Title of Unit: Reaction kinetics and Mechanism

Module Name: Lability and inertness of octahedral complexes, Taube's classification

THERMODYNAMIC and KINETIC STABILITY

VBT: Inner and Outer orbital complexes.

CFT approach: Crystal field Activation Energy

INTRODUCTION

In Metal Complexes there are two types of stability,

- THERMODYNAMIC STABILITY **and**
- KINETIC STABILITY

On the basis of Thermodynamic stability, Complexes are classified as, **Stable complexes**: Retain their identity in solution. **Unstable Complexes:** Reversibily dissociate in solution.

Henry Taube, who studied the mechanisms of ligand exchange reactions, classified transition metal complexes as **labile** if their reaction half-life was one minute or less, and **inert** if they took longer to react.

$[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$

These cyano complexes are stable from thermodynamic point of view, kinetically they are different. Rates of exchange of radiocarbon labeled cyanide vary much.

$[Ni(CN)_4]^{2-}$exchanges cyanide ions rapidly in 30s

$[Mn(CN)_6]^{3-}$ exchanges moderately in 1 hour

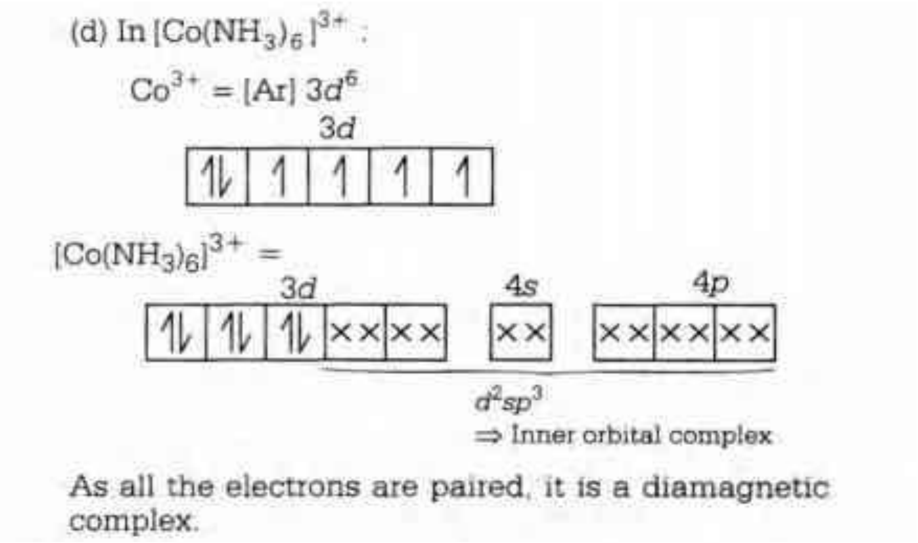
$[Cr(CN)_6]^{3-}$ is somewhat inert in ≈ 24 days

In the first transition series, virtually all octahedral complexes, are normally labile.
Except those of Co(III), Cr(III) and sometimes Fe(II),
$[Co(NH_3)_6]^{+3}$ is thermodynamically unstable, but kinetically it is inert
The complex in solution remains undecomposed even over a period of several days, NH_3 not exchanged by H_2O.

INTERPRETATION OF LABILITY AND INERT TRANSITION METAL COMPLEXES.

VALENCE BOND THEORY
CRYSTAL FIELD THEORY
Interpretation of Lability and Inertness of Transition Metal Complexes on the basis of **VBT** and CFT.
All outer orbital complexes would be labile and all inner orbital complexes would be inert if substitution reaction proceeds through S_N1 mechanism.

VALENCE BOND THEORY, the octahedral complexes are of two types; 1) inner orbital complexes d^2sp^3 hybridisation**, inert**.
and 2) outer orbital complexes sp^3d^2 hybridization**, labile**
This lability is correlated to the weakness of the bonds of sp^3d^2 as compared to d^2sp^3 bonds.



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

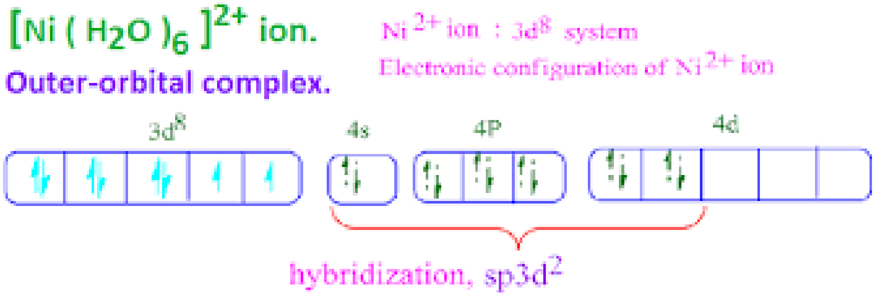
$Co^{3+} = [Ar]\ 3d^6$

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

d^2sp^3

⇒ Inner orbital complex

As all the electrons are paired, it is a diamagnetic complex.

