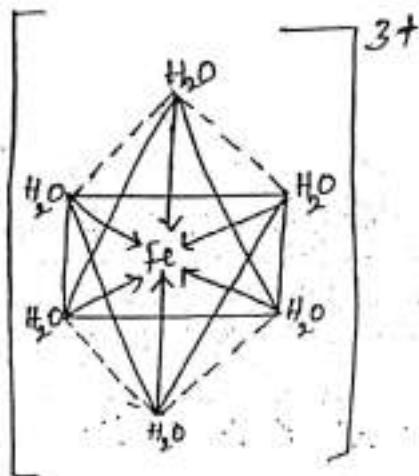
when the metal ion Iron is approached by 6 water liganols (aqua ligand) which are weak field ligand. the electrons of 4d-orbitals are filled up by ligand. The metal ion undergoes sp^3d^2 hybridisation.

The electronic configuaration of given complex ion.

$[Fe(H_2O)_6]^{3-} \longrightarrow [Ar]^{18}$

	3d					4s	4p			4d				
	↑	↑	↑	↑	↑	××	××	××	××	××	××				
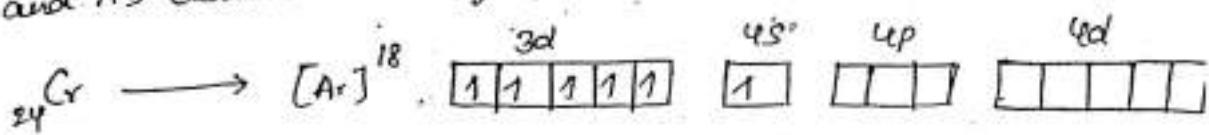
sp^3d^2

Since, there is unpaired electrons. the complex ion is paramagnetic. in nature. due to sp^3d^2 hybridisation octahedra ion shape. It is an outer sphere complex.

⑥ $[Cr(H_2O)_6]^{3+}$
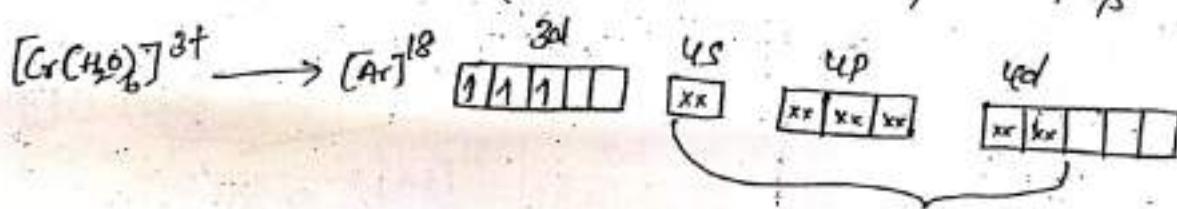
In Hexa aqua chromium (III) the transition metal is chromium and it's electronic configuaration is,

$_{24}Cr \longrightarrow [Ar]^{18}$.

	3d					4s°	4p	4d

$\uparrow\uparrow\uparrow\uparrow\uparrow$ (3d) $\uparrow$ (4s) ☐☐☐ (4p) ☐☐☐☐☐ (4d)

∴ In given complex chromium is in $+3$ oxidation state Therefore, electronic configuaration is,

$_{21}Cr^{3+} \longrightarrow [Ar]^{18}$

3d $\uparrow\uparrow\uparrow$ ☐☐ 4s ☐ 4p ☐☐☐ 4d ☐☐☐☐
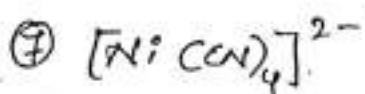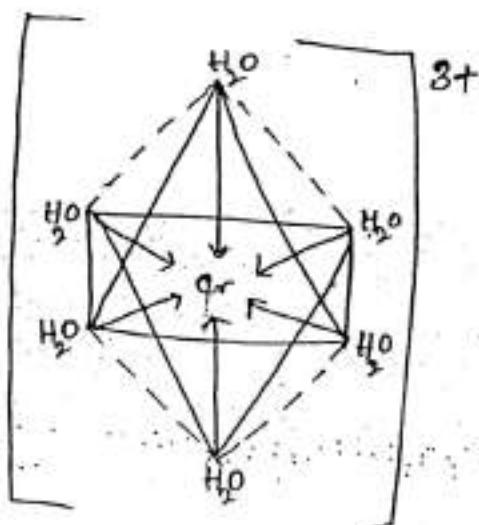
when the metal ion is approached by 6 aqua ligands which are weak field ligands. the metal ion 4d-provides outer d-orbital for hybridization. undergoes sp^3d^2 hybridisation

The electronic configuaration of given complex ion is

$[Cr(H_2O)_6]^{3+} \longrightarrow [Ar]^{18}$

3d $\uparrow\uparrow\uparrow$☐☐ 4s xx 4p $xx|xx|xx$ 4d $xx|xx|$☐☐

sp^3d^2

Due to sp^3d^2 hybridisation octahedral ion shape. Since, unpaired electrons are present it is paramagnetic in nature. It is an outer orbital complex.

$$\textcircled{7} \quad [Ni(CN)_4]^{2-}$$
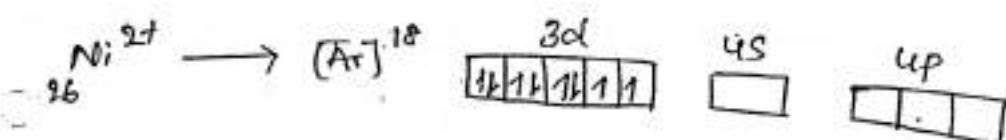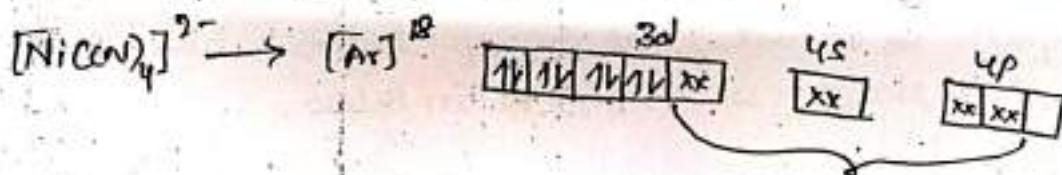
In tetra cyano nickelate (II) ion the transition metal is nickel. It's atomic no 28.

$$_{28}Ni \longrightarrow [Ar]^{18} \quad \underset{3d}{\boxed{\uparrow\downarrow | \uparrow\downarrow | \uparrow\downarrow | \uparrow | \uparrow}} \quad \underset{4s}{\boxed{\uparrow\downarrow}} \quad \underset{4p}{\boxed{||}}$$
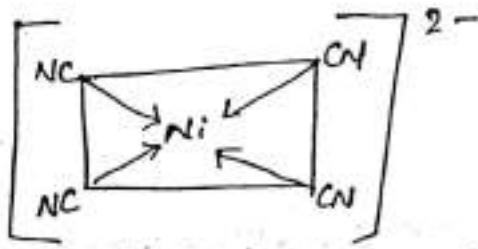
the given complex ion. Ni is in +2 oxidation state. It's Electronic configuaration is,

$$_{26}Ni^{2+} \longrightarrow [Ar]^{18} \quad \underset{3d}{\boxed{\uparrow\downarrow | \uparrow\downarrow | \uparrow\downarrow | \uparrow | \uparrow}} \quad \underset{4s}{\boxed{}} \quad \underset{4p}{\boxed{||}}$$

when metal ion is approached by four cyanide ligands which are strong field ligands the electrons of the inner 3d-orbital are ferried to pair up. Hence metal ion under -goes dsp^2 hybridisation.
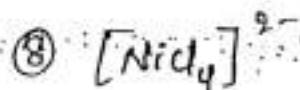
$$[Ni(CN)_4]^{2-} \longrightarrow [Ar]^{18} \quad \underset{3d}{\boxed{\uparrow\downarrow | \uparrow\downarrow | \uparrow\downarrow | \uparrow\downarrow | xx}} \quad \underset{4s}{\boxed{xx}} \quad \underset{4p}{\boxed{xx|xx|}}$$

$$dsp^2$$

Since, there is no unpaired electrons in the complex ion is Diamagnetic in nature. Due to dsp^2 hybridisation It is Square planar in shape. as shown below.

$$[NC-Ni-CN]^{2-}$$ (diagram with NC, CN ligands and Ni)
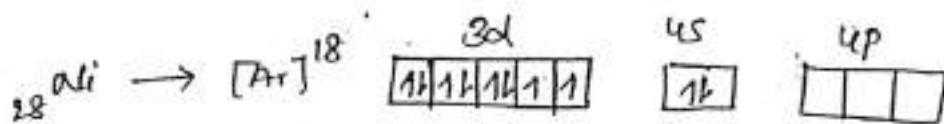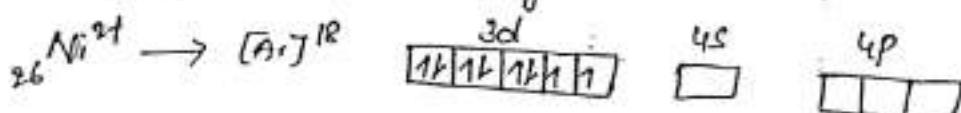
It is inner orbital complex., low spin ® spin paired Complex.

