Electron Transfer Reactions With and Without Ion Transfer

A. J. Appleby

238 Wisenbaker Engineering Research Center
Texas A&M University, College Station, TX 77843-3402

I. INTRODUCTION

The most frequent molecular model used for electrolytic electron transfer since the 1930s is similar to the Franck-Condon (FC) principle\(^1\) for spectral electronic transitions. Kinetic activation occurs until a rapid radiationless electronic transition becomes possible. Following FC and the equivalent Born-Oppenheimer approximation,\(^2\) it is assumed that classical nuclear motion during the electronic transition is slow enough to be negligible. In condensed media, the potential energy of a reactant involves an extended number of nuclei and many degrees of freedom. To reconcile the energy requirements in condensed media with electron transfer has resulted in many ingenious mechanistic proposals. Charged molecules surrounded by rather tightly-bound solvent dipoles have potential energies different from vacuum values because of the presence of the surrounding dielectric solvent. These tightly-bound “Inner Sphere” solvent dipoles may or may not be free to move before rapid electron transfer of FC type.

Since the 1950s, the surrounding dielectric solvent has usually been considered to determine kinetics because of its assumed immobility during rapid electron transfer. Efforts to summarize reaction rate evidence in the 1970s and more recently have failed to leave the theory in a satisfactory state.

This chapter reviews electron transfer models, develops molecular models of the solvent surrounding ions of different types to provide a more complete picture of the orientational changes taking place, especially in cases where electron transfer is combined with atom transfer, where assembly of a solvation sphere is required during the process. Finally, the activation energies of some charge-transfer processes are given.

II. THE FRANCK-CONDON PRINCIPLE AND ELECTRON TRANSFER

1. Historical Development

The electrochemical FC principle can be traced to 1931 papers by Franck and Haber on photochemical electron transfer\(^7\) and by Gurney on electrochemical hydrogen evolution.\(^8\) Landau’s publication on gaseous electron transfer followed in 1932.\(^9\) The electron makes a single, rapid transition from a donor to an acceptor state in which all heavy particle motions are frozen in time. The electronic transition may be adiabatic, i.e., with a transition probability of unity with no tunneling through an energy barrier, or non-adiabatic, i.e., with tunneling. Transitions may take place with or without radiation or photon absorption. Gurney’s model for proton dissociation from the \(\text{H}_2\text{O}^+\) ion with simultaneous electron acceptance from a metal energy level introduced the concept, accounting for the overpotential, the Tafel equation and its Butler-Volmer extension, then recently confirmed by Bowden. The \(\text{H}_3\text{O}^+\) ion was formalized as the oxonium or hydronium ion by Bernal and Fowler.\(^16\)

Gurney\(^8\) used Hund’s molecular orbital model for \(\text{H}_3\text{O}^+\) to deduce that its dissociation energy was 8.3 eV, close to the 7.9 eV value estimated using a thermochemical cycle. A thermally activated \(\text{H}_3\text{O}^+\) ion with one bond randomly stretched to a higher potential energy state was postulated to accept an electron from a metal electrode level and spontaneously “fly apart” (sic) to \(\text{H}_2\text{O} + \text{H}_\text{,}\) since the force between a neutral hydrogen atom and a water molecule would always be