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Introduction

Reflections on early days in electron transfer

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Abstract

As an introduction to this NATO workshop, some of the early electron transfer days, beginning with the late 1940s, are recounted.

My experience in the electron-transfer field began in 1955, when I chanced upon a 1952 symposium issue of the *Journal of Physical Chemistry* on these reactions. Because of the post-war availability of numerous isotopes, many researchers were able to study electron-transfer reactions of the isotopic exchange type. These reactions include those such as

$$MnO_4^- + Mn^*O_4^{2-} \rightarrow\rightarrow MnO_4^{2-} + Mn^*O_4^- \qquad (1)$$

where no chemical bonds are broken or formed (the asterisk denotes a radioactive isotope). Their simplicity stems from this fact and from the absence of a "driving force" in these reactions (*i.e.* $\Delta G^\circ = 0$). It was this dual simplicity which led to the new theoretical developments.

In an article in that *J. Phys. Chem.* issue, the late Bill Libby invoked the Franck–Condon principle to explain why the experimentally measured self-exchange reaction rates of small inorganic cations, such as $Fe^{2+,3+}$, were smaller than those of large complex ions such as $Fe(CN)_6^{3-,4-}$. Libby pointed out that, when the electronic charge is transferred, it is transferred abruptly; so abruptly that the nuclei do not have time to move during the actual transfer (the Franck–Condon principle). Thereby, the new charges each find themselves suddenly in a foreign environment. Moreover, the smaller the radius of each ion, the greater the electrostatic solvation forces, and so the more foreign the environment. Factors such as a negative standard free energy of reaction (ΔG°) as a driving force were absent and allowed the examination of other factors. Libby's description of the problem amounted to treating the transfer as a "vertical transition"; one from the initial electronic state (the reactants) to a final electronic state (the products) at the same nuclear configuration. (There is an equilibrium distribution of such initial configurations.) Such a transition, however, could only occur by absorption of light.

For a reaction to occur, instead, in the dark, *i.e.* a thermal reaction, it is necessary, I realized, for the solvent–reactants system to make some adjustments ("reorganize") before the electron transfer, and after, if total energy is to be conserved. With this idea as a basis, I developed the method described in a paper in 1956: after obtaining and utilizing a free-energy expression for fluctuations in the solvent dielectric polarization, found by finding a reversible path for forming these fluctuations and calculating the work done, I was then able to derive a simple expression for the rate of these reactions. I recall that, when it finally happened after a month of intense work, I experienced a sense of elation and excitement, because of the simplicity of the final result, not matched by any prior or perhaps later experience. Some of this history was described in a recent Nobel article and in a review article in 1964. I extended the 1956 study to electron transfers at electrodes in 1957 and 1959.

A quantum-mechanical description of the solvent in electron-transfer reactions, treating the solvent

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as a collection of harmonic oscillators, was given subsequently in the well-known work of Levich and Dogonadze in 1959. There have been other important contributions and extensions. One which is in common use today, due to Jortner in 1974, combined the classical result of the 1956 paper for low-frequency motions with the quantum result of the 1959 article for the high-frequency ones.

There was also, in 1947, an insightful one-dimensional treatment of electron transfers at electrodes by J.E.B. Randles, who used a potential energy curve for the reactants plus electrode, and one for the products plus electrode. There was also analysis of self-exchange reactions by George and Griffiths in 1956, who considered the changes in the individual vibrational bond lengths of the ligands in the reacting ions in self-exchange electron transfers. In a widely influential study in 1960, Gerischer formulated a phenomenological description of electron transfers at electrodes, by introducing a gaussian distribution for reactants' and products' states of the coordinates of the nuclei. In the 1960s and subsequently, Levich, Dogonadze and co-workers made basic contributions to reactions at electrodes.

Several theoretical ideas on other chemical reaction rates were prominent prior to this period, and continue, rightly, to be prominent today. For comparison, I comment on their nature here. In chemical reactions such as an atom or group transfer,

$$AB + C \longrightarrow A + BC \qquad (2)$$

the reaction is often visualized in terms of potential energy contour diagrams: idealizing the reaction as occurring on a line, there are only two coordinates, apart from that of the center of mass, needed to specify the relative positions of the atoms. Thus, plots of constant potential energy (contour plots) can be readily depicted, as in Fig. 1. Transition-state theory was commonly used for calculating reaction rates and, in the case of ionic reactions in polar solvents, a dielectric continuum model for the solvent was usually employed to treat the ion–ion and ion–solvent interactions.

