ANGEWANDTE CHEMIE
International Edition in English

Volume 32 · Number 8
August 1993
Pages 1111–1222

Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture)**

By Rudolph A. Marcus*

Since the late 1940s, the field of electron transfer processes has grown enormously, both in chemistry and biology. The development of the field, experimentally and theoretically, as well as its relation to the study of other kinds of chemical reactions, presents to us an intriguing history, one in which many threads have been brought together. In this lecture, some history, recent trends, and my own involvement in this research are described.

1. Electron Transfer Experiments since the Late 1940s[***]

The early experiments in the electron transfer field were on "isotopic exchange reactions" (self-exchange reactions) and, later, "cross reactions." These experiments reflected two principal influences. One of these was the availability after the Second World War of many radioactive isotopes, which permitted the study of a large number of isotopic exchange electron transfer reactions in aqueous solution such as depicted in Equations (1) and (2), where the asterisk denotes a radioactive isotope.

$$Fe^{2+} + {}^*Fe^{3+} \rightleftharpoons Fe^{3+} + {}^*Fe^{2+} \quad (1)$$

$$Ce^{3+} + {}^*Ce^{4+} \rightleftharpoons Ce^{4+} + {}^*Ce^{3+} \quad (2)$$

There is a two-fold simplicity in typical self-exchange electron transfer reactions (so-called because other methods beside isotopic exchange were later used to study some of them): 1) the reaction products are identical with the reactants, thus eliminating one factor that usually influences the rate of a chemical reaction in a major way, namely the relative thermodynamic stability of the reactants and products; and 2) no chemical bonds are broken or formed in simple electron transfer reactions. Indeed, these self-exchange reactions represent, for these combined reasons, the simplest class of reaction in chemistry. Observations stemming directly from this simplicity were to have major consequences, not only for the electron transfer field, but also, to a lesser extent, for the study of other kinds of chemical reactions as well (see Shaik et al.[21]).

A second factor in the growth of the electron transfer field was the introduction of new instrumentation, which permitted the study of the rates of rapid chemical reactions. Electron transfers are frequently rather fast compared with many reactions that undergo, instead, breaking of chemical bonds and forming of new ones. Accordingly, the study of a large body of fast electron transfer reactions became accessible with the introduction of this instrumentation. One example was the stopped-flow apparatus, pioneered for inorganic electron transfer reactions by N. Sutin. It permitted the study of bimolecular reactions in solution in the millisecond time scale (a fast time scale at the time). Such studies led to the investigation of what has been termed electron transfer

---

[*] Prof. Dr. R. A. Marcus
Noyes Laboratory of Chemical Physics
California Institute of Technology
MS 127-72
Pasadena, CA 91125 (USA)
Telefax: Int. code + (91)818-792-8485

[**] Copyright © The Nobel Foundation 1993. – We thank the Nobel Foundation, Stockholm, for permission to print this lecture.

[***] This article has not been consistently annotated. The relevant articles in the reference section have been arranged as follows: In [1] some of my important articles, largely from the 1956–1965 period, are listed. Some general references which review the overall literature are listed in [2], and several additional references for Table 1 and for the Figures in [3]. Classic texts on unimolecular reactions are given in [4].

cross reactions, that is, electron transfer reactions between two different redox systems, as in Equation (3), which sup-

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+} \qquad (3)$$

plemented the earlier studies of the self-exchange electron transfer reactions. A comparative study of these two types of reaction, self-exchange and cross-reactions, stimulated by theory, was also later to have major consequences for the field and, indeed, for other areas.

Again, in the field of electrochemistry, the new post-war instrumentation in chemical laboratories led to methods that permitted the study of fast electron transfer reactions at metal electrodes. Prior to the late 1940s, only relatively slow electrochemical reactions, such as the discharge of an H_3O^+ ion at an electrode to form H_2, had been investigated extensively. They involved the breaking of chemical bonds and the forming of new ones.

Numerous electron transfer studies have now also been made in other areas. Some are depicted in Figure 1. Some of these investigations were made possible by newer technology, in particular that of lasers, and now include studies in the picosecond and subpicosecond time regimes. Just recently, the non-laser technique of nanometer-sized electrodes has been introduced to study electrochemical processes that are still faster than those hitherto investigated. Still other recent investigations, important for testing aspects of the electron transfer theory at electrodes, involve the new use of an intervening, ordered, adsorbed monolayer of long-chain organic compounds on the electrode to facilitate the study of several effects such as varying the metal–solution potential difference on the electrochemical electron transfer rate.

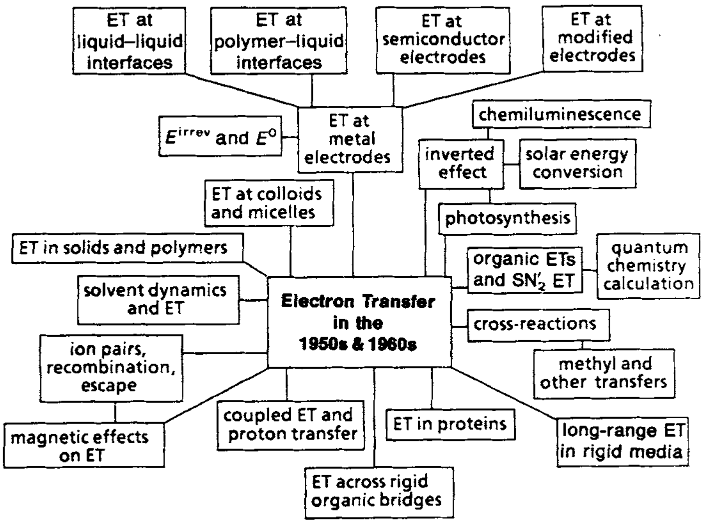

Fig. 1. Examples of topics in the electron transfer (ET) field (Marcus and Siddarth [2]).

In some studies of electron transfer reactions in solution, there has also been a skillful blending of these measurements of chemical reaction rates with organic or inorganic synthetic methods, as well as with site-directed mutagenesis, to obtain more hitherto unavailable information. The use of chemically modified proteins to study the distance dependence of electron transfer, notably by Gray and co-workers, has opened a whole new field of activity.

The interaction of theory and experiment in these many electron transfer fields has been particularly extensive and exciting, and each has stimulated the other. This lecture addresses the underlying theory and this interaction.

2. Early Experience

My own involvement in the electron transfer field began in a rather circuitous way. My background was in experimental measurements of reaction rates as a chemistry graduate student at McGill University (1943–1946) and as a post-doctoral associate at the National Research Council of Canada (NRC, 1946–1949). A subsequent post-doctoral study at the University of North Carolina (1949–1951) on the theory of reaction rates resulted in what is now known as RRKM theory (Rice, Ramsperger, Kassel, Marcus).

This field of unimolecular reactions reflects another long and extensive interaction between theory and experiment. RRKM theory enjoys widespread use and is now usually referred to in the literature only by its acronym (or by the texts written about it[41]), instead of by citation of the original articles.

