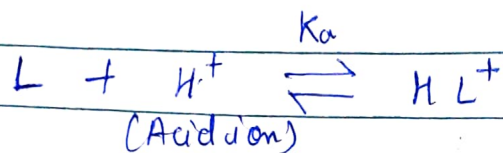
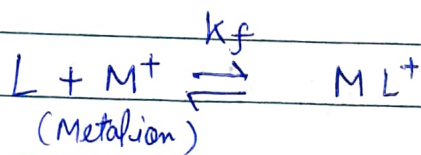


Photentiometric method or pH method / Photentiometric

=> When a ligand is either a weak acid or a weak base. there is a competition b/w H^+ ions and metal ions for the ligand and this can be used for the determination of the formation constant.



$$K_a = \frac{[HL^+]}{[L] \cdot [H^+]} \quad \text{where } K_a = \text{Acid dissociation Constant.}$$



$$K_f = \frac{[ML^+]}{[L][M^+]} \quad \text{where } K_f = \text{Formation Constant.}$$

Suppose C_H , C_m and C_L are the total amounts of acid H^+ metal ion and basic ligand (L) respectively. we have :-

$$C_H = [H^+] + [HL^+]. \quad \text{--- (3)}$$

$$C_m = [M^+] + [ML^+]. \quad \text{--- (4)}$$

$$C_L = [L] + \frac{[HL^+]}{[H^+]} + [ML^+]. \quad \text{--- (5)}$$

From equ. (5), we get.

$$[ML^+] \leq C_m \leq [M^+]$$

$\Rightarrow$ From eqn (5), we have

$$[ML^+] = C_L - [L] - [HL^+] \quad \text{--- (6)}$$

$\Rightarrow$ Now, Substituting the value of $[HL^+]$ from equation (3) in (6), we get

$$[ML^+] = C_L - [L] - C_H + [H^+] \quad \text{--- (7)}$$

and from (1), we get

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

$$[L] = \frac{[HL^+]}{K_a \cdot [H^+]} \quad \text{--- (8)}$$

Put value of (8) in (7), we get

$$[ML^+] = C_L - \frac{[HL^+]}{K_a \cdot [H^+]} - C_H + [H^+] \quad \text{--- (9)}$$

from eqn (4), we get

~~$[M^+] = C_M - [ML^+] - [HL^+]$~~

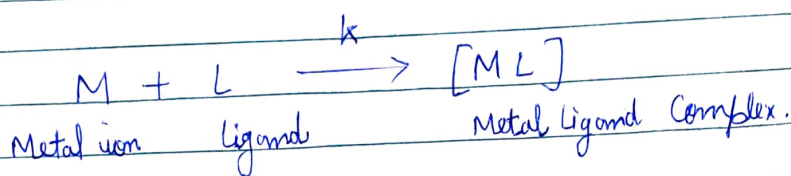
$$\Rightarrow [M^+] = C_M - [ML^+] \quad \text{--- (10)}$$

$\Rightarrow$ Now Substituting the values of ~~(8)~~ $[L]$, $[ML^+]$ and $[M^+]$ in K_f ~~we get~~

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

Stability of Metal Complexes and Factors affecting the formation constant.

=> A Stability Constant is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents to form complexes.



$k =$ is formation constant.

=> Factors affecting the stability of complexes:-

1> Nature of the central metal ion.



→ The nature of metal ion (like size) effect the stability constant

→ If the size of the metal ion increases the stability also increases.

→ ~~If the size of the~~ charge on metal ion increases the stability also increases.

2> Ionic charge :-



Ionic charge

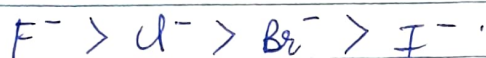
→ The Ionic charge effect the stability of the complex.

→ If the charge on metal ion increases the stability constant also increases.

- 3) Electronegativity of the central metal ion
 → If central metal ion have high electronegativity then it attracts more strongly the ligand to form a stable complexes.

4) Size and charge of ligand :-

Ligand with small size form the stable complexes.



