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Period

Group →

↓1

Legend / Key:

ATOMIC WEIGHT — 1.008
ATOMIC NUMBER — 1
SYMBOL — H
NAME — Hydrogen
ELECTRONIC CONFIGURATION — $1s^1$

BLACK : SOLID
MAROON : LIQUID
YELLOW : GAS

Group labels:
(1) IA | (2) IIA | (3) IIIB | (4) IVB | (5) VB | (6) VIB | (7) VIIB | (8)(9)(10) VIII | (11) IB | (12) IIB | (13) IIIA | (14) IVA | (15) VA | (16) VIA | (17) VIIA | (18) 0 (Zero)

Period 1

1.008, 1, H, Hydrogen, $1s^1$	4.003, 2, He, Helium, $1s^2$

Period 2

| 6.941, 3, Li, Lithium, $2s^1$ | 9.012, 4, Be, Beryllium, $2s^2$ | 10.811, 5, B, Boron, $2s^22p^1$ | 12.011, 6, C, Carbon, $2s^22p^2$ | 14.007, 7, N, Nitrogen, $2s^22p^3$ | 15.999, 8, O, Oxygen, $2s^22p^4$ | 18.998, 9, F, Fluorine, $2s^22p^5$ | 20.180, 10, Ne, Neon, $2s^22p^6$ |

Period 3

| 22.990, 11, Na, Sodium, $3s^1$ | 24.305, 12, Mg, Magnesium, $3s^2$ | 26.982, 13, Al, Aluminium, $3s^23p^1$ | 28.086, 14, Si, Silicon, $3s^23p^2$ | 30.974, 15, P, Phosphorus, $3s^23p^3$ | 32.065, 16, S, Sulphur, $3s^23p^4$ | 35.453, 17, Cl, Chlorine, $3s^23p^5$ | 39.948, 18, Ar, Argon, $3s^23p^6$ |

Period 4

| 39.098, 19, K, Potassium, $4s^1$ | 40.078, 20, Ca, Calcium, $4s^2$ | 44.956, 21, Sc, Scandium, $3d^14s^2$ | 47.867, 22, Ti, Titanium, $3d^24s^2$ | 50.942, 23, V, Vanadium, $3d^34s^2$ | 51.996, 24, Cr, Chromium, $3d^54s^1$ | 54.938, 25, Mn, Manganese, $3d^54s^2$ | 55.845, 26, Fe, Iron, $3d^64s^2$ | 58.933, 27, Co, Cobalt, $3d^74s^2$ | 58.693, 28, Ni, Nickel, $3d^84s^2$ | 63.546, 29, Cu, Copper, $3d^{10}4s^1$ | 65.38, 30, Zn, Zinc, $3d^{10}4s^2$ | 69.723, 31, Ga, Gallium, $4s^24p^1$ | 72.64, 32, Ge, Germanium, $4s^24p^2$ | 74.922, 33, As, Arsenic, $4s^24p^3$ | 78.96, 34, Se, Selenium, $4s^24p^4$ | 79.904, 35, Br, Bromine, $4s^24p^5$ | 83.798, 36, Kr, Krypton, $4s^24p^6$ |

Period 5

| 85.468, 37, Rb, Rubidium, $5s^1$ | 87.62, 38, Sr, Strontium, $5s^2$ | 88.906, 39, Y, Yttrium, $4d^15s^2$ | 91.224, 40, Zr, Zirconium, $4d^25s^2$ | 92.906, 41, Nb, Niobium, $4d^45s^1$ | 95.96, 42, Mo, Molybdenum, $4d^55s^1$ | 97.91, 43, Tc, Technetium, $4d^55s^2$ | 101.07, 44, Ru, Ruthenium, $4d^75s^1$ | 102.906, 45, Rh, Rhodium, $4d^85s^1$ | 106.42, 46, Pd, Palladium, $4d^{10}$ | 107.868, 47, Ag, Silver, $4d^{10}5s^1$ | 112.411, 48, Cd, Cadmium, $4d^{10}5s^2$ | 114.818, 49, In, Indium, $5s^25p^1$ | 118.710, 50, Sn, Tin, $5s^25p^2$ | 121.760, 51, Sb, Antimony, $5s^25p^3$ | 127.60, 52, Te, Tellurium, $5s^25p^4$ | 126.904, 53, I, Iodine, $5s^25p^5$ | 131.29, 54, Xe, Xenon, $5s^25p^6$ |

Period 6

| 132.905, 55, Cs, Caesium, $6s^1$ | 137.327, 56, Ba, Barium, $6s^2$ | 138.906, 57, La*, Lanthanum, $5d^16s^2$ | 178.49, 72, Hf, Hafnium, $5d^26s^2$ | 180.948, 73, Ta, Tantalum, $5d^36s^2$ | 183.84, 74, W, Tungsten, $5d^46s^2$ | 186.207, 75, Re, Rhenium, $5d^56s^2$ | 190.23, 76, Os, Osmium, $5d^66s^2$ | 192.217, 77, Ir, Iridium, $5d^76s^2$ | 195.078, 78, Pt, Platinum, $5d^96s^1$ | 196.967, 79, Au, Gold, $5d^{10}6s^1$ | 200.59, 80, Hg, Mercury, $5d^{10}6s^2$ | 204.383, 81, Tl, Thallium, $6s^26p^1$ | 207.2, 82, Pb, Lead, $6s^26p^2$ | 208.980, 83, Bi, Bismuth, $6s^26p^3$ | 208.98, 84, Po, Polonium, $6s^26p^4$ | 209.99, 85, At, Astatine, $6s^26p^5$ | 222.02, 86, Rn, Radon, $6s^26p^6$ |

Period 7

| 223.02, 87, Fr, Francium, $7s^1$ | 226.03, 88, Ra, Radium, $7s^2$ | 227.03, 89, Ac**, Actinium, $6d^17s^2$ | 265.12, 104, Rf, Rutherfordium | 268.13, 105, Db, Dubnium | 271.13, 106, Sg, Seaborgium | 270, 107, Bh, Bohrium | 277.15, 108, Hs, Hassium | 276.15, 109, Mt, Meitnerium | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 |

Lanthanoids *

| 140.116, 58, Ce, Cerium, $4f^15d^16s^2$ | 140.908, 59, Pr, Praseodymium, $4f^35d^06s^2$ | 144.24, 60, Nd, Neodymium, $4f^45d^06s^2$ | 144.91, 61, Pm, Promethium, $4f^55d^06s^2$ | 150.36, 62, Sm, Samarium, $4f^65d^06s^2$ | 151.964, 63, Eu, Europium, $4f^75d^06s^2$ | 157.25, 64, Gd, Gadolinium, $4f^75d^16s^2$ | 158.925, 65, Tb, Terbium, $4f^95d^06s^2$ | 162.50, 66, Dy, Dysprosium, $4f^{10}5d^06s^2$ | 164.930, 67, Ho, Holmium, $4f^{11}5d^06s^2$ | 167.26, 68, Er, Erbium, $4f^{12}5d^06s^2$ | 168.934, 69, Tm, Thulium, $4f^{13}5d^06s^2$ | 173.05, 70, Yb, Ytterbium, $4f^{14}5d^06s^2$ | 174.967, 71, Lu, Lutetium, $4f^{14}5d^16s^2$ |

Actinoids **

| 232.038, 90, Th, Thorium, $5f^06d^27s^2$ | 231.036, 91, Pa, Protactinium, $5f^26d^17s^2$ | 238.029, 92, U, Uranium, $5f^36d^17s^2$ | 237.05, 93, Np, Neptunium, $5f^46d^17s^2$ | 244.06, 94, Pu, Plutonium, $5f^66d^07s^2$ | 243.06, 95, Am, Americium, $5f^76d^07s^2$ | 247.07, 96, Cm, Curium, $5f^76d^17s^2$ | 247.07, 97, Bk, Berkelium, $5f^96d^07s^2$ | 251.08, 98, Cf, Californium, $5f^{10}6d^07s^2$ | 252.08, 99, Es, Einsteinium, $5f^{11}6d^07s^2$ | 257.10, 100, Fm, Fermium, $5f^{12}6d^07s^2$ | 258.10, 101, Md, Mendelevium, $5f^{13}6d^07s^2$ | 259.10, 102, No, Nobelium, $5f^{14}6d^07s^2$ | 262.11, 103, Lr, Lawrencium, $5f^{14}6d^17s^2$ |

UNIT-III

Coordination Chemistry-I
Stability of Complexes

M.Sc., CHEMISTRY – I SEMESTER

INORGANIC CHEMISTRY-I

Coordination Chemistry-I   (Unit: III)

References:

1. Inorganic Chemistry – James E. Huheey

2. Inorganic Chemistry – D.F.Shriver, P.W.Atkins & Langford

3. Inorganic Chemistry – Keith F.Purecell & John C Kotz.

4. Inorganic Chemistry – Gary L.Miessler & Donald A. Tarr

5. Advanced Inorganic Chemistry – Vol.I-Gurdeep Raj

6. Selected Topics in Inorganic Chemistry – Malik, Tuli & Madan

7. Concise Coordination Chemistry – R. Gopalan & V. Ramalingam

Stability of Complexes:

❖ In studying the formation of complexes in solution, **two kinds** of stability of complexes come into question. They are Thermodynamic Stability and Kinetic Stability.

(i) Thermodynamic Stability:

❖ "The Thermodynamic stability of a complex is a measure of the extent to which the complex will form from or will be transformed into another species under certain conditions, when the system has reached equilibrium".

❖ When we are interested in thermodynamic stability, we must deal with metal-ligand bond energies (bond strength), stability constants (formation constants) and the other thermodynamic variables derivable from them.

❖ From a thermodynamic point of view, it is more appropriate to call the complexes as 'Stable complexes' or 'unstable complexes'.