After the theoretical post-doctoral period, I joined the faculty of the Polytechnic Institute of Brooklyn in 1951 and wondered what theoretical research to do next after writing the RRKM papers (1951–1952). I remember vividly how a friend of mine and a colleague at Brooklyn Poly, Frank Collins, came down to my office every day with a new idea on the liquid-state transport theory that he was developing, while I had none for my theoretical research. Perhaps this gap of not doing anything immediately in the theoretical field was, in retrospect, fortunate: In not continuing with the study of the theory of unimolecular reactions, for which there were too few legitimate experimental data at the time to make the subject one of continued interest, I was open for investigating quite different problems in other areas. I did, however, begin a program of experimental studies in gas phase reactions prompted by my earlier studies at NRC and by the RRKM work.

I also recall how a student in my statistical mechanics class in this period (Abe Kotliar) asked me about a particular problem in polyelectrolytes. It led to my writing two papers on the subject (1954–1955), one of which required a considerable expansion in my background in electrostatics to analyze different methods for calculating the free energy of these systems: in polyelectrolyte molecules, the ionic charges along the organic or inorganic molecular backbone interact with each other and with the solvent. In the process I read the relevant parts of the texts that were readily available on electrostatics (Caltech's Mason and Weaver's book was later to be particularly helpful!) When shortly thereafter I encountered some papers on electron transfer, a field entirely new to me, I was reasonably well prepared for treating the problems that lay ahead.

3. Developing an Electron Transfer Theory

3.1. Introduction

My first contact with electron transfer reactions came in 1955 as a result of chancing upon a 1952 symposium issue on the subject in the Journal of Physical Chemistry. An article by Bill Libby caught my eye—a use of the Franck–Condon principle to explain some experimental results, namely, why some isotopic exchange reactions that involve electron transfer between pairs of small cations in aqueous solution, such as reaction (1), are relatively slow, whereas electron transfers involving larger ions, such as $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ and MnO_4^-/MnO_4^{2-}, are relatively fast.

Libby explained this observation in terms of the Franck–Condon principle, as discussed in Section 4.1. The principle was used extensively in the field of spectroscopy for interpreting spectra for the excitation of the molecular electronic–vibrational quantum states. An application of that principle to chemical reaction rates was novel and caught my attention. In that paper Libby gave a "back-of-the-envelope" calculation of the resulting energy barrier for solvation that slowed the reaction. However, I felt instinctively that even though the idea—that somehow the Franck–Condon principle was involved—seemed strikingly right, the calculation itself was incorrect. The next month of study of the problem was, for me, an especially busy one. To place the topic in some perspective I first digress and describe the type of theory that was used for other types of chemical reaction rates at the time and continues to be useful today.

3.2. Reaction Rate Theory

Chemical reactions are often described in terms of the motion of the atoms of the reactants on a potential energy surface. This potential energy surface is really the electron energy of the entire system, plotted against the positions of all the atoms. A very common example is the transfer of an atom or a group B from molecule AB to form BC [Eq. (4)].

$$AB + C \longrightarrow A + BC \qquad (4)$$

An example of reaction (4) is the transfer of a hydrogen atom, such as in $IH + Br \rightarrow I + HBr$, or the transfer of a CH_3 group from one aromatic sulfonate to another. To aid in visualizing the motion of the atoms in this reaction, the potential energy function for reaction (4) is frequently plotted as constant energy contours in a space whose axes are chosen to be two important relative coordinates such as a scaled AB bond length and a scaled distance from the center of mass of AB to C, as in Figure 2.

A point representing the reactants of this reacting system begins its trajectory in the lower right region of the figure in a valley in this plot of contours. When the system has enough energy, appropriately distributed between the various motions, it can cross the "mountain pass" (saddle-point region) separating the initial valley from the products' valley in the upper left of Figure 2, and so form the reaction products. The line xy in Figure 2, analogous to the continental divide in the Rocky Mountains in the United States separates systems that could spontaneously flow into the reactants' valley from those that could flow into the products' one. In chemists' terminology this line represents the transition state of the reaction.

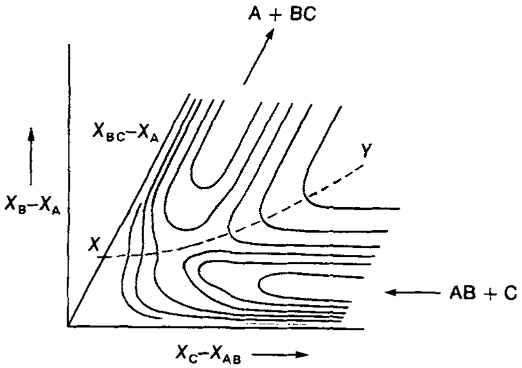

Fig. 2. Potential energy contours for reaction (4) in the collinear case. X_A = coordinates of A, etc.

In transition state theory, a quasi-equilibrium between the transition state and the reactant is frequently postulated, and the reaction rate is then calculated with equilibrium statistical mechanics. A fundamental dynamical basis, which replaces this apparently ad hoc but common assumption of transition state theory and which is perhaps not as well known in the chemical literature as it deserves to be, was given in 1938 by the physicist and one-time chemical engineer, Eugene Wigner. He used a classical mechanical description of the reacting system in the many-dimensional space (of coordinates and momenta). Wigner pointed out that the quasi-equilibrium would follow as a dynamical consequence, if each trajectory of a moving point representing the reacting system in this many-dimensional space did not recross the transition state (and if the distribution of the reactants in the reactants' region were a Boltzmann one). In recent times, the examination of this recrossing has been a common problem in classical mechanical trajectory studies of chemical reactions. Usually, recrossings are relatively minor, except in nonadiabatic reactions, where they are readily treated (see Section 4.1).

In practice, transition state theory is generalized to include as many coordinates as are needed to describe the reacting system. Further, when the system can tunnel quantum mechanically through the potential energy barrier (the pass) separating the two valleys, as for example frequently happens at low energies in H-transfer reactions, the method of treating the passage across the transition state region needs, and has received, refinement. (The principal problem encountered here has been the lack of "dynamical separability" of the various motions in the transition state region.)

4. Electron Transfer Theory: Formulation

4.1. Fundamental Considerations

In contrast to the above picture, we have already noted that in simple electron transfer reactions no chemical bonds are broken or formed, and so a somewhat different picture of the reaction is needed.

In his symposium paper in 1952, Libby noted that when an electron is transferred from one reacting ion or molecule to another, the two new molecules or ions formed are in the wrong environment of the solvent molecules, since the nuclei do not have time to move during the rapid electron jump: in reaction (1) an Fe^{2+} ion would be formed in some configuration of the many nearby dipolar solvent molecules that was appropriate to the original Fe^{3+} ion. Analogous remarks apply to the newly formed Fe^{3+} ion in the reaction. On the other hand, in reactions of complex ions, such as those in the $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ and MnO_4^-/MnO_4^{2-} self-exchange reactions, the two reactants are larger, and so the change of electric field in the vicinity of each ion, upon electron transfer, would be smaller. The original solvent environment would therefore be less foreign to the newly formed charges, and so the energy barrier to reaction would be less. In this way Libby explained the faster self-exchange electron transfer rate for these complex ions. Further confirmation was noted in the ensuing discussion in the symposium: the self-exchange $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$ reaction is very slow, and it was pointed out that there was a large difference in the equilibrium Co–N bond lengths in the Co^{III} and Co^{II} ions. Again, each ion would be formed in a very foreign configuration of the vibrational coordinates, even though the ions are complex ions.