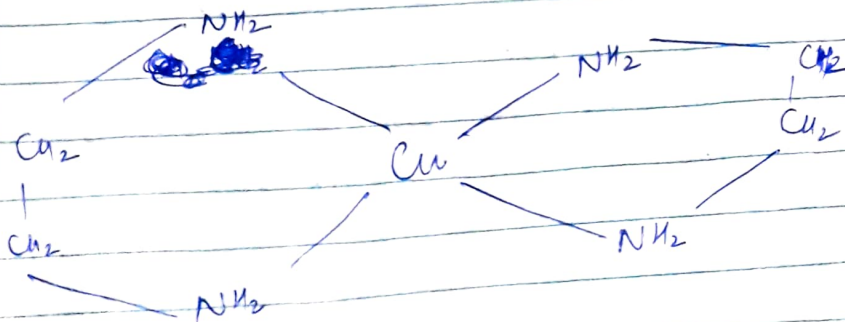
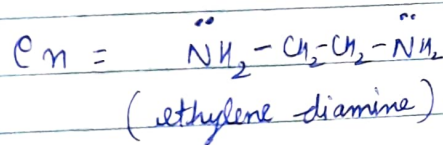
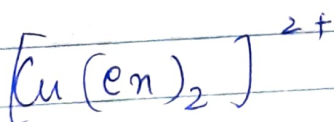
5) Basic nature of ligand :-

Which can donate lone pair of electrons easily form stable complexes.

Example :- F^- , and $\ddot{N}H_3$

6) Effect of chelation :-

- In chelation the cyclic ring formation take place.
 → Stability increases with chelate ring formation.



#

Chelate effect

#

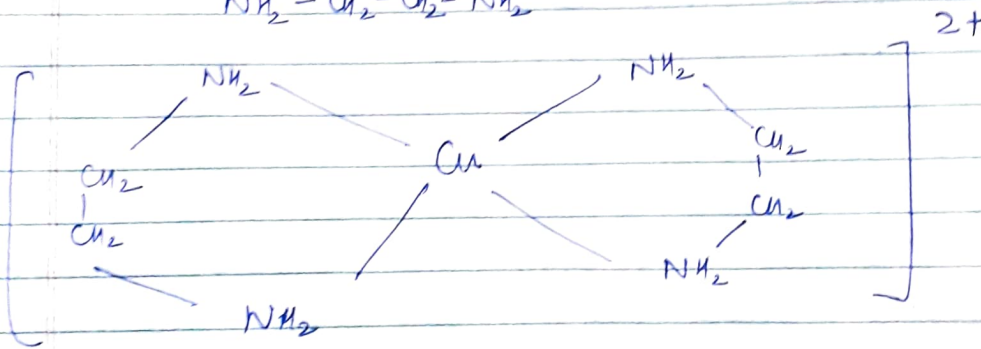
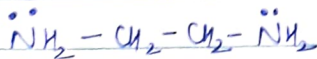
=>

=> When a bidentate or a polydentate ligand is attached by two or more atoms to the central atom forming a ring, the ligand is called chelating ligand and the complex is called chelate, the effect is called chelate effect.

Example:- $[\text{Cu}(\text{En})_2]^{2+}$

En is bidentate ligand

En is ~~ethyrene~~ ethylene diamine



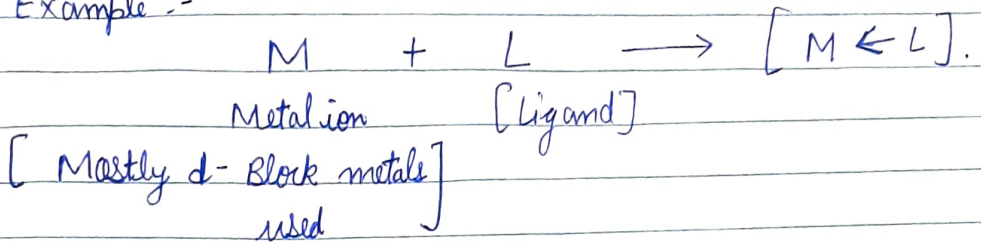
=> Chelate effect increases the stability of the complex.

- 1) ~~If~~ the size ring formation increases the stability of complex.
- 2) The ~~big~~ number of rings increases the stability of complex.
- 3) The chelated complex is always more stable than the non-chelated complex.