⑧ $[NiCl_4]^{2-}$

chloro

In tetracyano Nickelate(ii) ion, the transition metal is Ni. and it's Electronic configuaration is,

$_{28}Ni \longrightarrow [Ar]^{18}$ 3d [↑↓|↑↓|↑↓|↑|↑] 4s [↑↓] 4p [| |]
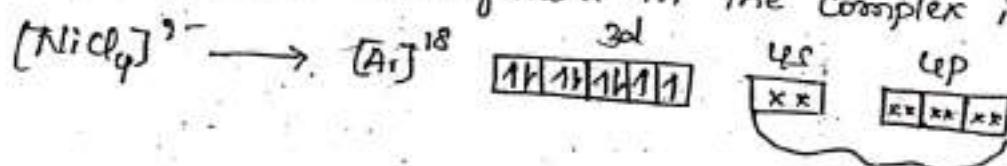
In given complex anion. Ni is in +2 oxidation state therefore, Electronic Configuaration.

$_{26}Ni^{2+} \longrightarrow [Ar]^{18}$ 3d [↑↓|↑↓|↑↓|↑|↑] 4s [ ] 4p [| |]
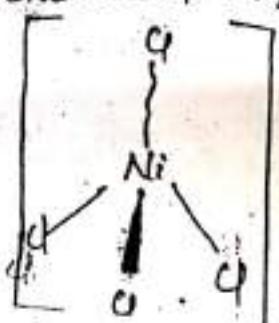
when metal ion approached by four $Cl^{\ominus}$ ligands. which are weak field ligands. the electrons of 3d-orbital doesnot pair up. Hence, metal undergoes Sp^3 hybridisation.

The electronic arrangement in the complex is

$[NiCl_4]^{2-} \longrightarrow [Ar]^{18}$ 3d [↑↓|↑↓|↑↓|↑|↑] 4s [x x] 4p [xx|xx|xx]

$\underbrace{\qquad\qquad}_{Sp^3}$

Since, there are unpaired Electrons the complex is paramagnetic in nature.. Due to sp^3 hybridisation it is Tetrahedral in shape, which shown in below.


$$[Ni(Cl)_4]^{2-}$$ (tetrahedral diagram with Cl ligands and Ni)

It is outer orbital complex. Spin free Complex. ® High spin complex.

Scanned by CamScanner
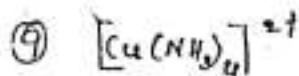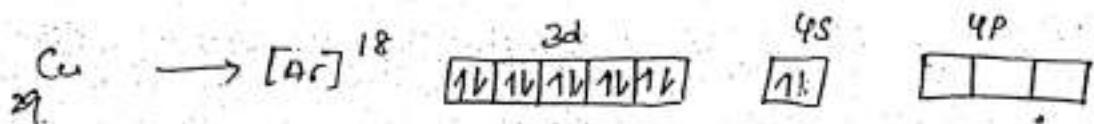
Type of Hybridization in metal complexes.

Coordination number	Type of hybridization	Geometry	Example.
2	sp	Linear	$[Ag(NH_3)_2]^+$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$
5	dsp^3	Trigonal bipyramid	$[Fe(CO)_5]$
6	d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$
6	sp^3d^2	Octahedral	$[CoF_6]^{4-}$

⑨ $[Cu(NH_3)_4]^{2+}$
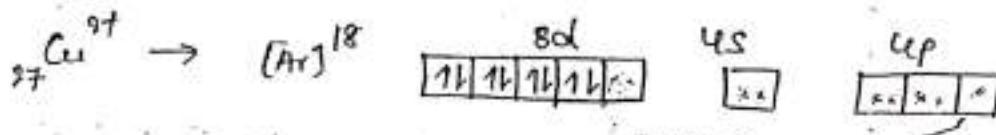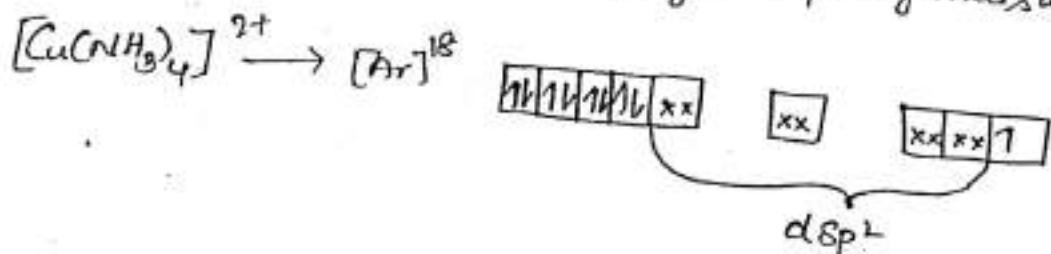
In Tetra ammino copper(II) ion, the transition metal is Cu.
It's Electronic Configuaration.

$Cu \atop 29$ ⟶ $[Ar]^{18}$ | 3d: ⇅|⇅|⇅|⇅|⇅ | 4s: ⇅ | 4p: ☐☐☐
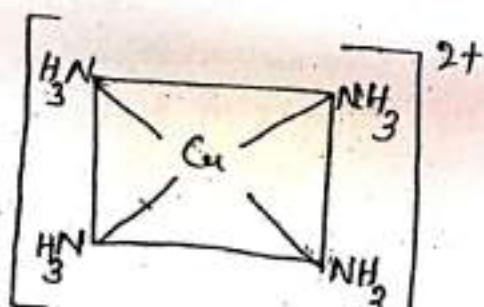
In given complex ion. Cu is in +2 oxidation state
therefore, Electronic Configuaration

$Cu^{2+} \atop 27$ ⟶ $[Ar]^{18}$ | 3d: ⇅|⇅|⇅|⇅|·· | 4s: ×× | 4p: ××|×·|·
 $\underbrace{\qquad}_{dsp^2}$
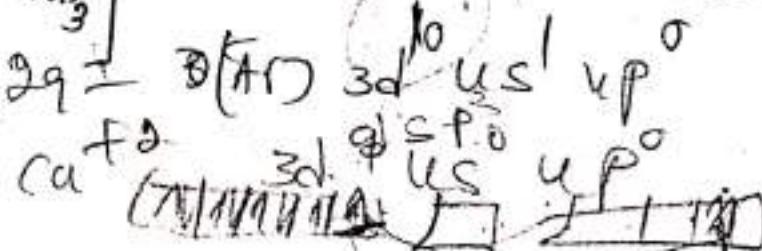
when metal approached by four NH_3 ligands. which are strong field ligands, the electrons of inner 3d-orbital are forced to pair up resulting in one electron jump from 3d to 4p orbital. Hence, This undergoes dsp^2 hybridisation.

$[Cu(NH_3)_4]^{2+}$ ⟶ $[Ar]^{18}$ | ⇅|⇅|⇅|⇅|×× | ×× | ××|××|↑
                                              $\underbrace{\qquad}_{dsp^2}$

Since. There is a unpaired electron in complex it is paramagnetic
in nature. due to dsp^2 hybridisation. It is square planar in shape. as shown below:

It is an inner orbital complex. low spin ⊖ spin paired complex.
dsp^2

$29 = θ(Ar) 3d^{10} 4s^1 4p^0$
$Cu^{+2} 3d^9 4s^0 4p^0$

· Isomerism in Coordination Compounds.

Compounds having same molecular formula but differ in their structural formula are called Isomers and the phenomenon is called Isomerism.

⟹ There are two types of Isomerism in complex compounds.

(1) Structural Isomerism
(11) Stereo Isomerism
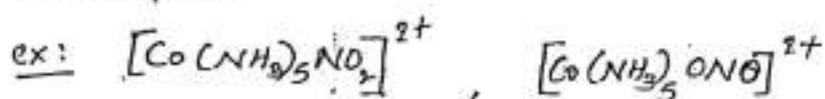
(1) Structural Isomerism.

Complex compounds with same molecular formula but differ in their structure are called "Structural Isomers" and the phenomenon is called as structural isomerism.

