

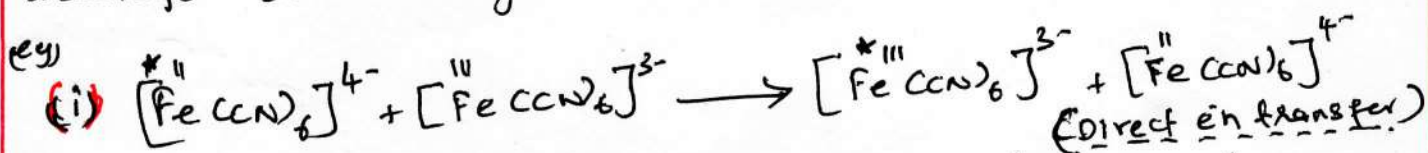
UNIT-III - Coordination Chemistry - IV (Redox reactions)

References:

1. 'Concepts and Models of Inorganic Chemistry' - Douglas, McDaniel & Alexander
2. 'Inorganic Chemistry' - Purcell & Kotz
3. Shriver & Atkins' Inorganic Chemistry - Atkins, Overton, Rourke, Weller, Armstrong
4. 'Inorganic Chemistry' - Principles of structure and Reactivity - James E. Huheey, Keiter, Richard & Medhi
5. 'Inorganic chemistry' - Gary L. Miessler & Donald A. Tarr.
6. 'Adv. Inorganic Chemistry' - Gurdeep Raj (Vol-II)
7. 'Concise Coordination Chemistry' - R. Gopalan & V. Ramalingam.
8. 'Principles of Inorganic Chemistry' - B.R. Puri, L.R. Sharma & K.C. Kalia.

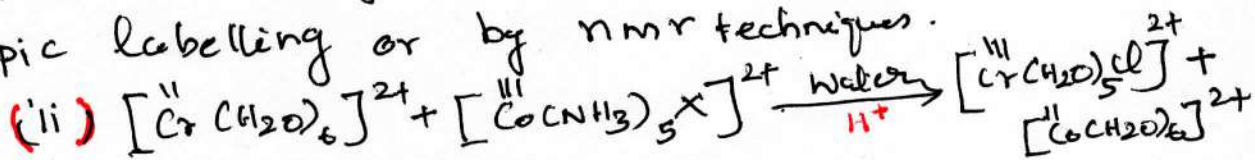
Electron transfer Reactions (Redox ~~redox~~ reactions)

Oxidation-reduction reactions involving transition metal complexes can occur either through atom or group transfer or through direct electron transfer



Here an electron transfer occurs between two complexes of the same metal, the metal being present in two different oxidation states in the two reactants. There is no net chemical changes during this e<sup>-</sup> transfer reaction as all the concentrations apparently remain unchanged. No net free energy change occurs ( $\Delta G^\ddagger = 0$ ) in this reaction.

These are called electron-exchange reactions. These reactions can be followed indirectly, for example, by isotopic labelling or by NMR techniques.



In these e- transfer reactions, atom

transfer also takes place. In these reactions, there is net chemical change and so, they can be followed by many standard chemical and physical methods including chemical analysis of the products, stopped-flow spectrophotometry, etc.

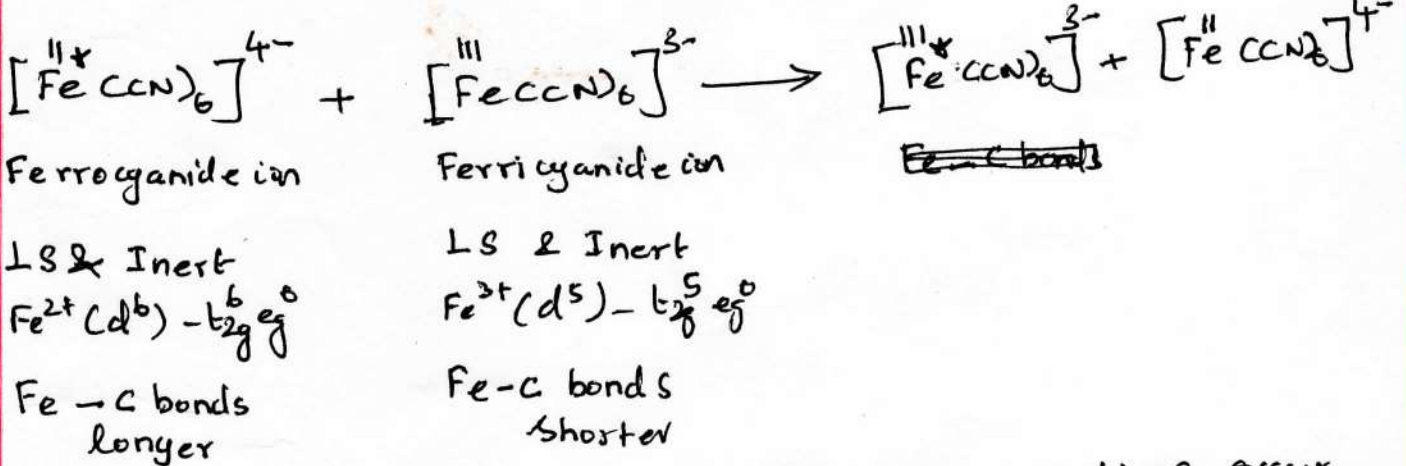
Mechanism of one electron transfer Reactions:

Most of one e- transfer reactions are believed to occur by two mechanisms.

- (i) Non-bridging (or) Direct electron transfer (or) Outer Sphere Mechanism (or) Tunnelling mechanism.
- (ii) Bridging (or) Inner-Sphere mechanism.

I Direct electron transfer (or) Outer Sphere Mechanism (OSM)

(or) Tunnelling Mechanism



① Outer sphere electron transfer reactions occur between those metal ions which are either both inert with their coordination shells saturated or one of the reactant is inert with its coordination shell saturated and none of the coordinated ligands should be a bridging ligand.

② In this mechanism, the electron effectively hops across from the reductant (R) to the oxidant (O) and the ligands acts as electron conduction media. The two coordination spheres remain unaffected. The ligands in the two reactants remain as such and bonds (M-L) are ~~neither~~ neither made nor broken. The electron is set to tunnel through the

medium from the reductant to the oxidant.

③ Critical requirement for electron transfer:

In this mechanism, direct transfer of  $e^-$ s occurs. For this process to occur, there is an essential ~~requirement~~ <sup>requirement</sup> which is given by Frank-Condon principle, which states that there can be no appreciable change of atomic arrangement during the time of electronic transition, i.e., very light  $e^-$ s move much more rapidly than much heavier atoms.

So this principle prescribes equal energies for the participating electronic orbitals. In the above example  $([Fe(CN)_6]^{4-} [Fe(CN)_6]^{3-})$ , an  $e^-$  is transferred from  $t_{2g}$  orbital of  $Fe(II)$  to a  $t_{2g}$  orbital of  $Fe(III)$ . The energies of these two orbitals are not equal, because the bond lengths (Fe-C) in  $Fe^{2+}$  and  $Fe^{3+}$  complexes are unequal. If the  $e^-$  transfer occurs without an input of energy, we would obtain the products  $Fe(II)$  with bond lengths characteristics of  $Fe(III)$  and the  $Fe(III)$  complex with bond lengths characteristics of  $Fe(II)$ . Since such a situation is unacceptable, there must be energy input before  $e^-$  transfer.

The energy input causes shortening of bonds in  $Fe(II)$  reactant complex and lengthening of the bonds in  $Fe(III)$  reactant complex, so that the participating orbitals are modified to have the same energy. After the readjustments of the bond lengths (required configuration), the electron jumps (transfer) occurs. The energy involved in the readjustment of bond lengths is small because the geometries of the two reactants are similar.

④ The energy of activation ( $E_a$ ) may be expressed as sum of three terms.

$$E_a^* = \Delta G_e^* + \Delta G_i^* + \Delta G_o^*$$

where

$\Delta G_e^*$  - is the energy required to bring the oxidant and reductant (R) into a configuration in which they are separated by a required distance.   
 ie energy

Tunnelling refers to a process where the  $e^-$ s do not have sufficient energy to overcome the energy barrier but penetrates into or through it.

ie the energy required to overcome coulombic repulsion between the reactants of like charge.

$\Delta G_i^*$  - is the energy required for bond compression and bond stretching to achieve orbitals of equal energy (so-called inner-sphere reorganization energy)

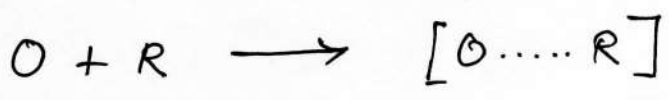
$\Delta G_o^*$  - is the energy required for solvent reorganization (alteration in solvent polarisation) outside the coordination sphere (so-called outer-sphere reorganization energy)

(5) Outer Sphere reactions are first order with respect to each reactant, so the overall order being two.

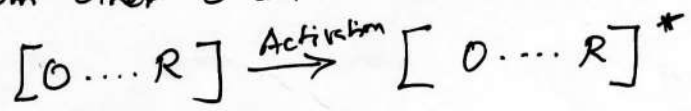
Rate = k [Reductant][Oxidant]

(6) An outer sphere electron transfer can be denoted by the following reaction scheme.

