Lability And Inertness Of Octahedral Complexes:-

Labile Complexes:- Complexes which permit quick exchange of one or more ligands from their coordination sphere by other ligands are called Labile complexes. Half-life $(t_{1/2})$ of labile complexes for substitution reaction is less than one minute.

Inert Complexes:- Complexes which either do not permit exchange of ligands or in which the exchange of ligands is slow are known as inert complexes. Half-life $(t_{1/2})$ of inert complexes for substitution reaction is greater than one minute.

Lability and inertness can be measured in the form of kinetic stability. Kinetic stability can be refers to the rate of reaction which is governed by its activation energy, E_a or rate constant. Kinetic stability relates to how fast compounds reacts rather than to how stable it is.

The thermodynamic stability refers to the tendency of a complex to exist under equilibrium conditions and it is related to the change in free energy, enthalpy and entropy of reaction. The compound may be unstable with respect to particular condition or reagent such as heat, light, acid or base.

The kinetic stability (lability and inertness) refers to the rate of reaction and stability of the reactions such as substitution and electron transfer reaction.

Thermodynamics and kinetics stability will discusses with some suitable example the complexes $[Ni(CN)_4]^{2^-}$, $[Mn(CN)_6]^{3^-}$ and $[Cr(CN)_6]^{3^-}$. All these complexes are thermodynamically stable but kinetically stability is different.

$$[\operatorname{Ni}(\operatorname{CN})_4]^{2-} + 4^{14}CN^{-} \xrightarrow{\operatorname{Very fast}} [\operatorname{Ni}({}^{14}CN)_4]^{2-} + 4\operatorname{CN}^{-} t_{1/2} = 30 \operatorname{sec}$$

$$[Mn(CN)_{6}]^{3-} + 6^{14}CN^{-} \xrightarrow{slow} [Mn(^{14}CN)_{6}]^{3-} + 6CN^{-} t_{1/2} = 1 hr$$

$$\left[\operatorname{Cr}(\operatorname{CN})_{6}\right]^{3^{-}} + 6^{14}CN^{-} \xrightarrow{slowest} \left[\operatorname{Cr}\left({}^{14}CN\right)_{6}\right]^{3^{-}} + 6\operatorname{CN}^{-} t_{1/2} = 24 \text{ days}$$

If we consider the example $[Co(NH_3)_6]^{3+}$ complex ion is inert to substitution but it is thermodynamically unstable in acid solution.

 $[Co(NH_3)_6]^{3+}+6H_3O^+ \longrightarrow [Co(H_2O)_6]^{3+}+6NH_4^+$ The formation constant of this reaction is very large (10³⁰). On the other hand it takes several days at room temperature to form $[Co(H_2O)_6]^{3+}$ complexes.

Interpretation of lability and inertness of transition metal complexes:-

(1) Valence bond theory: - According to VBT

- Transition metal complexes undergoing substitution reaction through the dissociation SN¹ mechanism would be labile if the bond holding central atom ion are comparatively weak and would be inert when such bonds are comparatively strong.
- All the nd orbital have higher energy than (n-1)d orbital. The outer orbital octahedral complexes in which metal ion utilise ns,np³,nd² hybridised orbitals for metal ligand bonding would weaker than the

bond form with $(n-1)d^2$, ns, np^3 hybride orbital. Thus it is known as inner orbital complexes.

- According to VBT all outer orbital complexes are labile and inert orbital complexes would be inert if substitution reaction proceed through SN¹ mechanism.
- In the inner orbital complexes the dissociation reaction proceed via SN^2 mechanism.

Lability and inert octahedral complexes according to Valence Bond Theory:- According to VBT

- (I) Outer orbital complexes which involves sp^3d^2 hybridisation.
- (II) Inner orbital complexes which result from d^2sp^3 hybridisation. The two d orbital in the bond formation is dx^2-y^2 and dz^{2+} .
 - (1) Outer Orbital Octahedral Complexes:-

Outer Orbital Octahedral Complexes (sp³d² hybridisation) are generally labile e.g. octahedral complexes of $Mn^{2+}(3d^5)$, $Fe^{2+}(3d^6)$, $Fe^{3+}(3d^5)$, $Co^{2+}(3d^7)$, $Ni^{2+}(3d^8)$, $Cu^{2+}(3d^9)$ and $Cr^{2+}(3d^4)$ exchange ligands rapidly thus labile. By VBT sp³d² have weak bond than d²sp³.

(2) Inner Orbital Octahedral complexes:-

Inner Orbital Octahedral complexes are formed by d^2sp^3 hybridisation. Six hybride orbitals are filled with the six electron pair donated by six ligands. The labile and inertness of inner orbital octahedral complex shown by following points.

(a) In the labile inner orbital octahedral complexes there is at least one d-orbital of t_2g set empty so that this empty d-orbital may be used to accept the electron pair from the incoming ligand in forming transition state (unstable intermediate) with coordination number of seven.

The reaction will be very fast.



(b) In the inert inner orbital Oh complexes every d orbital of t₂g set (dxy,dyz,dxz) contains at least one electron.

| Inner orbital labile Oh complexe | d^0, d^1, d^2 | |
|----------------------------------|------------------------|--|
| Inner orbital inert Oh complexe | s d^3, d^4, d^5, d^6 | |

Labile and Inert Oh Complexes According to Crystal Field Theory:-

Crystal Field Activation Energy (CFAE):-

Crystal Field Activation Energy is defined as the change in the crystal field stabilization energy (CFSE) when the reacting complex is transformed into the transition state (i.e. the intermediate). Thus CEAE = CESE of intermediate. CESE of meeting complexes

CFAE = CFSE of intermediate - CFSE of reacting complexes

According to Crystal Field Theory

- (1) If the CFSE of the activated complex is greater than that of octahedral complex or CFAE is negative or zero or low the reacting complex require less energy for its transformation into intermediate thus it becomes labile.
- (2) If the calculated CFAE is high , the reacting complex would require more energy for its transformation into the intermediate.