❖ **Thermodynamically stable complexes** have large positive free energy of reaction, **ΔG (roughly, the reaction energy), i.e., the thermodynamic stability of a complex depends on the difference in energy between the reactants and the products, namely the reaction energy (ΔH) (Fig.1). Greater this positive reaction energy, greater will be the thermodynamic stability.**

❖ **The magnitude of the formation constant (or stability constant) is a measure of the thermodynamic stability of a metal complex.**

(ii) Kinetic Stability:

❖ **"The kinetic stability of a complex refers to the speed with which transformations leading to the attainment of equilibrium will occur"**

Exothermic Reaction
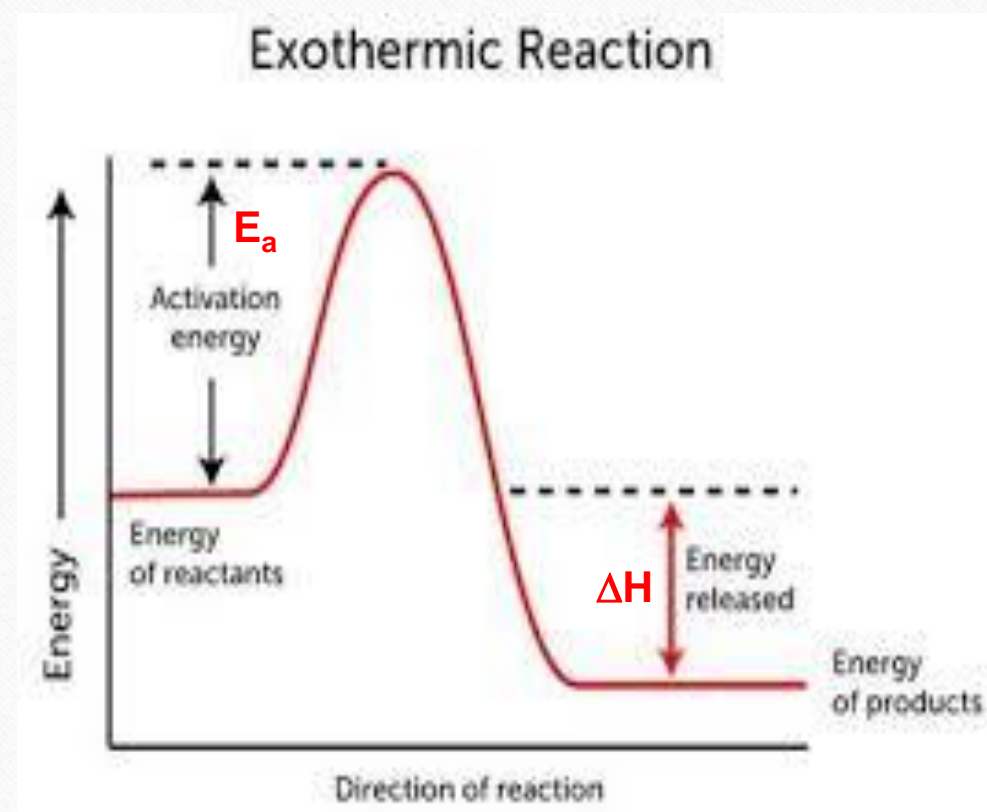
❖ When we are interested in kinetic stability, we must deal with the rates and mechanism of chemical reactions and also with the energies (ΔG^* or E_a) involved in the formation of the activated complex.

❖ From the kinetic point of view, it will be more proper to call the complexes as inert or labile complexes rather than stable or unstable complexes.

❖ Kinetic stability of a complex depends on the difference in energy between the reactants and the activated complex, namely the activation energy E_a.

❖ Kinetically inert complexes have large positive free energy of activation, ΔG^* (E_a) i.e., Greater this activation energy, lesser will be the reaction rate, implying that the complex is inert.

Depending upon the reactivity of complexes, Taube classified the complexes into two types.

(i) Labile (or) non-inert complexes: These are the complexes which react rapidly.

(ii) Inert (or) non-labile complexes. These are the complexes which react slowly.

❖ In order to make this distinction quantitatively, taube suggested that complexes of 0.1 M which react completely within about one minute should be considered **as labile** and those that take longer time should be considered **as inert.**

❖ These two terms, 'labile' and 'inert' relatively refer to the rates of reactions and are not related to 'instability' and 'stability terms, which refers to the thermodynamic character of the complex, to exist under equilibrium conditions.

❖ Thermodynamically stable complexes may be inert or labile and thermodynamically unstable complexes may be labile or inert.

❖ For example, $[Hg(CN)_4]^{2-}$ complex is thermodynamically very stable, because its formation constant is very high.

$$Hg^{2+} + 4\ CN^- \rightleftharpoons [Hg(CN)_4]^{2-} \qquad \beta = 1 \times 10^{42}$$

❖ **But, it can react fast with some reagents, i.e., kinetically labile. For example, its exchange reaction with isotopically labeled cyanide ion is extremely rapid.**

$$[Hg(CN)_4]^{2-} + {}^*CN^- \longrightarrow [Hg(CN)_3]\ [({}^*CN)]^{2-} + CN^- \quad (t_{1/2} < 1\ min)$$

❖ **On the other hand, $[Co(NH_3)_6]^{3+}$ complex is thermodynamically highly unstable (low β value)**

$$Co^{3+} + 6NH_3 \rightleftharpoons [Co\ (NH_3)_6]^{3+} \qquad \beta = 1 \times 10^{-25}$$

❖ **However, the above complex can be stored in aqueous solution containing some acid in the laboratory for several days without any noticeable change. This is possible, because its reaction with H_2O in acid medium is very slow due to high energy of activation, (E_a Value) for the reaction.**

$$[Co(NH_3)_6]^{3+} + 6\ H_3O^+ \longrightarrow [Co(H_2O)_6]^{3+}\ 6NH_4^+ \qquad \text{very slow.}$$
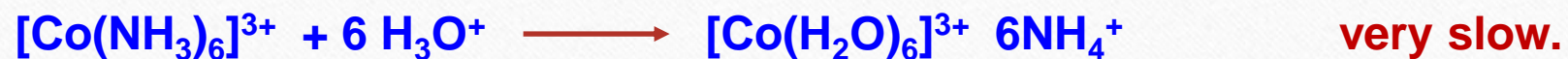
Thus, the above complex is kinetically inert.

❖ But the complex, $[Fe(CN)_6]^{4-}$ ion is thermodynamically stable and also kinetically inert.

(ii) Thermodynamic aspects of complex formation:

❖ The Thermodynamic stabilities of complexes are expressed in terms of stepwise stability constants (K) and overall stability constants (β). The stability constant of a complex denotes the extent of stability of the complex and denoted by 'β'

Stability constant and instability constant:

❖ When ammonia (monodentate, neutral ligand) is added to an aqueous solution of Ni^{2+} ions, there is noticeable colour change, because some of $[Ni(H_2O_6]^{2+}$ ions are converted into $[Ni(NH_3)_6]^{2+}$ ions, the system at equilibrium may be described by the equation,

$$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$$

The equilibrium constant (K) for the above reaction is

$$K_{eq} = \frac{[Ni(NH_3)_6]^{2+}\ [H_2O]^6}{[Ni(H_2O)_6]^{2+}\ [NH_3]^6} \qquad ....(1)$$

❖ **Here, we assume that the concentration of H_2O is a constant in a dilute solution of the complex and it is incorporated in the equilibrium constant, then the equation (1) becomes**

$$K_f = \frac{[Ni(NH_3)_6]^{2+}}{[Ni(H_2O)_6]^{2+}\ (NH_3)]^6} \qquad ....(2)$$

❖ **The equilibrium constant (K or K_f) is known as the stability constant or formation constant of the complex ion, $[Ni(NH_3)_6]^{2+}$. The higher the value of stability constant for a complex ion, the greater is its stability.**

Instability constant (1/K)

❖ The **reciprocal** of stability constant (1/K) is known as instability constant of the complex. A high value of instability constant indicates that the complex ion is highly unstable.

Stepwise stability constants and overall stability constant:

❖ According to J.Bjerrum, the formation of a complex (ML_n) is aqueous solution occurs by the stepwise addition of ligands to the metal ion which is accompanied by the stepwise replacement of coordinated water molecules by the ligand molecules or ions.

❖ We write the equilibrium reaction in a simplified and generalized form without referring to the coordinated water molecules as follows: The different steps involved in the formation of a complex, (ML_n) may be represented as follows:

Step 1:
$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

Step 2:

$$ML + L \xrightleftharpoons[]{K_2} ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

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nth Step:

$$ML_{n-1} + L \xrightleftharpoons[]{K_n} ML_n \qquad K_n = \frac{ML_n}{[ML_{n-1}][L]}$$
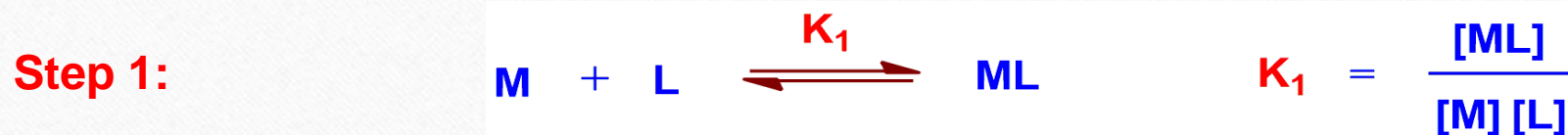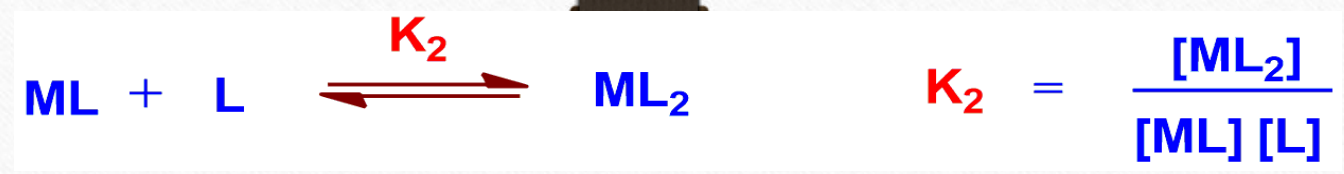
where 'n' represents the maximum coordination number of the metal ion for the ligand, L. (for the sake of simplicity, the charges of the complexes are ignored)

The equilibrium constants K_1, K_2, K_3,…….K_n are called stepwise formation constants or stepwise stability constants.

If the above reaction takes place in a single step, then the following equation applies,

$$M + nL \underset{}{\overset{\beta_n}{\rightleftharpoons}} ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

❖ **The equilibrium constant (β_n) of the above reaction is called as overall formation constant or overall stability constant or cumulative stability constant.**

Relationship between stepwise stability constants

K_1, K_2, K_3,…….K_n and overall stability constant (β_n)

Consider the formation of the complex **[ML_3]** from the aquated cation by the **stepwise replacement of coordinated water molecules** by the ligand molecules or ions. These reactions are represented in a simplified way by the following equations.

$$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML \qquad K_1 = \frac{[ML]}{[M][L]} \qquad \text{………(1)}$$

$$ML + L \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]} \qquad \ldots\ldots\ldots(2)$$

$$[ML_2] + L \underset{}{\overset{K_3}{\rightleftharpoons}} ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]} \qquad \ldots\ldots\ldots(3)$$

where K_1, K_2, and K_3 are called stepwise stability constants.