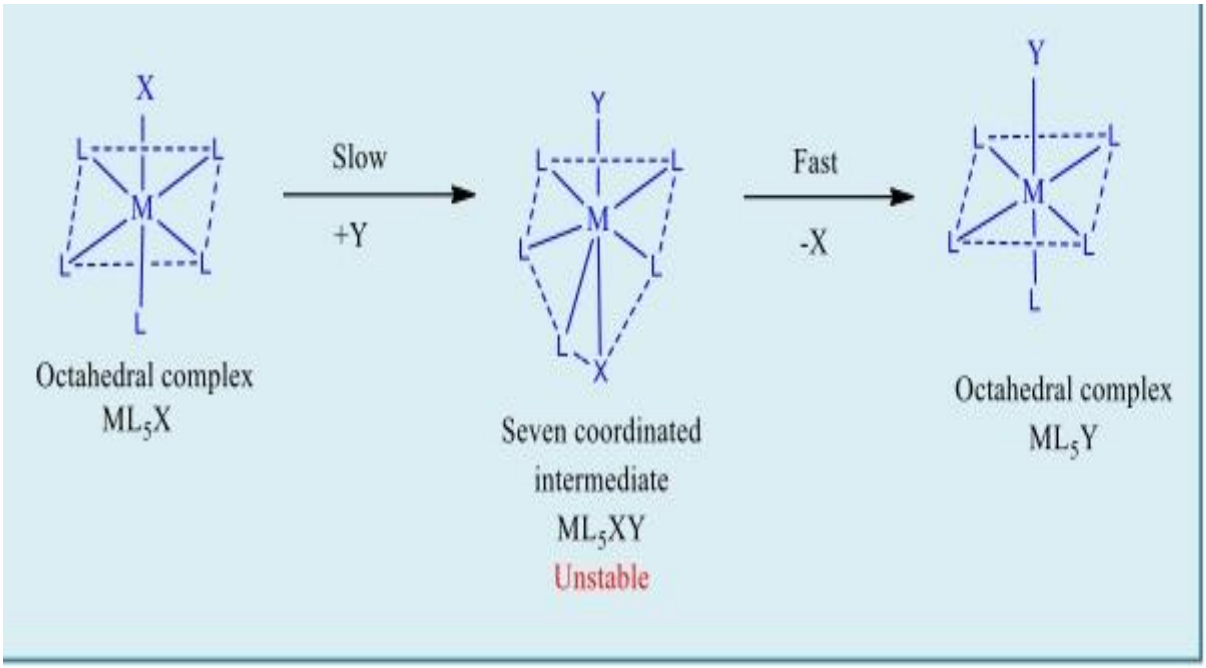


In the case of inner orbital complexes, if all the three t2g levels are filled either singly or doubly, then they are labile.

$[V(H_2O)_6]^{3+}$ an inner orbital complex, d^2 configuration contains two electrons in the t_{2g} set, hence, one orbital will be vacant, to accept the electron pair donated by the incoming ligand to form a 7-coordinated intermediate which is less stable.

To get itself stabilized, one of the original six ligands is expelled leading to a substitution product and **hence $[V(H_2O)_6]^{3+}$ is labile**.

A complex with fewer than three d electrons , d^0 d^1 d^2 will be relatively labile.



But in $[Cr(H_2O)]^{3+}$

d^3 configuration there is no vacant d level to accept the electron pair donated by the incoming ligand, hence $[Cr(H_2O)]^{3+}$ is inert.

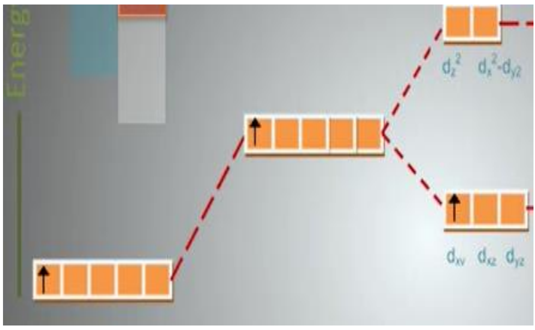
The Taube definition of lability is a useful one for classifying reactions into those that have low and high activation energies.

