

Stability of complex \rightarrow

The stability of complex can be discussed in two ways.

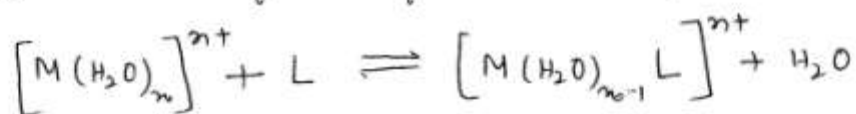
- ① Thermodynamic stability (stable or unstable)
- ② Kinetic stability (Inert or labile)

① Thermodynamic stability \rightarrow

It is referred to the extent to which the complex will form or will be transformed into another species when the system reaches the equilibrium. Simply we can say that a stable complex is the complex which possesses sufficient stability to retain ~~the~~ its identity in solⁿ while unstable complex is that complex which is dissociated in solution into its components.

When talk about the thermodynamic stability it deals with the properties like M-L bond energies, stability const. and redox potentials.

Let us consider the formation of ML complex ~~is~~



$n =$ No of water molecules

$n =$ Oxidation state of the complex/metal atom.

All the water molecules can be replaced by the ligand L.

This equilibrium reaction can be written in simplified & generalised form as



The equilibrium const. K_f can be written as

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

K_f = Equilibrium const or formation const.

If large amount of complex ML is formed, the concentration of $[ML]$ will be large. So K_f will be large, which means that ligand 'L' is attached to the metal 'M' more tightly than the H_2O molecule. So larger K_f means more stable of the complex in thermodynamic sense & the magnitude of K_f (formation const) is a measure of stability of a complex.

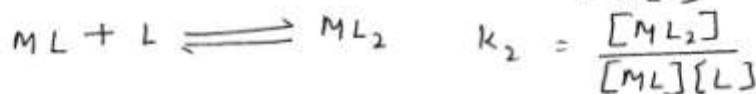
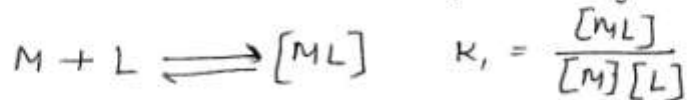
K_f large \rightarrow stable complex

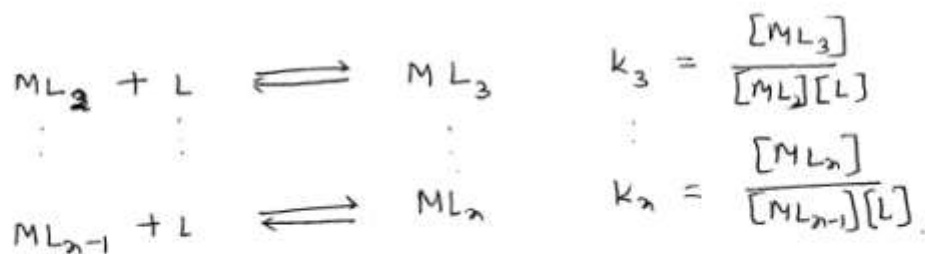
K_f small \rightarrow unstable complex.

Step wise formation const and overall formation const and their relationship

The formation of a complex ML_n can be expressed in two ways.

① ~~Step wise~~ let us consider the formation of $[ML_n]$ complex as





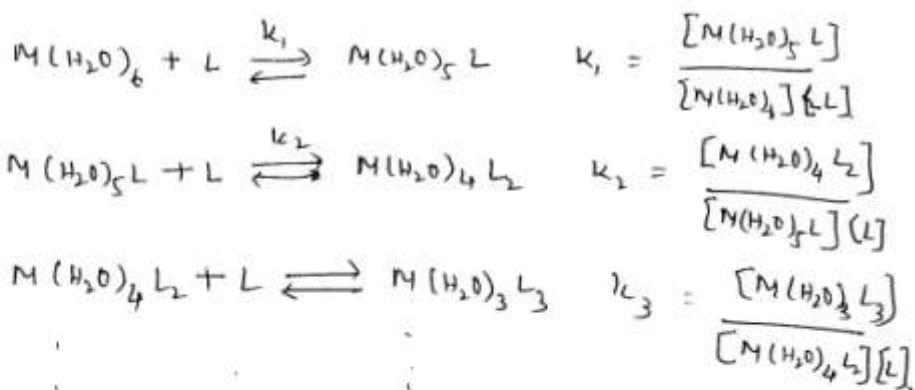
Here $k_1, k_2, k_3 \dots k_n$ are called stepwise formation or stepwise stability constants.