If we assume that the final product $[ML_3]$ is formed in a single step, then the reaction equation will be,

$$M + 3L \underset{}{\overset{\beta_3}{\rightleftharpoons}} ML_3$$

Therefore, overall stability constant, $\qquad \beta_3 = \dfrac{[ML_3]}{[M][L]^3} \qquad \ldots\ldots\ldots(4)$

On multiplying both the numerator and denominator of eqn-(4) by [ML] [ML$_2$], we get

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \qquad \ldots\ldots\ldots(5)$$

On rearranging the above equation (5), we get

$$\beta_3 = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \qquad \ldots\ldots\ldots(6)$$

$$\boxed{\beta_3 = K_1 . K_2 . K_3} \qquad \ldots\ldots\ldots(7)$$

Thus, for a system having n steps,

$$\beta_n = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \cdots \cdots \frac{[ML_n]}{[ML_{n-1}][L]} \qquad \ldots\ldots\ldots(8)$$

$$\beta_n = K_1 . K_2 . K_3 \dots\dots K_n$$

❖ Hence, overall stability constant, β_n is equal to the product of the stepwise stability constants $(K_1. K_2. \dots .K_n)$ of the system.

❖ The overall stability constant (β_n) is a measure of the stability of the complex. For extremely stable complexes such as $[Fe(CN)_6]^{4-}$, β_n is of the order of 10^{30} and for extremely unstable complexes β_n may even be less than unity. On account of this wide range, the values of β_n are given on a logarithmic scale.

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 +\dots\dots+ \log K_n$$

❖ As a rough guide, a log β value greater than '8' represents a 'stable' complex.

Trend in 'K' Values:

❖ The K values generally decrease gradually with increasing substitution of H_2O by ligand, L i.e, the stepwise stability constants lie typically in the order $K_1 > K_2 > K_3 \dots\dots > K_n$

For eg: **Effect of Ligand number on the stabilities of complexes.**

System	log K_1	log K_2	log K_3	log K_4	log β_4
$[Cd(NH_3)_4]^{2+}$	4.15	3.50	2.89	2.13	12.67
$[Ni((NH_3)_4]^{2+}$	2.80	2.24	1.73	1.19	7.96

❖ **This gradual decrease in K values is attributed to three factor, namely (i) the statistical factor (ii) steric factor and the (iii) the electrostatic factor.**

(i) Statistical factor:

   As the coordinated water molecules are replaced by ligands (L), the number of water molecules available to fresh ligands for replacement, decreases. As a result, stepwise formation constants (K) decreases gradually.

(ii) Steric factor:

This factor arises only when the incoming ligands are bulkier in size than the coordinated water molecules. As the small sized H_2O molecules are replaced by bulkier ligands (L), the steric crowding around the central metal ion increases. As a result of these steric repulsions, the subsequent steps are retarded. Hence, the 'K' values gradually decrease.

(iii) Electrostatic factor (or) columbic factors : (mainly in the case of charged ligands)

❖ In the first step of complex formation, one ligand (L) replaces one coordinated H_2O molecule to give $[M(H_2O)_{n-1}L]$. In the second step, another ligand (L) of the same charge approaches the first stage product. Now, there is an electrostatic repulsion between the incoming ligand and a similar ligand already present in the complex. As a result of electrostatic repulsion between the ligands, the subsequent steps are retarded. Moreover, with progressive intake of ligands the metal ion becomes less electron greedy. Hence, K values decreases gradually.

Exceptions to the usual relationship (trend) $K_1 > K_2 > K_3 \ldots \ldots > K_n$

❖ **Stepwise formation constants lie typically in the order $K_n > K_{n+1}$ as expected statistically. A reversal of this trend, $K_n < K_{n+1}$ is usually an indication of a major change in the structure and bonding at the metal center as more ligands are added. Examples: (i)**

System	log K_1	log K_2	log K_3	log K_4	log β_4
Cd^{2+}/Br^-	1.56	0.54	0.06	0.37	2.53

❖ **In the above example, K_4 is larger than K_3. This anomaly in the trend in K values suggests a major structural change. Generally the aqua complexes are six-coordinated, whereas the halo complexes are tetrahedral. In Cd^{2+}/Br^- system, the reaction of the fourth Br^- group and the complex with three Br^- group is**

$$[Cd\,Br_3\,(H_2O)_3]^- \; + \; Br^- \underset{K_4}{\overset{aq.medium}{\rightleftharpoons}} [Cd\,Br_4]^{2-} \; + \; 3H_2O$$

Octahedral   **Tetrahedral**

(2 particles)   **(4 particles)**

❖ **This reaction is accompanied by an increase in the number of particles and hence, it is entropically favored; (ΔS = +ve) this in turn results in an increase in K value.**

(ii) Another example is that tris(bipyridyl) complex of Fe(II) is very stable complex than bis (bipyridyl) complex of Fe(II) . This observation can be correlated with the change from a weak field Fe(II) ($t_{2g}^4 eg^2$) configuration (for bis (bipyridyl) cpx) to a strong field Fe(II) ($t_{2g}^6 eg^0$) configuration (for tris(bipyridyl) cpx). CFSE is more for $t_{2g}^6 eg^0$ configuration than $t_{2g}^4 eg^2$ configuration.

Relation between entropy and stability constant

❖ **The standard free energy change (ΔG^0) is related to the equilibrium constant (K) by the relation,**

$$\Delta G^0 = - RT \ln K \quad \dots \quad (1)$$

Where R is the gas constant and T is the absolute temperature. ΔG^0 is also related to ΔS^0 & ΔH^0 by the following relation, $\Delta G^0 = \Delta H^0 - T \Delta S^0$ ……. (2). By comparing (1) & (2),

$- RT \ln K = \Delta H^0 - T\Delta S^0 \quad ..... \quad (3)$

$\ln K = \dfrac{\Delta S^0}{R} - \dfrac{\Delta H^0}{RT}$

$$\therefore K = e^{\Delta S^0/R} \cdot e^{-\Delta H^0/RT} \quad ......(4)$$

❖ **From the above equation (4), it follows that complex formation is favoured by positive entropy changes (ΔS = +ve) and negative enthalpy changes (ΔH = -ve)**

Factors affecting the stability of Complexes:

❖ **The stability of a complex will be related mainly to (i) the complexing ability of the metal ion involved (ii) the characteristics of the ligand and (iii) the other factors which following from the above two important factors.**

(1) Complexing ability of Metals / Metal ions:

a) Charge and size of the central metal ion:

❖ In general, the metal ion with larger positive charge and smaller size form most stable complexes. A smaller but more highly charged metal ion permits a more closer approach of the ligands and greater will be the electro static attraction between the central metal ion and the ligands which results in the greater stability of the complex.

❖ For example, the stability of the complexes having the central metal ion with almost equal size but with different charges increases with the increase of the charge of the central metal ion. The stability constants (log β) of some complexes with two different charges are given here. The $\log_{10}\beta$ values of the complexes with the metals in their higher oxidation states are higher.

Complex	log β	Complex	log β	Complex	log β
1) Co^{2+}-EDTA cpx	16.2	$[Fe^{2+}(CN)_6]^{4-}$	8.3	V^{2+} - EDTA	12.7
2) Co^{3+}-EDTA cpx	36.0	$[Fe^{3+}(CN)_6]^{3-}$	31.0	V^{3+} - EDTA	25.9

❖ **Keeping the charge constant, as the size of the metal ion decreases, the specific charge per unit surface area increases. Hence, the metal's attraction for the ligand increases. So, the stability of complexes ↑se with decrease in size of the metal ion. This will be illustrated by the gradual ↑se in stability of the tri positive lanthanide ion – EDTA complexes from La to Lu due to lanthanide contraction. This contraction leads to a steady ↓se in size of the M^{3+} ion, hence stability ↑ses. ($\log_{10}\beta$ value).**

(e.g.) La^{3+} (15.50) < Ce^{3+} (15.98) < Gd^{3+} (17.37)…< Yb^{3+} (19.51) < Lu^{3+} (19.83)

❖ **Combination of the above two factors, i.e. charge / size (or) charge / radius ratio which is called the 'ionic potential (or) 'polarizing power' of the central metal ion becomes important in deciding the stability of the cpx. Therefore, as the ionic potential of the central metal ↑ses, the stability of the complexes with a particular ligand will also ↑se. For example, among the alkali metals, the stability of the cpx with a ligand ↑ses in the order**

Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ (ionic potential ↑ses in this order)

b) <u>Outer electronic configuration of the central metal ion.</u>

(i) <u>Cation with noble gas electronic configuration</u> ($s^2 p^6$) (Class 'a' metals)

❖ The alkali metal ions (M⁺), alkaline earth metal ions (M²⁺) and Al³⁺ ions belong to this group. In these cases, electrostatic forces dominate in complex formation, so interactions between small ions of high charge are particularly strong and lead to stable complexes.

❖ Thus, fluoro (F⁻) complexes of these metal ions are more stable and water (H_2O) is strongly bound than ammonia (NH_3) ligand which has smaller dipole moment. CN⁻ has little tendency to form complexes with these cations, because CN⁻ exists only in alkaline solutions, where it cannot compete successfully with OH⁻ ions.

(ii) <u>cations with completely filled d-sub shells</u> (or) pseudo-noble gas configuration ($d^{10} S^2 P^6$) (class 'b' metals)

❖ Cu^+, Ag^+, Au^+, Cd^{2+} & Hg^{2+} cations belong to this group. These ions, due to poor shielding effect of d-electrons, (high Z_{eff}) have high polarizing power and the bonds formed in their complexes have appreciable covalent character.

❖ Hence, this type of cations form stable complexes with the donor atom of the ligand which is less electronegative. This, Cd^{2+} and Hg^{2+} cations form strong complexes with I^- and CN^- ligands; but weak complexes with F^- ligand.