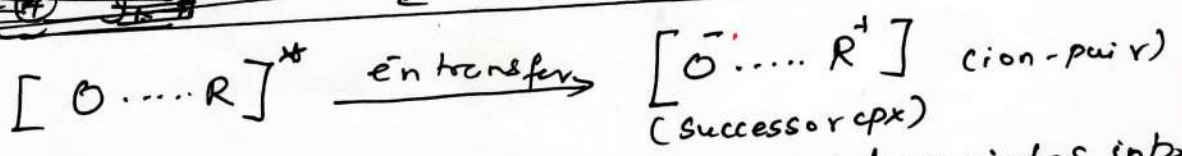
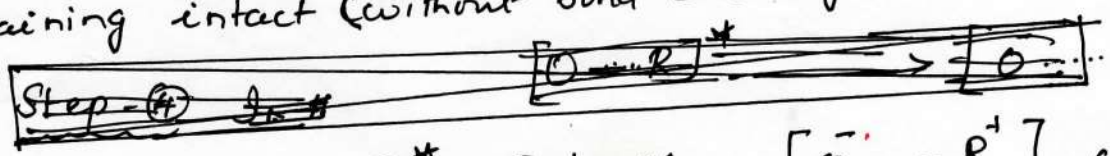
Step-1 The oxidant (O) and the reductant (R) come together to form a precursor complex.



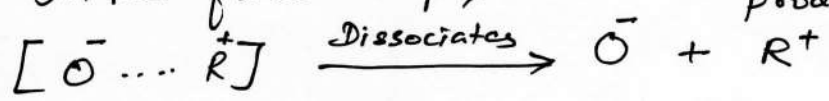
Step-2 In the 2nd step, the precursor complex is activated which is a prerequisite for the reaction. Activation of the precursor complex includes reorganisation of solvent molecules and changes in M-L bond lengths. The energy of activation (Ea) can be acquired by the [O.....R] from other O and R molecules or from the solvent molecules.

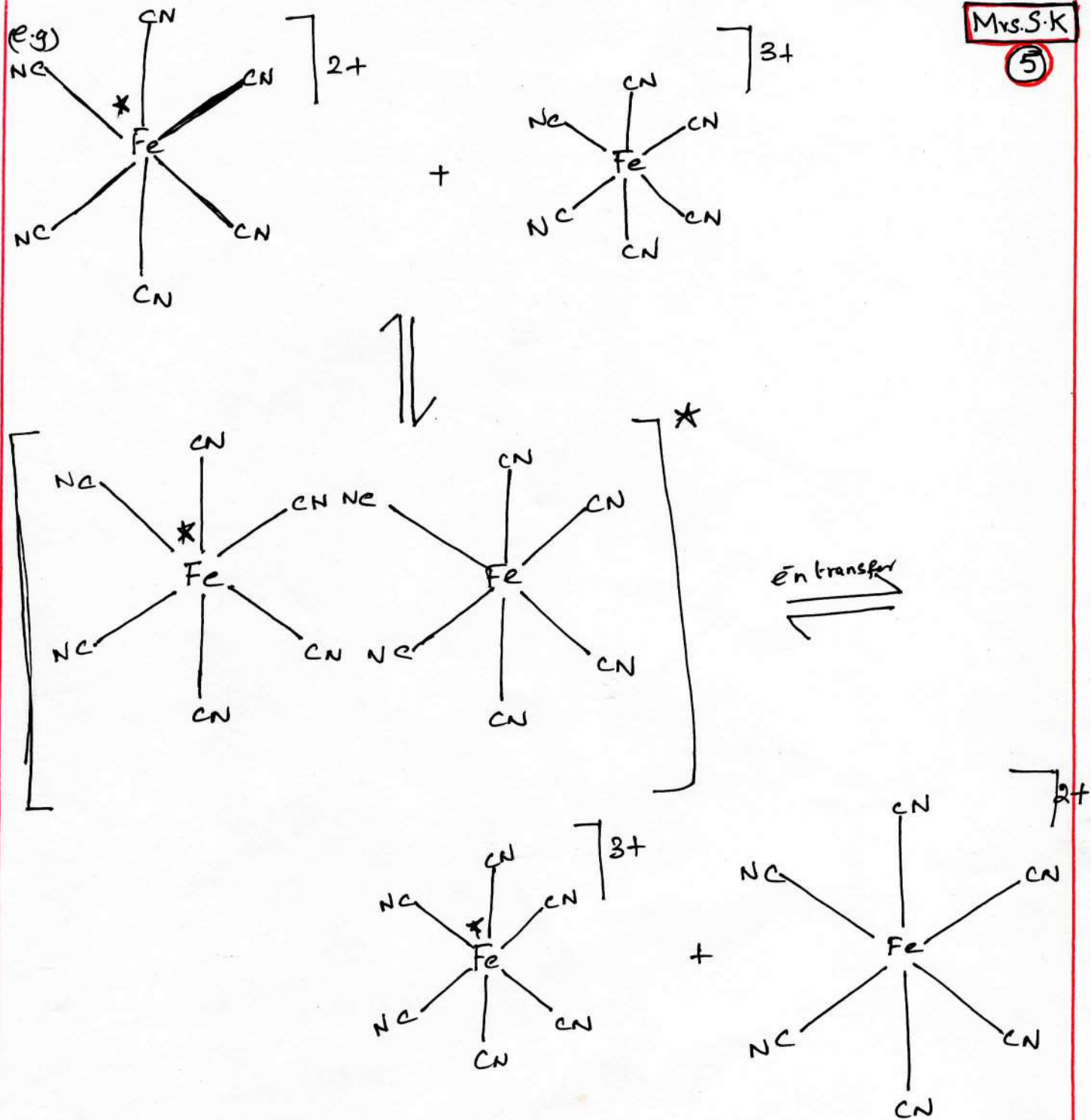


Step-3 Then electron transfer takes place from 'R to O' to form the ion-pair, and the molecular frame work remaining intact (without bond breaking)



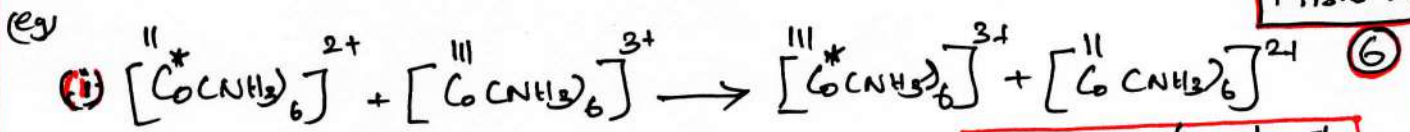
Step-4 In the final step, ion-pair dissociates into product ions.





Factors affecting the rates of Direct electron transfer reactions (OSM)

① In outer sphere reactions, the electron transfer is fast if the changes in M-L bond distance are lesser. If the electron being transferred is present in the 'eg' orbitals the change in bond length (M-L) will be larger, and the rate of OSM reaction is slow. Because, the eg orbitals are antibonding removal of electrons from these orbitals results in a more stable compound with shorter bond distance.



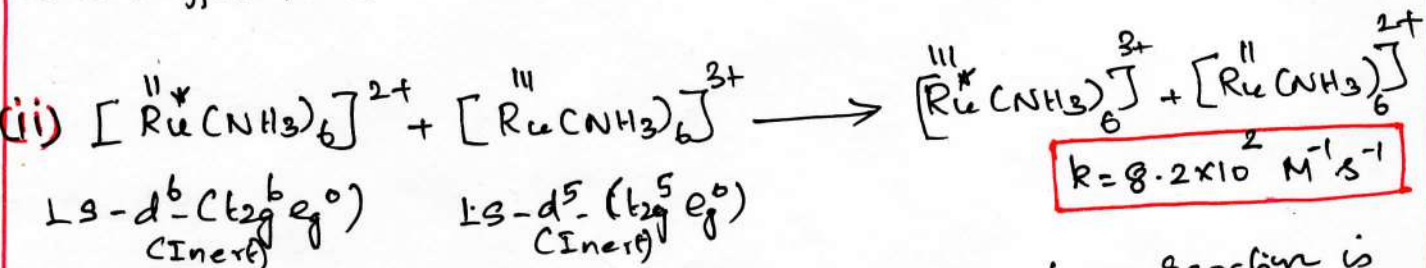
HS- $d^7$  ( $t_{2g}^5 e_g^2$ ) LS- $d^6$  ( $t_{2g}^6 e_g^0$ ) - Inert  
(Labile)

$k = 1 \times 10^{-6} M^{-1} s^{-1}$

Co(II) - N bond length =  $2.114 \text{ \AA}$   
 Co(III) - N bond length =  $1.936 \text{ \AA}$

The rate of outer sphere electron transfer reaction for the above example is very slow because of the following reasons.

- a) Since the Co-N bond distances in the reductant and oxidant complex ions are appreciably different, (bond length difference =  $0.178 \text{ \AA}$ ) considerable energy of activation ( $E_a^*$ ) is required to excite the two reactant ions to have identical Co-N bond distances. (after that only  $e^-$  transfer would occur). So rate is slow.
- b) The  $e^-$  being transferred from  $[Co(CNH_3)_6]^{2+}$  occupies an  $e_g$  orbital (antibonding orbital). which is ~~already engaged in M-L sigma bonding.~~ ( $d_{z^2}, d_{x^2-y^2}$  orbitals along with s p orbitals of N are involved in M-L sigma bonding)  
 $\therefore$  the removal of this  $e_g$  electron from Co(II) would require more energy. So the rate is slow.
- c) The spin states of Co(II) and Co(III) in the reacting complexes are different (HS & LS). So it is spin-forbidden.