There are four types.
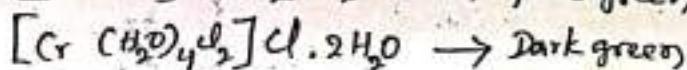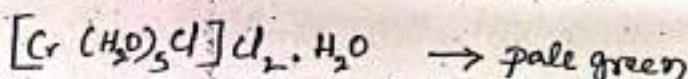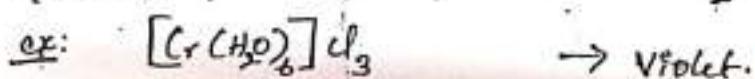
(a) Linkage Isomers:-

A pair of Structural isomers in which the ligands linked to the metal ion with different donor atoms are called Linkage Isomers and the phenomenon is called Linkage Isomerism.

ex: $[Co(NH_3)_5 NO_2]^{2+}$, $[Co(NH_3)_5 ONO]^{2+}$
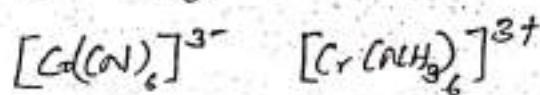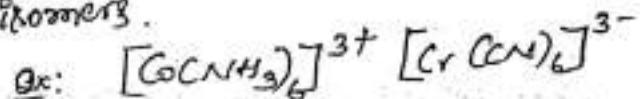
(b) Hydrated Isomers:-

A pair of Structural Isomers in which different no of water molecules serves as a ligands are called Hydrated Isomers.

ex: $[Cr(H_2O)_6] Cl_3$ ⟶ Violet.

$[Cr(H_2O)_5 Cl] Cl_2 . H_2O$ ⟶ pale green

$[Cr(H_2O)_4 Cl_2] Cl . 2H_2O$ ⟶ Dark green

(c) Co-ordination isomers:-

A pair of structural isomers which differ in their the co-ordination of ligands b/w the metal ions are called 'co-ordination isomers'.

ex: $[Co(NH_3)_6]^{3+} [Cr(CN)_6]^{3-}$

$[Cd(CN)_6]^{3-} [Cr(NH_3)_6]^{3+}$

(d) Ionization isomerism:-

A pair of structural isomers which produces different ions when dissolved in water are called 'Ionization isomerism'.

ex: $[Co(NH_3)_5 Br] SO_4 \xrightarrow{Aq} [Co(NH_3)_5 Br]^{2+} + SO_4^{2-}$

$[Co(NH_3)_5 SO_4] Br \xrightarrow{Aq} [Co(NH_3)_5 SO_4]^{+1} + Br^{-}$

(II) Stereo Isomerism

A pair of complex compounds with same chemical composition but differ in their arrangement of ligands in space are called "stereo isomers". the phenomenon is called stereo isomerism.
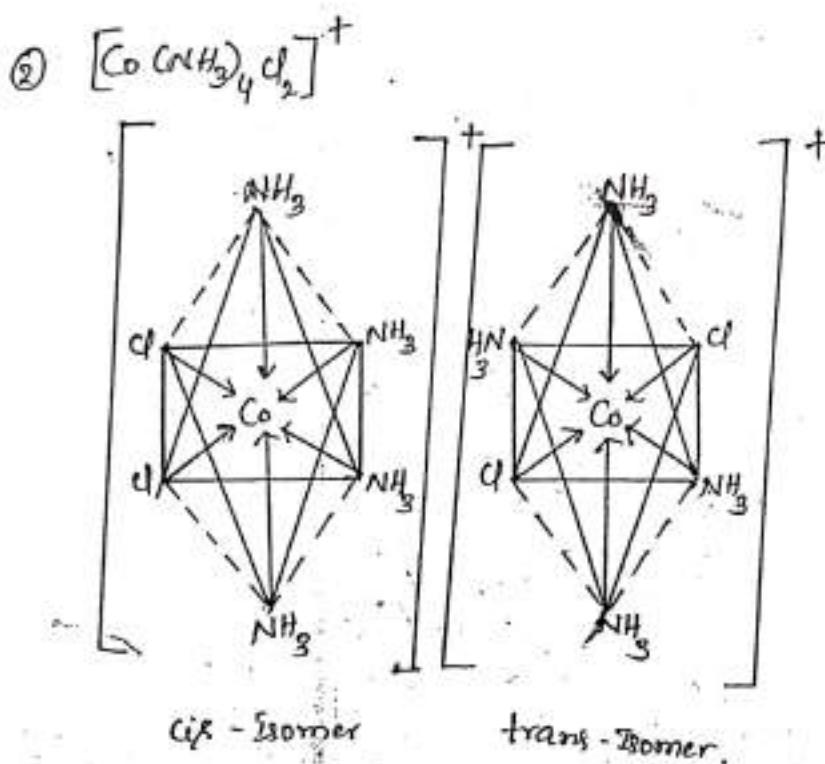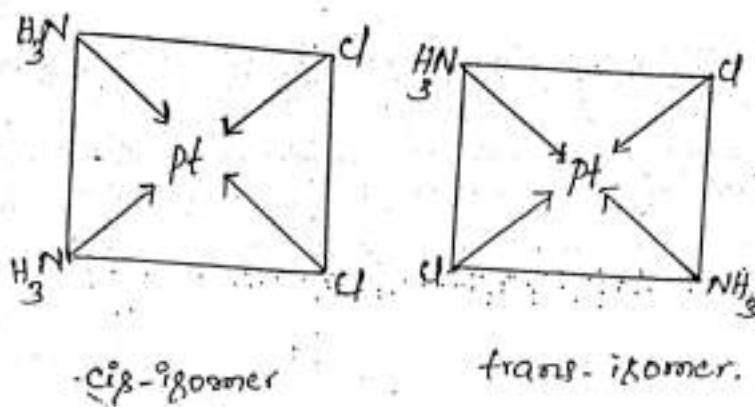
There are two types of stereo isomers namely.

(a) Geometrical isomers:-

Isomers which differ in their arrangement of ligands around the central metal ion in space are called Geometrical isomers.

A geometrical isomer in which similar ligands are present at same side of metal ion called cis-isomer and the other in which similar ligands present at opposite side of the metal ion is called trans isomer.

ex: ① $[Pt(NH_3)_2Cl_2]$ ⑧

cis-isomer   trans-isomer.

② $[Co(NH_3)_4Cl_2]^+$


cis-isomer   trans-isomer.
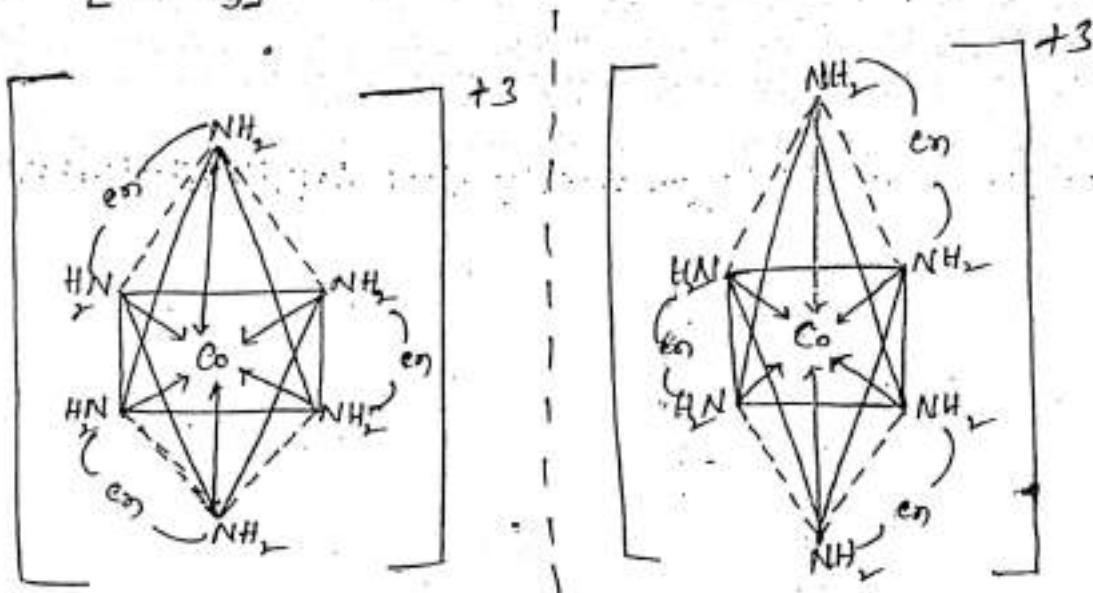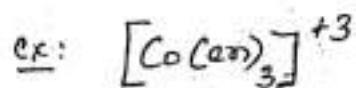
(b) Optical Isomerism :-

A pair of stereo isomers having same structural formula but differ only in direction of rotating plane polarised light are called optical isomers. and the phenomenon is called optical isomerism.

"Optical isomers are related with each other an object and mirror image and they are non-superimposable on one another."

An isomer which rotate the plane polarised light towards right is called Dextro rotatory (+) and an another isomer which rotates plane polarised light towards left is called as Laevo rotatory (−).

ex: $[Co(en)_3]^{+3}$

Crystal Field theory. (9)

This theory was developed by Bethe and Van vleck in 1930, to study the metal ions trapped in crystalline lattices and later on used by chemists to study co-ordination compounds. Hence, it is called as crystal field theory.

According to this theory :-

⇒ the electrostatic force of attraction between the central metal ion and the ligands (which are anions @ polar molecules) is responsible for the bond formation.