Note The stepwise formation constant (k_n) is generally decreased with the increase of no. of ligand L in the complex except few exceptions

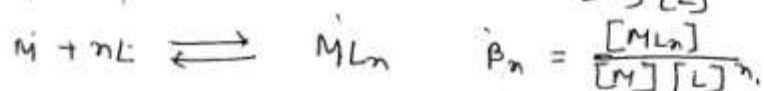
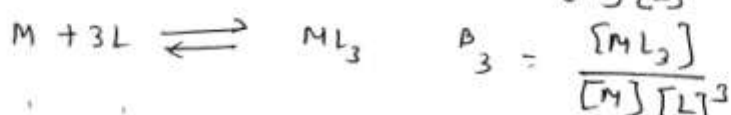
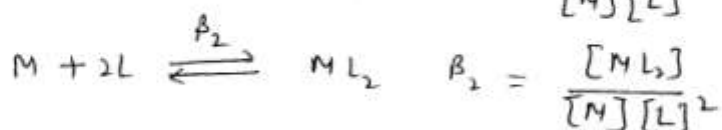
$$k_1 > k_2 > k_3 > k_4 > \dots > k_n$$

This is because of the less and less H_2O molecules are available for replacement with the increase of more and more ligand 'L'. ~~As~~ It means that k_1 has more water molecule to ligand L for replacement than k_2 which is again has more more water molecule than k_3 and so on.

example:



② The formation of ML_n can also be expressed as



$\beta_1, \beta_2, \beta_3 \dots \beta_n$ are called overall stability constant or overall formation constant.

Relationship between stepwise stability constant and overall stability constant

Let us take an example of the formation ML_3 complex.

By overall stability constant we can write β_3 as.

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \quad \text{--- (i)}$$

Multiply both the numerator and denominator of equation (i) by $[ML][ML_2]$, then we get:

$$\beta_3 = \frac{[ML_3][ML_2][ML]}{[ML_2][ML][L]^3[M]} \quad \text{--- (ii)}$$

We can rearrange this eqn (ii) as

$$\beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} = k_1 \times k_2 \times k_3$$

$$\therefore \beta_3 = k_1 \times k_2 \times k_3$$

$$\therefore \beta_n = k_1 \cdot k_2 \cdot k_3 \dots k_n$$

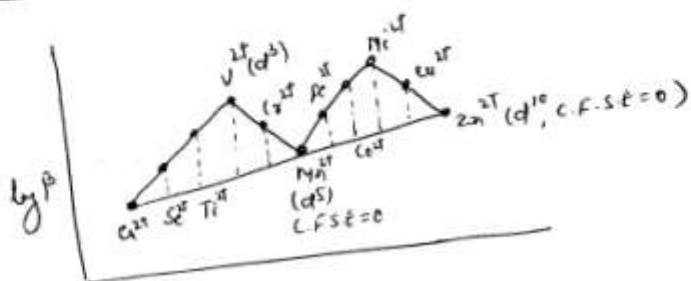
Factors affecting the stability of complexes \rightarrow

(i) Charge and size of metal atom \rightarrow

charge \propto stability

Size $\propto \frac{1}{\text{stability}}$

(ii) C.F.S.E effects [ML₆]



Note, $V^{2+} (d^3)$ + $Ni^{2+} (d^8)$ have higher stability because of large C.F.S.E. This is for the high spin complex.
 Mn^{2+} & Zn^{2+} have zero C.F.S.E. So lowest stability.

(iii) Electronegativity of central atom \rightarrow

As tendency is due to the absorption of electron to the central metal atom (to some extent) by the ligand, the increase of electronegativity of central metal atom means strong electron-attracting tendency, so more stable complex is formed.