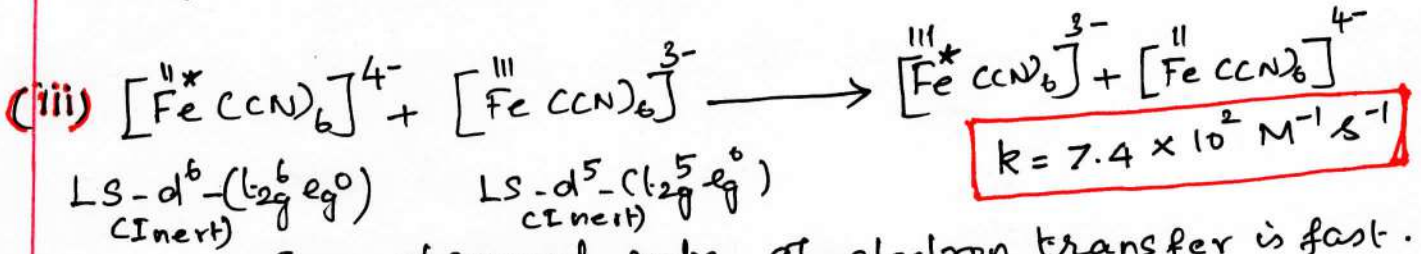


The rate of  $e^-$  transfer for the above reaction is very fast due to the following reasons.

- a) The Ru-N bond lengths ~~different~~ in the two reactant ion are almost the same. The bond length difference is  $0.04 \text{ \AA}$  (very ~~small~~ <sup>low</sup>). Hence very little energy is required to make the Ru-N bond lengths in two complexes identical so that  $e^-$  transfer may occur. So the rate is high.

b) If an electron is removed or added to a non-bonding orbital ( $t_{2g}$ ), the change in the metal-ligand bond length will be the least. So energy of activation is less. Here, the  $e^-$  under transfer is in  $t_{2g}$  orbital ( $Ru(II)-t_{2g}^6$ ) which is not engaged in M-L sigma bonding. So removal of this  $e^-$  from  $Ru(II)$  is very easy.

c) Leaving aside the  $e^-$  that is to be transferred, both the metal ions have the same electron spin. This facilitates the transfer of electrons.



The observed rate of electron transfer is fast.

This may be due to the following reasons.

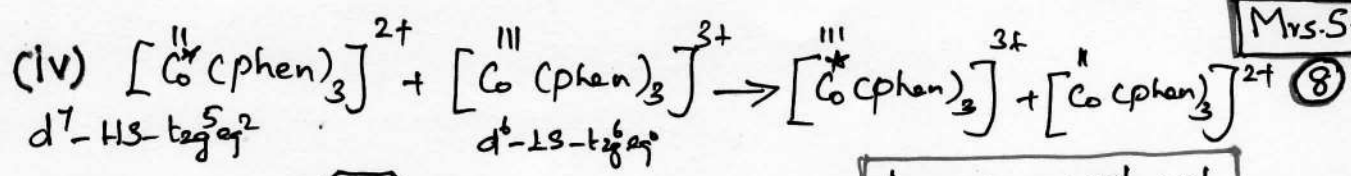
a) The Fe-C bond distances in both the reactant complexes are almost the same. Hence very little energy is required to make the Fe-C distances in the two complex ions identical which is a prerequisite for electron transfer.

b) Leaving aside the  $e^-$  that is to be transferred, both the complex ions have the same electronic spin ( $t_{2g}^5$ ). This facilitates the transfer of electrons.

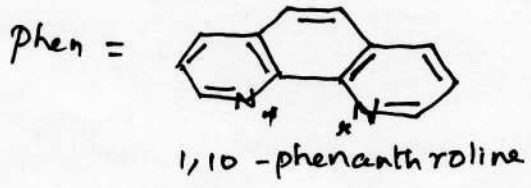
c) The electron to be transferred is present in the non-bonding  $t_{2g}$  orbital ( $Fe^{2+}-t_{2g}^6$ ) which is not engaged in M-L sigma bonding. Therefore the removal of this  $e^-$  from  $Fe(II)$  is easy.

d) The ligand  $CN^-$  is unsaturated ( $e \equiv N^-$ ) and the presence of unsaturated or conjugate ligands on the reductant provide ~~facilitate~~ good pathways for the electron to tunnel through the ligands.

e)  $CN^-$  is a  $\pi$ -acceptor ligand, i.e., it can form  $M \rightarrow L \pi$ -bond by accepting electrons from the  $t_{2g}$  orbitals of the metal ion. Such ligands always stabilize the lower oxidation state of the metal ion ( $Fe^{3+} + e^- \rightarrow Fe^{2+}$ ), which implies that such ligands stabilize the product formed ( $Fe^{2+}$ ) due to the transfer of  $e^-$ .

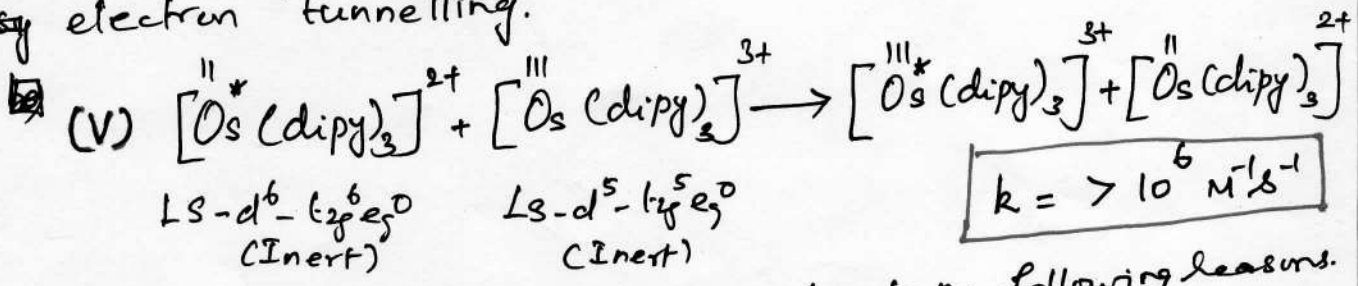


$k = 40 \text{ M}^{-1} \text{ s}^{-1}$



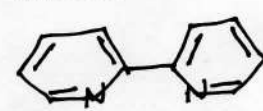
The observed rate for the above  $\text{Co}^{2+}/\text{Co}^{3+}$  OS reaction is many orders of magnitude <sup>(10<sup>7</sup> times)</sup> faster than for the cobalt-amine system. It is due to the following reasons.

1) The nature of the bound ligand has a significant influence on the reaction rate. Phen-ligand is a ligand with  $\pi$ -system provide easy passage of electrons i.e this (phen) ligand is a  $\pi$ -acceptor ligand and it is highly conjugated. This facilitates ~~easy~~ electron tunnelling.



The observed rxn. rate is fast due to the following reasons.

a) The Os-N bond distances in both the complexes are almost the same. Hence very little energy is needed to make the Os-N bond distances in the two complexes identical.

b) The ligand dipeyridine  is a  $\pi$ -acceptor and is highly conjugated. This facilitates electron tunnelling.

c) The  $e^-$  being transferred is present in the non-bonding  $t_{2g}$  orbital which is not engaged in M-L sigma bonding. Hence, this electron can be easily detached from Os(II) metal ion.

d) Except <sup>for</sup> the  $e^-$  which is being transferred, the two metal ions have the same electronic spin. ( $t_{2g}^5 e_g^0$ )

Summary of factors affecting Rn. Rates of OSM

Thus, (i) Electron transfer between ions of the same metal is fast if M-L bond distances in the reductant and the oxidant are very nearly the same. (ii) Electron transfer is fast if  $e^-$ s are able to ~~reach~~ <sup>reach</sup>



the surface of the complex either through unsaturated ligands or through highly conjugated ligands.

(iii) Electron transfer is fast if the ~~oxidation~~ e<sup>-</sup> being transferred is present in a t<sub>2g</sub> orbital and it is slow if it is present in the e<sub>g</sub> orbital.

(iv) Electron transfer is fast if the coordinated ligands present in the system are π-acceptors.

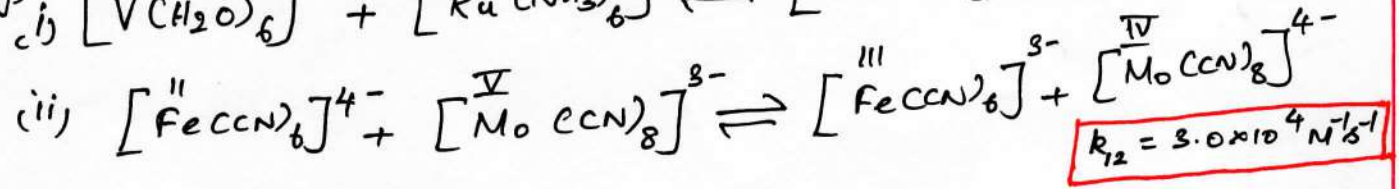
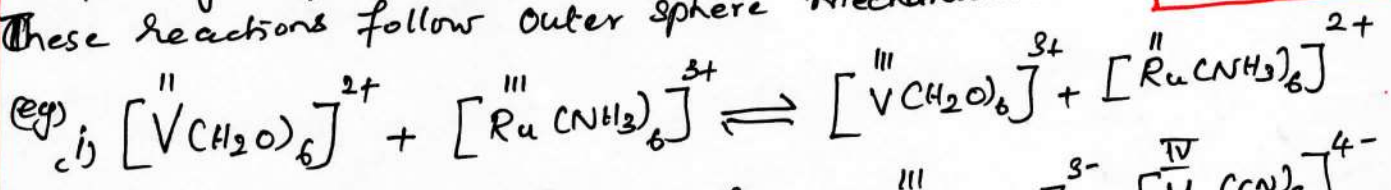
(v) Electron transfer is fast if the e<sup>-</sup> spins of the two complex ions (leaving aside the e<sup>-</sup>s being transferred) are the same.

