

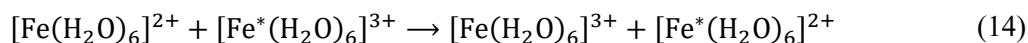
❖ Electron Exchange

On the basis of the mechanism involved, the redox reactions of transition metal complexes have been divided into two types; outer-sphere and inner-sphere. We have already studied the same in the previous section. However, these electron-transfer reactions can also be classified on the basis of the metal centers involved as given below.

- i) The electron transfer between two different oxidation states of the same metal ion. These reactions are generally called as self-exchange reactions.
- ii) The electron transfer between two completely different metal complexes. These reactions are called as the cross-reactions.

The *electron exchange or self-exchange reactions may simply be defined as the redox reactions involving the transfer of electrons between two complexes having the same ligands and metal ions but with different oxidation states.*

In other words, the reactants in electron-exchange reactions are indistinguishable from the products. These reactions result in no net chemical change and can be studied only by special experimental techniques.



All of the above are electron-exchange reactions proceeding via the outer-sphere electron transfer mechanism. The rate measurement of these reactions is quite difficult to record as the reactants are chemically equivalent to the products. Out of various techniques such as isotopic tracer, optical activity and EPR-NMR spectroscopy; isotopic labeling is the most convenient and widely accepted method to study the process of self-exchange. After mixing the reactants, the rate at which the radioactivity disappears in $\text{M}^*(\text{III})$ complex is the rate of electron exchange in the two complexes. Similarly, the rate at which the radioactivity appears in the $\text{M}^*(\text{II})$ complexes can also be used to estimate the rate of electron exchange.

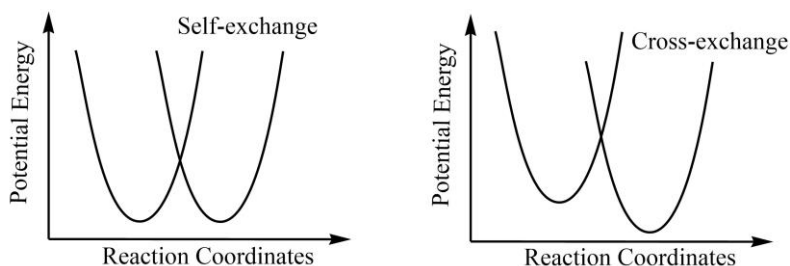


Figure 27. The comparison of potential energy curves of self-exchange and cross-exchange.

Table 2. The values of rate constants for some electron-exchange processes of type $[\text{ML}_6]^{2+} + [\text{M}^*\text{L}_6]^{3+} \rightarrow [\text{ML}_6]^{3+} + [\text{M}^*\text{L}_6]^{2+}$.

Complex	Electronic configuration $\text{M(II)} \rightarrow \text{M}^*(\text{III})$		k ($\text{M}^{-1}\text{s}^{-1}$)	T ($^\circ\text{C}$)
$\text{Cr}(\text{H}_2\text{O})_6$	$t_{2g}^3 e_g^1$	$t_{2g}^3 e_g^0$	2×10^{-5}	25
$\text{Fe}(\text{H}_2\text{O})_6$	$t_{2g}^4 e_g^2$	$t_{2g}^3 e_g^2$	4.2	25
$\text{Co}(\text{H}_2\text{O})_6$	$t_{2g}^5 e_g^2$	$t_{2g}^4 e_g^2$	5	25
$\text{Co}(\text{en})_3$	$t_{2g}^5 e_g^2$	$t_{2g}^6 e_g^0$	7.7×10^{-5}	25
$\text{Fe}(\text{phen})_3$	$t_{2g}^6 e_g^0$	$t_{2g}^5 e_g^0$	1.3×10^7	3
$\text{Co}(\text{phen})_3$	$t_{2g}^6 e_g^1$	$t_{2g}^6 e_g^0$	12	25

Now, as the electron-exchange reactions are the simplest type of outer-sphere mechanism; factors like transition-type, orbital overlap, and reorganization of electronic configuration can be used to explain the large differences in the electron-exchange rates listed in Table 2.