Nature of ligand: \rightarrow

(i) Size & charge of ligand: \rightarrow

charge \propto stability

Size $\propto \frac{1}{\text{stability}}$

(ii) Basic character of ligand:

Basic character of ligand \propto More stability.

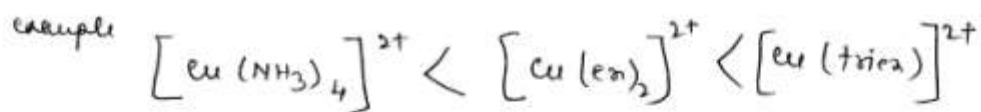
(More basic is the ligand, more easily the e^- can be donated to the central atom, so more stability)

(iii) Chelate effect: \rightarrow

Chelate complexes are more stable than the non-chelated complex because of the increase of entropy in chelated complex.

$$-RT \ln \beta = \Delta G = \Delta H - T\Delta S$$

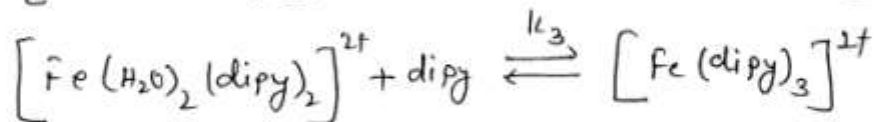
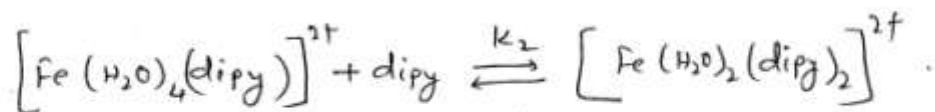
More -ve value of ΔG , more stability.



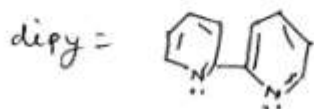
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1.

Co-ordinated water molecules in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ can be successively replaced by 2,2' dipyridyl, finally resulting in the formation of $[\text{Fe}(\text{dipy})_3]^{2+}$. In this process, the third equilibrium constant k_3 is observed to be greater than the second one k_2 . Explain it.

→ From the questions we know that:



~~$k_1 > k_3$~~ $k_1 > k_2 < k_3$



i.e. $k_3 > k_2$

$k_1 > k_2$ → Because more H_2O molecules present in $[\text{Fe}(\text{H}_2\text{O})_4(\text{dipy})]^{2+}$ complex than in $[\text{Fe}(\text{H}_2\text{O})_2(\text{dipy})_2]^{2+}$ complex.

The reason is that in the complex $[\text{Fe}(\text{H}_2\text{O})_4(\text{dipy})]^{2+}$ ^{high spin complex} ^{4 unpaired e⁻ ions}

$[\text{Fe}(\text{H}_2\text{O})_2(\text{dipy})_2]^{2+}$, due to the presence of H_2O molecules, high spin complex is formed. So the configuration of Fe^{2+} will be $t_{2g}^4 e_g^2$, therefore the crystal field stabilizing energy (CFSE) would be -0.44_0 . However in case of complex $[\text{Fe}(\text{dipy})_3]^{2+}$ Fe^{2+} has low spin complex due to absence of H_2O molecules. So the configuration would be $t_{2g}^6 e_g^0$, therefore C.F.S.E = -2.44_0 . Which is more -ve than -0.44_0 . So $k_3 > k_2$.

②

Kinetic Stability

It is refer to the speed with which transformation leading to the attainment of equilibrium will occur. Kinetic stability deals with rate of reaction in sol^n .

Kinetically stable complex is said as inert complex while kinetically unstable complex is ~~said~~ called as labile complex.