CROSS REACTIONS (Marcus - Hush Principle)

Marcus Theory (Hetero nuclear Redox reactions)

Direct electron transfer reactions between two completely different complex ions are called cross reactions. These reactions follow outer sphere mechanism.

$k_{12} = 1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$



$k_{12} = 3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$

A cross reaction involves large activation energy ( $E_a^*$ ), however, it is fast because the large  $E_a^*$  requirement is partly compensated by an attendant negative free energy change ( $-\Delta G^*$ ). For cross reaction,  $\Delta G^* < 0$ , i.e., the products are thermodynamically more stable than reactants. In a cross rxn, the rate is maximum when the e<sup>-</sup> is transferred from a π\* to a π\* orbital.

The rate constant of a cross reaction involving OSM can be predicted by an equation proposed by Marcus and Hush, which is called Marcus equation.

$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \sqrt{k_{11} k_{22} K_{12} f_{12}}$  where  $k_{12}$  is the rate constant for the cross reaction.

$k_{11}$  and  $k_{22}$  are the rate constants for the electron-exchange reactions of the same metal.

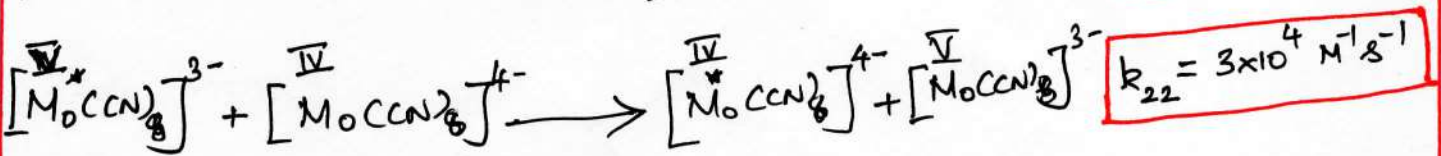
$K_{12}$  - is the equilibrium constant for the cross reaction.

Then, for the Heteronuclear redox rxn (cross rxn), the values are



The equilibrium constant  $K_{12} = 1.0 \times 10^2$

The self-exchange rate constants  $k_{11}$  &  $k_{22}$  for the respective two reaction partners are



The factor ' $f_{12}$ ' has been described as a correction for the difference in the free energies of the two reactants and its value is often close to unity. (In this case, it is 0.85).

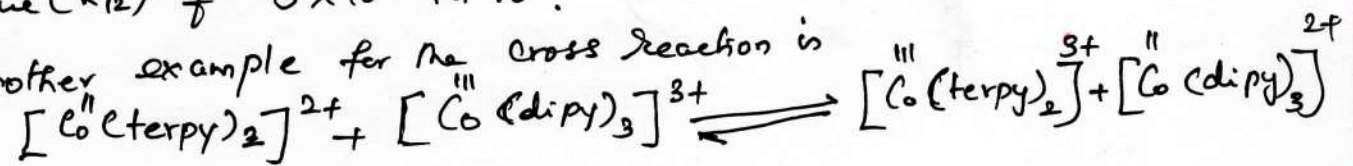
The factor  $f_{12}$  is given by the equation,

$$\log f_{12} = (\log K_{12})^2 / 4 \log \frac{k_{11} \cdot k_{22}}{z^2}$$

The term ' $z$ ' is the collision frequency of two uncharged particles in solution and it is taken as  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ .

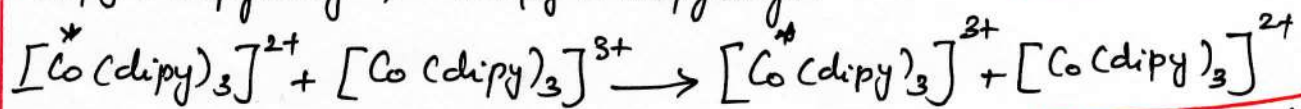
By substituting the experimental values of  $k_{11}$ ,  $k_{22}$ ,  $K_{12}$  &  $f_{12}$  in the Marcus-Hush equation, the rate constant for the cross reaction can be calculated. It is found to be  $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  which is in good agreement with the experimental value of  $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

Another example for the cross reaction is

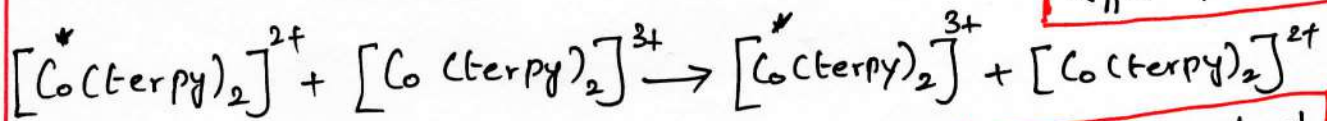


The equilibrium constant  $K_{12}$  for the above redox rxn is  $\boxed{3.57}$  Mrs. S.K  
(11)

dipy = dipyridyl ; terpy = terpyridyl.



$$k_{11} = 9 \text{ M}^{-1} \text{ s}^{-1}$$



$$k_{22} = 48 \text{ M}^{-1} \text{ s}^{-1}$$

$$f_{12} = 0.99 \approx 1$$

$$\therefore k_{12} = (k_{11} \cdot k_{12} \cdot K_{12} \cdot f_{12})^{1/2} = (9.0 \times 48 \times 3.57 \times 1)^{1/2} = 39 \text{ M}^{-1} \text{ s}^{-1}$$

The calculated  $k_{12}$  value compares reasonably well with the experimental value which is  $64 \text{ M}^{-1} \text{ s}^{-1}$ .

The Marcus equation connects thermodynamics and kinetics as shown by the dependence of  $k_{12}$  on  $K_{12}$ . As  $K_{12}$  increases, the reaction rate ( $k_{12}$ ) increases. Thus outer sphere reactions which are thermodynamically more favourable tend to proceed faster than those which are less favourable. The Marcus equation breaks down (not valid) when  $K_{12}$  becomes very large. The complete theory reveals that rate increases rapidly with increasing spontaneity, reaching a maximum when the change in free energy ( $\Delta G^\ddagger$ ) is equal to the sum of reorganisation energies ( $E_a^\ddagger$ ) and then the rate decreases as the spontaneity increases further.

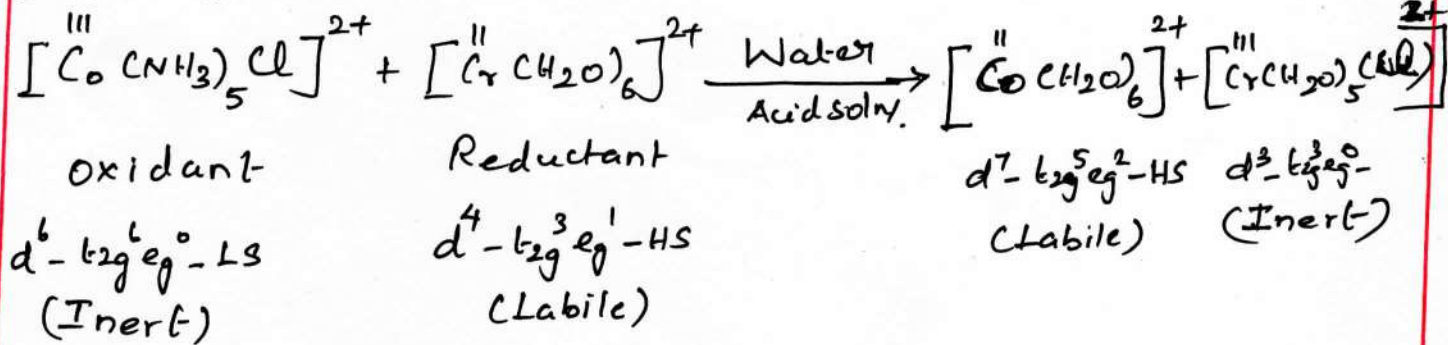
## II Inner-Sphere Mechanism (or) Bridging Mechanism. (ISM)

1. Electron transfer reactions which follow ISM are more complicated than OS reaction, because, in addition to the e<sup>-</sup> transfer, M-L bonds are broken and made.

2. Electron transfer reactions proceeding through ISM generally have one inert reactant and one labile reactant. The inert reactant has a coordinated ligand which is capable

of forming a bridge between the metal ions of reductant and oxidant.

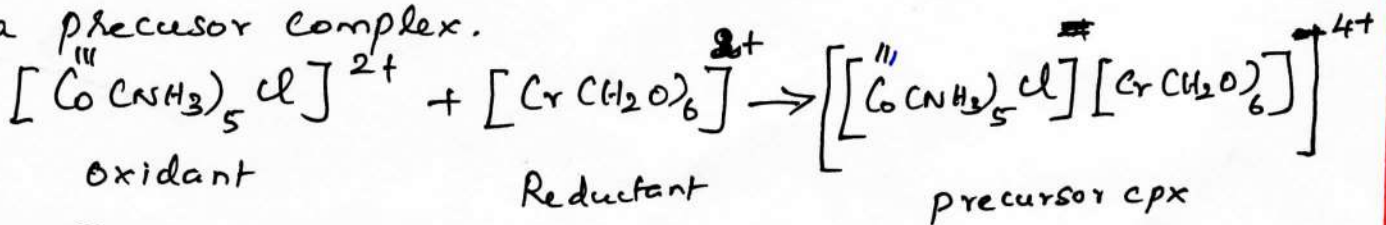
The classical example of this type of mechanism was provided by Taube and his coworkers. Their system involved in the reduction of Co(III) in  $[\text{Co}(\text{CNH}_3)_5\text{Cl}]^{2+}$  by Cr(II) in  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ .