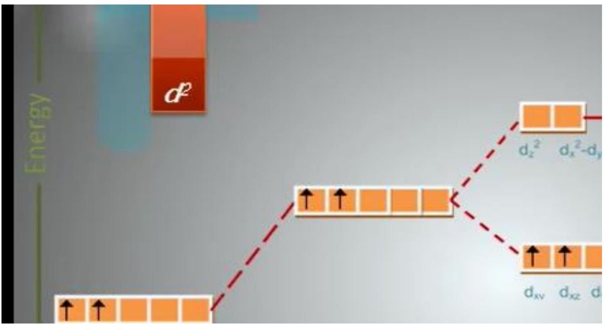
Crystal Field Stabilization Energy (CFSE) plays a key role in determining the activation energy and therefore the rate of ligand substitution.

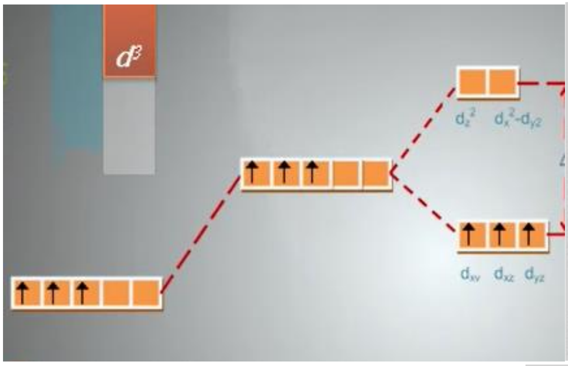
According to Taube, the degree of lability or inertness of a transition metal complex can be correlated with the d electronic configuration of the metal ion.

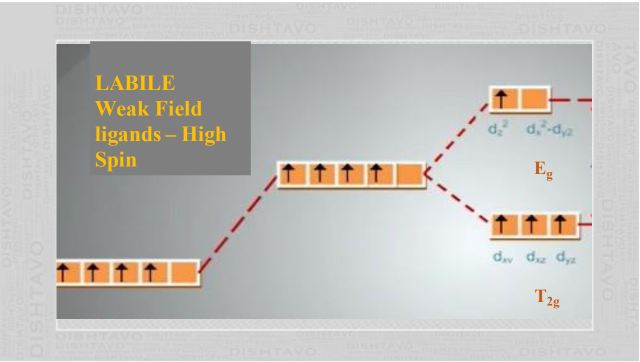
A complex with fewer than three d electrons or one or more eg* electrons should be relatively labile and

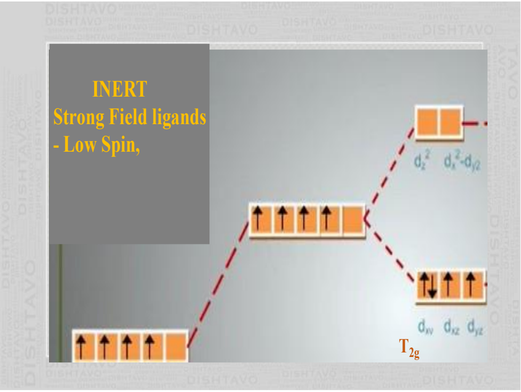
A complex with any other electronic configuration should be relatively inert.

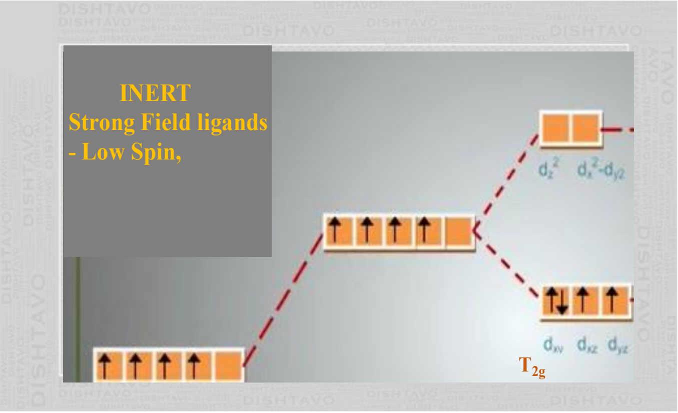












In Crystal Field Theory, Crystal Field Activation Energy is defined as the change in the Crystal Field Stabilisation Energy when the reacting complex is transformed into the transition state (intermediate).

CFAE = CFSE of intermediate – CFSE of reacting complex

Thus, it infers that octahedral complexes having negative or zero CFAE would be LABILE whereas those having positive CFAEs would be INERT

References and Credits

1. Principles of INORGANIC CHEMISTRY – G. S. Sodhi

2. Selected Topics in INORGANIC CHEMISTRY-for BSc (Hons) Dr. Wahid U. Malik et al

3. Principles of INORGANIC CHEMISTRY – B.R. Puri, L.R.Sharma, K.C. Kalia. 31st Edition