

Marcus equation

In the late 1950s to early 1960s Rudolph A. Marcus developed a theory for treating the rates of outer-sphere electron-transfer reactions. Outer-sphere reactions are reactions in which an electron is transferred from a donor to an acceptor without any chemical bonds being made or broken. (Electron-transfer reactions in which bonds are made or broken are referred to as inner-sphere reactions.) Marcus derived several very useful expressions, one of which has come to be known as the Marcus cross-relation or, more simply, as the Marcus equation. It is widely used for correlating and predicting electron-transfer rates. For his contributions to the understanding of electron-transfer reactions, Marcus received the 1992 Nobel Prize in Chemistry.

In common with ordinary chemical reactions, an electron-transfer reaction can be described in terms of the motion of the system on an energy surface. As the reaction proceeds the system moves from the reactant minimum (initial state) to the product minimum (final state). The nuclear configurations of the reactants and products and the configuration of the surrounding solvent are constantly changing as a consequence of thermal motion. Marcus showed that, subject to certain assumptions, these fluctuations can be described in terms of displacements on harmonic free-energy curves that are a function of a single reaction coordinate. Two harmonic free-energy curves are needed to describe the reaction — one refers to the reactants plus surrounding medium and the other to the products plus surrounding medium. The two free-energy curves have identical force constants and the reaction coordinate is the difference between the reactant and product free energies at a particular nuclear configuration.

The free energy of the close-contact reactants plus surrounding medium (Curve R) and the free energy of the close-contact products plus surrounding medium (Curve P) are plotted vs. the reaction coordinate in Figure 1. The plot is for an electron-transfer reaction with zero standard free-energy change (an electron self-exchange reaction). The free-energy curves intersect where the reactants plus surrounding solvent and the products plus surrounding solvent have the same nuclear configurations and energies. This intersection defines the transition state for the reaction: the energy required to reach the intersection is the free energy of activation for the reaction. Also shown is λ , the reorganization parameter, which is the vertical difference between the free energies of the (noninteracting) reactants and products of a self-exchange reaction at the