3. Mechanism of IS reactions: The first two steps of the IS are the formation of a precursor complex and the formation of the bridged binuclear intermediate. Then e<sup>-</sup> transfer takes place from R to O to form the successor cpx and then it dissociates to give the products, accompanied by transfer of bridging ligand. The various steps are:

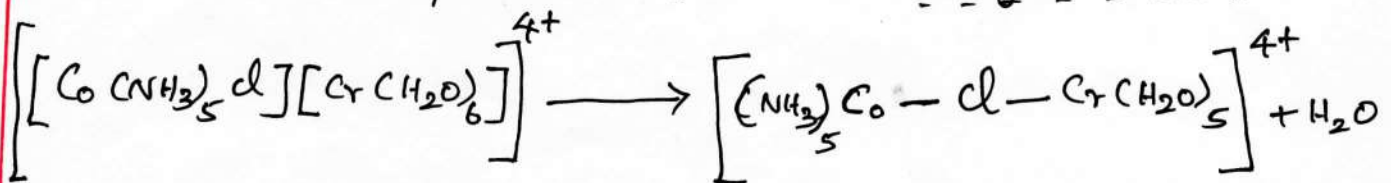
Step-① Formation of precursor complex.

The oxidant (O) and the reductant (R) come together to form a precursor complex.



Step-② Formation of bridged binuclear intermediate.

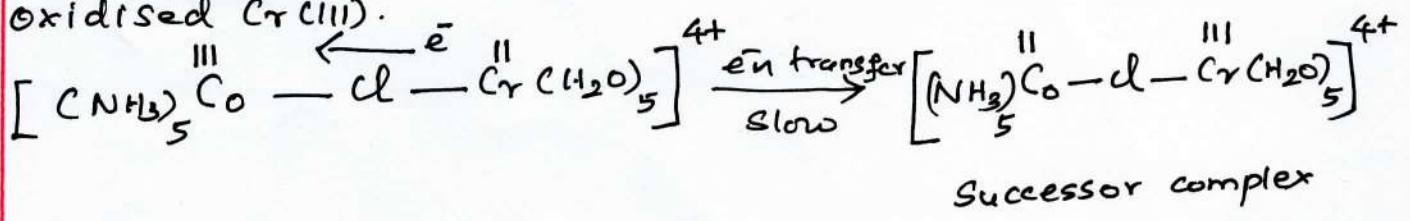
Here, the chloride ion, which is firmly attached to the inert Co(III) ion, can displace a water molecule from the labile Cr(II) complex to form the bridged binuclear intermediate.



Bridged binuclear intermediate

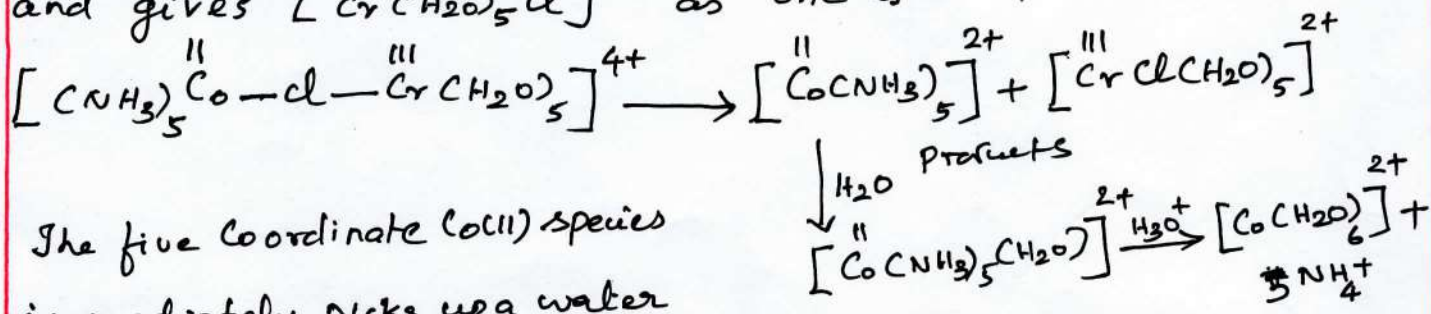
Step-③ Transfer of electron from reductant to oxidant

Electron transfer takes place from reductant to oxidant through the bridging ligand to give the successor complex which contain reduced Co(II) and oxidised Cr(III).

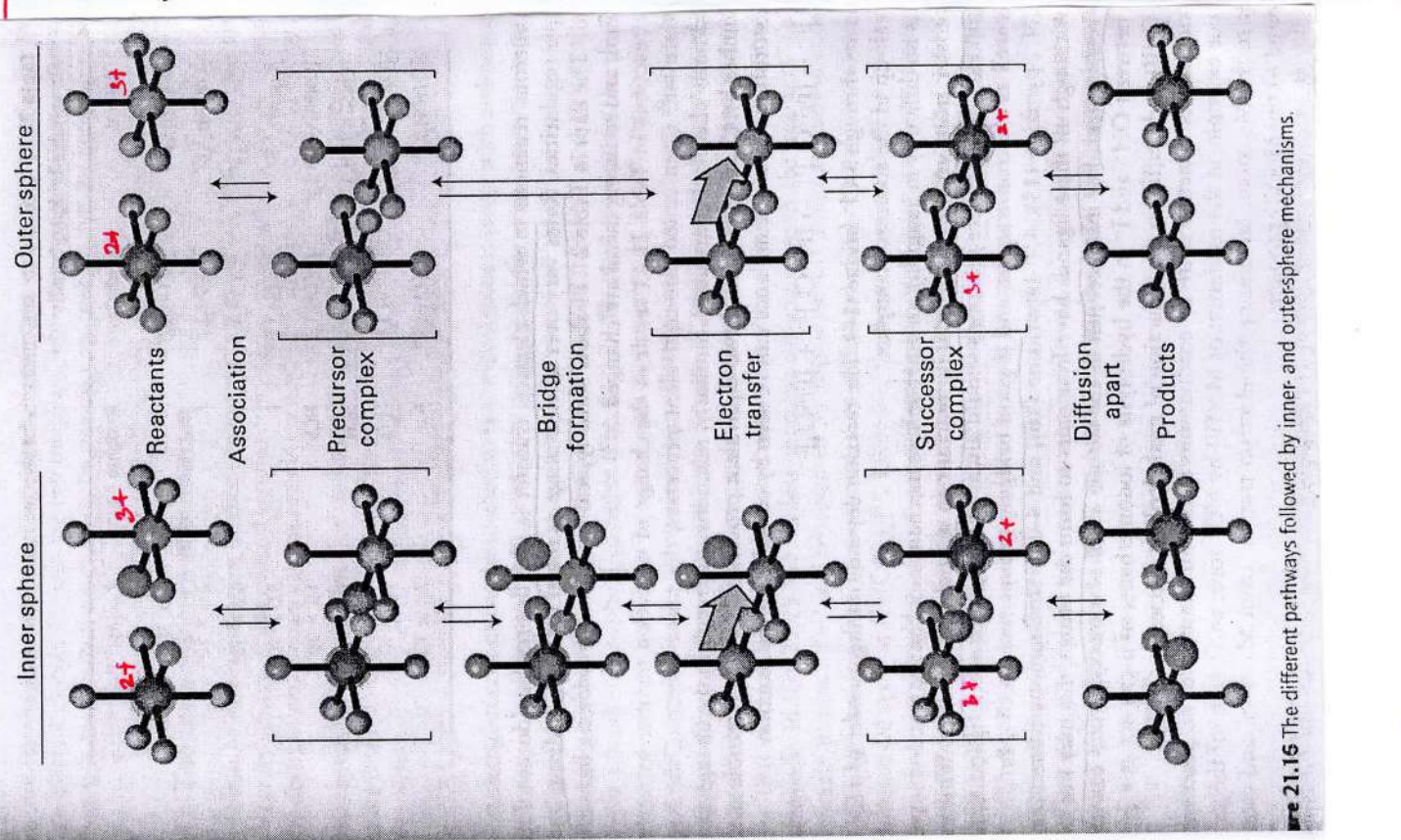


Step - 4 Dissociation of successor complex to give the products:

Since Cr(III) is inert to substitution and Co(II) is labile, the transfer of bridging ligand occurs from Co(II) to Cr(III) and gives  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$  as one of the product



The five coordinate Co(II) species immediately picks up a water molecule to fill its sixth coordination site and then hydrolyses in acid medium to  $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$  readily



4. Proof for Inner Sphere mechanism (ISM)

The important aspect of ISM is the transfer of a particular ligand from one coordination sphere to another coordination sphere through the formation of bridged binuclear intermediate. Therefore, the proof for this mechanism must prove the above fact. This can be done as follows.

When the same reaction is conducted in the presence of added radioactive  $^{36}\text{Cl}^-$  ion in solution, no radioactive  $^{36}\text{Cl}^-$  is incorporated in the product  $\text{Cr(III) cpx}$ ,  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ . If  $\text{Cl}^-$  had dissociated from the reactant  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and then the free  $\text{Cl}^-$  migrated to  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  through the solvent, then some added radioactive  $^{36}\text{Cl}^-$  would have been incorporated in the Cr(III) product. The absence of radioactive  $^{36}\text{Cl}^-$  in the product  $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$  species proves that the  $\text{Cl}^-$  is transferred directly from Cobalt cpx to Chromium complex through the bridge formation and not through the solvent. All the  $\text{Cl}^-$  in the product came from the reactant, not from the excess  $\text{Cl}^-$  in the solution.