(iii) Transition metal ions with incomplete sub-shells ($d^{10-n} S^2 P^6$)

❖ These metal ions are classified using the concept of Hard and soft Acids and Bases. (It will be discussed later)

❖ Transition metal ions of small size, high +ve oxidation state and lesser number of outer 'd' electrons for excitation are good electron acceptors and are called hard acids. Transition metal ions of large size, low (or) zero oxidation state with plenty of outer 'd' electrons for excitation are called soft acids.

❖ **Generally hard acid-hard base interaction leads to a complex of greater stability than one formed from Hard-soft interaction. Hard acids prefer to coordinate with hard bases such as N, O & F donor atoms and soft acids prefer to coordinate with soft bases such as P, As, Cl, Br, I donor atoms.**

Outer electronic configuration of the Central metal ion. (continued…)

❖ **The outer electronic configuration of the metal ion plays an important role in determining the stability of complexes. The complexes given by metal ions possessing inert gas (8e⁻ns) configuration, Pseudo inert gas (18e⁻ns) configuration and Pseudo inert gas plus two (18+2e⁻ns) electronic configuration are less stable than those given by transition metal ions which have some empty (n-1)d-orbitals available for accepting the e⁻n pairs donated by the ligands.**

❖ **In case of metal ions which have the same radius and same charge (e.g. Na⁺ and Cu⁺; K⁺ and Cu⁺; Ca²⁺ and Cd²⁺; Sc³⁺ and Ga³⁺ ions) (belonging to two sub-groups of same periodic family) when we compare the stabilities of complexes of those metal ions with a particular ligand, the transition metal cpx is more stable than non-transition metal complex.**

❖ **The cations of non-transition elements(K⁺) have the inert gas configuration, s^2p^6 in its outer most shell, whereas the cations of transition metals (eg. Cu⁺) have Pseudo-inert gas configurations, $d^{10}s^2p^6$ in its outer most shell. Due to poor shielding effect of d-electrons, the transition metal ions (Cu⁺) have high effective nuclear charge (Z_{eff}). So, the transition metal ions (Cu⁺) have greater (more polarizing power) attraction for the electrons donated by the ligands. Thus cu⁺ forms more stable complex than K⁺ with a particular type of ligand.**

(C) Crystal Field Effects and natural order of stability (or Irving – William Order)

❖ The **stabilities of high spin complexes of** divalent transition metal ions **between** Mn^{2+} **and** Zn^{2+} with a given ligand follows the order,

	Mn^{2+}	< Fe^{2+}	< Co^{2+}	< Ni^{2+}	< Cu^{2+}	> Zn^{2+}
Ionic Radius (A^o)	0.91	0.83	0.82	0.78	0.69	0.74

❖ **This order is known as "Irving-William order" or** natural **order of stability which is consistent with** charge-to-radius ratio concept, **the high spin complexes of these ions are primarily octahedral with the** exception of those of Cu^{2+} **which forms tetragonally distorted octahedral complexes due to** John-Teller distortion.

❖ **The relative stability of high spin octahedral [ML$_6$]$^{2+}$ complexes of the first-row transition elements as predicted by crystal field theory is shown in the following figure.**
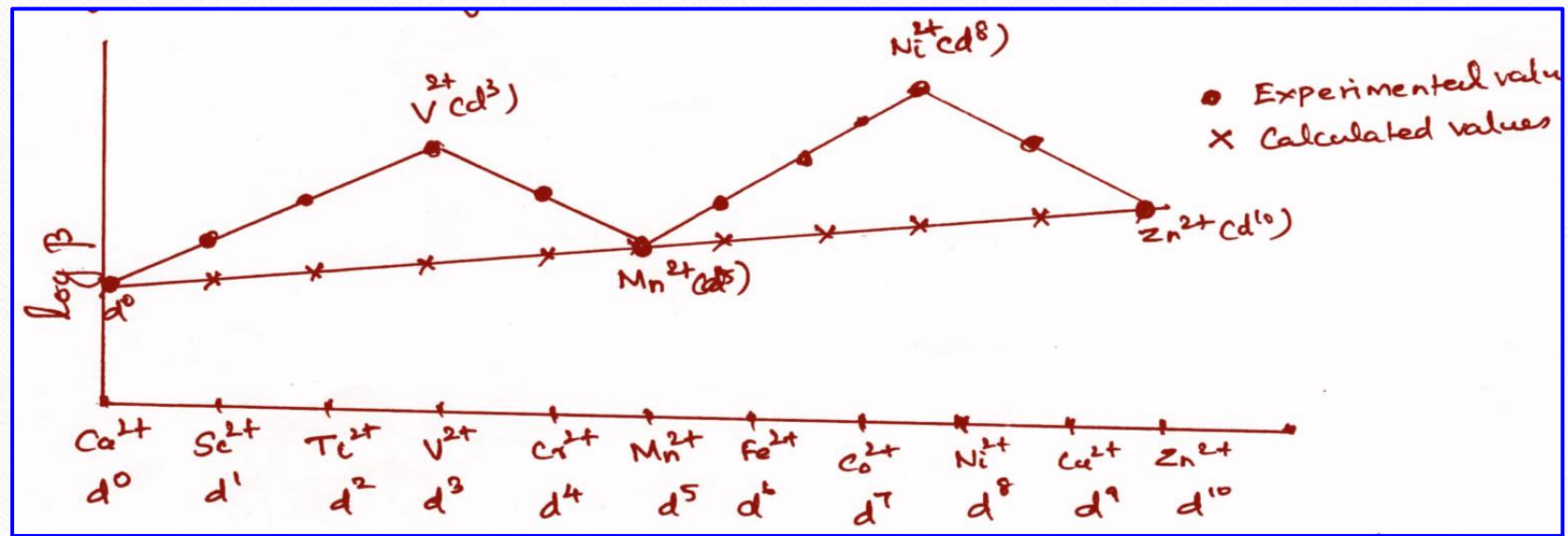
❖ **It is obvious from this figure that the Oh complexes of V^{2+} (d^3 ion) and Ni^{2+} (d^8) ions are the most stable with respect to their neighbours. This is because of the fact that high spin Oh complexes of these ions have the greatest CFSE values.**

$d^1 = -0.4\ \Delta_o$; $d^2 = -0.8\ \Delta_o$; $d^3 = -1.2\ \Delta_o$; $d^4 = -0.6\ \Delta_o$; $d^5 = 0\ \Delta_o$

$d^6 = -0.4\ \Delta_o$; $d^7 = -0.8\ \Delta_o$; $d^8 = -1.2\ \Delta_o$; $d^9 = -0.6\ \Delta_o$; $d^{10} = 0\ \Delta_o$

(Without Paring energy)

❖ **The order of stability as predicted by crystal Field Theory is the same as natural order of stability for complexes of these metal ions except for Cu^{2+}. The stability of Cu^{2+} complexes is greater than that of Ni^{2+} despite the fact that $cu^{2+}(d^9)$ has an additional e⁻n in the e_g orbital. This anomaly is a consequence of the stabilizing influence of the Jahn- Teller distortion, which enhances the log β value. In a tetragonally distorted complex, there is a strong binding of the four ligands in the square plane and the remaining distorted axial positions are more weakly bound.**

❖ **$Ca^{2+}(d^0)$, $Mn^{2+}(d^5)$ and $Zn^2+(d^{10})$ ions which do not have CFSE, have their experimental values in agreement with the calculated values. (on the smooth curve)**

(d) Class 'a' and class 'b' metals:

❖ **Chatt and Ahrland have classified the metals into three categories:** **(i) class 'a' metals (ii) class 'b' metals and (ii) borderline metals,** **on the basis of their electron-acceptor properties.**

(i) **Class 'a' metals:**

H^+, alkali metal ions, alkaline earth metal ions, Sc^{3+}, Ti^{4+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Ga^{3+}, In^{3+}, Sn^{4+}, Sb^{3+}, lanthanide ions (M^{3+}) and actinide ions.

(ii) **Class 'b' metals:**

Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}, Hg^{2+}, Pd^{2+}, Pt^{2+}, Rh^+, Ir^{2+}

(iii) **Border line metals:**

Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},

$Tl \rightarrow Po$, Mo, Te, Ru, W, Re, OS, Cd **(in the normal valence states)**

❖ **Class 'a'** metals form most stable complexes with ligands having the coordinating atoms from the 2nd period elements (eg. N, O, F) than those of an analogous ligand in which the donor atom is from 3rd or later period. (eg. P, S, Cl).

❖ Trend in complex stability with ligand donor atom type for class 'a' & 'b' metals are given below:

$F^- > Cl^- > Br^- > I^-$

$O >> S > Se > Te$ — Tendency to complex with

$N >> P > AS > Sb > Bi$ — class 'a' metals

`

$F^- < Cl^- < Br^- < I^-$ — Tendency to complex with

$O << S \approx Se \approx Te$ — class 'b' metals

$N << P < AS < Sb < Bi$

❖ **Class 'b' metals are characterized by the presence of a number of 'd' electrons beyond an inter-gas core. These d-electrons are used to form π-bond with ligand atoms. It is believed that the stability of complexes of class 'b' metals results from covalent contribution to metal-ligand bonds and the transfer of e⁻n density from the metal to the ligand via π-bonding. The most stable complexes of class 'b' metals are formed with ligands like PMe$_3$, S^{2-} and I⁻ which have vacant d-orbitals or like CO, CN⁻ which have vacant molecular orbitals of low energy.**

❖ **For borderline metals, the stability constants do not display either class 'a' or class 'b' behavior uniquely.**

 2) Characteristics of the Ligand:

   a) **Nature of the ligand: (size & charge of ligand)**

❖ **For anionic ligands, the higher the charge and the smaller the size, the more stable is the complex formed. Thus, F⁻ ion gives more stable complexes than does Cl⁻ ion. (e.g.) The stability constant (K$_1$) values of [FeF]$^{2+}$ and [FeCl]$^{2+}$ ions are 10^6 and 20 respectively.**

❖ **Thus, for class 'a' metals**, the order of stability of the halide complexes is $F^- > Cl^- > Br^- > I^-$. But this order is reversed for class 'b' metals (Pt^{2+}, Cu^+, Ag^+, Hg^{2+}, Te^+ etc.)

