

Perspective

Perspective on “On the theory of oxidation–reduction reactions involving electron transfer. I”

Marcus RA (1956) *J Chem Phys* 24: 966–978

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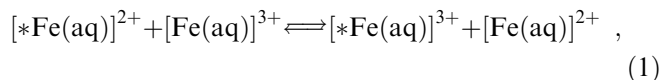
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Abstract. This paper provides a retrospective overview of the title paper written by Marcus around the middle of the twentieth century. A description of the history that led to this work, the basic features of the theory of electron-transfer reactions in solution developed in it, and a comment on its huge influence on succeeding developments are presented.

Key words: Electron-transfer reactions – Marcus theory – Solvent fluctuations – Free-energy barriers – Inverted region

Electron transfers are perhaps the simplest of all chemical reactions, at least when no chemical bonds are broken or formed. The availability of many radioactive isotopes due to nuclear developments in World War II made possible the early experiments in the electron-transfer field. Artificial radioactivity made it possible to measure the rates of a large number of isotopic-exchange (self-exchange) electron-transfer reactions in aqueous solution. Prior to about 1950, it was commonly believed that a self-exchange reaction such as [where the asterisk marks a radioactive isotope]



could proceed very rapidly (even almost instantaneously), because an electron could jump from the ferrous ion to the ferric ion, with no change in energy, across long distances. However, as several systems were explored, it soon became apparent that self-exchange reactions of simple cations in aqueous solutions, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Eu}^{2+}/\text{Eu}^{3+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$, are generally slow, while electron transfers in most systems involving complex

ions, such as $\text{MnO}_4^-/\text{MnO}_4^{2-}$ and $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, were faster by several orders of magnitude. In 1951, an important symposium on electron-transfer processes was held at the University of Nôtre Dame, and the proceedings were reported in the 1952 symposium issue of *J Phys Chem*. In his paper in that issue, Libby [1] noted that the surprising results could be rationalized by considering the role of the solvent molecules. For instance, in the reaction depicted in Eq. 1 the direct electron jump is much faster than the nuclear motion of the solvent, the new $[\text{Fe}(\text{aq})]^{3+}$ and $[\text{Fe}(\text{aq})]^{2+}$ being generated with the hydration configurations appropriate for the original $[\text{Fe}(\text{aq})]^{2+}$ and $[\text{Fe}(\text{aq})]^{3+}$, respectively. This idea comes from the Franck–Condon principle of molecular spectroscopy. The large change in initial and final equilibrium solvations around each of the two ions would account for the large energy barrier to the electron transfer. In self-exchange reactions involving complex ions, the change in equilibrium solvation would be smaller owing to the larger radii, thus leading to a smaller energy barrier to electron-transfer reactions.

Meanwhile, Marcus joined the faculty of the Polytechnic Institute of Brooklyn (New York) in 1951. After writing the 1952 RRKM papers, he was looking for a new field of theoretical research in which to work. As a result of a question posed by a student in his statistical mechanics class, Marcus focused on polyelectrolytes and their electrostatic free energy. To this aim, he had to expand considerably his electrostatics background, which turned out to be very useful for him when, in 1955, he found by chance the above-mentioned 1952 symposium issue on electron-transfer reactions. Reading that issue, Marcus realized that Libby’s proposal involved a vertical transition, which violated the energy-conservation principle unless absorption of radiation took place. As a result he intended to understand how thermal electron transfers in the dark could occur satisfying both the Frank–Condon and energy-conservation principles. A month later, Marcus found the solution to the problem and published his results in the

title paper, in which the first quantitative microscopic description of a chemical reaction in solution was made.

The basic features of the theory of electron-transfer reactions in solutions developed by Marcus in that paper can be summarized as follows. The electron transfer between the two reacting molecules is described in terms of a diabatic two-state model consisting of a system having the electronic configuration of the reactants (precursor complex) and a system having the electronic configuration of the products (successor complex) after the electron transfer. Each state gives rise to the corresponding diabatic potential energy hypersurfaces U_p (precursor) and U_s (successor), respectively, which are functions of the ensemble of nuclear coordinates of the entire system. Both U_p and U_s have minima that correspond to the equilibrium configuration of the solvent around the reacting molecules and the reaction products, respectively. Assuming a classical frame, the radiationless electron transfer takes place at the intersection region (X) between U_p and U_s , which constitutes the transition state of the reaction. This implies that reorganization of the solvent is required before the electron transfer takes place. Random thermal fluctuations in the solvent configurations of the precursor complex occur until that X region is reached, then the energies of both diabatic states become equal and the electron jump happens. The transfer at X occurs at fixed positions and momenta of the nuclei, the Franck–Condon principle being satisfied. The appearance of the proper fluctuations costs free energy. It is this free energy that determines the rate of the reaction. The electronic coupling between both diabatic states is supposed to be large enough to permit the conversion from reactants to products at the intersection region, but small enough to be neglected in order to ignore the splitting of the two hypersurfaces in the vicinity of their intersection.