5. Inner sphere reactions, though involving more steps than outer sphere reactions, they can be fast than OS reactions.

6. In most of the inner sphere reactions, the rate-determining step is electron-transfer step and not the bridged complex formation step.

7. Both OSM and ISM follow the same rate law. They are second order reactions.

$$\text{rate} = k[\text{oxidant}][\text{Reductant}]$$

8. An important feature of IS reaction is that the rate of inner sphere reaction is always slower than the rate of exchange of the bridging ligand in the absence of redox rxn. This is justifiable because the exchange of the ligand in an integral part of the ISM. Thus, in IS reactions,

Rate of ligand exchange  $>$  rate of electron transfer.

Mrs. S.K

15

But in OS reactions,  $e^-$  transfer proceed faster than ligand exchange.

9. Importance of <sup>the</sup> nature of the Bridging ligand

The importance of the nature of bridging ligand in an IS reaction is shown in the following examples:

Reductant	oxidant	Bridging ligand	Second order rate constant $k_2$ in $M^{-1}s^{-1}$ .
1. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_6]^{3+}$	.....	$8.9 \times 10^5$
2. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5F]^{2+}$	$F^-$	$2.5 \times 10^5$
3. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5Cl]^{2+}$	$Cl^-$	$6 \times 10^5$
4. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5Br]^{2+}$	$Br^-$	$1.4 \times 10^6$
5. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5I]^{2+}$	$I^-$	$3 \times 10^6$
6. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5N_3]^{2+}$	$N_3^-$	$3 \times 10^5$
7. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5H_2O]^{3+}$	$H_2O$	0.5
8. $[Cr(CH_2O)_6]^{2+}$	$[Co(NH_3)_5OH]^{2+}$	$OH^-$	$1.5 \times 10^6$

The bridging ligand significantly influences ~~the~~ the rates of IS  $e^-$  transfer reactions.

(i) The reduction of  $[Co(NH_3)_5Cl]^{2+}$  by  $[Cr(CH_2O)_6]^{2+}$  is about  $10^{10}$  times faster than the reduction of  $[Co(NH_3)_6]^{3+}$  by the same reductant. The bound  $NH_3$  ligand in the oxidant has no non-bonding pairs of electron to donate to a second metal to form a bridged intermediate. Thus the reduction of  $[Co(NH_3)_6]^{3+}$  complex cannot proceed by a ISM. It occurs only by OSM.

(ii) It has also been observed that the rate of  $e^-$  transfer in the IS reactions depends upon the nucleophilic

Character of the bridging  $X^-$  ligand. Thus the rates are in the order  $I^- > Br^- > Cl^- > F^-$ . It is obvious that the stronger the nucleophilic character of the halide ion (least electronegativity), the greater would be its capacity to form  $Co-X-Cr$  bridge, through which  $e^-$  transfer takes place.

(iii) By comparing the rates of IS  $e^-$  transfer reactions when the bridging ligand is  $H_2O$  or  $OH^-$ , the rates are in the order  $OH^- > H_2O$ . In reaction-⑦, the oxygen atom of the coordinated water (in  $[Co(CNH_3)_5(H_2O)]^{2+}$ ) has one ~~un-engaged~~ un-engaged (extra) lone pair of  $e^-$ s through which it can associate with the reductant ( $Cr(II)$ ) to form the aqua-bridged intermediate,  $[C(NH_3)_5Co - \overset{H}{O} - Cr(CH_2O)_5]^{5+}$ . Aqua bridge is weak one.

In reaction-⑧, the oxygen atom of the coordinated  $OH^-$  ligand ( $[Co(CNH_3)_5(OH)]^{2+}$ ) has two unshared  $e^-$  pairs through which it can associate with the reductant ( $Cr(II)$ ) to form the  $OH$  bridged intermediate  $[C(NH_3)_5Co - \overset{H}{O} - Cr(CH_2O)_5]^{4+}$ . Since  $OH$  bridge is stronger (i.e. stabler) than aqua bridge, the energy of activation required to form  $OH$ -bridged intermediates is less than that for aqua-bridge. So the  $sn$ -⑧ is faster than  $sn$ -⑦.

(iv) In reaction-⑥, the azide ligand ( $N_3^-$ ) acts as a bridging ligand and produces resonance stabilized bridged binuclear intermediate and hence accelerates the electron transfer IS reaction.

$$k = 8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

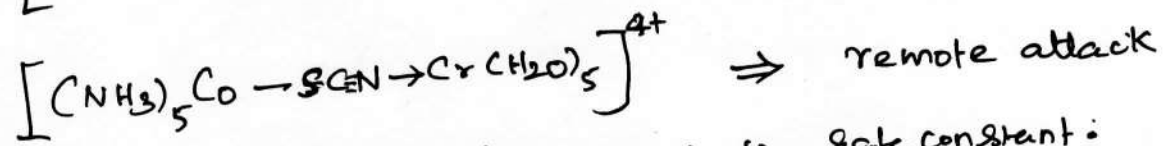
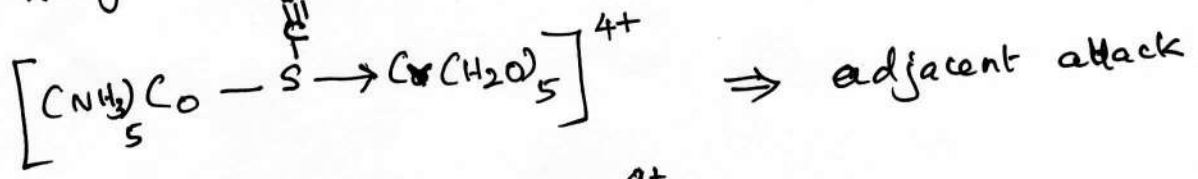
$[C(NH_3)_5Co - \overset{+}{N} = \overset{-}{N} = \overset{+}{N} - Cr(CH_2O)_5]^{4+}$  (resonance stabilized bridged intermediate)

⑩ If the bridging ligand contains only one atom (e.g.  $Cl^-$ ), both the metal atoms of oxidant and reductant must be bound to it. However, if the bridging ligand contains more than one atom (e.g.  $SCN^-$ ,  $NO_2^-$ ,  $CN^-$ , etc), the two metal atoms may or may not bound to the same bridging-ligand atom.



The two conditions are called adjacent attack and remote attack. A remote attack may lead to both linkage isomers. eg)

$[Co(CNH_3)_5(SCN)]^{2+} + [Cr(CH_2O)_6]^{2+}$  In this reaction, the  $SCN^-$  bridging ligand attacks  $Cr(II)$  in two ways.



Q.No. Rationalise the following difference in the rate constant:

Reductant	Oxidant	Product	k in $M^{-1}s^{-1}$
(i) $[Cr(CH_2O)_6]^{2+}$	$[Co(CNH_3)_5(NCS)]^{2+}$	<del>Bridging ligand</del> $[Cr(SCN)(CH_2O)_5]^{2+}$	$1.9 \times 10^1$
(ii) $[Cr(CH_2O)_6]^{2+}$	$[Co(CNH_3)_5(SCN)]^{2+}$	$[Cr(NCS)(CH_2O)_5]^{2+}$ (71%) + $[Cr(SCN)(CH_2O)_5]^{2+}$ (29%)	$1.9 \times 10^5$

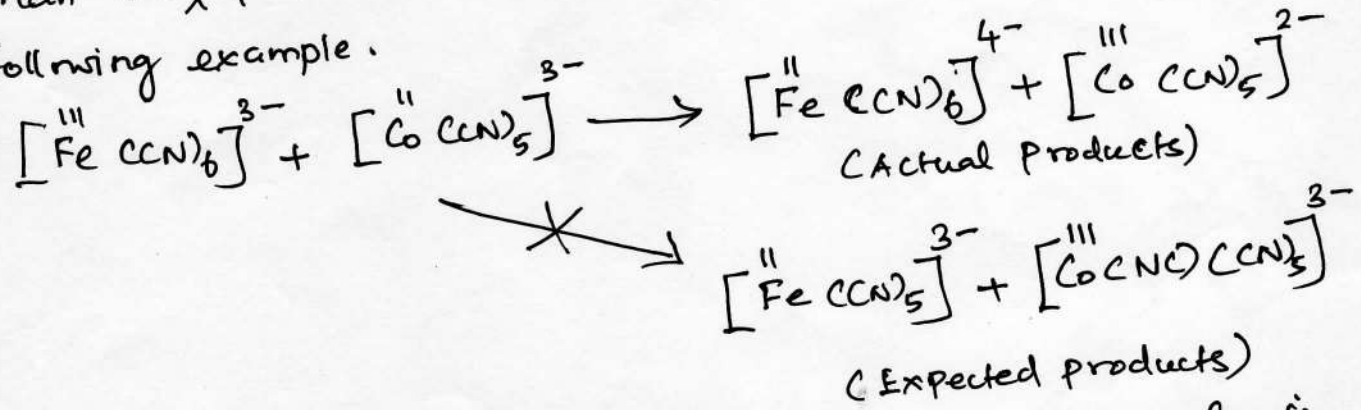
In the reaction (i), the only site available for bridging in  $[Co(CNH_3)_5(NCS)]^{2+}$  is on 's' atom which is remote from the metal ~~center~~ center. The product  $[Cr(SCN)(CH_2O)_5]^{2+}$  indicates that remote attack occurs on 's'. On standing, the product  $[Cr(SCN)(CH_2O)_5]^{2+}$  rearranges to the more stable  $[Cr(NCS)(CH_2O)_5]^{2+}$  isomer. Because  $Cr^{2+}$  is a hard acid, it prefers to bond with hard base 'N'. This preference is reflected in a lesser stability of the intermediate,  $-Co - NCS - Cr -$  and accounts for the rate differences between  $\delta$ -bonded  $Cr^{2+}$  and N-bonded chromium complexes.

