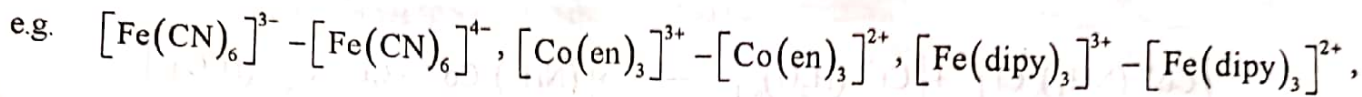


## **Redox Reactions**

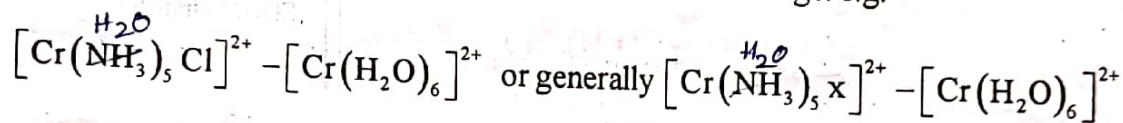
Redox reactions are the reactions in which transfer of electron/electrons from one atom to the other occurs, and hence the oxidation state of some atoms change. These reactions are divided into following two classes :

i) Electron transfer reactions in which there is no net chemical change. These are called electron-exchange processes.



$[\text{Co}(\text{NH}_3)_6]^{3+} - [\text{Co}(\text{NH}_3)_6]^{2+}$  etc. These reactions can be followed only indirectly, such as by isotopic labelling or NMR.

ii) Electron transfer reactions in which there is net chemical change. e.g.



where X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NCS<sup>-</sup> etc.

### Mechanism of one electron transfer reactions

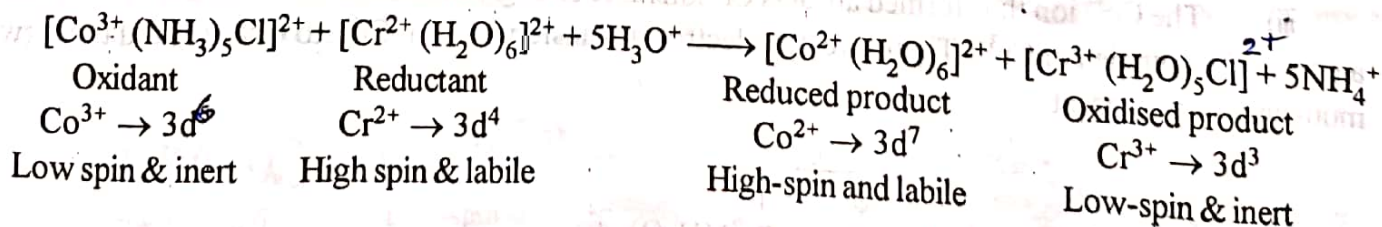
One electron transfer reactions mainly occur by following two mechanism : a) Bridge or inner - sphere mechanism, and b) electron - transfer or outer-sphere mechanism.