In the octahedral complex when substitution reaction proceed vai SN^1 mechanism then intermediate is five coordinated square pyramidal transition state.

when substitution reaction proceed val SN^2 mechanism then transition intermediate is seven coordinated pentagonal bipyramidal complexes.

The octahedral complexes formed by the ions for which there is large loss in CFSE are least labile such complexes are inert.

| System | weak field | complexes(hig | h spin | Strong field | complexes(low | v spin |
|----------------|-------------------|---------------|--------|-------------------|---------------|--------|
| | complex) CFSE For | | | complex) CFSE For | | |
| | Oh(CN=6) | Squ.py(CN=5) | CFAE | Oh. (CN.=6) | Squ.py(CN=5) | CFAE |
| d^0 | 0 | 0 | 0 | 0 | 0 | 0 |
| d^1 | -4 | -4.57 | -0.57 | -4 | -4.57 | -0.57 |
| d^2 | -8 | -9.14 | -1.14 | -8 | -9.14 | -1.14 |
| d^3 | -12 | -10.00 | 2.00 | -12 | -10.00 | 2.00 |
| d^4 | -6 | -9.14 | -3.14 | -16 | -14.57 | 1.43 |
| d^5 | 0 | 0 | 0 | -20 | -19.14 | 0.86 |
| d^6 | -4 | -4.57 | -0.57 | -24 | -20.00 | 4.00 |
| d^7 | -8 | -9.14 | -1.14 | -18 | -19.14 | -1.14 |
| d^8 | -12 | -10.00 | 2.00 | -12 | -10.00 | 2.00 |
| d ⁹ | -6 | -9.14 | -3.14 | -6 | -9.14 | -3.14 |
| d^{10} | 0 | 0 | 0 | 0 | 0 | 0 |

Table:- CFAE (inDq) of Octahedral complexes undergoing SN¹ Reaction through formation of square pyramidal complexes as intermediates.

From the above table we can conclude that

- Both high spin and low spin octahedral complexes of d⁰, d¹, d², ions will react rapidly i.e. labile complexes.
- According to VBT inner orbital complexes of d³, d⁴, d⁵ and d⁶ are inert. These inner orbital complexes are called low spin or spin paired complexes by CFT. CFT also predict that low spin complexes of these ions are also inert whether the mechanism is assumed to be SN¹ or SN².

Order of inertness = $d^6 > d^3 > d^4 > d^5$ or Order of reactivity= $d^6 < d^3 < d^4 < d^5$

Both high spin and low spin octahedral complexes of d^8 ion (Ni²⁺) are inert because CFAE is positive either by strong field or weak field ligands but in case of VBT d^8 ion $(3d_{xy}^2, 3d_{yz}^2, 3d_{xz}^2, 3d_{x2-y2}^1, 3d_z^2)$ will form outer orbital complexes which will be labile.

In case of d⁸ ions VBT and CFT give different predictions.

H.S. and L.S. complexes of d^{10} are labile. In H.S. complexes d^0 , d^1 , d^2 , d^4 , d^5 , d^6 , d^7 , d^9 and d^{10} , configuration are labile in nature.

| System | weak field | complexes(hig | h spin | Strong field | complexes(low | v spin |
|----------------|-------------------|---------------|--------|-------------------|---------------|--------|
| | complex) CFSE For | | | complex) CFSE For | | |
| | Oh(CN=6) | Pentagonal | CFAE | Oh. (CN.=6) | Pentagonal | CFAE |
| | | bipyramidal | | | bipyramidal | |
| d^0 | 0 | 0 | 0 | 0 | 0 | 0 |
| d^1 | -4 | -6.08 | -2.08 | -4 | -6.08 | -2.08 |
| d^2 | -8 | -8.68 | -0.68 | -8 | -8.68 | -0.68 |
| d^3 | -12 | -10.20 | 1.80 | -12 | -10.20 | 1.80 |
| d^4 | -6 | -8.79 | -2.79 | -16 | -16.26 | -0.26 |
| d^5 | 0 | 0 | 0 | -20 | -18.86 | 1.14 |
| d^6 | -4 | -6.08 | -2.08 | -24 | -20.37 | 3.63 |
| d^7 | -8 | -8.68 | -0.68 | -8 | -8.68 | -0.68 |
| d^8 | -12 | -10.20 | 1.80 | -12 | -10.20 | 1.80 |
| d ⁹ | -6 | -8.79 | -2.79 | -6 | -8.79 | -2.79 |
| d^{10} | 0 | 0 | 0 | 0 | 0 | 0 |

Table:- CFAE (in Dq) of Octahedral complexes undergoing SN^2 Reaction through formation of Pentagonal Bipyramidal intermediates in octahedral substitution reaction .

From both table data we conclude that

 d^3 (both L.S. and H.S.) and spin paired d^5 and d^6 (and to some extent d^4) would be slow to react by SN^1 and SN^2 mechanism similarly oh complexes with metal ion configuration of d^8 (e.g. complexes of NI(II)) would be slow.

 d^0 , d^1 , d^2 spin free d^4 , d^5 , d^6 , d^7 , d^9 and d^{10} would be labile by either of the two mechanism.