In the rxn. (ii)  $[Co(CNH_3)_5(SCN)]^{2+}$ , both adjacent

attack and remote attack occur. So both isomers are obtained as products. The remote attack leads to more stable bridged intermediate,  $(Cr(II)-hard N-hard)$   
 $[ (CNH_3)_5 Co(III) - S - Cr(II) (CH_2O)_6 ]^{4+}$ , hence the rate of  $e^-$  transfer is very high.

(11) The rate of  $e^-$  transfer from  $Fe(II)$  to various  $FeX^{2+}$  complexes (where  $X = F^-, Cl^-, Br^-, I^-$ ) do not differ much. As the rates do not differ much, the bridging mechanism is ruled out. They likely to follow OSM in which  $X^-$  ligands do not play any significant role so as to affect the reaction rate.

(12) In most of the inner-sphere  $e^-$  transfer reactions, the bridging ligand is transferred from oxidant to reductant. But, it is not always the case that the bridging ligand is transferred in IS reaction. The bridging ligand may be left with its original metal, after  $e^-$ -transfer has occurred through it. Thus, ligand transfer, though common in IS reactions, it is not a necessity always. The ligand transfer is not favoured if the bridging ligand stabilised the original complex more than the <sup>normally expected</sup> product complex. This ~~can~~ can be illustrated from the following example.



The retention of the  $CN^-$  ligand in the Fe-complex is rationalised based on the fact that the  $e^-$ -bound  $CN$  group stabilizes the  $d^6 (Fe^{2+})$  configuration of  $[Fe(CN)_6]^{4-}$  more

than the N-bound cyano group would stabilize a  $d^6 (Co^{3+})$  configuration in  $[Co(CNC)(CN)_5]^{3-}$

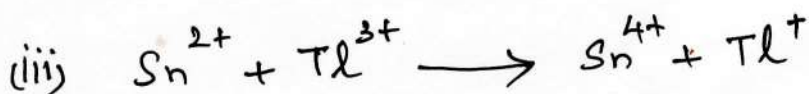
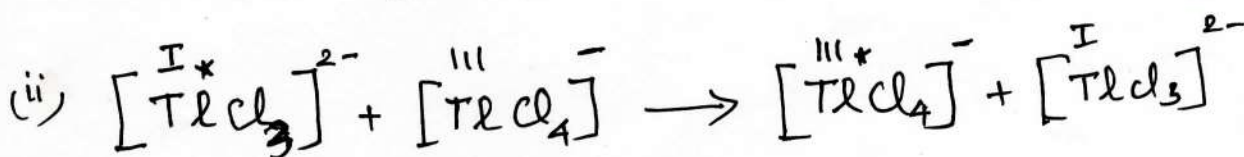
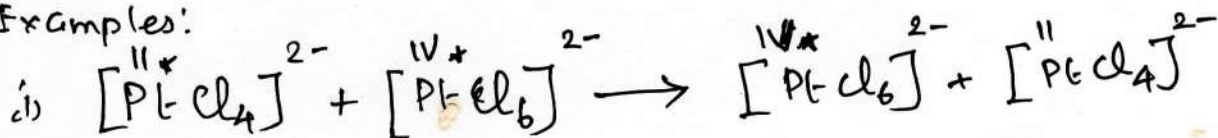
Two-Electron Transfer Reactions:

Reactions in which the oxidant and reductant change by only one unit in their formal oxidation state are called one electron transfer reaction.

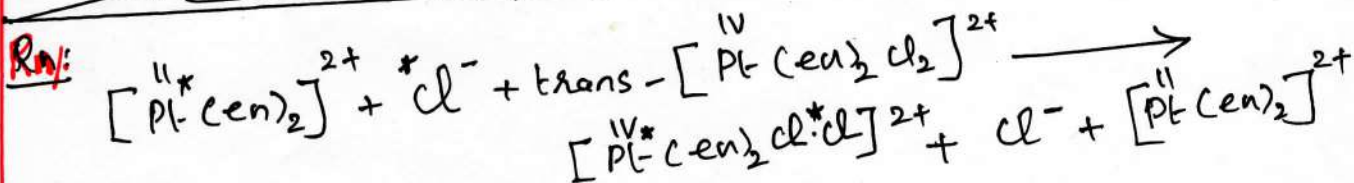
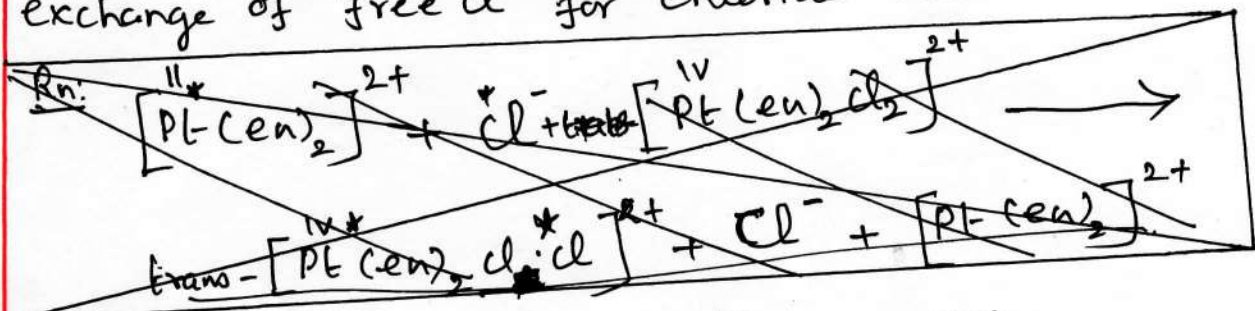
Reactions in which the oxidant and reductant change by two units in their oxidation states are called two-electron transfer reactions.

Some elements exist in two stable oxidation states differing by two electrons. (e.g)  $Pt^{2+}$  &  $Pt^{4+}$ ;  $Tl^+$  and  $Tl^{3+}$ . When a complex of  $Tl^+$  reacts with a complex  $Tl^{3+}$ , two electrons are transferred from the reductant to the oxidant. Such a reaction is called a two e<sup>-</sup> transfer reaction.

Examples:



One of the best understood two-electron transfer reactions in transition metal chemistry is the Pt(II)-catalysed exchange of free  $Cl^-$  for chloride bound to Pt(IV) compound.



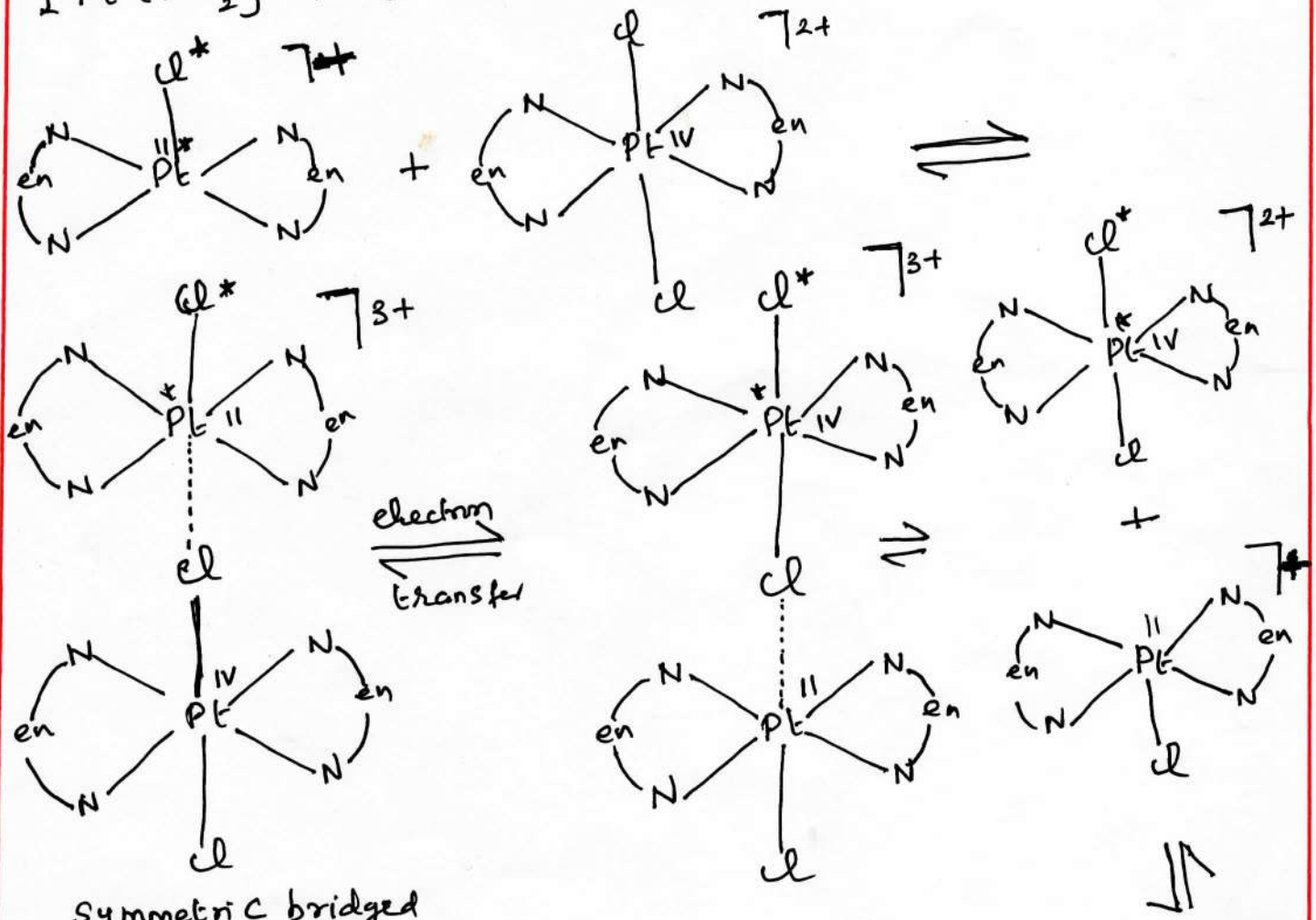
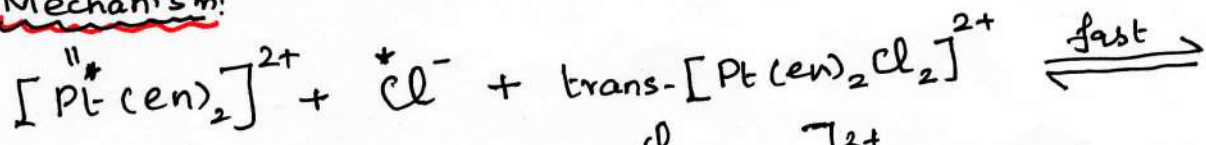
The rate law for the reaction is