After studying Libby's paper and the symposium discussion, I realized that what troubled me in this picture for reactions occurring in the dark was that energy was not conserved: the ions would be formed in the wrong high-energy environment, but the only way such a non-energy-conserving event could happen would be by the absorption of light (a vertical transition), and not in the dark. Libby had perceptively introduced the Franck–Condon principle to chemical reactions, but something was missing.

In the present discussion, as well as in Libby's treatment, it was supposed that the electronic interaction of the reactants that causes the electron transfer is relatively weak. That view is still the one that seems appropriate today for most of these reactions. In this case of weak-electronic interaction, the question becomes: how does the reacting systm behave in the dark so that it satisfies both the Franck–Condon principle and energy conservation? I realized that fluctuations had to occur in the various nuclear coordinates, such as in the orientation coordinates of the individual solvent molecules and indeed in any other coordinates whose most probable distribution for the products differs from that of the reactants. With such fluctuations, values of the coordinates could be reached which satisfy both the Franck–Condon and energy conservation conditions and so permit the electron transfer to occur in the dark.

An example of an initial and final configuration of the solvent molecules for reaction (1) is depicted in Figure 3. Fluctuations from the original equilibrium ensemble of configurations were ultimately needed, prior to the electron transfer, and were followed by a relaxation to the equilibrium ensemble for the products after electron transfer.

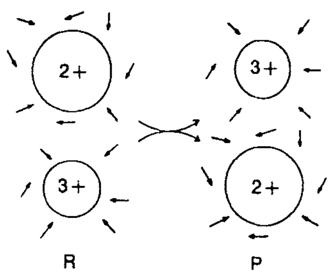

Fig. 3. Typical arrangement of solvent molecules surrounding reactants and products in reaction (1). The longer M–OH_2 bond length in the cation is indicated schematically by the larger ionic radius (Sutin, [2]).

The theory then proceeded as follows. The potential energy U_r of the entire system, reactants plus solvent, is a function of the many hundreds of relevant coordinates of the system, coordinates which include, among others, the position and orientation of the individual solvent molecules (and hence of their dipole moments, for example), and the vibrational coordinates of the reactants, particularly those in any inner coordination shell of the reacting ions. (For example, the inner coordination shell of an ion such as Fe^{2+} or Fe^{3+} in water is known from EXAFS (*e*xtended *X*-ray *a*bsorption *f*ine *s*tructure) experiments to contain six water molecules.) No longer were there just the two or so important coordinates that were dominant in reaction (4).

Similarly, after the electron transfer, the reacting molecules have the ionic charges appropriate to the reaction products, and so the relevant potential energy function U_p is that for the products plus solvent. These two potential energy surfaces will intersect if the electronic coupling which leads to electron transfer is neglected. For a system with N coordinates this intersection occurs on an $(N-1)$ dimensional surface, which then constitutes in our approximation the transition state of the reaction. The neglected electronic coupling causes a well-known splitting of the two surfaces in the vicinity of their intersection. A schematic profile of the two potential energy surfaces in the N-dimensional space is given in Figure 4. (The splitting is not shown.)

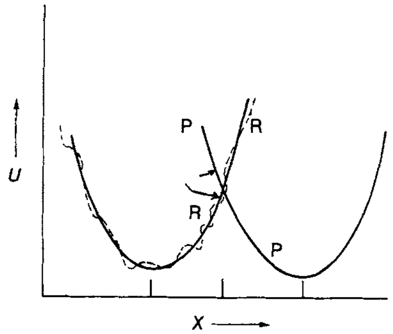

Fig. 4. Profile of potential energy surfaces for reactants plus environment (R) and for products plus environment (P). Solid curve: schematic. Dashed curve: schematic but slightly more realistic. The typical splitting at the intersection of the potential energy curves U_r and U_p is not shown (Marcus and Siddarth [2]). X = nuclear coordinates.

Due to the effect of the previously neglected electronic coupling and the coupling between the electronic motion and the nuclear motion near the intersection surface S, an electron transfer can occur at S. In classical terms, the transfer at S occurs at fixed positions and momenta of the atoms; the Franck–Condon principle is satisfied. Since U_r equals U_p at S, energy is also conserved. The details of the electron transfer depend on the extent of electronic coupling and how rapidly the point representing the system in this N-dimensional space crosses S. (It has been treated, for example, by using as an approximation the well-known one-dimensional Landau–Zener expression for the transition probability at the near-intersection of two potential energy curves.)

When the splitting caused by the electronic coupling between electron donor and acceptor is large enough at the intersection, a system crossing S from the lower surface on the reactants' side continues onto the lower surface on the products' side; an electron transfer in the dark has then occurred. When the coupling is, instead, very weak, ("nonadiabatic reactions") the probability of successfully reaching the lower surface on the products' side is small and can be calculated by using quantum mechanical perturbation theory—for example, by using Fermi's "Golden Rule," an improvement over the 1-dimensional Landau–Zener treatment.

Thus, there is some difference and some similarity with a more conventional type of reaction such as reaction (4), whose potential energy contour plots were depicted in Figure 2. In both cases, fluctuations of coordinates are needed to reach the transition state, but since so many coordinates can now play a significant role in the electron transfer reaction because of the major and relatively abrupt change in charge distribution on passing through the transition state region, a rather different approach from the conventional one was needed to formulate the details of the theory.

4.2. Electron Transfer Theory: Treatment

In the initial paper (1956) I formulated the picture of the mechanism of electron transfer described in the previous section and, to make the calculation of the reaction rate tractable, treated the solvent as a dielectric continuum. Because of the orientation and vibrations of the solvent molecules, the position-dependent dielectric polarization $P_u(r)$ of the solvent in the transition state was not the one in equilibrium with the reactants' or the products' ionic charges. It represented instead, some macroscopic fluctuation from them. The electronic polarization of the solvent molecules, on the other hand, can rapidly respond to any such fluctuations and therefore is that dictated by the reactants' charges and by the instantaneous $P_u(r)$.

With these ideas as a basis, what was then needed was a method of calculating the electrostatic free energy G of this system and its still unknown polarization function $P_u(r)$. I obtained this free energy G by finding a reversible path for reaching this state of the system. Upon then minimizing G, subject to the constraint imposed by the Franck–Condon principle (reflected in the electron transfer occurring at the intersection of the two potential energy surfaces), I was able to find the unknown $P_u(r)$ and, hence, to find G for the transition state. That G was then introduced into transition state theory, and the reaction rate calculated.

During this research I also read and was influenced by a lovely paper by Platzmann and Franck (1952) on the optical absorption spectra of halide ions in water and later by work of physicists such as Pekar and Fröhlich (1954) on the closely related topic of polaron theory. As best as I can recall now, my first expressions for G during this months of intense activity seemed rather clumsy, but then with some rearrangement a simple expression emerged that had the right "feel" to it and that I could also derive by a somewhat independent argument. The expression also reduced reassuringly to the usual one, when the constraint of arbitrary $P_u(r)$ was removed. Obtaining the result for the mechanism and rate of electron transfer was indeed one of the most thrilling moments of my scientific life.