#### a) Atom (or Group) - Transfer of Inner - Sphere Mechanism

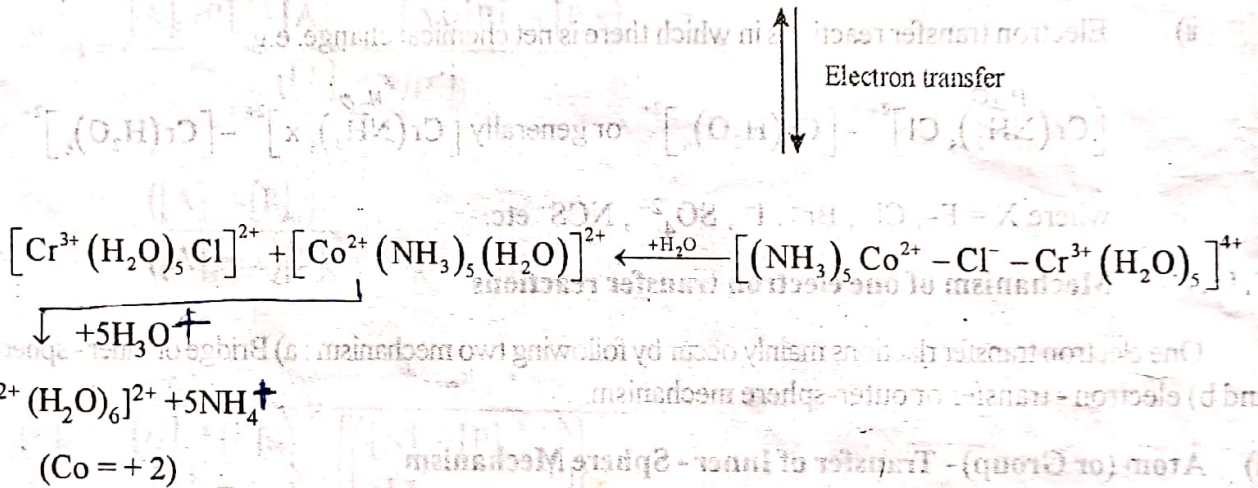
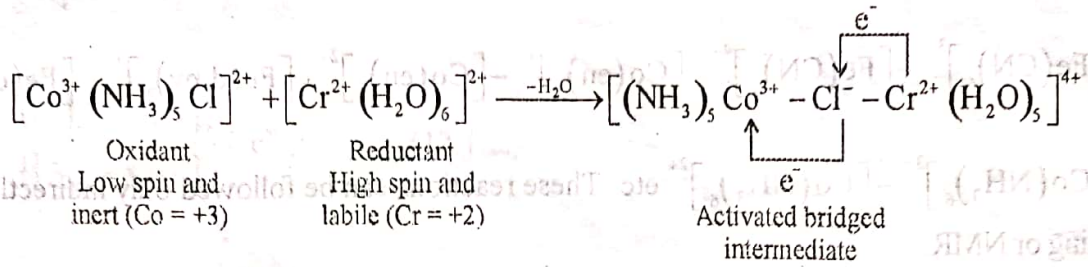
These are electron-transfer reactions in which concomitant electron transfer and ligand transfer occur. In such reactions the essential requirement is the intimate contact between oxidant and reductant. This requirement can only be achieved only when a bridged activated complex is formed as a result of an intimate attachment between the oxidant and reductant. Therefore, this activated complex has at least one ligand which is common to the coordinate sphere of both the reacting complexes and this forms a bridge between them. Hence the name inner sphere mechanism and for obvious reason this mechanism is also called ligand-bridged, atom (or group) transfer or bridged activated complex mechanism.

#### Example

Oxidation of aqueous Cr (II),  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  by pentammine cobalt (III) chloride,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{3+}$  in acidic medium as shown below



The above reaction can be explained by the following mechanism :



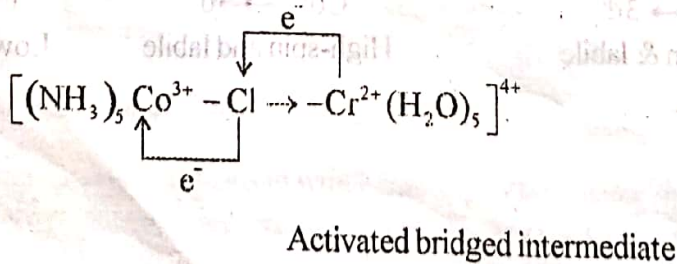
The above reaction proceeds through the following steps:

i) A molecule of water is readily released from the  $[\text{Cr} (\text{H}_2\text{O})_6]^{2+}$  for its labile nature to form an activated bridged intermediate which contains  $\text{Co}^{3+}$  and  $\text{Cr}^{2+}$  ions linked together through  $\text{Cl}^-$  ion which acts as a bridge between the two co-ordinate spheres.