$$\text{Rate} = k [\text{Pt(II)}] [\text{Pt(IV)}] [\text{Cl}^-]$$

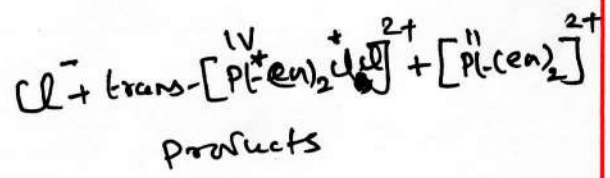
Hence, the mechanism of the two electron-transfer reaction is as follows.

In the first step, rapid addition of free chloride ( $\text{Cl}^-$ ) to the  $\text{Pt(II)}$  compound to form a five coordinate monovalent ion. Then  $\text{Cl}^-$  forms a six-coordinate, inner sphere ~~complex~~ bridged complex with the  $\text{Pt(IV)}$  reactant. The two platinum atoms are now in symmetrical environments, and the transfer of two  $\sigma^*$  electrons with anion ( $\text{Cl}^-$ ) ~~transfer~~ in the opposite direction can readily occur.

Mechanism:

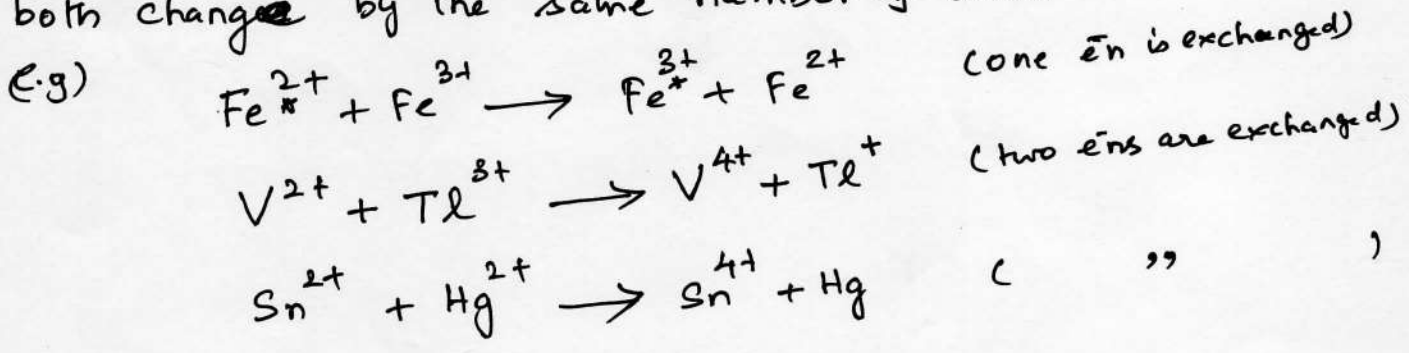


Symmetric bridged transition state



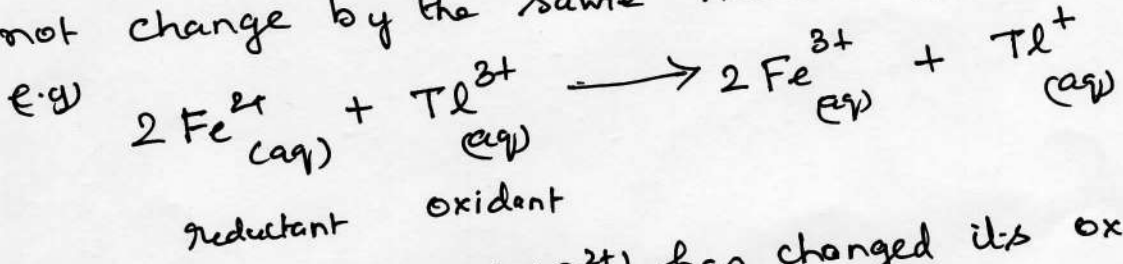
# Complementary Electron Transfer Reactions

Electron transfer reactions in which the oxidant gains the same number of electrons as the reductant loses are called Complementary electron transfer reactions. That is, the formal oxidation states of the oxidant and reductant both change by the same number of units.



## Non-Complementary Electron Transfer Reactions.

Non-complementary redox reactions are those in which the electrons released by reductant is not equal to the number of electrons gained by the oxidant. That is the oxidation states of the oxidant and reductant do not change by the same number of units.

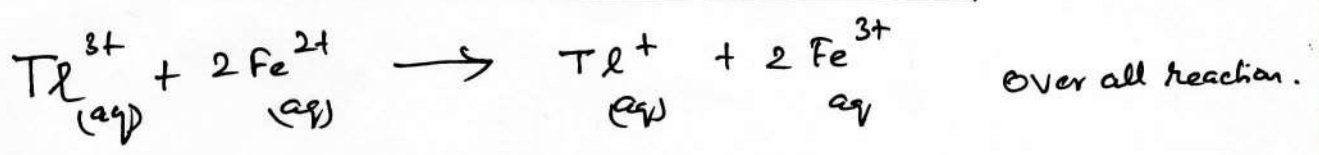
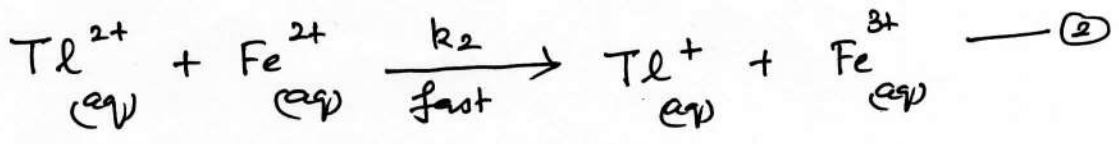
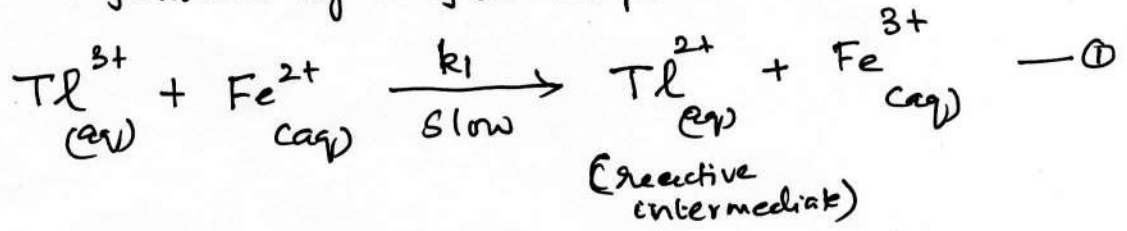


Here the reductant ( $\text{Fe}^{2+}$ ) has changed its oxidation state by one unit ( $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ ) whereas the oxidant has changed its oxidation state by two units ( $\text{Tl}^{3+} \rightarrow \text{Tl}^{+}$ ).

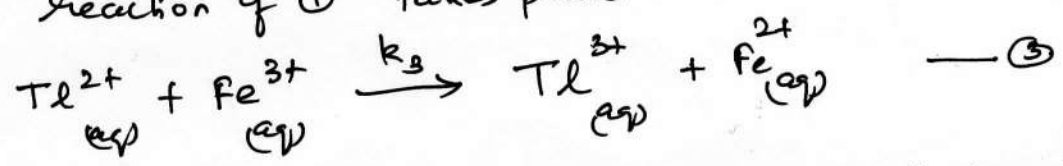
Such reactions generally proceed through a multi-step path and they are slower than Complementary reactions, because <sup>in the</sup> non-complementary reactions, termolecular collision is required, this is more difficult than the bimolecular collision in a Complementary reaction.

Mechanism: The experimental data show that a reactive intermediate  $\text{Tl}^{2+}(\text{aq})$  is produced in the slow step which

is then followed by a fast step.



When  $Fe^{3+}_{(aq)}$  builds up in the course of reaction, the reverse reaction of (1) takes place.



The complete rate expression for this mechanism is given as

$$\text{rate} = \frac{k_1 k_2 [Tl^{3+}] [Fe^{2+}]^2}{k_2 [Fe^{2+}] + k_3 [Fe^{3+}]}$$

Some of the best examples of non-complementary redox processes in transition metal chemistry are chromate ion oxidations.



The various steps are