The expression for the rate constant k of the reaction is given by Equation (5), where ΔG^* is represented by Equation (6).

$$k = A\exp\left(\frac{-\Delta G^*}{k_B T}\right) \tag{5}$$

$$\Delta G^* = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \tag{6}$$

The term A in Equation (5) depends on the nature of the electron transfer reaction (e.g., bimolecular or intramolecular), ΔG^0 is the standard free energy of reaction (and equals zero for a self-exchange reaction), and λ is a "reorganization term" composed of solvational (λ_0) and vibrational (λ_i) components [Eq. (7)].

$$\lambda = \lambda_0 + \lambda_i \tag{7}$$

In a two-sphere model of the reactants, λ_0 was expressed in terms of the two ionic radii a_1 and a_2 (which encompass the radii of any inner coordination shell), the center-to-center separation distance R of the reactants, the optical (D_{op}) and static (D_s) dielectric constants of the solvent, and the charge transferred (Δe) from one reactant to the other [Eq. (8)].

$$\lambda_0 = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{8}$$

For a bimolecular reaction, work terms, principally electrostatic, are involved in bringing the reactants together and in separating the reaction products, but are omitted from Equation (6) for notational brevity. The expression for the vibrational term λ_i is given by (9), where Q_j^r and Q_j^p are equilibrium values for the jth normal mode coordinate Q, and k_j is a reduced force constant $2k_j^r k_j^p/(k_j^r + k_j^p)$ associated with it. The superscripts r and p refer to reactants and products. (I introduced a "symmetrization" approximation for the vibrational part of the potential energy surface to obtain this simple form of (6)–(9), and tested it numerically.)

$$\lambda_i = \frac{1}{2}\sum_j k_j\,(Q_j^r - Q_j^p)^2 \tag{9}$$

In 1957 I published the results of a calculation of the λ_i arising from a stretching vibration in the innermost coordination shell of each reactant, (the equation used for λ_i was given in the 1960 paper). An early paper on the purely vibrational contribution calculated by using chemical bond length coordinates and neglecting bond–bond correlation had already been published for self-exchange reactions by George and Griffiths in 1956.

I also extended the theory to treat electron transfers at electrodes, and distributed it as an Office of Naval Research

Report in 1957. The equations were published later in a journal paper in 1959. I had little prior knowledge of the subject, and my work on electrochemical electron transfers was facilitated considerably by reading a beautiful and logically written survey article of Roger Parsons on the equilibrium electrostatic properties of electrified metal–solution interfaces.

In the 1957 and 1965 work I showed that the electrochemical rate constant is given by (5)–(9), but A now is a value appropriate to the different "geometry" of the encounter of the participants in the reaction. The term $1/(2a_2)$ in Equation (8) is now absent because only one reaction ion is present, and R denotes twice the distance from the center of the reactant's charge to the electrode (it equals the ion–image distance). A term $e\eta$ replaces ΔG^0 in Equation (6), where e is the charge transferred between the ion and the electrode, and η is the activation overpotential, namely, potential difference between metal and solution relative to the value it would have if the rate constants for the forward and reverse reactions were equal. These rate constants are equal when the minima of the two free energy curves in Figure 5 have the same value for G.

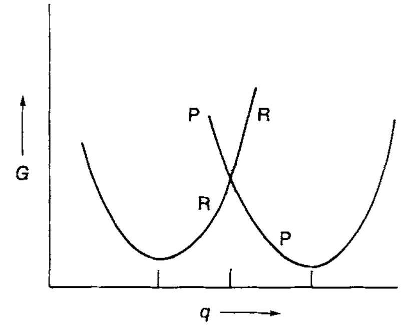

Fig. 5. Plot of the free energy of reactants plus environment vs. the reaction coordinate q (R) and of the free energy of products plus environment vs. reaction coordinate q (P). The three vertical lines on the abscissa denote, from left to right, the value for the reactants, the transition state, and the products (Marcus and Siddarth [2]).

When $|e\eta| < \lambda$, most electrons go into or out of quantum states in the metal that are near the Fermi level. However, because of the continuum of states in the metal, the inverted effect described below was now predicted to be absent for this process; that is, the electrochemical counterpart of Eq. (6) is applicable only in the region $|e\eta| < \lambda$: In the case of an intrinsically highly exothermic electron transfer reaction at an electrode, the electron can remove the immediate "exothermicity" by (if entering) going into a high, unoccupied quantum state of the metal, or (if leaving) departing from a low, occupied quantum state, each far removed from the Fermi level. (The inverted region effect should, however, occur for the electron transfer when the electrode is a narrow-band semiconductor.)

After these initial electron transfer studies, which were based on a dielectric continuum approximation for the solvent outside the first coordination shell of each reactant, I introduced a purely molecular treatment of the reacting system. The solvent was treated by statistical mechanics as a collection of dipoles in the 1960 paper, and later in 1965 a general charge distribution was used for the solvent molecules and the reactants. At the same time I found a way in this 1960 paper of introducing rigorously a global reaction coordinate in this many-dimensional (N) coordinate space of the reacting system. The globally defined coordinate so introduced was equivalent to using $U_p - U_r$, the potential energy difference between the products plus solvent (U_p) and the reactants plus solvent (U_r) (see A. Warshel, 1987). This coordinate is thus defined everywhere in this N-dimensional space.

The free energy G_r of a system containing the solvent and the reactants, and that of the corresponding system for the products, G_p, could now be defined along this globally defined reaction coordinate. (By contrast, in reactions such as that depicted by Figure 2, it is customary, instead, to define a reaction coordinate locally in the vicinity of a path leading from the valley of the reactants through the saddle point region and into the valley of the products.)

The potential energies U_r and U_p in the many-dimensional coordinate space are simple functions of the vibrational coordinates, but complicated functions of the hundreds of relevant solvent coordinates: there are many local minima corresponding to locally stable arrangements of the solvent molecules. However, I introduced a "linear response approximation," in which any hypothetical change in charge of the reactants produces a proportional change in the dielectric polarization of the solvent. (Recently I utilized a central limit theorem to understand this approximation better than is possible with simple perturbation theory and plan to submit the results for publication shortly.) With this linear approximation the free energies G_r and G_p became simple quadratic functions of the reaction coordinate.

Such an approach had major consequences. It depicted the reaction in terms of parabolic free energy plots in simple and readily visualized terms, as in Figure 5. With these plots the trends predicted from the equations were readily understood. It was also important to use the free energy curves, instead of oversimplified potential energy profiles, because of the large entropy changes which occur in many electron transfer cross-reactions, caused by changes in strong solvent interactions between ions and polar solvent. (The free energy plot is legitimately a one-coordinate plot, whereas the potential energy plot is at most a profile of the complicated U_r and U_p functions in N-dimensional space.)

With the new statistical mechanical treatment of 1960 and 1965 one could also see how certain relations between rate constants initially derivable from the dielectric continuum-based equations in the 1956 paper could also be valid more generally. The relations were based, in part, on Equations (5) and (6) and (initially via (8) and (9)) on the approximate relation (10), where λ_{12} is the reoganization term for

$$\lambda_{12} \cong \tfrac{1}{2}(\lambda_{11} + \lambda_{22}) \qquad (10)$$

the cross-reaction, and λ_{11} and λ_{22} are those of the self-exchange reactions.