⇒ There are five d-orbitals d_{z^2} and $d_{x^2-y^2}$ orbitals are oriented along the axes while d_{xy}, d_{yz} and d_{zx} are oriented in b/w the axes.

⇒ In case of free metal ion all these orbitals are of equal energy. Hence, there is only one set of degenerate orbitals.

⇒ when ligands approach the metal ion, these experience greater repulsion from d_{z^2} and $d_{x^2-y^2}$ electrons and less repulsion from d_{xy}, d_{yz} and d_{zx} electrons dueto this d-orbitals are split into two sets of degenerate orbitals.

⇒ One set of orbitals of higher energy comprising of two degenerate orbitals named e_g orbital and another set of three degenerate orbitals of lower energy called t_{2g} orbitals.

⇒ This splitting of five fold degenerate orbitals into two sets of degenerate orbitals with different energies is called "Crystal field Splitting".

⇒ The difference in energy between the two sets of degenerate orbitals i.e e_g and t_{2g} is called crystal field splitting Energy (Δ)

Merits of crystal field theory.

1) This theory used to predict most favourable geometry for the complex.

2) This theory gives an account for why some complexes are tetrahedral and others square planar.

3) Useful in interpreting magnetic properties.

4) The colours of many transition metal complexes can be rationalised.

Demerits of crystal field theory

1. The assumption that the interaction b/w metal-ligand is purely electrostatic can't be said to be very realistic.

2. This theory takes only d-orbitals in to account. The s and p orbitals are not considered for study.

3. This theory fails to explain the behavior of certain metals which cause large splitting while others show small splitting.
   Ex: The theory has no evidence as to why H_2O is stronger ligand as compared to $OH^{\ominus}$

4. The theory gives no significance to the orbits of the ligands, therefore, it cannot explain any properties related to ligand orbitals.

Crystal field splitting in octahedral field. (10)

In octahedral environment, 6 ligands will approach metal ion along the three co-ordinate axes in both direction.

Due to electrostatic repulsion energy of d_{z^2} and $d_{x^2-y^2}$ orbitals which are oriented along the axes will raised slightly. These are called e_g orbitals. Energy d_{xy}, d_{yz} and d_{zx} orbitals are called t_{2g} orbitals which are oriented b/w the axes will be lowered by an equal amount.
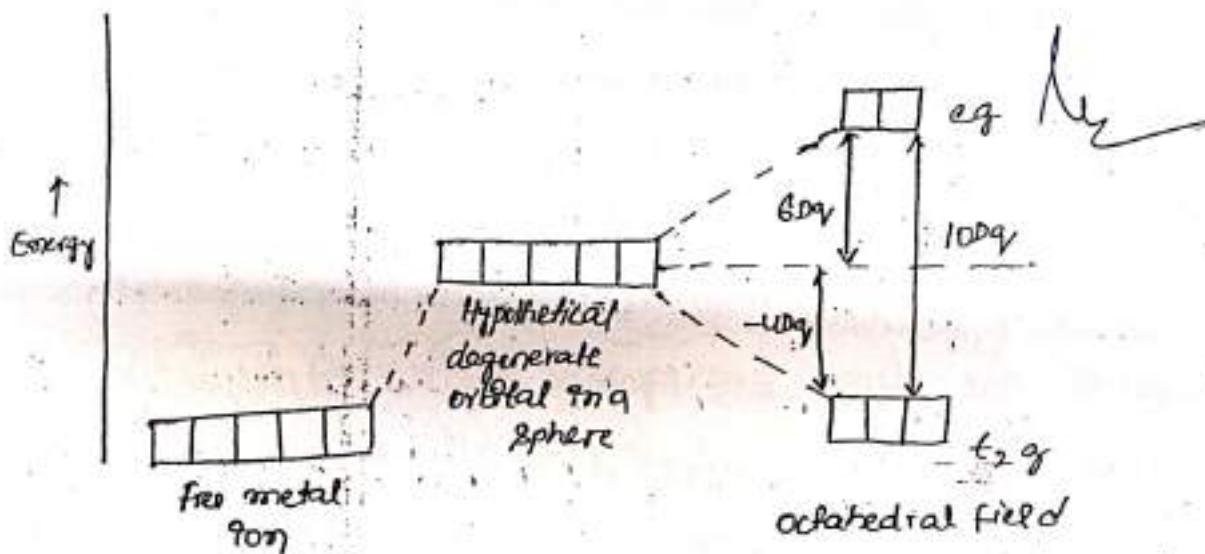
The difference in energy b/w t_{2g} and e_g orbital is called as crystal field splitting energy. It is denoted by Δ_0 (or) $10\,Dq$. Each orbital in e_g is destabilised by Δ_0 (or) $10Dq$ $\frac{3}{5}\Delta_0$ (or) 0.6 energy

∴ Total increase in energy is $12\,Dq$. Each orbital is stabilised by $\frac{2}{5}\Delta_0 = 4\,Dq = 0.4\,\Delta$

∴ Total decrease in energy $= 12\,Dq$.

∴ Net change in energy $= +12\,Dq - 12\,Dq = 0$.

This can be diagramatically represented as follows.

free metal ion | Hypothetical degenerate orbital in a sphere | octahedral field
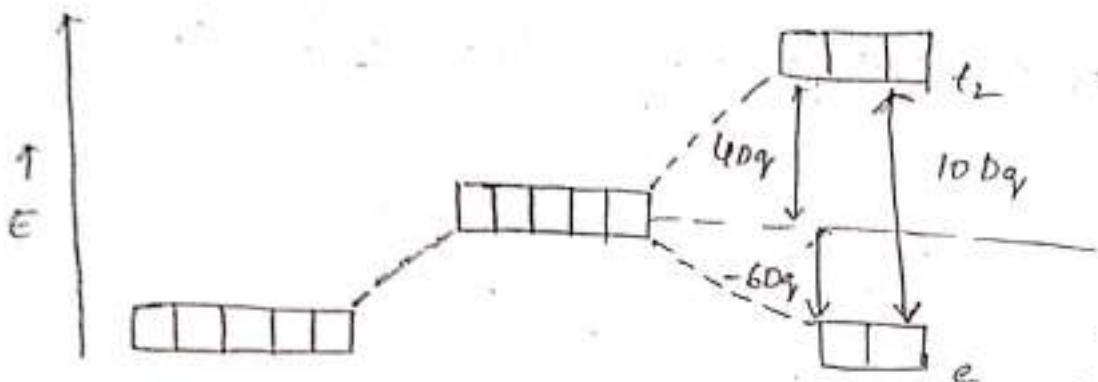
Each electron entering into t_{2g} orbital is stabilised by $4Dq$ energy. Each electron entering into e_g orbital is destabilised

by 6 Dq energy. Sum of the stabilisation energies associated with addition of electrons (present in d-orbitals of metal ion) to t_{2g} and e_g orbitals is called "crystal field stabilization energy".

Splitting of d-orbitals in a tetrahedral field.

In some complex compounds, when the d-orbitals of a transition metal ion is approached by four ligands then it is a tetrahedral field. In the tetrahedral field the d-orbitals splits as follows.

't_2' set is triply degenerate which is raised in energy. e set is doubly degenerated which is lowered in energy. In t_2 set each orbitals is raised in energy by the value of '4Dq' and e set each orbital is lowered in energy by the value of '6Dq'. the energy gap b/w e and t_{2g} set is called "crystal field splitting energy". It is denoted by a symbol. 10Dq.

Ⓑ Δ_t

factors Influencing formation of Tetrahedral geometry
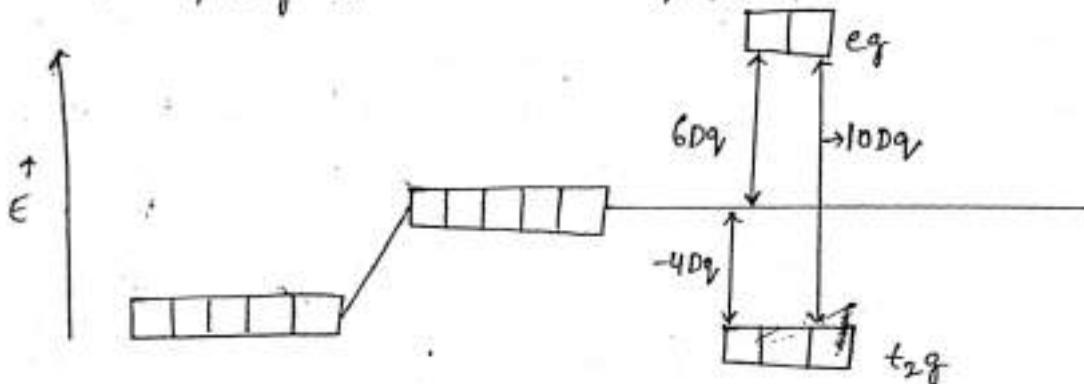
1. ligands are large, less ligand-ligand repulsion.