❖ **In class 'b' metals**, back donation from metal to ligand occurs in addition to be transfer of e^-ns from ligand to metal. For this back donation from M⟶L (**π – bonding**) to occur, the ligand must possess vacant orbitals capable of receiving elections. Iodine, being the least electronegative among the halogens, can easily accept the back donated e^-ns by the metal. Hence the order of stability is reversed in the case of class 'b' metals. (dπ - dπ back bonding)

(b) Basic Character of ligands:

❖ **Basicity is a measure of electron pair donation.** Greater the basic strength of the ligand, greater will be the tendency to donate electron pairs. This means that the **more basic ligands will form more stable complexes.**

❖ **Bjerrum studied the stabilities of the amine complexes of Ag⁺ and Hg²⁺ with reference to ligand basicities. He observed that, other things being equal, the increase in basicity of the ligands increases the stability of their complexes.**

❖ **The following table gives the effect of ligand basicity (K_b) on the stability (log K) of some Ag⁺ complexes.**

Ligand	$10^4 K_b$ (Basicity)	log K (Ag⁺) (Stability)
CH_3-NH_2	4.4	3.34
$CH_3-CH_2-NH_2$	4.6	3.65
$CH_3-CH_2-CH_2-NH_2$	4.7	3.84

(c) Chelating ability of the Ligand: (Chelate Effect)

❖ **The stabilities of complexes are greatly increased by the coordination of polydentate ligands. Coordination of polydentate ligands produces ring structures with the metal ion. Such ring-structured complexes are called chelates, and the ligand that forms a chelate is called chelating agent.**

❖ Due to chelation, **extra stability** is conferred on the complex. This **enhanced stability** of complexes containing chelated ligands than a similar and non chelated complexes is known as **Chelate Effect**.

❖ For example, **Cu^{2+}** forms a stabler complex with ethylene diamine than with **NH_3** because of chelate effect. $log_{10}\beta$ of $[Cu (en)_2]^{2+} > [Cu (NH_3)_4]^{2+}$ <u>**Reason for the chelate effect:**</u>

$[Ni (H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$
(aquated Ni^{2+})

1+3 = 4 Particles $\longrightarrow$ 1+6= 7 Particles
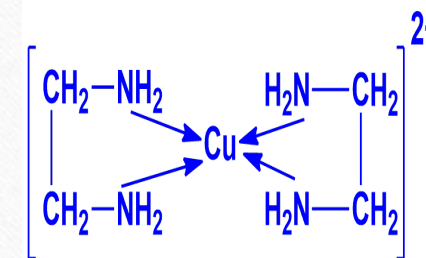
❖ The replacement of monodentate ligands (**H_2O**) by chelating ligands (**en**) results **in an increase** in the number of particles (4→7) present in the system. The increase in the number of particles results in an increase of the randomness (entropy) in the system. This in turn, results in a positive entropy change (**ΔS^o = +ve**) of the process which adds to the negative **ΔH^o** value, to give a more negative **ΔG^o**.

[ΔG° = ΔH° - TΔS° and ΔG° = -RTlnK]

❖ **Thus, a more positive value of ΔS° will lead to a more negative value of ΔG° and hence a more stable complex is formed.**

❖ **Thus the greater the amount of disorder produced in the products during the reaction relative to the reactants, the greater the increase in entropy during the reaction and hence greater the stability of the products (chelate) for eg, the stability of the following complexes increases in the order,**

$$[Cu(NH_3)_4]^{2+} < [Cu(en)_2]^{2+} < [Cu(trien)]^{2+}$$

logβ =   12.7   19.7   20.5   (entropy increases in this order)

(d) Ring size of Chelates:

❖ **One factor of greater importance in chelation is the size of the ring produced. Generally five or six membered ring complexes are formed as these ring system involve least strain and hence of greater stability.**

❖ When there is **no double bond** in the chelate ring, generally **a 5-membered ring will be the most stable. When there are double bonds, a 6-membered ring is the most stable.** Any ring containing less than 5 members or more than 6 members will be less stable.

❖ Thus, **[Co(EDTA)]⁻ cpx is the most stable complex as the hexadentate EDTA ligand forms 5 membered ring with Co³⁺.**

(e) Number or rings:

❖ When the chelating agent forms **more number of rings** with the metal ion, **stability ↑ses.** The greater stability of complexes having more number of rings is attributed to the **greater ↑se in the positive entropy of the system.**
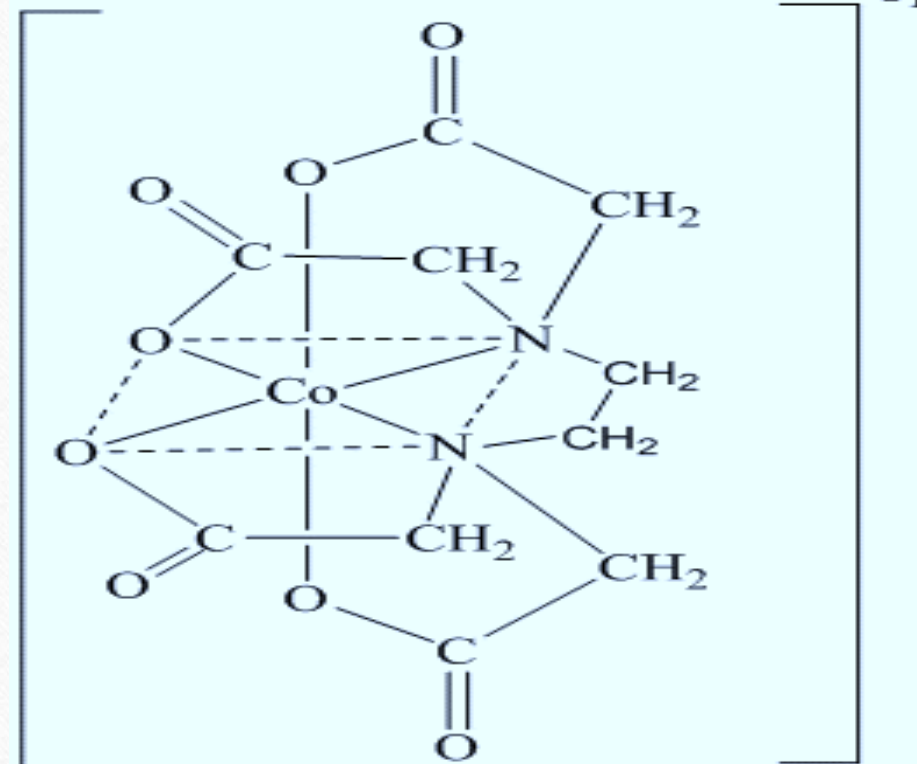
❖ **For example [N^{II}(EDTA)]$^{2-}$ complex is more stable than [N^{II}(en)$_3$]$^{2+}$ chelate cpx, because the former cpx involves 5 rings and the later cpx contains 3 chelate rings only.**

❖ **The following table shows the influence of the number of chelate rings on the stability of complexes formed by Ni^{2+} with en, dien and trien as chelating agents.**

Ligand	Complex	Change in the no. of particles	Number of rings	Log K$_1$
en	[Ni (en) (H$_2$O)$_4$]$^{2+}$	2 → 3	1	7.9
dien	[Ni (dien)(H$_2$O)$_3$]$^{2+}$	2 → 4	2	10.7
trien	[Ni (trien) (H$_2$O)$_2$]$^{2+}$	2 → 5	3	14.0

(Note: dien = diethylenetriamine;   trien = triethylenetetramine)

(dien)

(trien)
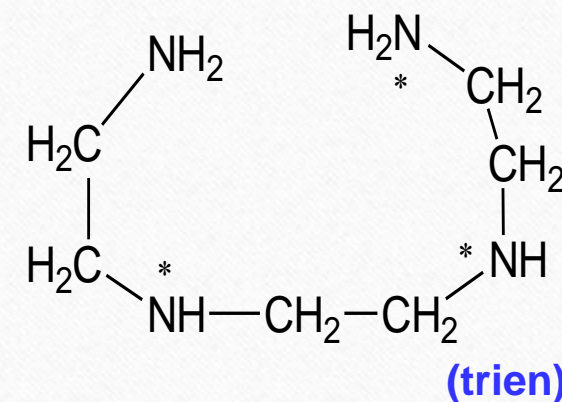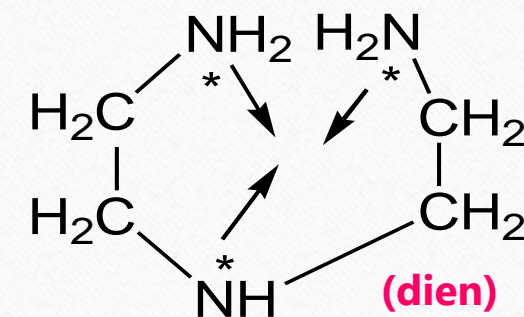
(f) Resonance Stabilization of Chelate ring:

❖ **Ligands possessing alternate double and single bonds, like acetyl acetone, porphyrin nucleus, form chelated complexes with extra stability which is attributed to the operation of resonance effects in the complex. In the case of acetyl acetone, the enol forms a chelated complex with metal ion having a six membered ring in which there is a greater delocalization of π e⁻ns over the whole ring which ↑ses the stability of this 6-membered ring system.**
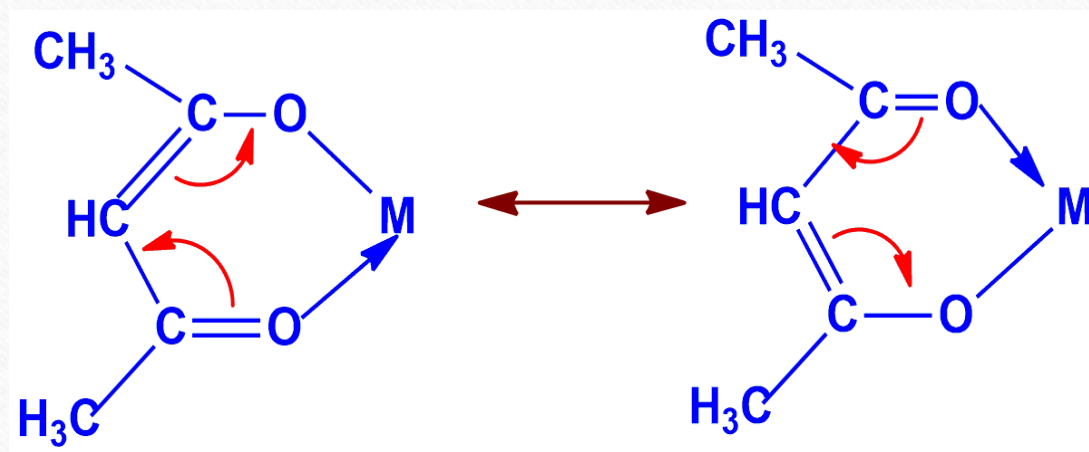
Fig.: **Resonance stabilization of M-acac chelate ring.**

(g) Steric Effects of ligands:

❖ One more factor of significance in chelation is the **steric factor.** When a **bulky group is either attached to** or **present near the donor atom of a ligand**, mutual repulsion among the ligands occurs which results in the **weakening of the metal to ligand bonds.** Thus, large bulky ligands form less stable complexes than do the analogous small ligands. This effect is commonly referred to as steric hindrance or steric effect. This effect can be illustrated by the following examples.