In order to get a wider view of the mechanism involved in electron-exchange, we need to recall the Frank-Condon principle which says the electronic rearrangements are so rapid that the nuclei can be considered as stationary. Moreover, the electron transfer from one complex to another is expected only when it has the same energy in both of the sites. Hence, the activation energy to achieve this goal is mainly governed by nuclear rearrangements. Consider the following reaction:



The potential energy curves for the reactants and products should be parabolic because the metal–ligand deformations are almost harmonic in nature. The activated complex is present at the intersection point of the two curves.

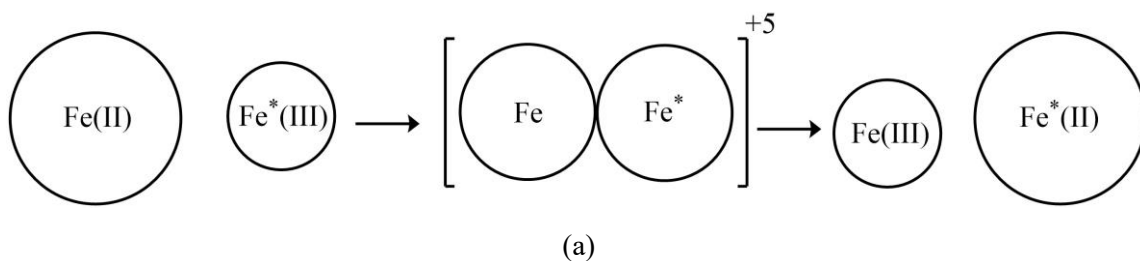


Figure 28. Continued on the next page...

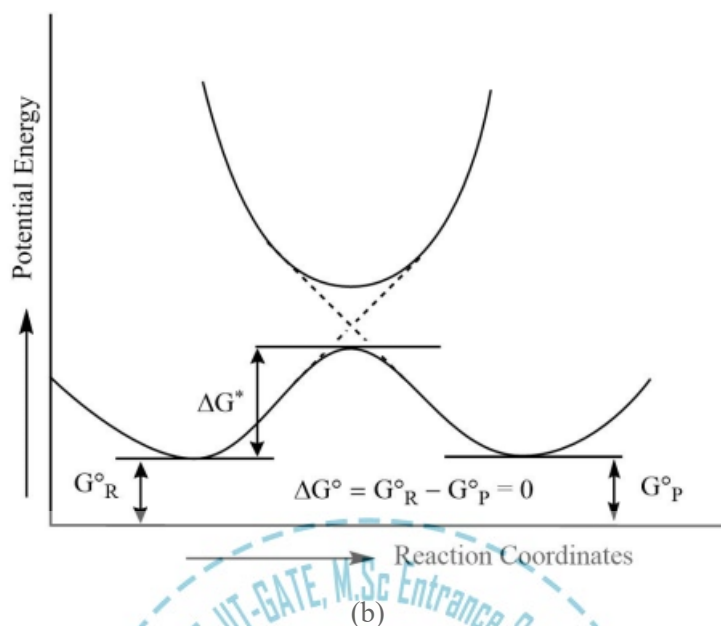


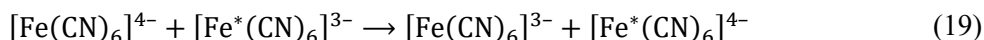
Figure 28. The (a) reaction course and (b) potential energy curve for electron-exchange reactions.

During the formation of activated complex, the Fe(II) bonds shorten while the Fe*(III) bonds lengthen which facilitates the transfer of electron. It is worth noting that the Gibbs free energy change for self-exchange reactions is zero but free energy of activation is still a non-zero term.