Detection of complex formation - in Solution.

=> The complex compound :- When the Metal ion accept a electron from a ligand a ligand it form a complex compound. and this complex compound cannot dissociate in water

Example :-



-> Ligand :- It is a substance which have extra electron. (it may be negative ligand or positive ligand or neutral ligand) these extra electron donated to central metal ion to form a complex.

-> Metal ion :- The metal ions are mostly d-block elements and they have vacant d-orbitals which accept electron from ligand to form complexes.

-> Metal ion act as Lewis Acid (electron acceptor).
-> Ligand act as Lewis Base (electron donor).

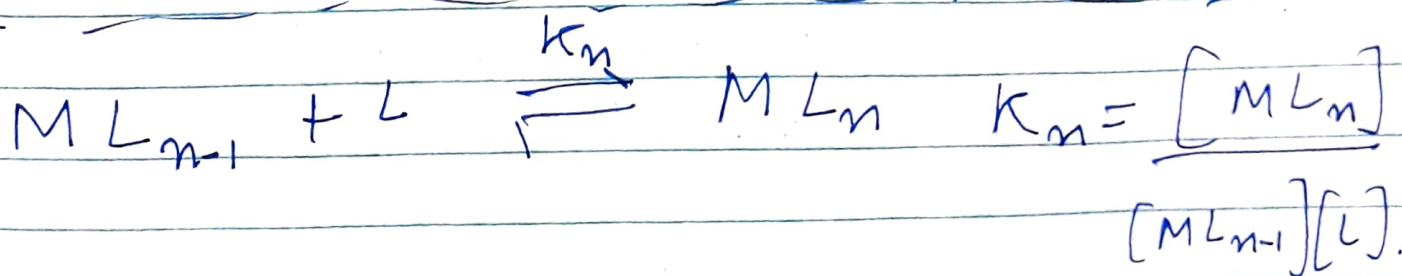
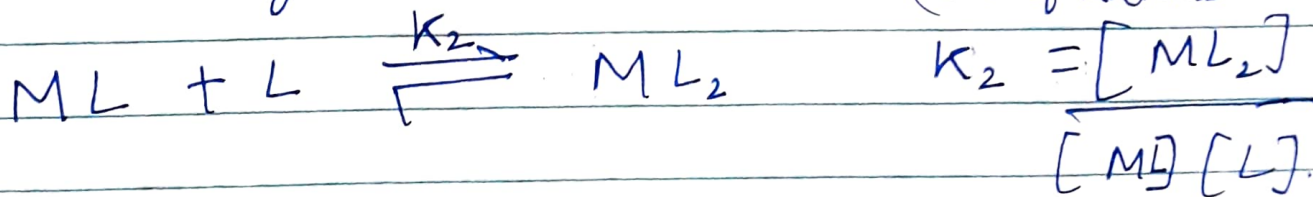
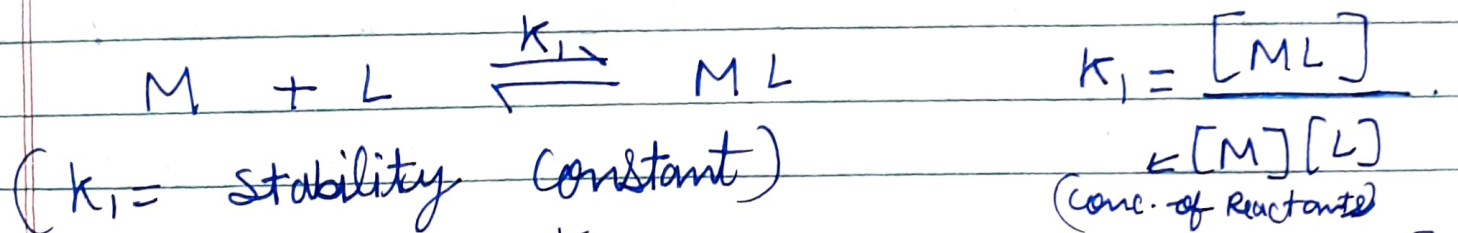
=> The formation of complex compounds can be detected by

- (i) Change in color
- (ii) Solubility
- (iii) pH
- (iv) Electrical Conductivity.

unit-2.
#

Formation Constant and its overall Stability Constant Stepwise and overall formation constants.