(i) $[Ni(en)_3]^{2+}$ cpx & $[Ni(N, N'\text{-dime-en})_3]^{2+}$

(N, N'-dime-en = N,N'–dimethyl ethylenediamine)

❖ **The first formation constant (log K_1) is higher** for the complex with **N,N'-dime-en**, because of its **higher basicity** than that with **en.** But the successive formation constants (log K_2 & log K_3) are less than that of the cpx with **en.** This is **due the steric repulsion** developed by methyl substituents in $[Ni(N, N^1 - \text{dime-en})_3]^{+2}$ cpx.

Table: **Steric effect on stability constants of complexes.**

Stability Constants	Ni^{2+}-en cpx	Ni^{2+}-N,N'-dime-en cpx
$\log K_1$	7.6	7.7
$\log K_2$	6.5	4.7
$\log K_3$	5.0	1.5

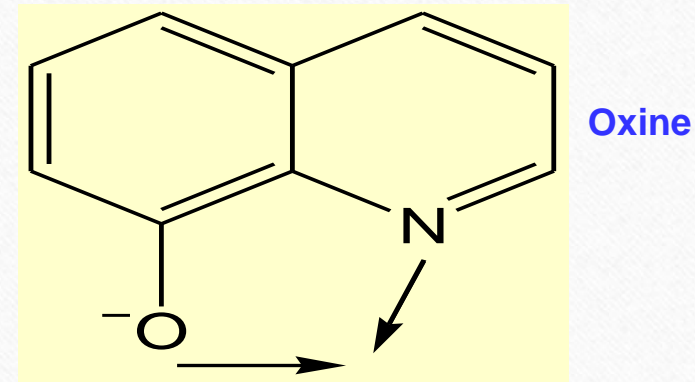(ii) **The metal complexes of 2-methyloxine are less stable than those of either oxine itself or its 4-methyl oxine.**

❖ **The log β_2 values values for Ni(II) metal complexes with these three ligands are given in the following table.**

Ligand	log β_2 of Ni^{2+} cpx
Oxine	21.4
2-methyloxine	17.8
4-methyloxine	22.3

Oxine

❖ **Among the three ligands considered in the above table, the 2-methyl derivative is the most basic one and hence it is expected to form the most stable complex. But, actually, it forms the least stable complex. The least stability of this cpx is attributed to the greater difficulty of chelation caused by the steric hindrance of the methyl group at position-2. Hence, the bulky methyl group is near enough to the donor atom (N) to cause mutual repulsion between the ligands.**

❖ **The 4-methl derivative is more basic than oxine itself. Since the bulky methyl group in this ligand is too far away from the donor nitrogen atom to sterically affect the process of complex formation, it forms the most stable cpx.**

(h) π-bonding capacity of ligands:

❖ The ligands like CN^-, CO, PR_3, AsR_3, NO, alkenes and alkynes which are capable of forming π-bonds with transition metal ions give more stable complexes.

Hard and soft Acids and Bases concept (HSAB Approach)

(or)

SHAB Principle and stability of complexes.

Definition of hard and soft acids and bases:

Hard Acids:

❖ Hard acids are those in which the **acceptor atoms** have the following characteristic features:

(i) They have small size and high positive oxidation state

(ii) They have noble gas electronic configuration (or) lesser no. of d- e-ns **i.e**, their outer electrons charge clouds or orbitals are not easily distorted i.e., polarized.

❖ **Hard acids includes ions of alkali metals, alkaline earth metals, lighter transition metals in higher oxidation state like Sc^{3+}, Ti^{4+}, Cr^{3+}, Fe^{3+}, Co^{3+} and the hydrogen ion (H+)**

Examples:

H^+ Li^+, Na^+, K^+, Be^{2+}, $Mg^{2+,}$ Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, Ti^{4+}, Zr^{4+}, Ge^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Cr^{6+}, La^{3+}, Th^{4+}, Si^{4+}, Mn^{2+}, Mn^{7+}, I^{5+}, I^{7+}, Cl^{7+}, BF_3, UO_2^{2+}, SO_3, CO_2, $(HF)_n$ **(Hydrogen bonded molecules)**

Soft Acids:

❖ **Soft acids are those in which the acceptor atoms have the following characteristic features:**

(i) They have large & zero or low positive oxidation state

(ii)They do not have a noble gas electronic configuration, i.e, they have plenty of available outer 'd' electrons for excitation, i.e, the outer electron charge clouds are easily distorted i.e, polarized. So, Soft acids includes heavier transition metals in lower oxidation states.

Examples:

Cu$^+$, Ag$^+$, Au$^+$, Cd^{2+}, Hg$^+$, Hg^{2+}, Pt^{2+}, Pd^{2+}, Tl$^+$, I$^+$, Br$^+$, Zero valent metal atoms, BH$_3$, π-acceptors like trinitro benzene, tetracyano ethylene etc.

Hard Bases:

❖ **Hard bases are those in which the donor atoms have the following characteristic features:**

(i) They have small size and high electronegativity with low polarizability.

(ii) The donor atoms tend to retain its electrons

(iii) Most of the donor atoms don't have empty orbitals. Some donor atoms are associated with empty orbitals of higher energy.

Examples:

F$^-$, Cl$^-$, OH$^-$, H$_2$O, O^{2-}, PO$_4$$^{3-}$, SO$_4$$^{2-}$, CO$_3$$^{2-}$, CH$_3COO^-$, ClO$_4$$^-$, NH$_3$, NO$_3$$^-$, ROH, R$_2O, RO^-$, R-NH$_2$, etc.

Soft bases:

❖ **Soft basis are those in which the donor atoms have the following characteristics:**

(i) The donor atoms have large size and low electronegativity with high polarizability.

(ii) The donor atoms tend to lose its electrons easily.

(iii) They are associated with empty low lying orbitals.

Examples:

CN^-, CO, SCN^-, I^-, $S_2O_3^{2-}$, R_3P, R_3As, R_2S, RSH, RS^-, H^-, C_2H_4, C_6H_6, R^-, etc.

Borderline Acids: (intermediate Acids)

Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, C_6H_5+, R_3C^+, SO_2, NO^+, etc.

Borderline Bases: (intermediate Bases)

$C_6H_5NH_2$, Pyrrole C_5H_5N, NO_2^-, SO_3^{2-}, N_3^-, Br^-

❖ **Pearson suggested that terms hard and soft acids can be used for class 'a' and class 'b' metals respectively.**

R.G.Pearson's hard-soft rule (or) SHAB Principle and stability of complex:

"Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases"

The typical Lewis acid-base reaction can be represented as

A	+	:B	⟶	A : B
(Lewis acid)		(Lewis base)		Complex
(Acceptor)		(Donor)		

❖ **Pearson's SHAB Principle is very helpful to predict, the stability of the complex A:B.**

❖ According to this principle, the complex A:B is most stable when A and B are either both soft or both hard. The complex A:B is least stable when one of the reactants is very hard and the other one is very soft. The concept of hard and soft character is qualitative.

Theories of Hardness and softness:

1) Electronic Theory:

❖ According to the theory, the bonding (interaction) between a hard acid and hard base is primarily ionic or electrostatic interaction and the bonding between soft acids and soft bases is primarily covalent.

❖ It is expected that small sized and highly charged positive ions (hard acids) would be favouring ionic bonding with hard bases which contain highly electronegative donor atom. Hard acids and hard bases like Na^+, K^+, F^-, OH^- form ionic bonds (NaF, KOH, NaOH, etc) because the electrostatic energy of an ion pair (Na^+F^-) is inversely proportional to the inter atomic distance, the smaller the ions involved, the greater is the electrostatic energy and greater is the attraction between the hard acid and hard base.

❖ **Since an electrostatic explanation cannot account for the apparent stability soft-soft interactions, (because the electrostatic energy of a pair of large ions should be relatively small) it has been suggested that the predominant factor here is covalent interaction. This correlates well for transition metals (Ag, Hg, etc.).**

❖ **In this regard, the polarizing power and polarizability of d-electrons becomes important. It has been pointed out that all soft acids are transition metals with six or more d-electrons (Pd^{2+}- d^8), with the d^{10} configuration (Ag^+, Hg^{2+}). The soft acids are having more polarizing power (shielding effect of d-e⁻ns is less) and the soft bases are having more polarizability (e.g. I⁻). Thus, polarization effects leads to covalent interaction between soft acids and soft bases.**

❖ **So, if hard-soft interaction takes place, the resulting species would be unstable.**

2) π-bonding Theory:

❖ **J. Chatt's π-bonding theory can be applied to explain the bonding between the soft-soft complexes.**

❖ π-bonding occurs most readily in those metal ions that have low oxidation states and large number of d-electrons. Lewis soft acids satisfy this criterion.

❖ According to this theory, the soft acids can form π-bonding (back bonding) by donating the loosely held outer d-electrons to ligands (soft bases) in which empty d-orbitals are available on the donor atoms, eg., P, As, S, I, etc., The presence of empty d-orbitals, on the ligand (except on CO) helps to strengthen the π-bonding.

❖ Thus, second row elements N, O and F are excluded from entering into this type of interaction.

Electronegativity and hardness and softness

❖ Hardness and softness have been found to be related to electronegativity. In general, species having relatively high electronegativities are hard and those having low electronegativities are soft.

❖ For example, Li, although it has a low electronegativity, the Li$^+$ ion has a relatively high electronegativity resulting from the extremely high second ionization energy.

❖ In contrast, transition metals in low oxidation states (cu^+, Ag^+, etc.,) have relatively low ionization energies and low electronegativities. Thus, Li^+ is hard acid and Cu^+, Ag^+ etc., are soft acids. The same may be said of hard and soft bases. (eg. F^- - hard base (high e.n) I^- soft base (low e.n)

❖ This relationship between electro negativity and hardness is used to explain why CF_3 -group is harder than CH_3 -group, and why BF_3 is harder than BH_3.