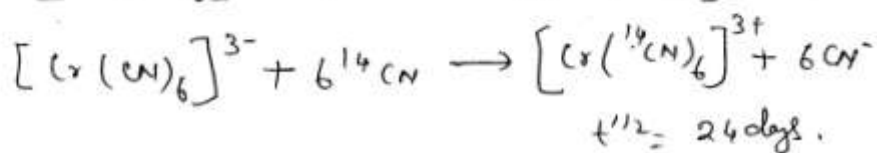
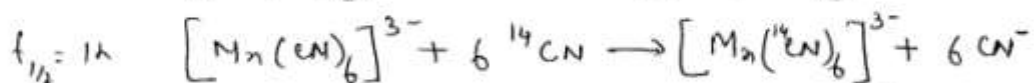
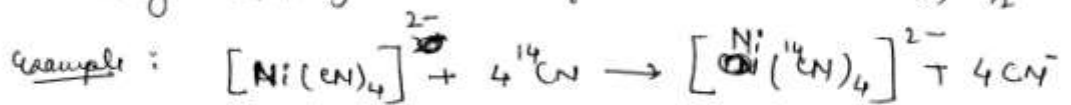
① If the ligand of a complex is replaced by other ligand ~~is~~ rapidly is called labile complex.

② If the ligand of a complex is not substitute by other ligand ~~is~~ easily is substitution takes place slowly, then it is called inert complex.

③ ~~Inert complex~~

Thermodynamically stable complex may be inert or labile complex. Thermodynamically unstable complex may be inert or labile.

④ Inert complex have high activation energy, i.e. high energy path way whereas thermodynamically stable complex have large ΔG , negative value of ΔG .



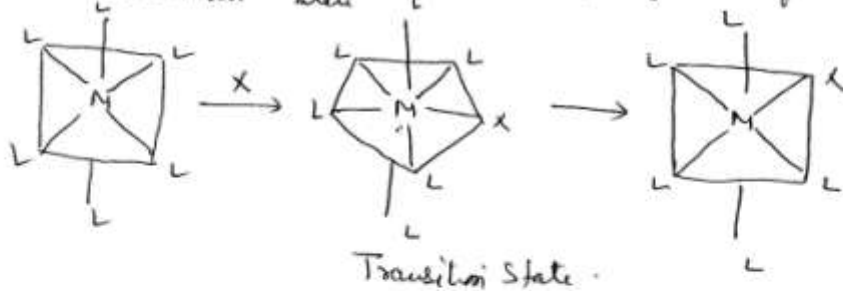
All these three complexes are extremely stable thermodynamically, however they have quite different kinetic stability when CN is replaced by radio carbon labelled ^{14}CN .

Factors affecting the lability and inertness of a complex:

(i) Outer orbital complex: Generally outer orbital complexes sp^3d^2 are more labile than inner orbital complex (d^2sp^3). This is because of the weakness of bond of outer orbital complex due to the d orbital used is from the higher principal quantum number than inner orbital complex. So exchange of ligands can get rapidly.

(ii) Inner orbital complex:

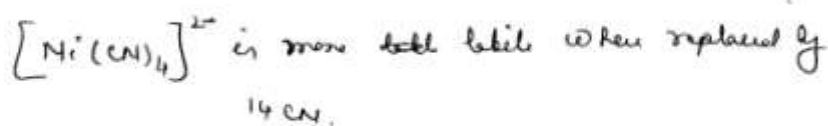
Inner orbital complex are generally inert, and if it is labile then there exists at least one vacant t_{2g} orbital to accept the lone pair donated by the incoming ligand & forming an unstable transition state.



(iii) Geometry of the complex :-

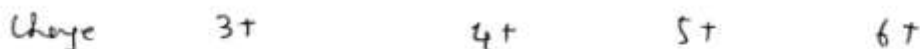
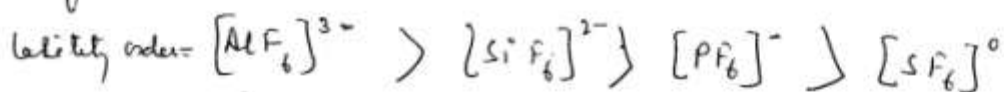
90° of the geometry of the complex is square planar, then it is more labile than the oct complex because there are two sides up + below that incoming ligand can enter easily. So because of the presence of sufficient room around the metal ion for the entry of the incoming ligand, to form a 5-coordinated activated complex, 4 coordinated square planar complex is more labile, whereas no such space is observed in octahedral complex. So it is more inert compare to square planar.

Therefore



(iv) Charge of the central atom :-

Increases the charge of the central atom increases the inertness of the complex.



(v) Radius of the central atom :-

[ionic radius \propto lability (more)]

Lability increases with the increases of size of the central metal atom.

