

6.4: Electron-Transfer Theory

The simplest electron transfer occurs in an outer-sphere reaction. The changes in oxidation states of the donor and acceptor centers result in a change in their equilibrium nuclear configurations. This process involves geometric changes, the magnitudes of which vary from system to system. In addition, changes in the interactions of the donor and acceptor with the surrounding solvent molecules will occur. The Franck-Condon principle governs the coupling of the electron transfer to these changes in nuclear geometry: during an electronic transition, the electronic motion is so rapid that the nuclei (including metal ligands and solvent molecules) do not have time to move. Hence, electron transfer occurs at a fixed nuclear configuration. In a self-exchange reaction, the energies of the donor and acceptor orbitals (hence, the bond lengths and bond angles of the donor and acceptor) must be the same before efficient electron transfer can take place.

The incorporation of the Franck-Condon restriction leads to the partitioning⁶⁰⁻⁶⁵ of an electron-transfer reaction into reactant (precursor complex) and product (successor complex) configurations. The steps in Equations 6.4.1 to 6.4.3 go from reactants to products: K is the equilibrium constant for the formation of the precursor complex $[A_{ox}, B_{red}]$, and k_{et} is the forward electron transfer rate to produce the successor complex $[A_{red}, B_{ox}]$.



Marcus pioneered the use of potential energy diagrams as an aid in describing electron-transfer processes.⁶⁰ For the sake of simplicity, the donor and acceptor are assumed to behave like collections of harmonic oscillators. Instead of two separate potential energy surfaces being used for the reactants, they are combined into a single surface that describes the potential energy of the precursor complex as a function of its nuclear configuration (i.e., the sum of the translational, rotational, and vibrational degrees of freedom of the reactant molecules and the molecules in the surrounding solvent-3N coordinates, where N is the number of nuclei present). Similarly, a single potential energy (3N-dimensional) surface is used to describe the potential energy of the successor complex as a function of its nuclear configuration. It has become conventional to simplify such potential energy diagrams by using one-dimensional slices through the reactant and product surfaces in order to visualize the progress of a reaction, as illustrated in Figure 6.21.

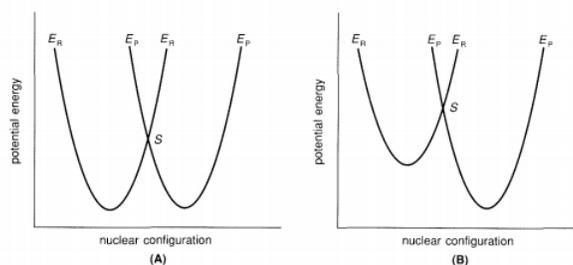


Figure 6.21 - Potential energy diagrams: (A) self-exchange reaction; (B) cross reaction. Point S represents the activated complex. E_R and E_P are the reactant and product surfaces, respectively.

The intersection of the reactant and product surfaces (point S) represents the transition state (or "activated complex"), and is characterized by a loss of one degree of freedom relative to the reactants or products. The actual electron-transfer event occurs when the reactants reach the transition-state geometry. For bimolecular reactions, the reactants must diffuse through the solvent, collide, and form a precursor complex prior to electron transfer. Hence, disentangling the effects of precursor complex formation from the observed reaction rate can pose a serious challenge to the experimentalist; unless this is gone, the factors that determine the kinetic activation barrier for the electron-transfer step cannot be identified with certainty.

The surfaces depicted in Figure 6.21 presume that the electrons remain localized on the donor and acceptor; as long as this situation prevails, no electron transfer is possible. Thus some degree of electronic interaction, or coupling, is required if the redox system is to pass from the precursor to the successor complex. This coupling removes the degeneracy of the reactant and product states at the intersection of their respective zero-order surfaces (points S in Figure 6.21) and leads to a splitting in the region of the intersection of the reactant and product surfaces (Figure 6.22). If the degree of electronic interaction is sufficiently small, first-order

perturbation theory can be used to obtain the energies of the new first-order surfaces, which do not cross. The splitting at the intersection is equal to $2H_{AB}$, where H_{AB} is the electronic-coupling matrix element.

The magnitude of H_{AB} determines the behavior of the reactants once the intersection region is reached. Two cases can be distinguished. First, H_{AB} is very small; for these so-called "nonadiabatic" reactions, there is a high probability that the reactants will "jump" to the upper first-order potential energy surface, leading to very little product formation. If the electronic interaction is sufficiently large, as it is for "adiabatic" reactions, the reactants will remain on the lower first-order potential energy surface upon passage through the transition-state region.

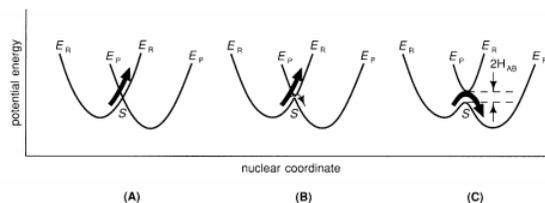


Figure 6.22 - Potential energy diagrams: (A) $H_{AB} = 0$, $\kappa = 0$ (no transfer); (B) H_{AB} small, $\kappa < 1$ (nonadiabatic transfer); (C) H_{AB} large, $\kappa = 1$ (adiabatic transfer). The arrows indicate the relative probability of crossing to the product surface (E_R to E_P).

The term adiabatic (Greek: *a-dia-bainein*, not able to go through) is used in both thermodynamics and quantum mechanics, and the uses are analogous. In the former, it indicates that there is no heat flow in or out of the system. In the latter, it indicates that a change occurs such that the system makes no transition to other states. Hence, for an adiabatic reaction, the system remains on the same (i.e., lower) first-order electronic surface for the entire reaction. The probability of electron transfer occurring when the reactants reach the transition state is unity. The degree of adiabaticity of the reaction is given by a transmission coefficient, κ , whose value ranges from zero to one. For systems whose H_{AB} is sufficiently large ($>k_B T$, where k_B is the Boltzmann constant), $\kappa = 1$. This situation occurs when the reacting centers are close together, the orbital symmetries are favorable, and no substantial changes in geometry are involved. The transmission coefficient is generally very small ($\kappa < 1$) for electron-transfer reactions of metalloproteins, owing to the long distances involved.

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