2. metal ion with zero CFSE (d^0, d^5, d^{10}) ⓑ small CFSE (d^2 and d^7) (central metal ion is in lower oxidation state)

3. when ligands are weak and CFSE loss is important.

Crystal Field Stabilisation Energy.

In an octahedral field the d-orbitals splits into two sets namely t_{2g} and eg. The three orbitals of 't_{2g}' set are lowered in energy where as two orbitals of 'eg' set are rised in energy. The energy gap b/w 't_{2g}' and 'eg' set is represented by a symbol '$10Dq$'. In t_{2g} set each orbital is lowered in Energy by a value of '$-4Dq$' and in 'eg' set each orbital is rised in energy by a value $+6Dq$.

The splitting of d-orbitals is represented as fallows.

Due to arrangement of electrons in t_{2g} and eg set, the complex is stabilised by certain amount of Energy.

Crystal field stabilisation energy is defined as

" The energy by magnitude of which the complex aquires stability due to the arrangement of electrons in different sets of d-orbitals"

Depending on <u>no</u> of electrons present in t_{2g} and eg set. CFSE is calculated as fallows.

$$CFS_nE = n(-4Dq) + n'(6Dq)$$

where, n and $n' \rightarrow$ no of Electrons present in t_{2g} and eg sets respectively.

Pairing Energy (P)

It is the energy required to make the electrons undergoes pairing in t_2g orbitals. (i) If $P < 10\,Dq$, the crystal field splitting energy, then electrons undergoes pairing.

(ii) If $P > 10\,Dq$, then electrons ocupy eg orbital without pairing in t_{2g}. orbitals

Factors Affecting CFSE. (Δ_0 Θ 10Dq):

The crystal field splitting energy (Δ_0 Θ Δ_t) depends on different factors as given below.

(1) Oxidation state of the central metal ion:

larger the charge on central metal ion, greater is the extent of splitting.

(2) Type of d-orbital:

generally magnitude of crystal field splitting is in the order of $3d < 4d < 5d$. thus a complex of Mo(4d) has larger the value of Δ_0 compared to Cr(3d).

(3) Geometry of Complex:

CFSE for Tetrahedral complex is nearly 50% of the octahedral complex (Δ_0) that is $\Delta_t = (4/9)\,\Delta_0$.

(Smaller the value of Δ_t than Δ_0 due to the lower number of ligands in Tetrahedral field)
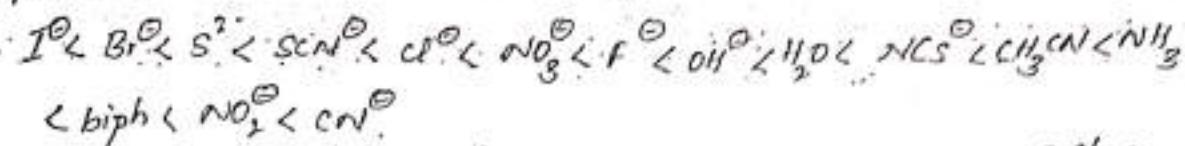
(4) Nature of ligands:

this is most important factor which influences the magnitude of crystal field splitting energy.

spectrochemical series. (14)

The field strength of different ligands have been determined by spectroscopic data. When different ligands are arranged in the increasing order of their ligand field strength, a series is obtained. This series is called spectrochemical series.

The order of ligands in the spectrochemical series is as follows,

$$I^{\ominus} < Br^{\ominus} < S^{2-} < SCN^{\ominus} < Cl^{\ominus} < NO_3^{\ominus} < F^{\ominus} < OH^{\ominus} < H_2O < NCS^{\ominus} < CH_3CN < NH_3$$
$$< biph < NO_2^{\ominus} < CN^{\ominus}$$

In spectrochemical series ligands which can comes after the water including water are called strong field ligands. For all strong field ligands 10Dq value is greater than pairing energy. Those ligands which are kept prior to water are called weak field ligands. For all weak field ligands 10Dq value is smaller than pairing energy.

Calculation of CFSE in octahedral Complexes.

CFSE can be calculated using formula.

$$CFSE = n(+0.4) - n'(0.6)$$

$n \rightarrow$ no. of Electrons in t_{2g} set.

$n' \rightarrow$ no. of Electrons in eg set.
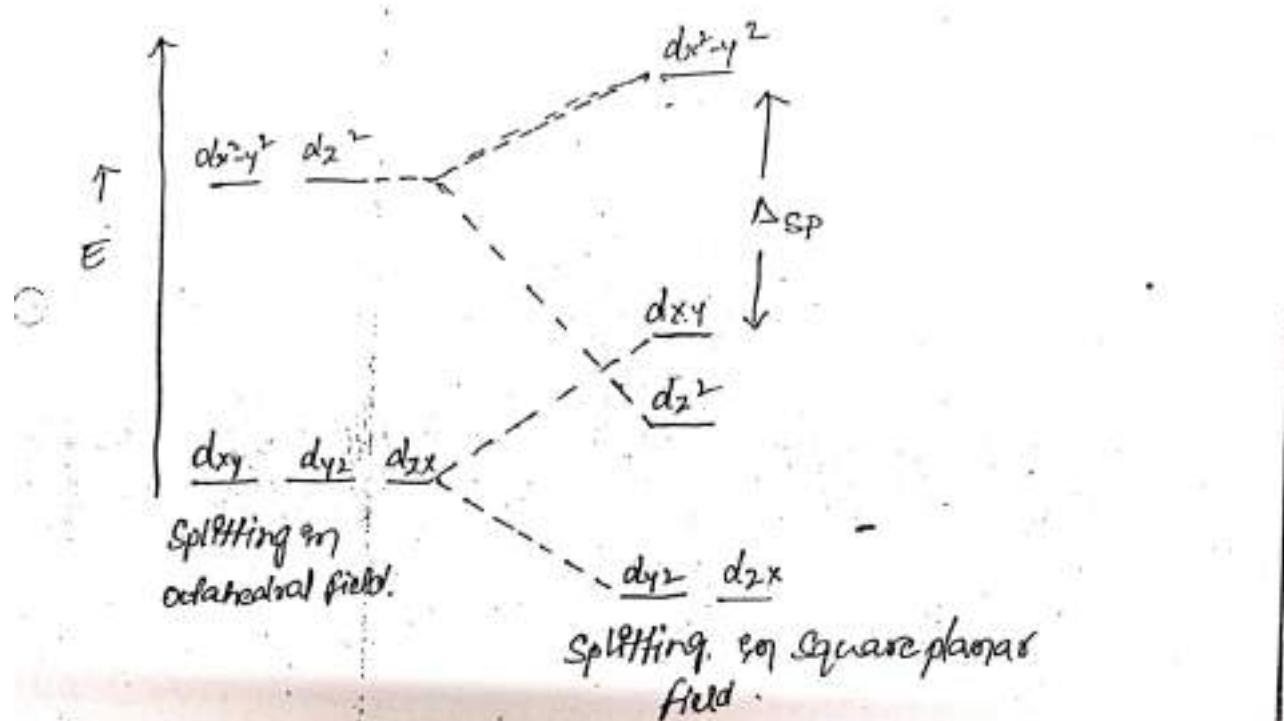
	Weak field			Strong field			
d^n	Configuration	No. of unpaired electrons	CFSE Δ_0	Configuration	No. of unpaired electrons	CFSE Δ_p	Examples
d^1	$t_{2g}^1 e_g^0$	1	0.4	$t_{2g}^1 e_g^0$	1	0.4	Ti^{3+}
d^2	$t_{2g}^2 e_g^0$	2	0.8	$t_{2g}^2 e_g^0$	2	0.8	V^{3+}
d^3	$t_{2g}^3 e_g^0$	3	1.2	$t_{2g}^3 e_g^0$	3	1.2	Cr^{3+}
d^4	$t_{2g}^3 e_g^1$	4	0.6	$t_{2g}^4 e_g^0$	2	1.6	Cr^{2+}
d^5	$t_{2g}^3 e_g^2$	5	0.0	$t_{2g}^5 e_g^0$	1	2.0	Fe^{3+}
d^6	$t_{2g}^4 e_g^2$	4	0.4	$t_{2g}^6 e_g^0$	0	2.4	Co^{3+}
d^7	$t_{2g}^5 e_g^2$	3	0.8	$t_{2g}^6 e_g^1$	1	1.8	Co^{2+}
d^8	$t_{2g}^6 e_g^2$	2	1.2	$t_{2g}^6 e_g^2$	2	1.2	Ni^{2+}
d^9	$t_{2g}^6 e_g^3$	1	0.6	$t_{2g}^6 e_g^3$	1	0.6	Cu^{2+}
d^{10}	$t_{2g}^6 e_g^4$	0	0.0	$t_{2g}^6 e_g^4$	0	0.0	

Crystal field splitting in square planar complexes.

Ligands approaching metal ion from opposite direction along the axes are called trans ligands.