In addition Marcus treated the solvent as a dielectric continuum in order to make the calculation of the free-energy barrier feasible. As a result of the slowness of the vibrations and orientation changes of the solvent molecules, the solvent electrical polarization at the transition state is not in equilibrium with the electric field produced by the ionic charges of the reacting molecules or reaction products. Marcus had to use a method to calculate the electrostatic free energy of states having nonequilibrium polarization that was developed by himself in the paper following the title paper in the same volume of *J Chem Phys* [2]. The title paper finally provided a simple expression for the free-energy barrier, which when introduced into transition-state theory leads to the reaction rate.

The title paper was enormously important by itself, but in addition it was the first step (and the cornerstone) in a long series of papers on electron-transfer reactions which were published by Marcus from 1956 to 1965. During those years he extended [3, 4] the theory to include, for instance, intramolecular vibrational effects, numerically calculated rates of self-exchange and cross reactions, electrochemical electron-transfer reactions (i.e. including electrodes), chemiluminescent electron transfers, the relation between nonequilibrium and

equilibrium solvation free energies for arbitrary geometries, and spectral charge-transfer processes.

One of the most fundamental achievements of the seminal Marcus theory on electron-transfer reactions is the nowadays widely used quadratic driving force–activation free energy Marcus relationship

$$\Delta G^\ddagger = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (2)$$

that relates the activation free energy ΔG^\ddagger to the standard reaction free energy ΔG^0 and the reorganization free energy λ (i.e., the free energy released when the system evolves from equilibrium configurations corresponding to reactants to those corresponding to products, while an electronic wave function, that can be directly related to products in a valence-bond structure sense, is maintained to describe the solute). This classical expression contains a most interesting prediction: as the driving force (negative of the standard reaction free energy) of the reaction increases, the reaction rate rises to a maximum when $\Delta G^0 = -\lambda$, but then unexpectedly falls off again. The initial decrease in ΔG^\ddagger with increasingly negative ΔG^0 is the expected trend in chemical reactions (similar, for instance, to the usual trend in Brønsted plots of acid- or base-catalyzed reactions and in Tafel plots of electrochemical reactions) and corresponds to the “normal” region. Instead, the prediction for the region where $\Delta G^0 < -\lambda$, the so-called “inverted region”, was one of the more startling and controversial results of Marcus theory. As a matter of fact, the first unambiguous experimental demonstration [5] of the existence of such an inverted region in solution electron-transfer reactions was not made until 1984, almost 25 years after Marcus had predicted it.

The huge impact of the title paper and the 1956–1965 series of papers originating from it on the field of theoretical chemistry (and on many new experimental developments in chemistry) was recognized by the Royal Swedish Academy of Sciences, which decided to award the 1992 Nobel Prize in Chemistry to Marcus for his contributions to the theory of electron-transfer reactions in chemical systems. Nowadays, the practical consequences of his theory extend over all areas of chemistry and many areas of biochemistry. Marcus theory describes and makes predictions concerning an increasingly growing set of widely differing phenomena, such as natural and artificial photosynthesis, metabolism, enzyme-catalyzed redox reactions, photochemical production of fuel, chemiluminescence, the conductivity of electrically conducting polymers, long-range electron transfer in proteins, corrosion, the methodology of electrochemical synthesis and analysis, and more. Much theoretical (and experimental) work on all these topics remains to be done, and it is expected that impressive progress on all of them will be achieved during the next century using new developments based on the Marcus theory initiated in the title paper. In this sense, computer simulations (Monte Carlo and molecular dynamics) will become excellent tools to study very important biological problems associated with electron-transfer reactions,

such as radical processes intervening in chemical carcinogenesis and cellular aging.

Finally, it has to be stressed that, being aware of the corresponding differences, some concepts of electron-transfer reactions have been extended to other types of chemical reactions, such as the transfer of methyl groups, atoms or, especially, protons. It is clear that, apart from electron transfer, proton transfer is the most important type of chemical reaction and, in particular, the most common enzyme-catalyzed reaction. Through proton transfers, the original ideas formulated by Marcus in the title paper for electron-transfer reactions have

found new fields to influence and in which to be successfully applied.

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