The bridging  $\text{Cl}^-$  ion is brought into the activated intermediate by the inert reactant viz  $[\text{Co} (\text{NH}_3)_5 \text{Cl}]^{2+}$ . The only source of  $\text{Cl}^-$  is  $[\text{Co} (\text{NH}_3)_5 \text{Cl}]^{2+}$ .

ii) In an activated intermediate an electron is transferred from  $\text{Cr}^{2+}$  to  $\text{Co}^{3+}$  through the bridging  $\text{Cl}^-$  ion to convert  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ .

iii) The  $\text{Cr}^{3+}$  ion thus formed attracts  $\text{Cl}^-$  ion more strongly than does  $\text{Co}^{2+}$ . As a result,  $\text{Cl}^-$  ion becomes a part of the complex of  $\text{Cr}^{3+}$ . Therefore, the electron is transferred from  $\text{Cr}^{2+}$  to  $\text{Co}^{3+}$  (I) and these two acts are mutually interdependent.



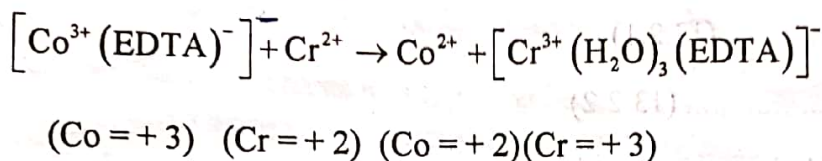
After electron transfer the initial labile partner  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  becomes inert to substitution and the inert partner  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  becomes labile.

The reaction is first order with respect to the oxidant and the reductant

$$v = k [\text{oxidant}] [\text{reductant}]$$

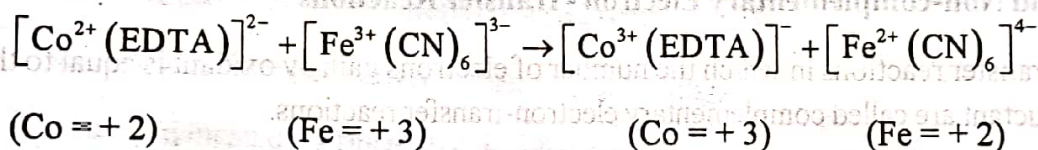
$$= k [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$$

There are some redox reactions which occur by multiple bridges. e.g. in the following reactions three oxygen atoms of EDTA serve as bridges



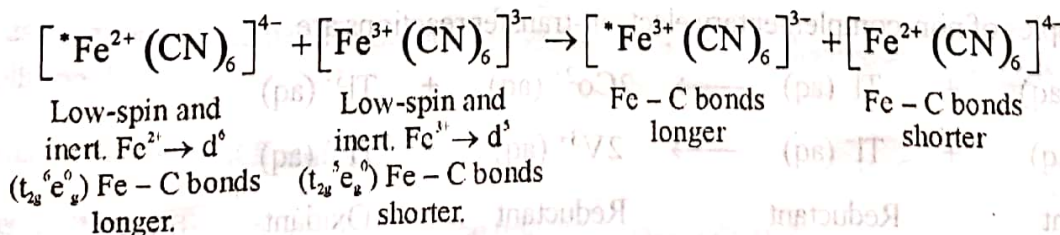
There are also examples in which two electrons but only one ligand is transferred. e.g. various  $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$  exchanges.

There is also a reaction in which electron transfer by an inner-sphere mechanism is not accompanied by ligand transfer, e.g.



### b) Direct Electron Transfer or Outer-Sphere Mechanism

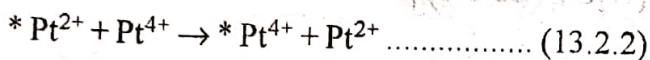
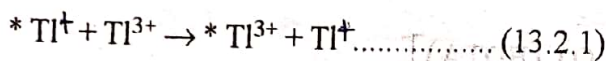
In these electron transfer reactions only the formal valence state of the metal ions changes. These reactions occur by direct electron transfer and the electron effectively hops from one species to the other and the ligands act as electron-conduction media. The electron transfer can occur by a mechanism which involves movement of an electron from the outside of a ligand in one coordination sphere over the outside of a second sphere. This mechanism is particularly appropriate with large conjugated ligands like bipyridine, phenanthroline etc. As in this mechanism direct electron transfer occur, the Frank-condon principle must be obeyed. Therefore very light electrons will move much more rapidly than much heavier atoms. In order to understand this mechanism, let us consider the transfer of an electron from  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  to  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ . The rate of this redox reaction can be studied by labelling either of the complexes with a radio active isotope of Fe or with  $^{14}\text{C}$ .