Applications of SHAB Principle:

❖ This principle finds applications in various domains of chemical reactions. Some of them are:

(i) Stability of species

❖ AgI_2^- is stable, but AgF_2^- does not exist. It is known that $Ag+$ is a soft acid, F^- is a hard base and I^- is a soft base. Hence, AgI_2^- (soft acid + soft base) is a stable complex and AgF_2^- (soft acid + hard base) does not exist.

❖ Similarly, it can also be shown that $[CoF_6]^{3-}$ (hard acid + hard base) is more stable than $[CoI_6]^{3-}$ (hard acid + soft base)

(ii) Feasibility of reaction:

❖ According to Pauling Rule, the most stable bonds are formed between elements of high electro negativity difference such as Cs and F Hence, the following reaction is expected to occur.

$$CsI + LiF \longrightarrow LiI + CsF \text{ (Highly endothermic)}$$

But, experimentally, the reverse reaction has been observed.

$$LiI + CsF \longrightarrow LiF + CsI \quad \Delta H = -63 \text{ (KJ/mol)}$$

❖ This can be explained by hard-soft acid-base rule. Here, soft iodide (I^-) prefers to combine with soft cesium ion (Cs^+) and the hard fluoride ion (F^-) prefers to combine with hard lithium ion (LI^+)

(iii) Occurrence of minerals:

❖ The kinds of **metal ores found in earth's crust** can be rationalized by using this principle. Thus hard acids such as Ca^{2+}, Mg^{2+} and Al^{3+} occur in nature as $CaCO_3$, $MgCO_3$ and Al_2O_3 and not as sulphides (**MgS, CaS, Al$_2$S$_3$**), since the anions CO_3^{2-} & O^{2-} are hard bases and S^{2-} is a soft base. However, soft acids such as **Cu+, Ag+, and Hg^{2+}** occur in nature as sulphides (**Cu$_2$S, Ag$_2$S & HgS**) because S^{2-} is a soft base. The **borderline acids such as Ni^{2+}, Cu^{2+}, Pb^{2+}** occur in nature both as carbonates and sulphides.

(iv) Poisoning of metal catalysts:

❖ This has been explained on the basis of SHAB principle. Soft metals (**e.g. Pd & Pt**) act as catalysts and they are easily poisoned with **CO, Olefins, phosphorus or arsenic ligands** (all are soft bases) These ligands **adsorb strongly** on the surface of the metal and block the active sites. The soft metal catalysts are not affected by hard bases such as **F, O, N**.
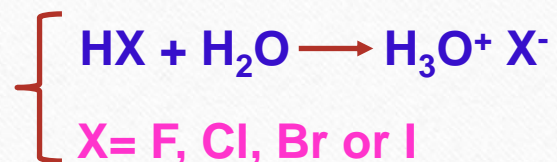
(v) Relative strengths of halogen acids in aqueous solution:

❖ **The relative strength of halogen acids in aq.solution can be explained on the basis of SHAB principle. The order is**

HF < HCl < HBr < HI

Weakest   Strongest
Acid   Acid

$HX + H_2O \longrightarrow H_3O^+ X^-$

X= F, Cl, Br or I

❖ **In HF, the hard acid (H⁺) combines with the hardest base F⁻ to form the undissociated acid (weakest acid) HF – stability is more. However, HI (hard-soft) is unstable and hence it is the strongest acid.**

(vi) Prediction of coordination in complexes of Ambidentate ligands

❖ **Ambidentate ligand is one which, although unidentate, may coordinate to the metal ion through either of its two coordinating atoms.**

❖ For example, SCN^- is an ambidentate ligand, it can coordinate through N atom to form the Cpx $[Co(NCS)_4]^{2-}$ whereas it coordinates through S atom to form the Cpx $[Pd(SCN)_4]^{2-}$. The reason is Pd^{2+} is a soft acid, so it prefers to coordinate through softer 'S' atom to form Pd-SCN linkage. Co^{2+} comparatively hard acid, it prefers to coordinate through the harder 'N' atom to form Co-NCS linkage.

❖ (vii) Out of the two complexes, $[Cd(NH_3)_4]^{2+}$ and $[Cd(CN)_4]^{2-}$ the later complex should be more stable (combination of soft acid Cd^{2+} with soft base CN^-) on the basis of SHAB principle.

Limitations of HSAB concept:

(i) Interpreting hard-hard interactions between small atoms as purely ionic and those between soft-soft involving larger atoms as covalent bonds is not accurate one. Example: covalent bonding between two smaller atoms is the strongest in H_2. (Bond energy = 431 KJ/mol)

(ii) With hard-soft principle, it is difficult to interpret acid-base relative strengths.

Symbiosis with respect to HSAB Principle:

❖ The hardness and softness of an acidic or basic site is not an inherent property of the particular atom at that site, but can be influenced by the substituent atoms. The addition of soft, polarizable substituents can soften the hard centre and the presence electron withdrawing substituents can reduce the softness of a site.

❖ For example, addition of three, hard electro negative fluorine ion (F^-) to the borderline acid, B^{3+}, hardens the boron atom and makes it a hard Lewis acid (BF_3). Conversely, addition of three soft hydride ion (H^-) to B^{3+}, softens the boron atom and makes it a soft Lewis acid (BH_3)

❖ Soft ligands have a tendency to combine with a Centre already associated with soft ligands and hard ligands have a tendency to combine with a Centre already associated with hard ligands. This tendency has been termed as "symbiosis" by Jorgenson. Thus, F^- ion, a hard ligand readily combines with BF_3 to form a stable cpx, BF_4^-, similarly H^- ion, a soft ligand, readily combines with BH_3 to form a stable cpx, BH_4^- .

$$BF_3 \ + \ F^- \longrightarrow BF_4^- \ ; \qquad BH_3 \ + \ H^- \longrightarrow BH_4^-$$

Hard   Hard   Soft   Soft

❖ **Mixed substituent are not preferred. Thus, cpds, such as BF_3H^- & BH_3F^- having mixed substituents, interact spontaneously to yield BF_4^- & BH_4^-**

$$BF_3H^- + BH_3F^- \longrightarrow BF_4^- + BH_4^- \qquad\qquad \text{Similarly,} \quad CH_3F + CF_3H \longrightarrow CF_4 + CH_4$$

DETERMINATION OF STABILITY CONSTANTS

❖ **Stability constants of complexes have been measured by different methods. Some of them are**

    (i) Spectrophotometric method

    (ii) Potentiometric method (Bjerrum method)

    (iii) Polarographic method

    (iv) Job's continuous variation method (Spectrometric method when only one complex is formed)

(i) Spectrophotometric method:

❖ **Most of the complexes absorb light at different wavelength than the free metal ions from which they are formed. The relationship between the absorbance or optical density (A) at a particular wavelength and concentration (c) is expressed by the Beer's Law.**

$$A = \varepsilon\, c\, l$$

Where A   =   Absorbance (or) Optical density

ε   =   Molar extinction coefficient

c   =   Concentration of the complex (in mol/lit)

l   =   length of the absorption cell

❖ **So, by using Beer's law equation, by measuring the absorbance (A) using a spectrophotometer, knowing the extinction coefficient (ε) at that wavelength and the cell length (l), the concentration (c) can be calculated.**

Fig: A representative absorption spectra of a metal ion, M^{2+} (shown by broken lines) and its complex ion, ML^{2+} (shown by unbroken lines) is shown in the diagram.

❖ It is also clear from the above spectrum, that the absorption by the complex takes place over the entire region of the metal ion absorption, while at **550 mµ**, only the cpx absorbs. i.e, the λ_{max} of complex is not interfered with that of M^{2+} ions.

The stability constant (K_f) for the reaction is

$$M^{2+} + L \underset{\longleftarrow}{\overset{K_f}{\rightleftharpoons}} ML^{2+} \qquad K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} \qquad \ldots\ldots\ldots(1)$$

❖ **In order to obtain the value of formation constant, the equilibrium concentration of $[ML^{2+}]$, $[M^{2+}]$ & $[L]$ should be known. For that, solutions, containing known amounts of total $[M^{2+}]$ and total $[L]$ are equilibrated. The absorbance of these solutions at 550 mμ is measured using spectrophotometer. The value of K_f is evaluated as follows:**

We know that,   The total concentration of M^{2+} $= C_M = [M^{2+}] + [ML^{2+}]$ ….(2)

The total concentration of L $= C_L = [L] + [ML^{2+}]$ ….(3)

From Beer's law, $A = Ɛ_{(ML^{2+})} \cdot [ML^{2+}] \cdot l$

$$[ML^{2+}] = \frac{A}{Ɛ_{(ML^{2+})} \cdot l} \quad ….(4)$$

❖ **The value of Ɛ for the $[ML^{2+}]$ can be determined first by measuring the absorbance of a solution of the complex of known concentration (such a solution can be prepared by mixing a known amount of M^{2+} with a large excess of L, so that all the M^{2+} is converted to the complex, ML^{2+})**

❖ **Substituting the value of [ML^{2+}] obtained from equation (4) in the equations (2) and (3) we get the equilibrium concentration values of [M^{2+}] & [L]. Thus,**
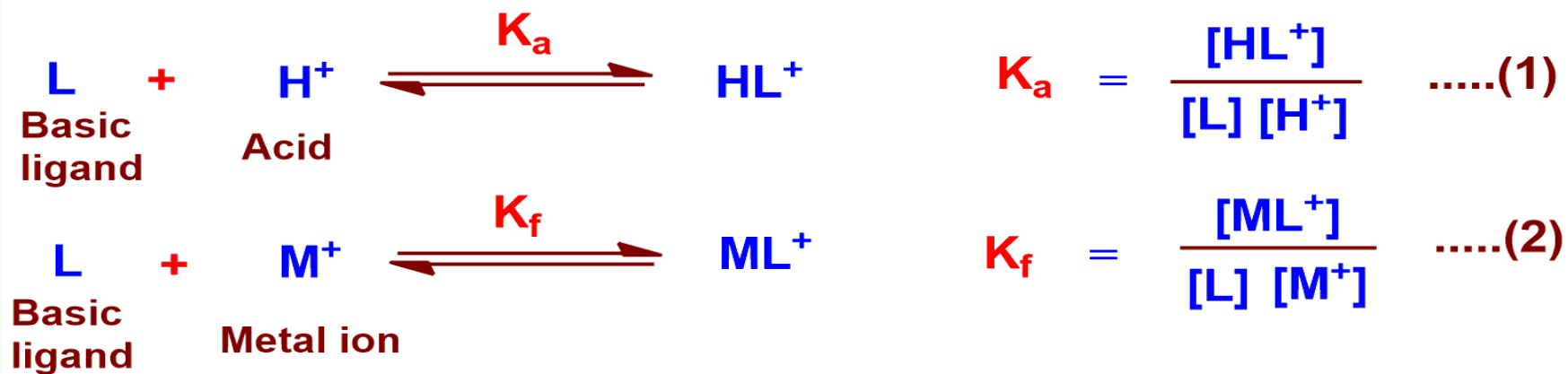
$$[M^{2+}] = C_M - \frac{A}{\varepsilon_{(ML^{2+})} \cdot l} \quad \ldots (5)$$

$$[L] = C_L - \frac{A}{\varepsilon_{(ML^{2+})} \cdot l} \quad \ldots (6)$$

❖ **Thus, if we put the equilibrium concentration values of [ML^{2+}], [M^{2+}] and [L] in equation (1), we get the formation constant or stability constant, K$_f$ of the complex ML^{2+}.**