In that treatment, one of two limiting models for the charge distribution in the transition state was typically used: in one of these, the transition state consisted of the separated charges of the reactants and the coulombic interaction between them was calculated. In an alternative limiting model of the transition state, the charges of the reactants were assumed to be collapsed and the free energy of solvation of this charged system was then calculated and compared with that of

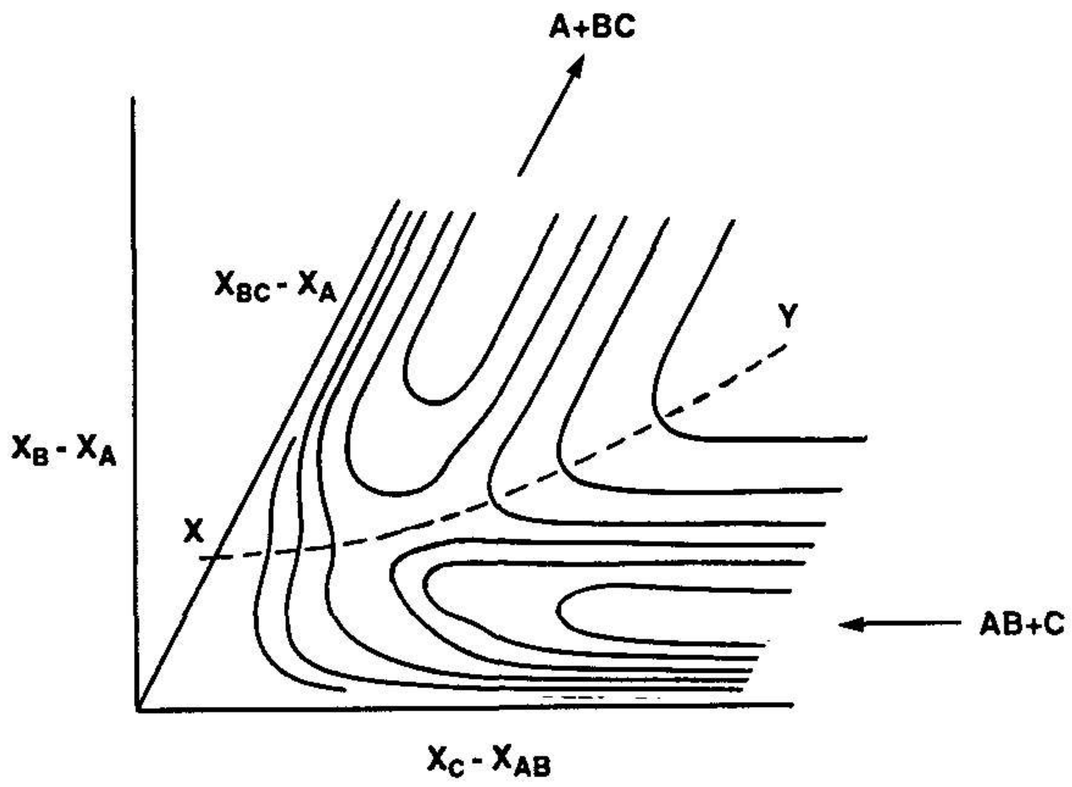

Fig. 1. Potential-energy contours for an atom or group transfer.

the separated charges in the same solvent.

However, for an electron transfer between a donor D and an acceptor A

$$D + A \longrightarrow D^+ + A^- \qquad (3)$$

these conventional models for the transition state of the reaction are inappropriate when the electronic interaction of D and A is relatively weak: in this latter instance, the change of charge distribution in reaction (3) occurs abruptly, and so leads to a system whose solvent dipoles do not have a distribution in equilibrium with the charges. One needs to consider, instead, the fluctuations in orientations, vibrations, and positions of the many relevant polar solvent molecules, and the fluctuations in the various vibrational coordinates of the reactants, prior to and after the electron transfer.

Having such fluctuations at the fixed initial charge distribution of the reactants was the unusual feature of these electron-transfer reactions and had not been explicitly encountered in other types of chemical reactions. In these other reactions, such as in eqn. (2), any change in charge distribution of the reactants varied smoothly as the system proceeded along a reaction coordinate (a concerted motion of the decrease in BC distance and increase in AB distance in the case of eqn. (2)). Accordingly, the standard type of theory was inadequate, and prompted the theory published in 1956.

There was also considerable experimental progress in research in electron transfers. Taube delineated the difference between "inner sphere" and "outer sphere" electron transfers. In the late 1950s and on, Sutin pioneered the study of fast inorganic electron-transfer reactions between different redox systems 1 and 2 ("cross reactions")

$$Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2 \qquad (4)$$

using a stopped-flow technique. In this way, reactions were studied in which $\Delta G°$ need not be zero and so its effect on the rate could then be investigated. This work nicely complemented the body of work on the self-exchange reactions. Other things being equal, when no chemical bonds are broken or formed, reaction (4) tended to be too fast to be studied by methods more conventional than the (millisecond) stopped-flow one.

Again, for investigating fast electron transfers at electrodes, Randles had used in 1947 an a.c. impedance method. Gerischer and others introduced further methods, particularly step techniques, for the study of rapid electrochemical electron transfers. Cyclic voltammetry and the rotating-disc electrode were among other new electrochemical methods employed. Prior to the use of fast reaction techniques, only relatively slow electrode reactions involving bond rupture and bond formation had been extensively investigated, as in the hydrogen over-potential reaction,

$$H_3O^+ + M(e) \longleftrightarrow \tfrac{1}{2}H_2 + H_2O + M \qquad (5)$$

where M is an electrode.