In square planar complex, trans ligands from z directions are removed. Hence, d_z^2, d_{xz} and d_{yz} electrons in metal ion experience less repulsion when compared to $d_{x^2-y^2}$ and d_{xy} electrons. Hence, energy of d_z^2, d_{xz} and d_{yz} electrons are lowered w.r.to octahedral field and energy of $d_{x^2-y^2}$ and d_{xy} electrons is increased w.r.to octahedral field.

This can be ~~diagram~~ diagramatically shown as.

$$\uparrow E$$

$d_{x^2-y^2}$ d_z^2

d_{xy} d_{yz} d_{zx}

Splitting in octahedral field.

$d_{x^2-y^2}$

Δ_{SP}

d_{xy}

d_z^2

d_{yz} d_{zx}

Splitting in square planar field.

Comparison of CFSE of Δ_t over Δ_0

The CFSE of Tetrahedral environment is smaller compared to octahedral complexes (Δ_0). This is due to.

1. there are only four ligands in a tetrahedral complex where as in octahedral complex there are six ligands Hence, one third decrease in the number of ligands. decreases the Δ_t values to some extent from Δ_0 value.

2. The high energy t_2g orbital in tetrahedral complex, Although nearer to the ligands. do not point directly at ligands. Hence. the extent of interaction is less. But, in octahedral complexes. The high energy eg. orbitals point directly at ligands. Therefore, the extent of interaction is more, Hence, Δ_0 is always greater than Δ_t.

—0—

Kushala P.S
IV sem

Introduction JAHN- TELLER EFFECT

It was stated by Jahn-and teller that any non-linear molecular system in orbitally degenerate electronic state (ie state which represents more than one electronic arrangements of the same energy) would be unstable and it would get stabilised by undergoing distortion in it's geometry and thus by causing a split in its orbitally degenerate electronic state.
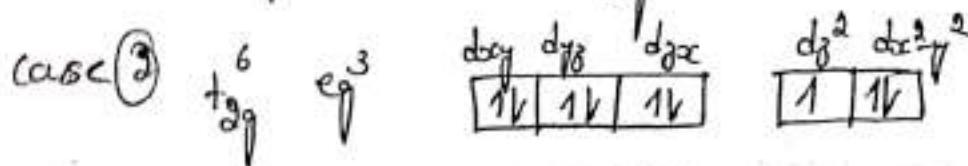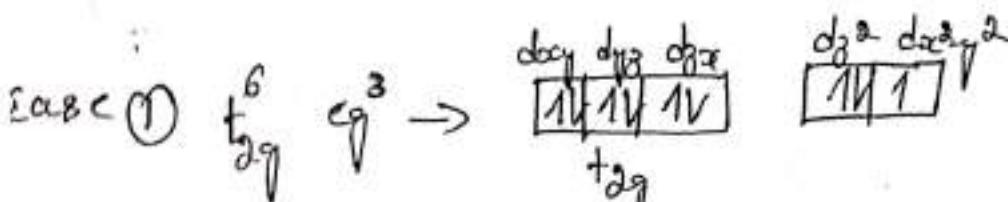
Definition:

Any non-linear molecular system in orbitally degenerate electronic state would be unstable and that it would get stabilised by undergoing distortion in it's geometry and is called Jahn teller effect

Tetragonal distortion caused by elongation of M-L bond along z-direction

let us consider an octahedral complex of Cu^{2+} ion.

The ground state electronic configuration is $t_{2g}^6 e_g^3$, which represents two electronic arrangjment.as follows.

Case ① $t_{2g}^6 \, e_g^3 \rightarrow$

$$d_{xy} \quad d_{yz} \quad d_{zx} \qquad d_{z^2} \quad d_{x^2-y^2}$$

| ↑↓ | ↑↓ | ↑↓ | | ↑↓ | ↑ |

t_{2g}

Case ② $t_{2g}^6 \, e_g^3$

$$d_{xy} \quad d_{yz} \quad d_{zx} \qquad d_{z^2} \quad d_{x^2-y^2}$$

| ↑↓ | ↑↓ | ↑↓ | | ↑ | ↑↓ |

In case ①

Electron charge density will obviously become higher in z direction than in x or y direction.

~~The Elect~~ The screening of the positive charge on Cu^{+2} nucleus by d-electrons will be more in z direction than in x or y direction.
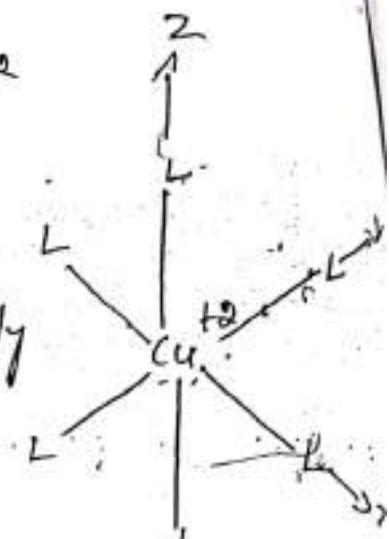
This is due to two electrons are present in d_{z^2} orbitals where as in $d_{x^2-y^2}$ only one Electron ~~as~~ is present.

Therefore the force of attraction between the Metal ion and the ligand decreases, ~~As a result~~ in z-axis. As a result, the ligand along z-direction will move away from the metal ion whereas the ligands along x and y direction will draw nearer to the metal ion.

In other words, the octahedral geometry of the complex will get distorted to tetragonal geometry. (which is elongated along z direction and compressed x and y directions)

Due to this, d_{z^2} orbital will be of lower energy and $d_{x^2-y^2}$ orbital will be of higher energy.

[case-2 refer page no.-03]

other examples, t_{2g} orbitals —
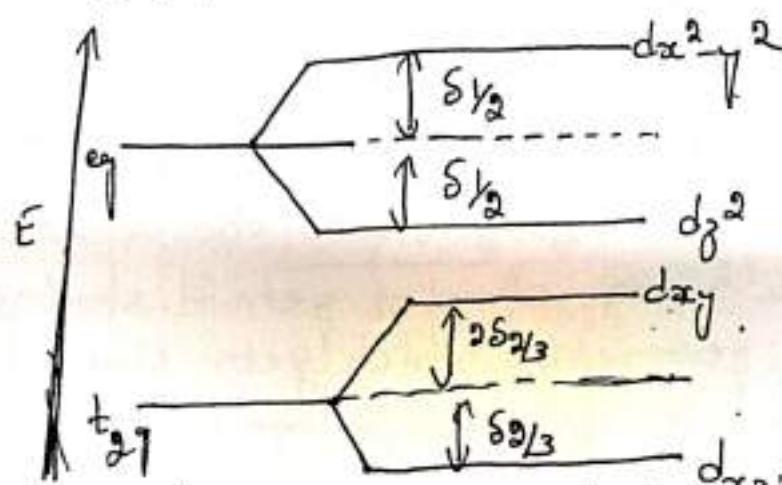
let us now consider an octahedral complex of metal ion with t_{2g}^1 configuration in ground state.

This electron can be present in any of the three t_{2g} orbitals.

If the electron is present in either of the d_{xz} and d_{yz} orbitals, it will screen the nucleus of the metal ion more effectively in the xz xy or the yz plane compared to the xy plane. This would result in a decrease of attraction between the metal ion and the ligands along the z-direction and an increase in such attraction along x and y direction.

As a result, the metal ligand bonds get elongated along the z direction whereby the octahedral geometry gets distorted to tetragonal geometry.

This increases the energy of d_{xy} orbitals and decreases the energies of d_{xz} and d_{yz} orbitals.
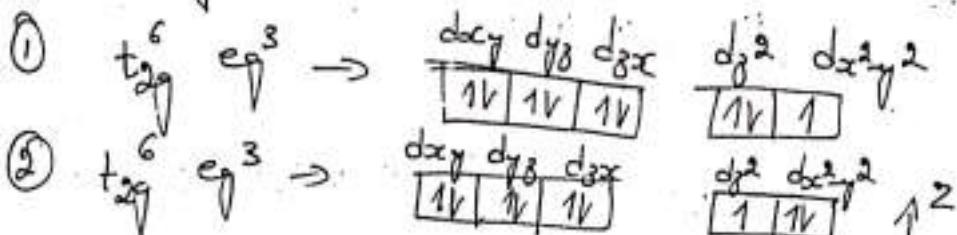
Tetragonal distortion caused by elongation of M-L bond along z-direction

Tetragonal distortion caused by compression of M-L bonds along z direction

Case ②

let us consider an octahedral complex of Cu^{+2} ion.
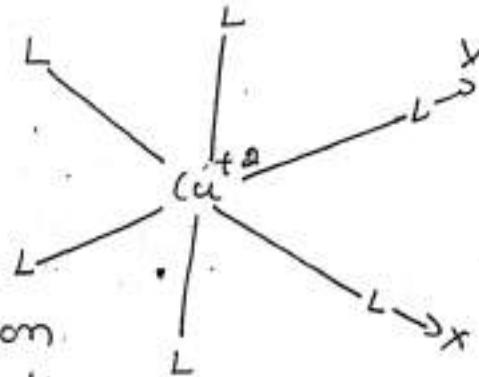
The ground state electronic configuration is $t_{2g}^6 e_g^3$ which represents two electronic arrangements as followas