Rudolph A. Marcus derived an equation using the first principle to predict the overall rate constant for outer-sphere electron transfer reactions from the self-exchange rate constants of each of the redox couples involved and overall equilibrium constant. The equation can be given as:

$$k = [k_1 k_2 K f]^{1/2} \quad (18)$$

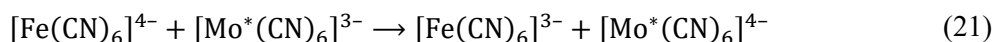
Where k_1 and k_2 are rate constants for two electron-exchange reactions and K is the equilibrium constant for the overall reaction. The factor f is a complex parameter composed of the rate constants and has been incorporated to correct the free energy differences of the two reactants. Consider the example,



$$k_1 = 7.4 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$$



$$k_2 = 3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$$



$$K = 1.0 \times 10^2$$

Now, putting the values of k_1 , k_2 and K from equation (19), (20) and (21) in equation (18); the value of rate constant for the overall reaction is found to be $4 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; and it is obviously pretty much comparable to the experimental value of $3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$.

In 1992, R. A. Marcus received the Nobel Prize in the field of Chemistry for his work on the theory of electron transfer reactions occurring in chemical systems. His theory is also named after him, the Marcus theory, and it provides a kinetic and thermodynamic framework for describing outer-sphere electron transfer reactions involving one electron.



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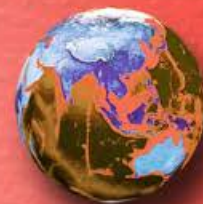
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Table of Contents

CHAPTER 1	11
Stereochemistry and Bonding in Main Group Compounds:	11
❖ VSEPR Theory	11
❖ $d\pi-p\pi$ Bonds	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems	42
❖ Bibliography	43
CHAPTER 2	44
Metal-Ligand Equilibria in Solution:	44
❖ Stepwise and Overall Formation Constants and Their Interactions	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems	68
❖ Bibliography	69
CHAPTER 3	70
Reaction Mechanism of Transition Metal Complexes – I:	70
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes	89
❖ Electrophilic Attack on Ligands	92
❖ Problems	94
❖ Bibliography	95

CHAPTER 4	96
Reaction Mechanism of Transition Metal Complexes – II:	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
CHAPTER 5	123
Isopoly and Heteropoly Acids and Salts:	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions	123
❖ Problems.....	152
❖ Bibliography.....	153
CHAPTER 6	154
Crystal Structures:	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI ₂ , BiI ₃ ; ReO ₃ , Mn ₂ O ₃ , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
CHAPTER 7	180
Metal-Ligand Bonding:	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ π -Bonding and Molecular Orbital Theory	198
❖ Problems.....	212
❖ Bibliography.....	213

CHAPTER 8	214
Electronic Spectra of Transition Metal Complexes:	214
❖ Spectroscopic Ground States	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States).....	248
❖ Calculation of Dq , B and β Parameters	280
❖ Effect of Distortion on the d -Orbital Energy Levels	300
❖ Structural Evidence from Electronic Spectrum	307
❖ Jahn-Teller Effect	312
❖ Spectrochemical and Nephelauxetic Series	324
❖ Charge Transfer Spectra	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems	340
❖ Bibliography	341
CHAPTER 9	342
Magnetic Properties of Transition Metal Complexes:	342
❖ Elementary Theory of Magneto-Chemistry	342
❖ Guoy's Method for Determination of Magnetic Susceptibility	351
❖ Calculation of Magnetic Moments	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field	362
❖ Application of Magneto-Chemistry in Structure Determination	370
❖ Magnetic Exchange Coupling and Spin State Cross Over	375
❖ Problems	384
❖ Bibliography	385
CHAPTER 10	386
Metal Clusters:	386
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes.....	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC).....	417
❖ Problems.....	424
❖ Bibliography.....	425
CHAPTER 11.....	426
Metal-II Complexes:	426
❖ Metal Carbonyls: Structure and Bonding.....	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems.....	469
❖ Bibliography.....	470
INDEX.....	471



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