Thus, the period beginning in the late 1940s and continuing through the 1950s into the 1960s and beyond has been a very fertile one for research in the electron-transfer field, both for homogeneous reactions in solution and for reactions at electrodes, and provided an excellent background for the many later developments which the field experienced.

This period was also a wonderful time for the interaction of theory and experiment, each stimulating the other, a feature which continues to this day. I have recalled elsewhere the excitement that Sutin and I felt when we tested in 1962 the "cross-relation" (1960) which relates the rate constants of cross-reactions (4) to those of the related self-exchange reactions, for example, and found that the cross-relation worked. There were a variety of other tests of the theory, but one of them, the "inverted effect", took about 25 years for its experimental confirmation (1984), in a story now well known. From the 1960s on, the field rapidly developed in many other directions, including the important one of charge-transfer spectra, where the theoretical work of N. Hush in 1967 played a seminal role, and the field of biological electron transfers.

A sketch of some of these many developments is given in Fig. 2. The electron-transfer field continues to expand, because of the recognized widespread occurrence of these reactions in chemistry, electrochemistry and biology.

The present remarks are intended only to give a "snapshot" of those early years, rather than a detailed history. Detailed descriptions of the field have been given by many authors; some recent reviews are listed as examples below [1].

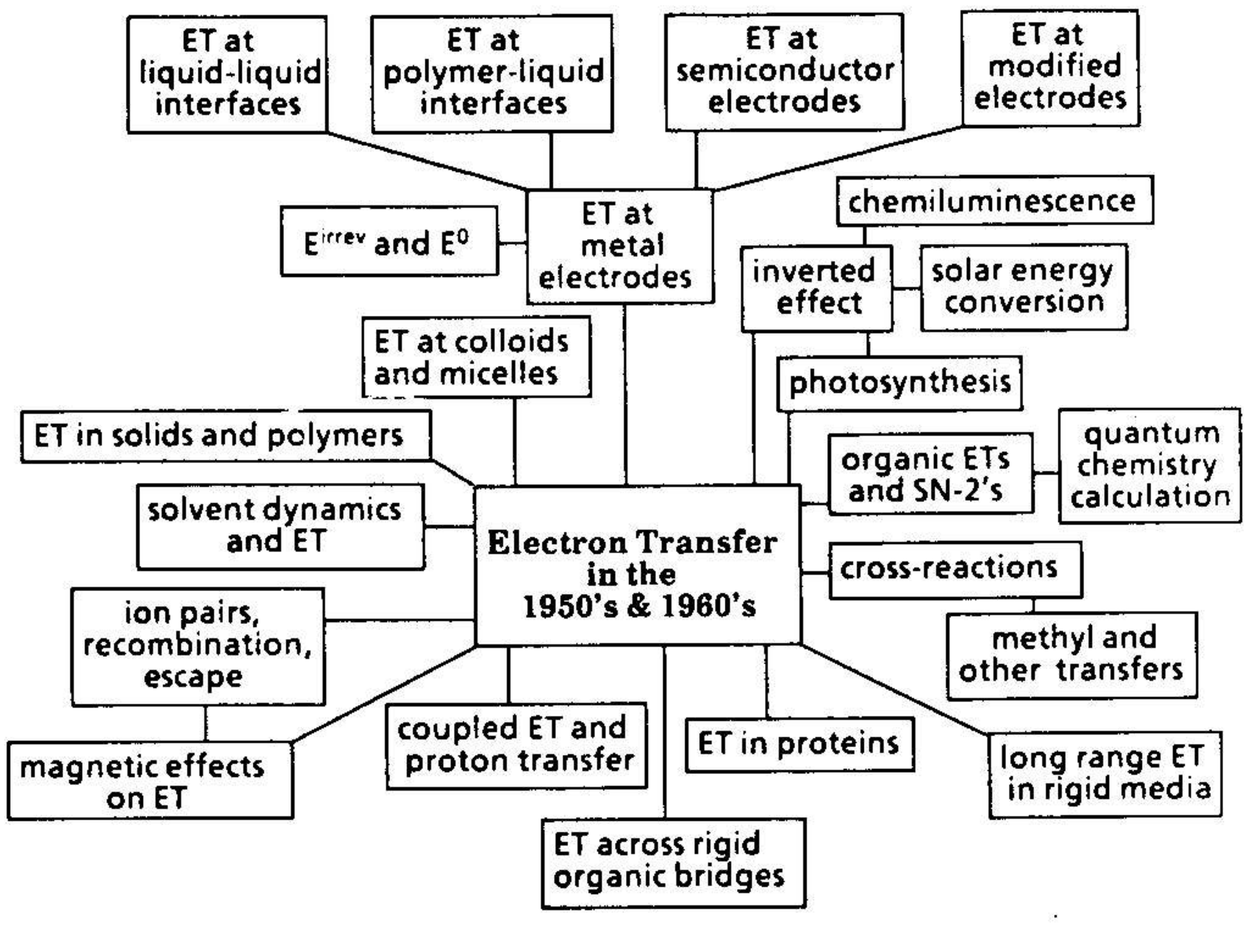

Fig. 2. Developments in electron-transfer (ET) reactions.

Acknowledgments

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Reference

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