5. Predictions Based on the Theory

In the 1960 paper I had listed a number of theoretical predictions resulting from these equations, in part to stimulate discussion with experimentalists in the field at a Faraday Society meeting on oxidation–reduction reactions, where this paper was to be presented. At the time I certainly did not anticipate the subsequent involvement of the many experimentalists in testing them. Among the predictions was one that became one of the most widely tested aspects of the theory, namely, the cross-relation. This expression, which follows from Equations (5), (6), and (10), relates the rate constant k_{12} of a cross-reaction to the two self-exchange rate constants, k_{11} and k_{22}, and to the equilibrium constant K_{12} of the reaction [Eq. (11)], where f_{12} is a known function of k_{11}, k_{22} and K_{12} and is usually close to unity.

$$k_{12} \cong (k_{11} k_{22} K_{12} f_{12})^{1/2} \qquad (11)$$

Another prediction in the 1960 paper concerned what I termed there the inverted region: In a series of related reactions, similar in λ but differing in ΔG^0, a plot of the activation free energy ΔG^* vs. ΔG^0 is seen from Equation (6) first to decrease as ΔG^0 is varied from zero to some negative value, to be zero at $\Delta G^0 = -\lambda$, and then to increase when ΔG^0 is made still more negative. The initial decrease of ΔG^* with increasingly negative ΔG^0 is the expected trend in chemical reactions and is similar to the usual trend in "Brønsted plots" of acid- or base-catalyzed reations and in "Tafel plots" of electrochemical reactions. I termed that region of ΔG^0 the "normal" region. However, the prediction for the region where $-\Delta G^0 > \lambda$, the inverted region, was the unexpected behavior, or at least unexpected until the present theory was introduced.

This inverted region is also easily visualized from Figures 6 and 7: Successively making ΔG^0 more negative by lowering the products' G curve vertically relative to the reactant curve, decreases the free energy barrier ΔG^* (given by the intersection of the reactants' and products' curves); that barrier is seen in Figure 6 to vanish at some ΔG^0 and then to increase again.

Other predictions dealt with the relation between the electrochemical and the corresponding self-exchange electron transfer rates, the numerical estimate of the reaction rate constant k, and, in the case of nonspecific solvent effects, the dependence of the reaction rate on solvent dielectric properties.

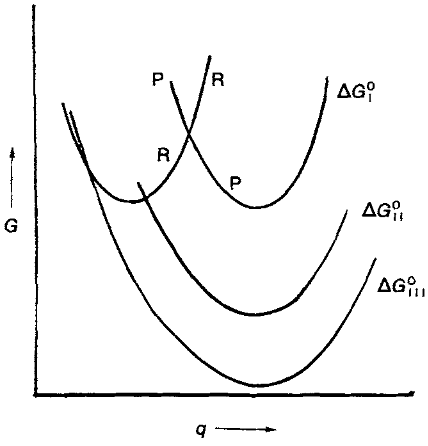

Fig. 6. Plot of the free energy G versus the reaction coordinate q for reactants (R) and products (P), for three different values of ΔG^0; the cases I to III refer to Figure 7 (Marcus and Siddarth [2]).

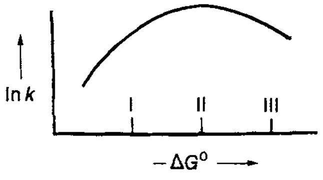

Fig. 7. Plot of $\ln k$, vs. $-\Delta G^0$. Points I and III are in the normal and inverted regions, respectively, while point II at which $\ln k_r$ is a maximum occurs at $-\Delta G^0 = \lambda$ (Marcus and Siddarth, [2]).

The testing of some of the predictions was delayed by an extended sabbatical in 1960–1961, which I spent auditing courses and attending seminars at the nearby Courant Mathematical Institute.

6. Comparison of Experiment and Theory

Around 1962 during one of my visits to Brookhaven National Laboratory, I showed Norman Sutin the 1960 predictions. Norman had either measured on his stopped-flow apparatus or otherwise knew rate constants and equilibrium constants that permitted the cross-relation [Eq. (11)] to be tested. He had about six such sets of data available. I remember vividly the growing sense of excitement we both felt as, one by one, the observed rate constants k_{12} more or less agreed with the predictions of the relation. I later collected the results of this and of various other tests of the 1960 predictions and published them in 1963. Perhaps by showing that the previously published expressions were not mere abstract formulae, but rather had concrete applications, this 1963 paper and many tests by Sutin and others appear to have stimulated numerous subsequent tests of the cross-rela-

Table 1. Comparison of calculated and experimental k_{12} values (Bennett [3]).

Reaction [a]	k_{12} [$\mathrm{M^{-1}\,s^{-1}}$] observed	calculated
$[\mathrm{IrCl_6}]^{2-} + [\mathrm{W(CN)_8}]^{4-}$	6.1×10^7	6.1×10^7
$[\mathrm{IrCl_6}]^{2-} + [\mathrm{Fe(CN)_6}]^{4-}$	3.8×10^5	7×10^5
$[\mathrm{IrCl_6}]^{2-} + [\mathrm{Mo(CN)_8}]^{4-}$	1.9×10^6	9×10^5
$[\mathrm{Mo(CN)_8}]^{3-} + [\mathrm{W(CN)_8}]^{4-}$	5.0×10^6	4.8×10^6
$[\mathrm{Mo(CN)_8}]^{3-} + [\mathrm{Fe(CN)_6}]^{4-}$	3.0×10^4	2.9×10^4
$[\mathrm{Fe(CN)_6}]^{3-} + [\mathrm{W(CN)_8}]^{4-}$	4.3×10^4	6.3×10^4
$\mathrm{Ce^{IV}} + [\mathrm{W(CN)_8}]^{4-}$	$> 10^8$	4×10^8
$\mathrm{Ce^{IV}} + [\mathrm{Fe(CN)_6}]^{4-}$	1.9×10^6	8×10^6
$\mathrm{Ce^{IV}} + [\mathrm{Mo(CN)_6}]^{4-}$	1.4×10^7	1.3×10^7
L-$[\mathrm{Co\{(-)pdta\}}]^{2-} + [\mathrm{Fe(bpy)_3}]^{3+}$	8.1×10^4	$\geq 10^5$
L-$[\mathrm{Fe\{(-)pdta\}}]^{2-} + [\mathrm{Co(edta)}]^{-}$	1.3	1.3
L-$[\mathrm{Fe\{(-)pdta\}}]^{2-} + [\mathrm{Co(ox)_3}]^{3-}$	2.2×10^2	1.0×10^3
$[\mathrm{Cr(edta)}]^{2-} + [\mathrm{Fe(edta)}]^{-}$	$\geq 10^6$	10^9
$[\mathrm{Cr(edta)}]^{2-} + [\mathrm{Co(edta)}]^{-}$	ca. 3×10^5	4×10^7
$[\mathrm{Fe(edta)}]^{2-} + [\mathrm{Mn(Cydta)}]^{-}$	ca. 4×10^5	6×10^6
$[\mathrm{Co(edta)}]^{2-} + [\mathrm{Mn(Cydta)}]^{-}$	0.9	2.1
$[\mathrm{Fe(pdta)}]^{2-} + [\mathrm{Co(Cydta)}]^{-}$	1.2	1.8
$[\mathrm{Co(terpy)_2}]^{2+} + [\mathrm{Co(bpy)_3}]^{3+}$	6.4	3.2
$[\mathrm{Co(terpy)_2}]^{2+} + [\mathrm{Co(phen)_3}]^{3+}$	2.8×10^2	1.1×10^2
$[\mathrm{Co(terpy)_2}]^{2+} + [\mathrm{Co(bpy)(H_2O)_4}]^{3+}$	6.8×10^2	6.4×10^4
$[\mathrm{Co(terpy)_2}]^{2+} + [\mathrm{Co(phen)(H_2O)_4}]^{3+}$	1.4×10^3	6.4×10^4
$[\mathrm{Co(terpy)_2}]^{2+} + [\mathrm{Co(H_2O)_6}]^{3+}$	7.4×10^4	2×10^{10}
$[\mathrm{Fe(phen)_3}]^{2+} + \mathrm{MnO_4^-}$	6×10^3	4×10^3
$[\mathrm{Fe(CN)_6}]^{4-} + \mathrm{MnO_4^-}$	1.3×10^4	5×10^3
$[\mathrm{V(H_2O)_6}]^{2+} + [\mathrm{Ru(NH_3)_6}]^{3+}$	1.5×10^3	4.2×10^3
$[\mathrm{Ru(en)_3}]^{2+} + [\mathrm{Fe(H_2O)_6}]^{3+}$	8.4×10^4	4.2×10^5
$[\mathrm{Ru(NH_3)_6}]^{2+} + [\mathrm{Fe(H_2O)_6}]^{3+}$	3.4×10^5	7.5×10^6
$[\mathrm{Fe(H_2O)_6}]^{2+} + [\mathrm{Mn(H_2O)_6}]^{3+}$	1.5×10^4	3×10^4