The above reaction is fast with second-order rate constant  $\sim 10^5$  at  $25^\circ\text{C}$ . Both  $[\text{Fe}(\text{CN})_6]^{4-}$  ( $t_{2g}^6 e_g^0$ ) and  $[\text{Fe}(\text{CN})_6]^{3-}$  ( $t_{2g}^5 e_g^0$ ) are low spin and are inert. Thus the loss or exchange of  $\text{CN}^-$  or any substitution reaction is very fast. As a result, the possibility of electron transfer through a bridged activated complex is eliminated, since formation of the activated complex requires to a substitution reaction. Therefore, when both the reactants are inert, the close approach of the metal atom is impossible and hence the electron transfer takes place by a tunneling or outer-sphere mechanism.

### Two Electron-Transfer Reactions

The reactions in which two electrons are transferred are known as two electron-transfer reactions. e.g. the reactions.



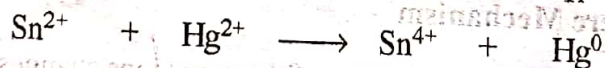
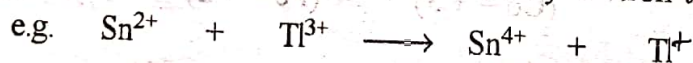
Occur in aqueous perchlorate solution.

The rate law for reaction (13.2.1) is in aqueous perchlorate solution is

$$v = K_1 [\text{Tl}^-] [\text{Tl}^{3+}] + K_2 [\text{Tl}^-] [\text{TlOH}^{2+}]$$

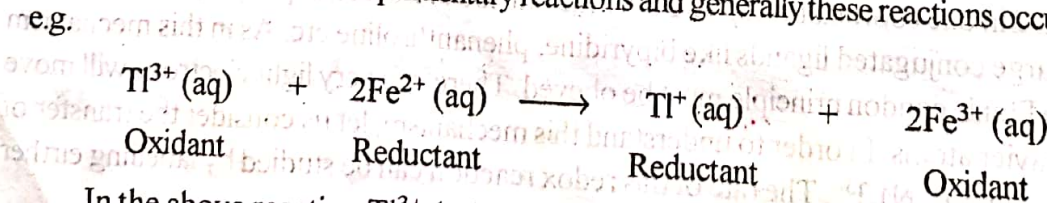
### Complementary and Non-complementary Electron -Transfer Reactions

The electron -transfer reactions in which the number of electrons gain by oxidant is equal to the number of electrons loss by reductant are called complementary electron-transfer reactions.



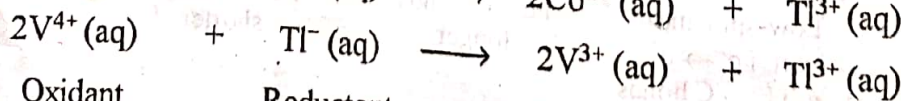
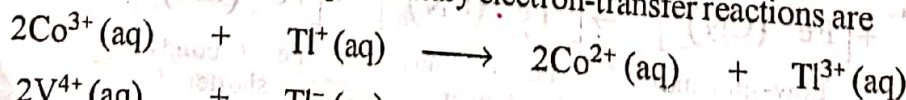
Reductant                      Oxidant                      Oxidant                      Reductant

When the number of electrons gained by oxidant and lost by reductant are different, the electron-transfer reactions are called non-complementary reactions and generally these reactions occur by more complicated mechanism.



In the above reaction  $\text{Tl}^{3+}(\text{aq}) \longrightarrow \text{Tl}^+(\text{aq})$  is a two electron transfer reaction while,  $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq})$  is one-electron transfer reaction.

The other examples of non-complementary electron-transfer reactions are



Oxidant                      Reductant                      Reductant                      Oxidant