① $t_{2g}^6 e_g^3$ →

d_{xy}	d_{yz}	d_{zx}
↑↓	↑↓	↑↓

d_{z^2}	$d_{x^2-y^2}$
↑↓	↑

② $t_{2g}^6 e_g^3$ →

d_{xy}	d_{yz}	d_{zx}
↑↓	↑↓	↑↓

d_{z^2}	$d_{x^2-y^2}$
↑	↑↓

In case ②

In which the $d_{x^2-y^2}$ orbital has two electrons and the d_{z^2} orbital one electron, thier L are the negative charges on the ligand along x and y directions which are less attracted by the nuclear charge on Cu^{+2} ion because of more effective screening of the latter by d electrons in x and y direction. This results in elongation of metal ligand bonds along x and y directions and a contraction of metal-ligand bonds along z-direction. This implies that the octahedral geometry of Cu^{+2} ion complex gets distorted to tetragonal geometry which gets elongated along x and y directions and compressed M-L along z-direction
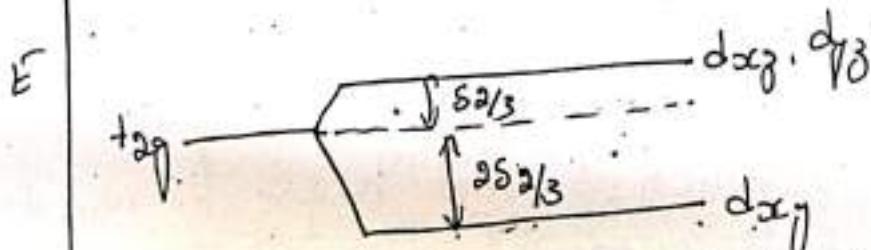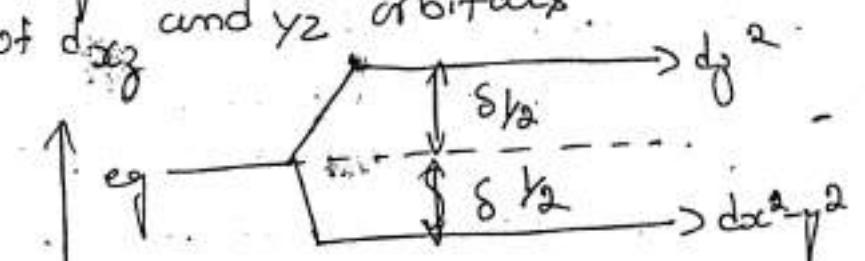
As a result, the dx^2-y^2 orbital becomes of lower energy and d_z^2 orbital becomes of higher energy.

let us now consider an octahedral complex of a metal ion with t_{2g}^1 configuration in ground state.

If the electron is present in d_{xz} ---- d_{xy} orbitals, it will screen the nucleus of the metal ion more effectively in the d_{xy} ---- plane compared to the d_{xz} & d_{yz} plane
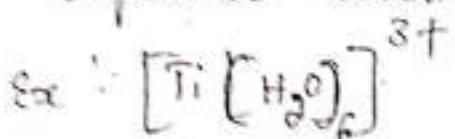
As a result, the octahedral geometry of the complex would get distorted by elongation of the metal-ligand bonds in x y plane, and contraction of the metal ligand bonds in xy and yz plane, resulting in a decrease in the energy of the d_{xy} orbital and an increase in energie of d_{xz} and yz orbitals.
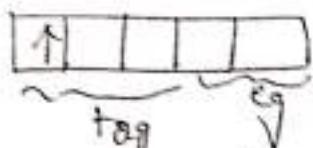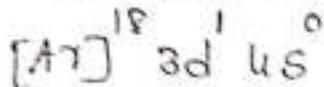
Tetragonal distortion caused by compression of M-L bonds along z-direction.

Electronic Spectra of Complex Compounds

It has been seen that the solution of transition metal complexes formed by metal cations having no unpaired electrons in d-orbitals are colourless while the solution of transition metal complexes given by transition metal cations having one or more unpaired electrons in d-orbitals are coloured.

Ex : $[Ti(H_2O)_6]^{3+}$
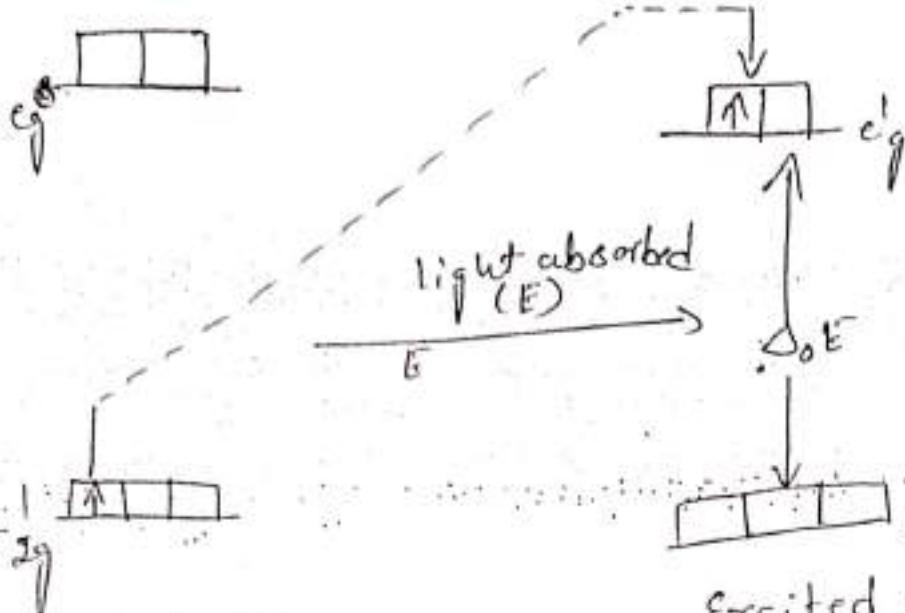
Ti^{3+} ion has the configuration $t_{2g}^1 e_g^0$

$[Ar]^{18} 3d^1 4s^0$

The unpaired electron present in t_{2g} set of orbitals moves from lower energy t_{2g} set to higher energy e_g set, since the energy of the radiation absorbed by unpaired t_{2g} electron is the same as the energy difference between t_{2g} and e_g sets.

This type of Electronic transition from t_{2g} to e_g level is called d-d or ligand field transition, which is the cause of the colour of $[Ti(H_2O)_6]^{3+}$ ion.

light absorbed (E)

