

# PG SEMESTER 1

## PAPER 1

### INORGANIC CHEMISTRY

### TOPIC – THEORIES OF REDOX REACTION

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#### 7.4 THEORIES OF REDOX REACTIONS

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Thus, for explanation of outer sphere reactions it is necessary to consider two concepts : (i) Born – Oppenheir Approximation and (ii) the energies of starting and end states.

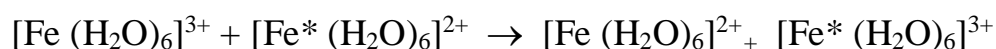
According to Born–Oppenheir approximation, electron distribution must be done, considering nuclei are stable at their place. If we consider the nuclei are stable in the transition state, then we can see distribution of wave function of the electron transferred on both the centres. On the basis

of energy, it will be more advantageous, the ion – ligand bond – length stabilize at the intermediate value. At this point electron transfer takes place at the bond – length of reactants.

According to the other concept, the possibility of electron transfer will be maximum when the energy of the initial and final states are equal.

Consideration of these two concepts clearly show that the rate of electron transfer and the activation energy for the process depends on the capability of nuclei to reorganise.

An example of the reaction of inert reactants is electron transfer reaction between solvated Fe (II) and Fe (III); which has been studied using radio active isotope of iron (Fe\*) :



In this reaction also electron transfer takes place through outer sphere or tunneling mechanism. At 25° second order rate constant is 3.0 L mol<sup>-1</sup> s<sup>-1</sup> and the activation energy is 32 KJ mol<sup>-1</sup>. The arrangements during electron transfer require changes in Gibbs energy; this is known as inner sphere rearrangement energy  $\Delta^*G_{\text{IS}}$ . In addition to this, the energy for the changes in the solvent outside the coordination sphere, i.e. Outer sphere rearrangement energy,  $\Delta^*G_{\text{OS}}$ , is also important. Further, the electrostatic interaction, energy between the two reactants, will be,  $\Delta^*G_{\text{ES}}$ . Hence the Gibbs energy of complete activation is the sum of all these energies :

$$\Delta^*G = \Delta^*G_{\text{IS}} + \Delta^*G_{\text{OS}} + \Delta^*G_{\text{ES}}.$$

For electron transfer it is necessary that the energies of the participating electronic orbitals are equal (Frank – Condon Principle). In

this reaction, one electron from  $t_{2g}$  orbital of Fe (II) is transferred to  $t_{2g}$  orbital of Fe (III). The bond-lengths in Fe (II) and Fe (III) complexes are different (In octahedral high spin complex of Fe (II) = 92 pm and that of Fe (III) = 78.5 pm), which indicates the energies of orbitals are not equivalent. If the electron transfer takes place without losing energy, then we will get the product in which bond-length of Fe (II), complex is equal to the characteristics bond – length of Fe (III) – complex and vice versa. But this will be against the first law of thermodynamics. Actually, it is necessary to give energy for electron – transfer. The actual reaction starts with smaller bonds in Fe (II) complex and larger bonds in Fe (III) – complex; unless the energy of participating orbitals become equal. The vibrational stretching and compressions of metal – ligand bond help in getting required configuration.

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#### 7.4 POTENTIAL ENERGY DIAGRAMS

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Potential energy diagrams also confirm the relation between molecular motion and electron transfer. For electron transfer it is necessary that there should be coupling in vibrational and electronic motion. The limit of these interactions is related with the energy difference,  $\Delta E$ , at the crossing of potential energy diagrams (fig. 7.1). If the coupling interaction is strong, distortion of bonds is very less and electron transfer is easy. If the interaction is weak, bond-distortion is high;  $\Delta G$  will be high and the reaction is slow. As the activated complex rests at the intersection of two curves; while according to the non-crossing rule, molecular potential energy curves of same symmetry – states do not cross each other, but divide into upper and lower curves (Fig. 7.1). The indication of non-crossing rule is that, if the reactants distort slowly in their ground states, then they are converted into products, in their ground states itself, following the lowest energy path.

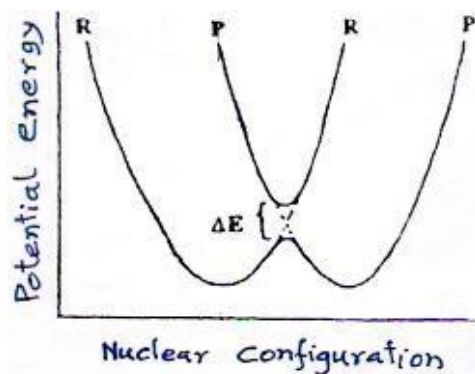


Fig. 7.1

In common red-ox reactions, Gibb's-energy of the reaction is not zero. If the product surface is high (Fig. 7.2 (a)), then the crossing point rises and the activation energy of the reaction will be high. On the other hand, when crossing point drops (Fig. 7.2 (c)), activation energy decreases. At the limit of exergonic reaction (Fig. 7.2 (d)) crossing point rises up and the rate again slowdowns.

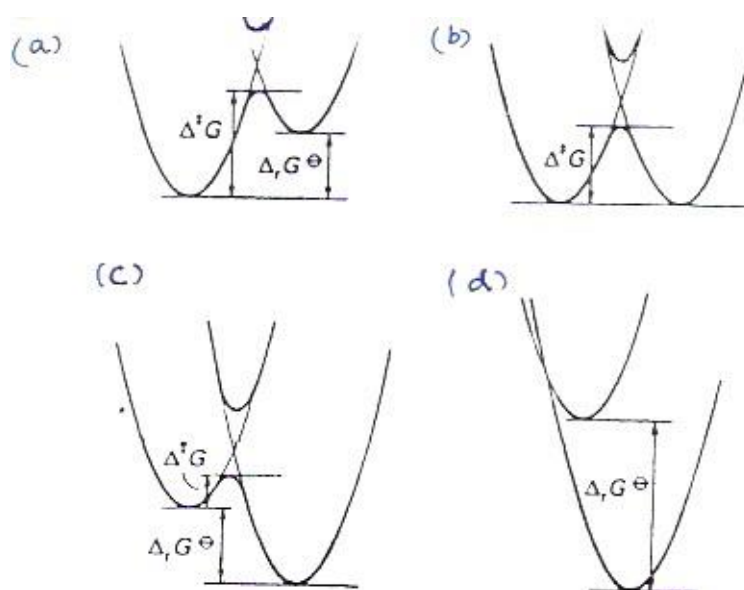


Fig. 7.2

In cyanide complexes of Fe (II) and Fe (III), according to LFT, the extra electron of Fe (II) in  $t_{2g}$  orbital, is in non-bonding molecular orbital; and is diffused partially on the ligand due to  $\pi$  bonding. During electron

transfer between complex ions,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , initially the products are in the excited state. If the shapes of reactant – species are very less distorted, as compared to the transition state, then the energy of activation required for electron exchange is very less and the reaction is fast. Although, the value of equilibrium constant for isotopic exchange is almost same and  $\Delta G^\circ$  is zero; still energy of activation is required due to following reasons :

- (i) For overcoming electronic repulsion between ions of same charge,
  - (ii) to distort coordination shells of both the species, and
  - (iii) to change the arrangement of solvent molecules surrounding the two species.
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