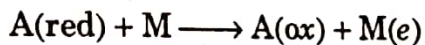


## □ QUANTUM ASPECTS OF CHARGE TRANSFER AT ELECTRODE-SOLUTION INTERFACE

We come across with a number of electron transfer reaction. The field of electron transfer processes has grown tremendously in the last decades of the last century. Suppose the transfer of an electron occurs from the reduced form of a reactant A, A (red) to the oxidised form of reactant B (ox) in solution.

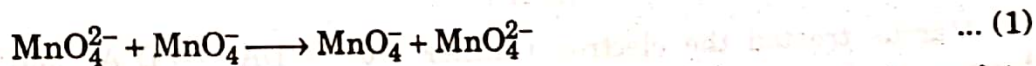


when one of the reactants B is an electrode M, the electrochemical reaction can be written as



Electron transfer processes occur for organic as well as inorganic ones, for reactions in solution and for those across interfaces, in complex biological systems and in very simple systems.

Consider a self exchange reaction in aqueous solution which is the simplest of all electron transfers.



Experimentally, the reaction rates of such reactions were initially measured, for a wide variety of central metal atoms and of ligands (here, Mn and O, respectively), by labelling one of the metal atoms in a particular valence state with a radioactive atom as a tracer and then its appearance was followed in the other valence state.

According to Marcus (1923) the main idea underlying the electron transfer is two fold and can be shown by using reaction (1), when the electron jumps from  $\text{MnO}_4^{2-}$  to  $\text{MnO}_4^-$ . It occurs so rapidly that the atoms in the reactants and in the solvent molecules do not have time to move in that brief time, as the atoms are much heavier than the electrons, *i.e.*, the transfer should obey Franck-Condon principle. It may be recalled that the solvent dipolar molecules are partially oriented, on an average, towards the ions and much more so towards the more highly charged ions. Therefore, each of the newly formed ions in reaction (1) finds itself in a wrong solvent environment. If the electron transfer occurred in this manner, the total energy of the system would suddenly increase. In case the transfer occurred in the absence of absorption of light, this mechanism would go against the law of energy conservation. Therefore, for a thermal electron transfer to occur, an appropriate redistribution of the orientations of the solvent molecules in the neighbourhood of each ion needs to happen prior to the electron transfer. With a suitable such fluctuation, both the energy

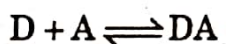


conservation and Franck and Condon principle would be simultaneously satisfied, while the former would be violated in the absence of fluctuation.

Marcus (1956) during the formulation of the electron transfer theory suggested a way for finding the needed redistribution, using it to mention the transition state and calculate the reaction rate. In the beginning, he used a dielectric continuum model for the solvent and set up an equation for the free energy ( $G$ ) of such a dielectric continuum undergoing fluctuations. The value of  $G$  was obtained by finding a reversible path for forming such a non-equilibrium state of the solvent, with an arbitrary dielectric polarisation  $P(r)$  at each point  $r$  in the system and then calculating the reversible work done to form that state. In order to find  $P(r)$  which characterises the transition state of the system,  $G$  was minimised subject to the constraint that the transition state was an ensemble of configurations of the system which satisfy both energy conservation and Franck-Condon principle on electron transfer.

### [I] Quantisation of Charge Transfer

Consider a charge transfer from a donor  $D$  ( $MnO_4^{2-}$  in reaction 1) to an acceptor  $A$  ( $MnO_4^-$ ) in solution. First  $D$  and  $A$  must diffuse through the solution and collide to form a complex  $DA$ , in which the donor and acceptor are separated by a distance,  $r$ . It is the distance between the edges of each species, i.e.,  $D$  and  $A$ . If  $D, A$  and  $DA$  exist in a pre-equilibrium then



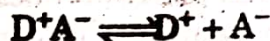
$$\therefore K_1 = \frac{[DA]}{[D][A]}$$

The charge (say electron) transfer occurs in  $DA$  to give  $D^+A^-$



$$\therefore \text{Reaction rate} = k_{et}[DA]$$

The complex  $D^+A^-$  breaks and the ions diffuse through the solution.



$$\therefore K_2 = \frac{[D^+][A^-]}{[D^+A^-]}$$

Marcus treated the electron transfer process  $DA \longrightarrow D^+A^-$  and from activated complex theory, we get

$$k_{et} = \kappa v \exp(-\Delta G^*/RT)$$

where  $\kappa$  is the transmission coefficient,  $v$  is vibrational frequency with which the activated complex nears the transition state and  $\Delta G^*$  is the free energy of activation. The two central ideas in the Marcus treatment of charge transfer reactions are as follows :

(i) Electrons are transferred by tunnelling through a potential energy barrier, the height of which is partly determined by the ionisation energies of  $DA$  and  $D^+A^-$  complexes, i.e., electron tunnelling affects the magnitude of  $\kappa v$ . Tunnelling is a purely quantum mechanical phenomenon and its examples are in semiconductors and superconductors.

(ii) The complex  $DA$  and the solvent molecules which surround it undergo structural rearrangement before the charge transfer. The energy associated with these rearrangements and the standard reaction Gibbs energy,  $\Delta_r G^\circ$ , determine  $\Delta G^*$ . Marcus gave the following equation,

$$\Delta G^* = \frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda}$$

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In this equation,  $\Delta_r G^\circ$  is the standard reaction Gibbs energy for the electron transfer reaction  $DA \longrightarrow D^+A^-$  and  $\lambda$  is the reorganisation energy, *i.e.*, energy associated with molecular rearrangements that must occur so that DA can acquire the equilibrium geometry  $D^+A^-$ . The molecular rearrangements include the relative orientation of the solvent molecules surrounding DA and the relative orientation of the D and A molecules in DA.