❖ **The experiment is then repeated with three or more different initial M^{2+} and L concentrations to check the constancy of K$_f$.**

(ii) Potentiometric Method (Bjerrum method)

❖ **When the ligand is a weak base, competition between H⁺ ions and metal ions for the ligand can be used for the determination of the formation constant.**

❖ **Let us consider the equilibria in which an acid and metal ions are added to a basic ligand in solution. The following equations hold good.**

$$L + H^+ \underset{}{\overset{K_a}{\rightleftharpoons}} HL^+ \qquad K_a = \frac{[HL^+]}{[L][H^+]} \quad .....(1)$$

Basic ligand   Acid

$$L + M^+ \underset{}{\overset{K_f}{\rightleftharpoons}} ML^+ \qquad K_f = \frac{[ML^+]}{[L][M^+]} \quad .....(2)$$

Basic ligand   Metal ion

Where K_a and K_f are the acid association constant of the ligand and formation constant of the complex respectively.

❖ **If C_H, C_M and C_L are the total concentrations in moles / lit of acid (H^+), metal ion (M^+) and the basic ligand (L),**

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

$$C_L = [L] + [ML^+] + [HL^+] \quad \text{……. (4)}$$

$$C_M = [M^+] + [ML^+] \quad \text{……. (5)}$$

Solving the last three equations [i.e. eqn. (3), (4), (5)] using the acid association constant of the ligand, K_a, we get,

From eqn. (4)

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

By substituting the value of $[HL^+]$ & $[L]$

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a \cdot [H^+]} \quad \text{….. (7)}$$

From eqn.3

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

From eqn.1

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

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

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

$$[M^+] = C_M - [ML^+] \quad ......(9) \quad \text{(from eqn.5)}$$

❖ **Thus, on putting the values of [ML⁺], [M⁺] and [L] in the equation (2), we can evaluate the formation constant, K_f of the complex, [ML⁺].**

$$K_f = \frac{[ML^+]}{[L] [M^+]} \quad .....(2)$$

❖ **For the determination of [ML⁺], [M⁺] & [L], we must know the values of C_H, C_M, C_L, K_a and [H⁺]. The last quantity, [H⁺], the equilibrium hydrogen ion concentration is generally determined Potentiometrically using glass electrode in a p^H-meter.**

Pt / 0.1M HCl / Glass / Experimental soln. of unknown p^H // KCl (sat.soln.), $Hg_2Cl_{2(S)}$ | H_g

$$E_G = E^0_G - 0.0591 p^H \qquad p^H = -log[H^+] \qquad \therefore [H+] = 10^{-PH}$$

(iii) Polarographic Method:

❖ **The half Wave potential (E$_{1/2}$) for the polarographic reduction of a metal ion is usually shifted to the more negative value as a result of complex formation. This implies that the metal ion in the complexed state is less easily reduced than the free metal ion.**

❖ **Therefore, Polarographic E$_{1/2}$ values can be used to determine the formation constants of complexes. This can be illustrated with a Pb(II) cpx. For the reduction of simple Pb^{2+}, the equation is**

$$Pb^{2+} + 2e^- \rightleftharpoons Pb$$

The Nernst equation for this reduction reaction is,

Fig: Essential features of a Polarograph

$$E_{Pb^{2+}/Pb} = E^o_{Pb^{2+}/Pb} - \frac{0.0591}{n} \log \frac{[Pb]}{[Pb^{2+}]} \quad ....(1)$$

Where, $E^0_{Pb2+/Pb}$ is the standard reduction potential of Pb^{2+}/Pb

n – is the number of electrons transferred in the reduction.

Let the complex formation of Pb^{2+} with the ligand, L be denoted as

$$Pb^{2+} + x\,L \rightleftharpoons Pb\,L_x \quad \text{(for simplicity, the charge on L is ignored here)}$$

Therefore, Stability constant $K = \beta_x = \dfrac{[PbL_x]}{[Pb^{2+}][L]^x}$ \quad (or)

$$[Pb^{2+}] = \frac{[PbL_x]}{K[L]^x} \quad ....(2)$$

Substituting the value of $[Pb^{2+}]$ in the equation (1), we get,

$$E_{Pb^{2+}/Pb} = E^0_{Pb^{2+}/Pb} - \frac{0.0591}{n} \log \frac{[Pb]}{[PbL_x]} - \frac{0.0591}{n} \log [K] - \frac{0.0591}{n} \cdot x \log [L] \quad ………(3)$$

❖ **Assuming that the complex is reversibly reduced, the values for [Pb] and [PbL_x] can be obtained from Lingane equation**

$$E_{Pb^{2+}/Pb} = E^0_{Pb^{2+}/Pb} - \frac{0.0591}{n} \log \frac{k}{k'} - \frac{0.0591}{n} \log \frac{I}{I_d - I} - \frac{0.0591}{n} \log [K] - \frac{0.0591}{n} \cdot x \log [L] \quad ………(4)$$

❖ **Where k and k' are the diffusion current constants of metal atom (Pb) in the amalgam and in the solution (Pb^{2+}) respectively. 'I' is the current at any point in the polarographic wave and I$_d$ is the diffusion current (I$_d$ = limiting current – residual current)**

$$\frac{[Pb]}{[PbL_x]} = \frac{k}{k'} \frac{I}{(I_d - I)}$$

For simplicity, let k be assumed to remain constant for the complex and for the simple metal ion (k ≈ k') and $E_{1/2} = E^0_{Pb2+/Pb} - \frac{0.0591}{2} \cdot \log \frac{k}{k'}$ $\quad \therefore E_{1/2} = E^0_{Pb2+/Pb}$

Where $E_{1/2}$ is the half wave potential for the simple metal ion couple. The equation (4) becomes

$$E_{Pb^{2+}/Pb} = E_{1/2} - \frac{0.0591}{n} \log \frac{I}{I_d - I} - \frac{0.0591}{n} \log [K] - \frac{0.0591}{n} \cdot x \log [L] \quad \text{........(5)}$$

When $I = I_{d/2}$ for the complex, $E_{Pb2+/Pb} = (E_{1/2})_{cpx}$

$$(E_{1/2})_{cpx} = E_{1/2} - \frac{0.0591}{n} \log [K] - \frac{0.0591}{n} \cdot x \log [L] \quad \text{........(6)}$$

The shift in half wave potential of the meal ion due to complexation is $= \Delta E_{1/2}$.

$$\Delta E_{1/2} = (E_{1/2})_{cpx} - E_{1/2}$$

Here, $(E_{1/2})_{cpx}$ & $E_{1/2}$ are the half wave potentials for the complexed and un-complexed metal ion respectively.

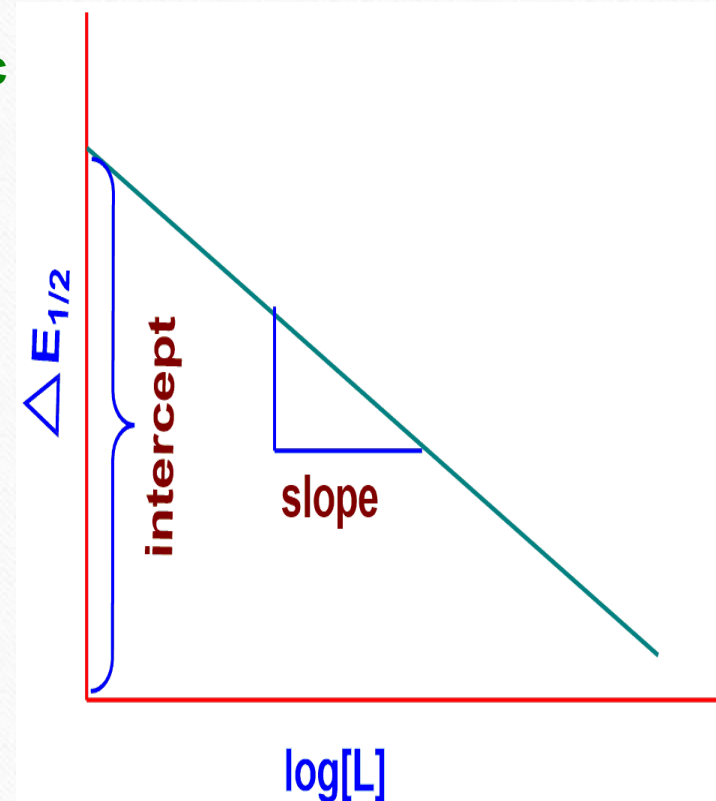$$\triangle E_{1/2} = -\frac{0.0591}{n} \log [K] - \frac{0.0591}{n} \cdot x \log [L] \quad \text{........(7)}$$

This equation - ⑦ is in the form of straight line equation Y = mx + c

A plot of $\Delta E_{1/2}$ against log[L] for several ligand concentrations give a straight line whose slope is equal to

$$\text{Slope} = -\frac{0.0591}{n} \cdot x$$

$$\text{Intercept} = -\frac{0.0591}{n} \log [K]$$

❖ **From the slope, the value of x, the number of ligands bonded to the metal ion can be calculated, provided 'n' is known.**

❖ **From the intercept, the stability constant, K can be calculated.**

THANK YOU

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