[a] pdta = propylenediaminetetraacetate, bpy = bipyridine, edta = ethylenediaminetetraacetate, Cydta = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate, terpy = terpyridine, phen = phenanthroline, en = ethylenediamine.

tion and of the other predictions. A few examples of the cross-relation test are given in Table 1.

The encouraging success of the experimental tests given in the 1963 paper suggested that the theory itself was more general than the approximations (for example, treating solvent as dipoles or employing unchanged force constants) used in 1960 and stimulated me to give a more general formulation (1965). The latter paper also contains a unified treatment of electron transfer reactions in solution and at metal electrodes, and served, thereby, to generalize my earlier (1957) treatment of the electrochemical electron transfer reactions.

The best experimental evidence for the inverted region was provided in 1984 by Miller, Calcaterra, and Closs, almost 25 years after it was predicted. This successful experimental test, which was later obtained for other electron transfer reactions in other laboratories, is reproduced in Figure 8. Possible reasons for not observing it in the earlier tests are severalfold and have been discussed elsewhere.

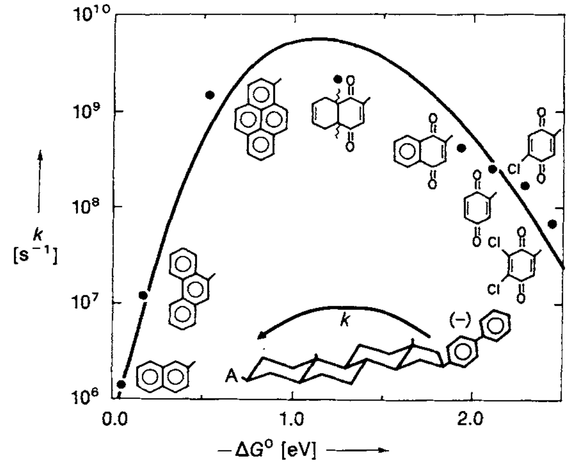

Fig. 8. Inverted region in the chemical electron transfer from a biphenyl group to an acceptor A. Dihydronaphthoquinone marks the changeover from normal (left) to inverse behavior (right). The solid curve was calculated for $\lambda_0 = 0.75$ and $\lambda_i = 0.45$ eV. The frequency of the high-frequency vibrations ω was 1500 cm^{-1} (Miller et al. [3]).

Previously, indirect evidence for the inverted region had been obtained by observing that electron transfer reactions with a very negative ΔG^0 may result in chemiluminescence: when the intersection of the G_r and G_p curves in such cases results in a high free energy of activation ΔG^* because of the effect of the inverted region, there may be an electron transfer to a more easily accessible G_p curve in which one of the products is electronically excited and which intersects the G_r curve in the normal region at a low ΔG^* (Fig. 9). Indeed, experimentally in some reactions 100% formation of an electronically excited state of a reaction product has been observed by Bard and co-workers, and results in chemiluminescence.

Another consequence of Equations (5) and (6) is the linear dependence of $k_BT\ln k$ on $-\Delta G^0$ with a slope of 1/2 when $|\Delta G^0/\lambda|$ is small. The behavior at electrodes is similar, but ΔG^0 is replaced by $e\eta$, that is, the product of the charge transferred and the activation overpotential. Extensive verification of both these results has been obtained. More recently, the curvature of plots of $\ln k$ vs. $e\eta$, expected from these equations, has been demonstrated in several experiments. The very recent use of ordered organic molecular monolayers on electrodes, either to slow down the electron transfer rate or to bind a redox-active agent to the electrode, but in either case to avoid or minimize diffusion control of the fast electron transfer processes, has considerably facilitated this study of the curvature in the $\ln k$ vs. $e\eta$ plot.

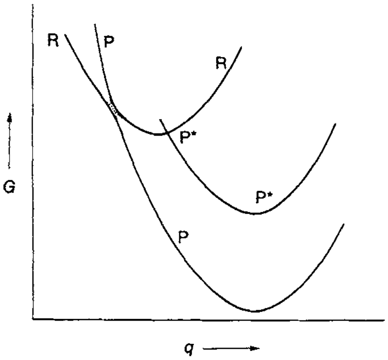

Fig. 9. The favored formation of an electronically excited state of the products (Marcus and Siddarth [2]), which prevents the observation of the inverse region.

Comparison of experiment and theory has also included the testing of absolute reaction rates of self-exchange reactions and the effect on the rate of varying the solvent (an effect sometimes complicated by ion pairing in the low dielectric constant media involved). The related problem of charge transfer spectra, as portrayed in (12) has also been examined. Here, the frequency of the spectral absorption maximum ν_{max} is given by Equation (13).

$$DA + h\nu \longrightarrow D^+A^- \tag{12}$$

$$h\nu_{max} = \lambda + \Delta G^0 \tag{13}$$

Comparisons with Equation (13) in which λ is expressed as in Equation (8) have included examples with effects of separation distance and solvent dielectric constant.