$\Delta_0 E$

e_g

e_g'
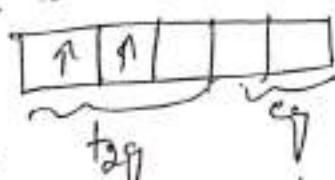
t_{2g}^1

t_{2g}^0

Ground state
of $[Ti(H_2O)_6]^{3+}$

$(t_{2g}^1\, e_g^0)$

Excited state
of $[Ti(H_2O)_6]^{3+}$

$[t_{2g}^0\, e_g^1]$

(purple colour)
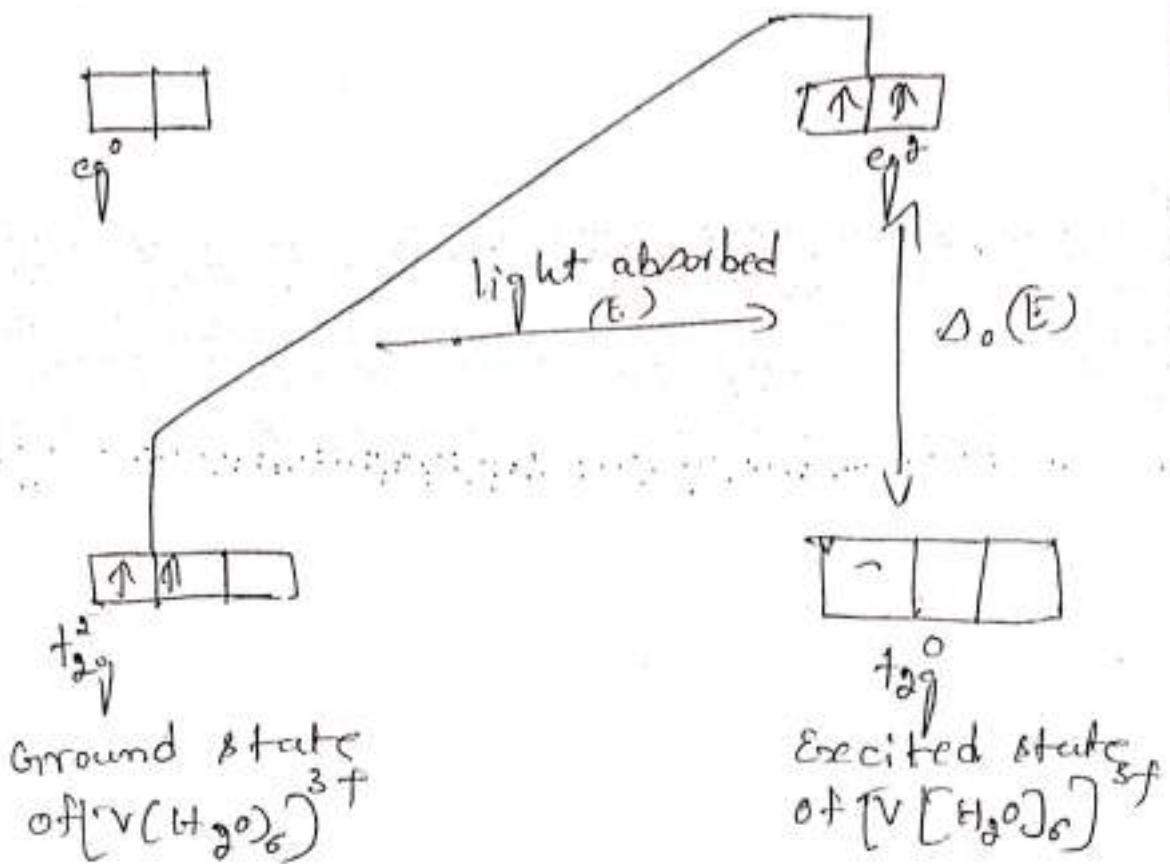
2.) $[V(H_2O)_6]^{3+}$

V^{+3} oxidation state

$t_{2g}^2\, e_g^0$

$[Ar]\, 3d^{18}\, 4s^{2\,0}$

t_{2g} e_g

The unpaired electrons present in lower t_{2g} orbitals get excited to higher e_g orbitals since energy of the radiation absorbed by unpaired electrons is the same as the energy difference between t_{2g} and e_g orbitals. This type of transition is called d-d transition or ligand field transition.

light absorbed
(E)

Δ_o (E)

e_g^0

e_g^2

t_{2g}^2

t_{2g}^0

Ground state
of $[V(H_2O)_6]^{3+}$

Excited state
of $[V[H_2O]_6]^{3+}$

Magnetic properties of complex compounds.

By measuring magnetic moment of a complex. It is possible to obtain information about diamagnetic ⓞ paramagnetic nature of the substance. and the no of unpaired electrons in the complex ion can be calculated.
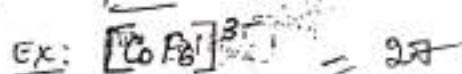
The magnetic moment of a substance can be approximately related to the number of unpaired electrons as

$$\mu_{spin} = \sqrt{m(m+2)} \ B.m.$$

where,

$m \rightarrow$ Number of unpaired electrons

The property of a magnet that interacts with an applied field to give mechanical moment.

the magnetic property of complex depends on number of unpaired electrons in a complex.

(i) Complexes of Cobalt (Co)

Ex: $[CoF_6]^{3-} = 27$

This is an octahedral complex. In this complex the transition metal cobalt is in +3 oxidation state. hence it has 6 electrons in d-orbital (d^6 configuration)
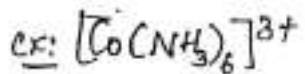
The d-orbitals in octahedral environment splits in to t_{2g} and e_g orbitals as follows
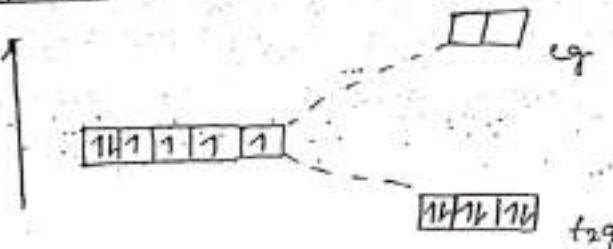
Here Δ_0 is small compared to pairing energy (P) high spin complex is formed with four unpaired electrons.

$$\mu_s = \sqrt{m(m+2)} = \sqrt{4(4+2)} = 4.89 \ Bm$$

Hence, the complex is paramagnetic.

ex: $[Co(NH_3)_6]^{3+}$

In this complex the transition metal is Cobalt. It is in +3 oxidation state. It has d^6 configuration. The d-orbitals in octahedral complex splits in to t_{2g} and e_g set. Here, the Δ_0 is large when compared to pairing energy (P) then it is preferre low spin complex with No unpaired electrons.
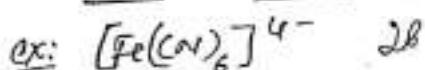

Since, there is no unpaired electrone.
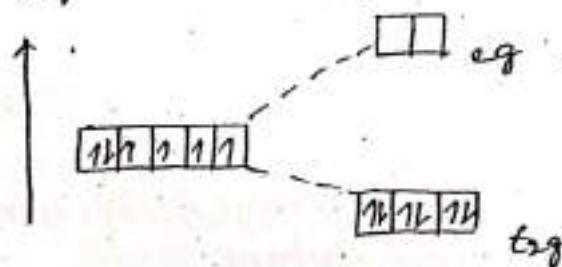
$$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0 \, B.m$$

Hence, the complex is diamagnetic.

(ii) Complexes of Iron (Fe)

ex: $[Fe(CN)_6]^{4-}$ 28
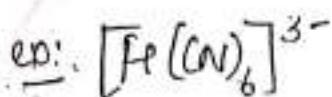
In this complex the transition metal is Iron. It is in +2 oxidation state. It has d^6 configuration. The d-orbitals in octahedral complex splits into t_{2g} and e_g set. Here, the CN^- ion has high crystal field splitting energy, Hence, Δ_0 is fairly large, larger than pairing energy (P). There is no unpaired electrons.


$$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0.B.m$$

Hence, The complex is diamagnetic.

ep: $[Fe(CN)_6]^{3-}$ (Y)
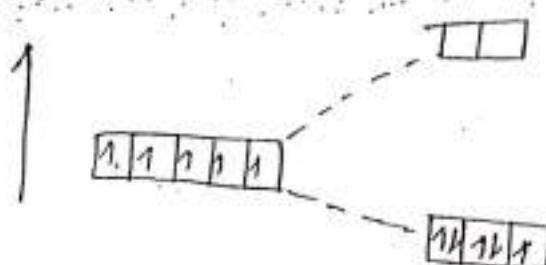
In this complex Iron is in +3 oxidation state, it has d^5 Configuration. The d-orbitals will splits in to t_{2g} and e_g sets. Here $CN^\ominus$ ion has high crystal field splitting energy.
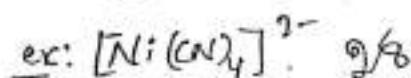
Δ_0 is large when compared to pairing energy (P). Then there is one unpaired electron in t_{2g} set. Then the complex is expected to be paramagnetic.
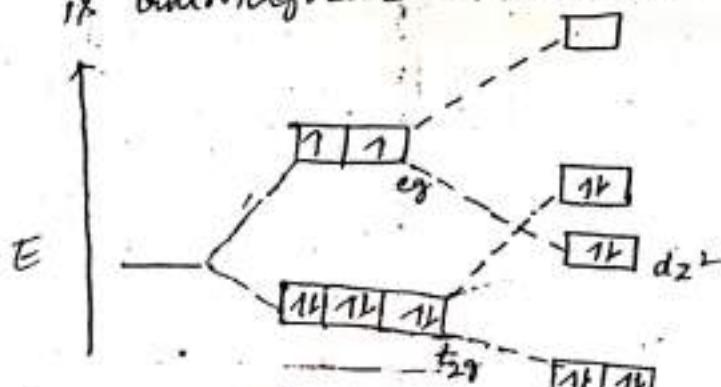

$\mu_s = \sqrt{1(1+2)} = 1.41$ B.m.

Hence the complex is paramagnetic.

(iii) Complexes of Nickel (Ni)

ex: $[Ni(CN)_4]^{2-}$ 9/8

Nickel is in +2 Oxidation state and has d^8 configuration. The complex is square planar. The $CN^\ominus$ ion being strong field ligand has a high crystal field splitting energy which is larger than the pairing energy (P). Thus, the electrons are forced to pair up and Ni(II) has an electronic configuration $t_{2g}^6 d_{z^2}^2$. Hence, there is no unpaired electrons, the complex ion is diamagnetic in nature.
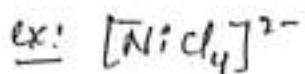

Since, There is no unpaired electrons.

$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$ B.m.

Hence, the complex is diamagnetic.

ex: $[NiCl_4]^{2-}$

In this is complex ion Nickel is in +2 oxidation state and d^8 configuaration. The complex is tehahedral. Since, the Cl^- is weak field ligand. pairing energy is large when compared to Δ_E (crystal field splitting energy) unable to forced to pair up electrons. there are two unpaired electrons.

Since, there are too unpaired electrons.

$$\mu_s = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.82 B.m.$$

Hence, the complex compound is paramagnetic.