⇒ According to L. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n may take place by the following n consecutive steps and equilibrium constants.



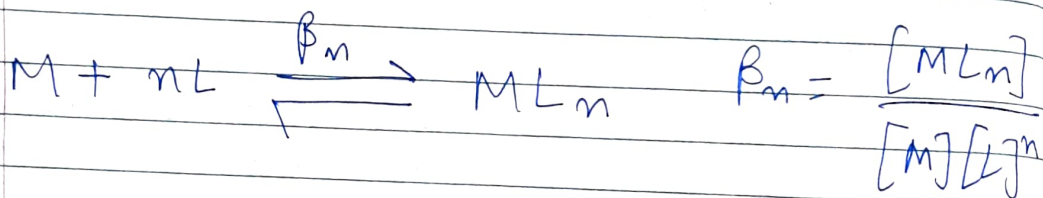
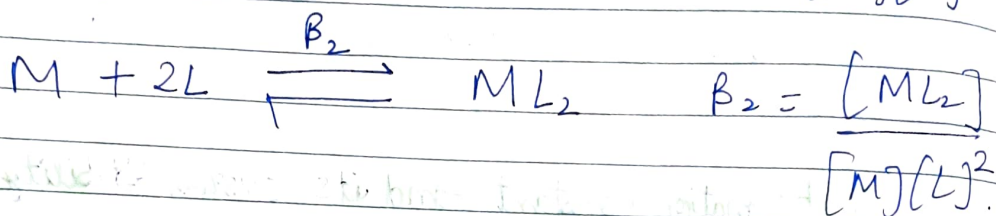
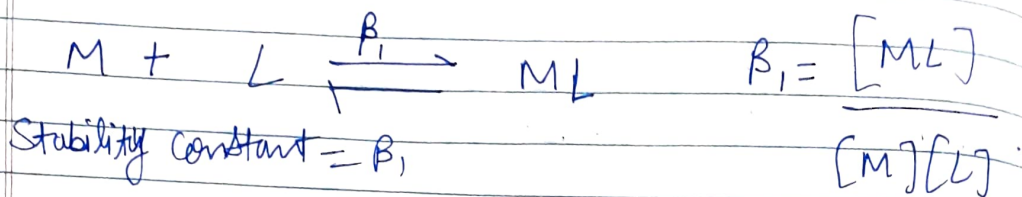
The equilibrium constants $K_1, K_2, \dots, K_n$ are called stepwise formation constants or stepwise stability constants. These constants are also

expressed as $\log_{10} K_1, \log_{10} K_2 \dots \log_{10} K_n$ respectively.

Date: _____

overall formation constant.

The formation of complex ML_n may also be expressed as below:-



The equilibrium constants $\beta_1, \beta_2 \dots \beta_n$ are called overall formation constants or overall stability constants. These constants are also expressed as $\log_{10} \beta_1, \log_{10} \beta_2 \dots \log_{10} \beta_n$ respectively.

Relation b/w Stepwise and overall formation constant:-

Stepwise and overall formation constants are related to one another. For example let us consider the expression for β_3 viz.

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

~~Multip~~

⇒ Multiplying numerator and denominator by $[ML][ML_2]$.

$$\Rightarrow \beta_3 = \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \times$$

$$\Rightarrow \beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[M][L]} \times \frac{[ML_3]}{[ML_2][L]}$$

$$\Rightarrow \beta_3 = k_1 \times k_2 \times k_3 \dots$$

or

$$\boxed{\beta_3 = k_1 \cdot k_2 \cdot k_3 \dots k_n} \quad \text{--- (1)}$$

$$\boxed{\log_{10} \beta_3 = \log_{10} k_1 + \log_{10} k_2 + \log_{10} k_3 \dots \log_{10} k_n} \quad \text{--- (2)}$$

From eqn (1) it is evident that the overall formation constant (β_n) is equal to the product of the stepwise formation constants.