Comparisons have also been made of the self-exchange reaction rates in solution with the rates of the corresponding electron transfer reactions at electrodes. An example of the latter is the plot given in Figure 10, where the self-exchange

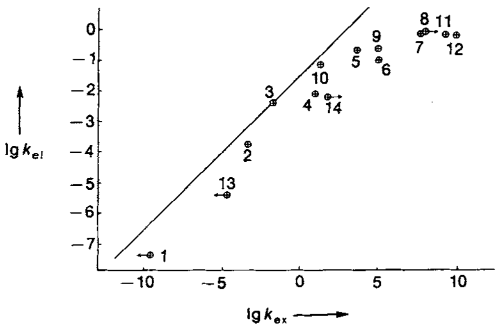

Fig. 10. Comparison of self-exchange electron transfer rates k_{ex} in solution, covering 20 orders of magnitude with rates of corresponding electron transfers at metal electrodes (k_{el}). The line with slope 1/2 shows the behavior predicted by theory (Cannon [2]).

rates are seen to vary by some twenty orders of magnitude. The discrepancy at high rate constants k is currently the subject of some reinvestigation of the fast electrode reaction rates, using the new nanotechnology. Most recently, a new type of interfacial electron transfer rate has also been measured: electron transfer at liquid–liquid interfaces. In treating the latter, I extended the cross relation to this two-phase system. It is clear that much is to be learned from this new area of investigation. (The study of the transfer of ions across such an interface, on the other hand, goes back to the time of Nernst and of Planck around the turn of the century.)

7. Other Applications and Extensions of the Theory

As noted in Figure 1, one aspect of the electron transfer field has been its continued and, indeed, ever-expanding growth in so many directions. One of these is in the biological field, where there are now detailed experimental and theoretical studies in photosynthetic and other protein systems. The three-dimensional structure of a photosynthetic reaction center, the first membrane protein to be so characterized, was obtained by Deisenhofer, Michel, and Huber, who received the Nobel Prize in Chemistry in 1988 for this work. A bacterial photosynthetic system is depicted in Figure 11; the protein framework holding fast the constituents in this reaction center is not shown.

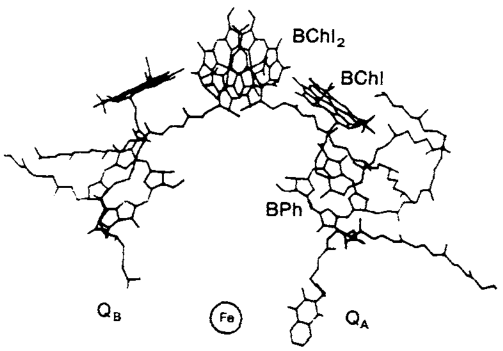

Fig. 11. The redox-active species involved in the initial charge separation in a bacterial photosynthetic center (Deisenhofer et al. and Yeates et al. [3]). The labels added conform to the present text; they include a missing Q$_B$.

In the photosynthetic system there is a transfer of electronic excitation from "antenna" chlorophylls (not shown in Figure 11) to a special pair BChl$_2$. The latter then transfers an electron to a pheophytin BPh within a very short time (≈ 3 ps), from it to a quinone Q$_A$ in 200 ps, and thence to the other quinone Q$_B$. (Other chemical reactions then occur with these separated charges at each site of the membrane, bridged by this photosynthetic reaction center.)

To avoid wasting the excitation energy of the BChl$_2^*$ unduly, it is necessary that $-\Delta G^0$ of this first electron transfer to BPh be small. (It is only about 0.25 eV out of an overall excitation energy of BChl$_2^*$ of 1.38 eV.) In order that this electron transfer also be successful in competing with two wasteful processes, the fluorescence and the radiationless transition of BChl$_2^*$, it is also necessary that ΔG^* for that first electron transfer step be small and hence, by Equation (6), that λ be small. The reactants are large, and the immediate protein environment is largely nonpolar, so leading to a small λ [see Eq. (8)]. Nature appears, indeed, to have constucted a system with this desirable property.

Furthermore, to prevent another form of energy wastage, it is also important that an unwanted back electron transfer reaction from the BPh$^-$ to the BChl$_2^+$ not compete successfully with a second forward electron transfer step from BPh$^-$ to Q$_A$. That is, it is necessary that the back transfer, a "hole–electron recombination" step, be slow, even though it is a very highly exothermic process (about 1.1 eV). It has been suggested that the small λ (about 0.25 eV) and the resulting inverted region effect play a significant role in providing this essential condition for the effectiveness of the photosynthetic reaction center.

There is now a widespread interest in synthesizing systems that can mimic the behavior of nature's photosynthetic systems, and so offer other routes for harnessing solar energy. The current understanding of how nature works has served to provide some guidelines. In this context, as well as in that of electron transfer in other proteins, there are also relevant experiments in long-range electron transfer. Originally the studies were of electron tansfer in rigid glasses, performed by Miller and co-workers. More recently the studies have involved a donor and receptor held together by constructed rigid molecular bridges. The effect of varying the bridge length has been studies in the various systems. A theoretical estimate of the dependence of electron transfers on distance in a photosynthetic system was first made by Hopfield, who used a square barrier as model and an estimate of the barrier height based on molecular considerations.

Recently, in their studies of long-range electron transfer in chemically modified proteins, Gray and co-workers have studied systematically the distance or site dependence of the electronic factor by attaching an appropriate electron donor or acceptor to a desired site. For each such site the reactant was chosen so that $-\Delta G^0 \approx \lambda$, that is, the rate constant k is at the maximum of the $\ln k$ vs. $-\Delta G^0$ curve (see Eqs. (5)–(6)). The value of k then no longer depends on ΔG^*. Since ΔG^* is distance-dependent [see Eq. (8)], it is particularly desirable to make $\Delta G^* \approx 0$, so that the relative k values at the various sites now reflect only the electronic factor. Dutton and co-workers have treated data similarly for a number of reactions by using, where possible, the k at the maximum of each $\ln k$ vs. ΔG^0 curve. Of particular interest in such studies is whether there is a simple exponential decrease of the electronic factor on the separation distance between donor and acceptor, or whether there are deviations from this monotonic behavior, due to local structural factors.

In a different development, the mechanism of various organic reactions has been explored by several investigators, notably by Eberson,[2] in the light of current electron transfer theory, and also by Shaik and Pross in their analysis of a possible electron transfer mechanism vs. a conventional mechanism.

Theoretical calculations of the donor–acceptor electronic interactions, initially by McConnell and by Larsson, and later by others, my group among them, have been used to treat long-range electron transfer. The methods have recently been adapted to large protein systems. In our studies with

Siddarth we used an "artificial intelligence" searching technique to limit the number of amino acids used in the latter type of study.

Another area of much current activity in the field of electron transfer is that of solvent dynamics, which follows the pioneering treatment for general reactions by Kramers (1940). Important later developments for electron transfer were made by many contributors. Solvent dynamics affects the electron transfer reaction rate when the solvent is sufficiently sluggish. As we showed recently with Sumi and Nadler, the solvent dynamics effect can also be modified significantly when there are vibrational (λ_i) contributions to λ.

Computational studies, such as the insightful one of David Chandler and co-workers on the Fe^{2+}/Fe^{3+} self-exchange reaction, have also been employed recently. Using computer simulations they obtained a verification of the parabolic G curves, even for surprisingly strong fluctuations in G. They also extended their studies to dynamic and quantum mechanical effects of nuclear motion. Studies of the quantum mechanical effects of the nuclear motion on electron transfer reactions were initiated in 1959 by Levich and Dogonadze, who assumed a harmonic oscillator model for the polar solvent medium and employed perturbation theory. Their method was related to that used for other problems by Huang and Rhys (1951) and Kubo and Toyozawa (1954).

