

# M.Sc. Semester-I, Paper: CC-01 (Inorganic Chemistry)

## Unit-4 Reaction Mechanism of Transition metal Complexes.

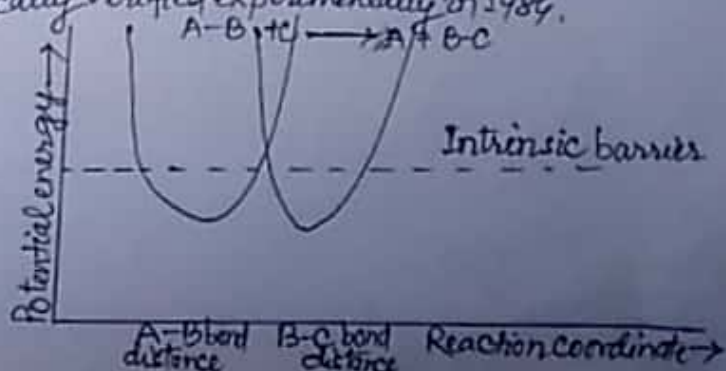
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### ⇒ Marcus-Hush Theory

Marcus theory is originally developed by Rudolph A. Marcus (in 1950) to explain the rates of electron transfer reactions. The rate at which an electron can move or jump from one chemical species (called an electron donor) to another (called the electron acceptor). It was originally formulated to address outer sphere electron transfer reactions in which the two chemical species only change in their charge with an electron jumping (e.g. the oxidation of an ion like  $Fe^{2+}/Fe^{3+}$ ), but do not undergo large structural changes. It was extended to include inner sphere electron transfer contributions, in which a change of distances or geometry in the solvation or coordination shells of two chemical species is taken into account (the Fe-O distances in  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{3+}$  are different)

For electron transfer reactions without making or breaking bonds, Marcus theory takes place of Eyring's transition state theory which has been derived for reactions with structural changes. Both theories lead to rate equations of the same exponential form. However, whereas in Eyring theory the reaction partners become strongly coupled in the course of the reaction to form a structurally defined activated complex, in Marcus theory they are weakly coupled and retain their individuality. It is the thermally induced reorganization of the surroundings, the solvent (outer sphere) and the solvent sheath or the ligands (inner sphere) which create the geometrically favourable situation prior to and independent of the electron jump.

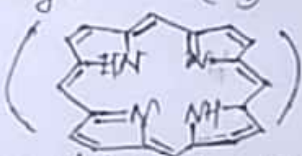
The original classical Marcus theory for outer sphere electron transfer reactions demonstrates the importance of the solvent and leads the way to the calculation of the Gibbs free energy of activation, using the polarization properties of the solvent, the size of the reactants, the transfer distance and the Gibbs free energy ( $\Delta G^\circ$ ) of the redox reaction. The most startling result of Marcus theory was the 'inverted region', whereas the reaction rates usually become higher with increasing exergonicity of the reaction, electron transfer should, according to Marcus theory become slower in the very negative  $\Delta G^\circ$  domain. Scientists researched the inverted region for proof of a slower electron transfer rate for 30 years until it was unequivocally verified experimentally in 1984.



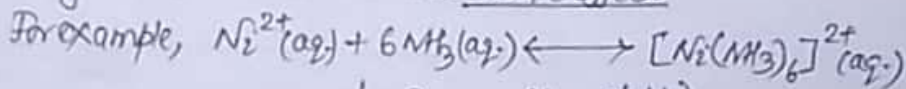
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 It is used to describe a number of important processes in chemistry and biology, including photosynthesis, corrosion, certain types of chemiluminescence, charge separation in some types of solar cells and more. Besides the inner and outer sphere applications. It has been extended to address heterogeneous electron transfer.

### ⇒ Chelate effect

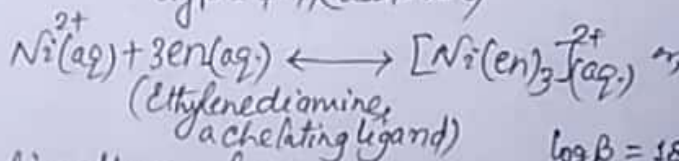
Chelation is a type of bonding of ions and molecules to metal ions. It involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand and a single central atom. These ligands are called chelants or chelating agents, chelators or sequestering agents.

Examples of some important chelating agents: Ethylenediamine ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ), Gluconic acid ( $\text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_2-\text{COOH}$ ), Glutamic acid ( $\text{HOOC}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{NH}_2$ ), 2,3-dihydroxybenzoic acid ( $\text{HOOC}-\text{C}_6\text{H}_3(\text{OH})_2$ ), Catechol ( $\text{HO}-\text{C}_6\text{H}_4-\text{OH}$ ), Acetylacetonone ( $\text{CH}_3-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\text{CH}_3$ ), Oxime ( $\text{R}_2\text{C}=\text{N}-\text{OH}$ ), Gallic acid ( $\text{HO}-\text{C}_6\text{H}_2(\text{OH})_3-\text{COOH}$ ), Porphine () etc.

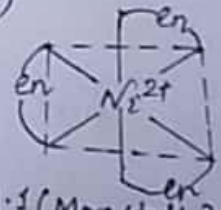
When a ligand attaches to the metal ion in a manner that forms a ring, then the metal-ligand (M-L) association is found to be more stable. In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the Chelate effect.



$\log \beta = 7.99$  (Less stable)



$\log \beta = 18.1$  (More stable)



Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on...

Hence, the order of chelating effect: bidentate < tridentate < tetradentate ...

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar non-chelating (monodentate) ligands for the same metal atom/ion.