Important subsequent developments by various authors on these quantum effects include the first discussion of quantum effects for the vibrations of the reactants by Sutin in 1962 and the important work of Jortner and co-workers in 1974–1975, who combined a Levich and Dogonadze type approach to treat the high frequency vibrations of the reactants with the classical expression that I described earlier for the polar medium. These quantum effects have implications for the temperature dependence of k, among other effects. Proceeding in a different (classical) direction Savéant recently showed how to extend Equation (6) to reactions involving the rupture of a chemical bond by electron transfer, which he had previously studied experimentally: $M(e) + RX \rightarrow M + R + X^-$, where R is an alkyl group, X a halide, and M a metal electrode.

A particularly important early development was that by Taube in the 1950s, who received the Nobel Prize for his work in 1983. Taube introduced the idea of different mechanisms for electron transfer, the outer sphere and inner sphere electron transfers, which he had investigated experimentally. His experimental work on charge transfer spectra of strongly interacting systems ("Creutz–Taube" ion, 1959, 1973) and of weakly interacting ones has been similarly influential. Also notable has been Hush's theoretical work on charge transfer spectra, both of intensities and absorption maxima (1967), which supplemented his earlier theoretical study of electron transfer rates (1961).

There has been a spin-off of the original electron transfer theory to other types of chemical reactions as well. In particular, the ΔG^* vs ΔG^0 relation and the cross-relation have been extended to these other reactions, such as the transfer of atoms, protons, or methyl groups. (Even an analog of Equations (6) and (10) for binding energies instead of energy barriers has been introduced to relate the stability of isolated proton-bound dimers AHB^+ to those of AHA^+ and BHB^+!)

Since the transfer of these nuclei involves strong electronic interactions, it is not well represented by intersecting parabolic free energy curves, and a different theoretical approach was needed. For this purpose I adapted in 1968, a "bond-energy–bond-order" model of H. Johnston in order to treat the problem for a reaction of type (4). The resulting simple expression for ΔG^* is similar to Equation (6) when $|\Delta G^0/\lambda|$ is not large ($<\frac{1}{2}$), but differs from it in not having any inverted region. It has the same λ property as that given by Equation (10) and has resulted in a cross-relation analogous to Equation (11). The cross-relation has been tested experimentally for the transfer of methyl groups by E. Lewis, and the ΔG^* vs ΔG^0 relation has been used or tested for other transfers by the groups of Albery and Kreevoy, among others.

It is naturally gratifying to see one's theories used. A recent article, which showed the considerable growth in the use of papers such as the 1956 and 1964 articles,[5] points up the impressive and continued vitality of the field itself. The remarks above on many areas of electron transfer and on the spin-off of such work on the study of other types of reactions represent a necessarily brief picture of these broad-based investigations.

I would like to acknowledge my many fellow researchers in the electron transfer field, notably Norman Sutin, with whom I have discussed so many of these matters for the past thirty or more years. I also thank my students and post-doctorals, whose presence was a constant source of stimulation to me, both in the electron transfer field and in the other fields of research which we have explored. In its earliest stage and for much of this period, my research was supported by the Office of Naval Research and also later by the National Science Foundation. The support of both agencies continues to this day, and I am very pleased to acknowledge its value and timeliness here.

In my Nobel lecture, I concluded on a personal note with a slide of my great-uncle, Henrik Steen (né Markus), who came to Sweden in 1892. He received his doctorate in theology from the Univeristy of Uppsala in 1915, and was an educator and a prolific writer of pedagogic books. As I noted in the biographical sketch in Les Prix Nobel, he was one of my childhood idols. During my trip to Sweden to receive the Nobel prize, visiting with my Swedish relatives – some thirty or so of his descendants – has been an especially heartwarming experience for me and for my family. In a sense I feel that I owed him a debt, and that it is most fitting to acknowledge that debt here.

Received: March 10, 1993 [A 914 IE]
German version: *Angew. Chem.* **1993**, *105*, 1161

---

[1] R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966, 979; *ibid.* **1957**, *26*, 867, 872; *Trans. N.Y. Acad. Sci.* **1957**, *19*, 423; *ONR Tech. Rep. 12*, Project NR 051-331, **1957**, reproduced in *Spec. Top. Electrochem.* **1977**, 181; *Can. J. Chem.* **1959**, *37*, 155; *Discuss. Faraday Soc.* **1960**, *29*, 21; *J. Phys. Chem.* **1963**, *67*, 853, 2889; *J. Chem. Phys.* **1963**, *38*, 1858; *ibid.* **1963**, *39*, 1734; *Annu. Rev. Phys. Chem.* **1964**, *15*, 155; *J. Chem. Phys.* **1965**, *43*, 679, 1261; *ibid.* **1965**, *43*, 2654, correction *ibid.* **1970**, *52*, 2803; *J. Phys. Chem.* **1968**, *72*, 891.

[2] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265; assorted articles in *Adv. Chem. Ser.* **1991**, *228*; M. D. Newton, N. Sutin, *Annu. Rev. Phys. Chem.* **1984**, *35*, 437; N. Sutin, *Prog. Inorg. Chem.* **1983**, *30*, 441; M. D. Newton, *Chem. Rev.* **1991**, *91*, 767; R. D. Cannon, *Electron Transfer*

Reactions, Butterworths, London, **1980**; L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, New York, **1987**; *Photoinduced Electron Transfer Vol. 1–4* (Eds.: M. A. Fox, M. Chanon), Elsevier, New York, **1988**; J. F. Endicott, D. H. Macartney in *Mechanisms of Inorganic and Organometallic Reactions, Vol. 7* (Ed.: M. V. Twigg), Plenum, New York, **1991**, Chapters 1, 2, and earlier volumes. R. A. Marcus, P. Siddarth in *Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules: Experiment and Theory* (Ed.: E. Kochanski), Kluwer, Norwall, MA, USA, **1992**, p. 49; S. S. Shaik, H. B. Schlegel, S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry*, J. Wiley, New York, **1992**; N. Sutin, *Pure Appl. Chem.* **1988**, *60*, 1817; assorted articles in *Chem. Rev.* **1992**, *92*, (3); *J. Phys. Chem.* **1986**, *90*, R. A. Marcus Commemorative Issue).

[3] L. E. Bennett, *Prog. Inorg. Chem.* **1973**, *18*, 1; J. R. Miller, L. T. Calcaterra, G. L. Closs, *J. Am. Chem. Soc.* **1984**, *106*, 3047; J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, *J. Mol. Biol.* **1984**, *180*, 385; R. Huber, *Angew. Chem.* **1989**, *101*, 849; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 848; J. Deisenhofer, H. Michel, *ibid.* **1989**, *101*, 872 or **1989**, *28*, 829; T. G. Yeates, H. Komiya, D. C. Rees, J. P. Allen, G. Feher, *Proc. Natl. Acad. Sci.* **1987**, *84*, 6438.

[4] P. J. Robinson, H. A. Holbrook, *Unimolecular Reactions*, J. Wiley, New York, **1972**; W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York, **1973**; see also the very recent publication by R. G. Gilbert, S. C. Smith, *Theory of Unimolecular and Recombination Reactions*, Blackwell, Oxford, **1990**.

[5] *Science Watch* **1992**, *3* (9), p. 8.