ELECTRON TRANSFER PAST AND FUTURE

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Electron transfers in the post–World War II era began in the small arcane field of isotopic self-exchange reactions, such as $Fe^{3+*} + Fe^{2+} \rightarrow Fe^{2+*} + Fe^{3+}$, in solution. There was an abundance of radioactive isotopes (denoted here by an asterisk), and chemists were using isotopic tracers after the war to determine the mechanisms of various chemical reactions. Their use in electron transfer was very fortunate, since it removed from consideration one of the dominant factors controlling chemical reaction rates, ΔG^0, the standard free energy of reaction or, as it is commonly called, the driving force of the reaction. This ΔG^0 vanishes for self-exchange reactions.

Thus the researchers were led to study the other factors influencing the reaction rate, which stimulated Libby (1952) to apply the Franck–Condon principle to explain these new data. In turn, this idea led to the formulation of an electron transfer theory in its classical (1956), quantum (1959), and mixed (1974) formulations (classical for the low-frequency and quantum for the high-frequency motions). A history of these developments and of the explosive subsequent proliferation of research areas to which the theory could be applied was given in my Nobel lecture. I have been asked by the editors of the present volume to focus, instead, on the more daunting question of where the electron transfer field might be going.

At the outset let me disclaim any predictive expertise for long-range predictions on research. When I happened in 1955 to see Libby's article, written in 1952, the electron transfer problem seemed merely an interesting puzzle. I didn't think in terms of it being the subsequent source of numerous applications. And perhaps that's the way it typically is in new directions in research.

Advances in Chemical Physics, Volume 106, Electron Transfer—From Isolated Molecules to Biomolecules, Part One, edited by Joshua Jortner and M. Bixon. Series Editors I. Prigogine and Stuart A. Rice.
ISBN 0-471-25292-1

We can ask in what direction the field might be going, perhaps by first looking back and asking whether we might have predicted the future from that vantage point.

So let us place ourselves in the very late 1940s. We have already noted that electron transfer (ET), in the form of the small research area of isotopic exchange reactions in solution, was beginning to develop at that time. A fast electrochemical technique, developed in the late 1940s in England, permitted fast electron transfers at electrodes also to be investigated. That work also represented a major step forward because of the simplification of the factors influencing electrochemical reaction rates. Formerly, studies of reaction rates in electrochemistry had been limited to reactions such as those in the hydrogen and oxygen overpotential processes, which involve ruptures of chemical bonds and formation of new ones. But with the new technique, electrode reactions in which no bonds are broken or formed could be studied—simple electron transfers, and they were fast. Other developments in rapid reaction techniques were soon to occur, probably stimulated by the extensive use of electronic and other technology during World War II. There has also been some prewar developments, particularly in the biological area. Their application to simple electron transfers, however, was at least a decade or more away in the late 1940s.

Eventually, by the early 1990s, the field had broadened to encompass numerous areas, such as those indicated in Figure 1, among others. (References to these developments are given in Ref. 1, and the history of the first 25 years of studies of electron transfer reactions in solution is described by Sutin in this volume.) One might ask: Which of the new areas might have been predicted in the late 1940s? The explosive growth itself was not predicted—I certainly did not predict it, even later in 1956, when I published my first paper on electron transfer. The study of ET in cross-reactions, for example, did not become an active area until a decade or so later, and it was not predicted nor was its connection to S_N2 reactions of the ET type, nor were other ideas that were developed: "intrinsic barriers," "driving force," in reactions such as methyl transfers, proton transfers, and others.

Indeed, Kramers' now famous theoretical article on solvent dynamics in chemical reactions (1940) remained largely unused by chemists until the late 1970s. Another idea—namely, that small magnetic effects could have a dramatic influence on certain chemical reactions rates by affecting the singlet–triplet splitting of a charge-separated pair (produced by a photoexcitation)—was not anticipated, and even the idea of an organic triplet state, described around 1945, was having difficulty in gaining acceptance. Electron transfer across rigid organic bridges had not been explored; the reactants plus the intervening organic bridge had to be synthesized, and that event was decades away. The dramatic and counterintuitive inverted effect,

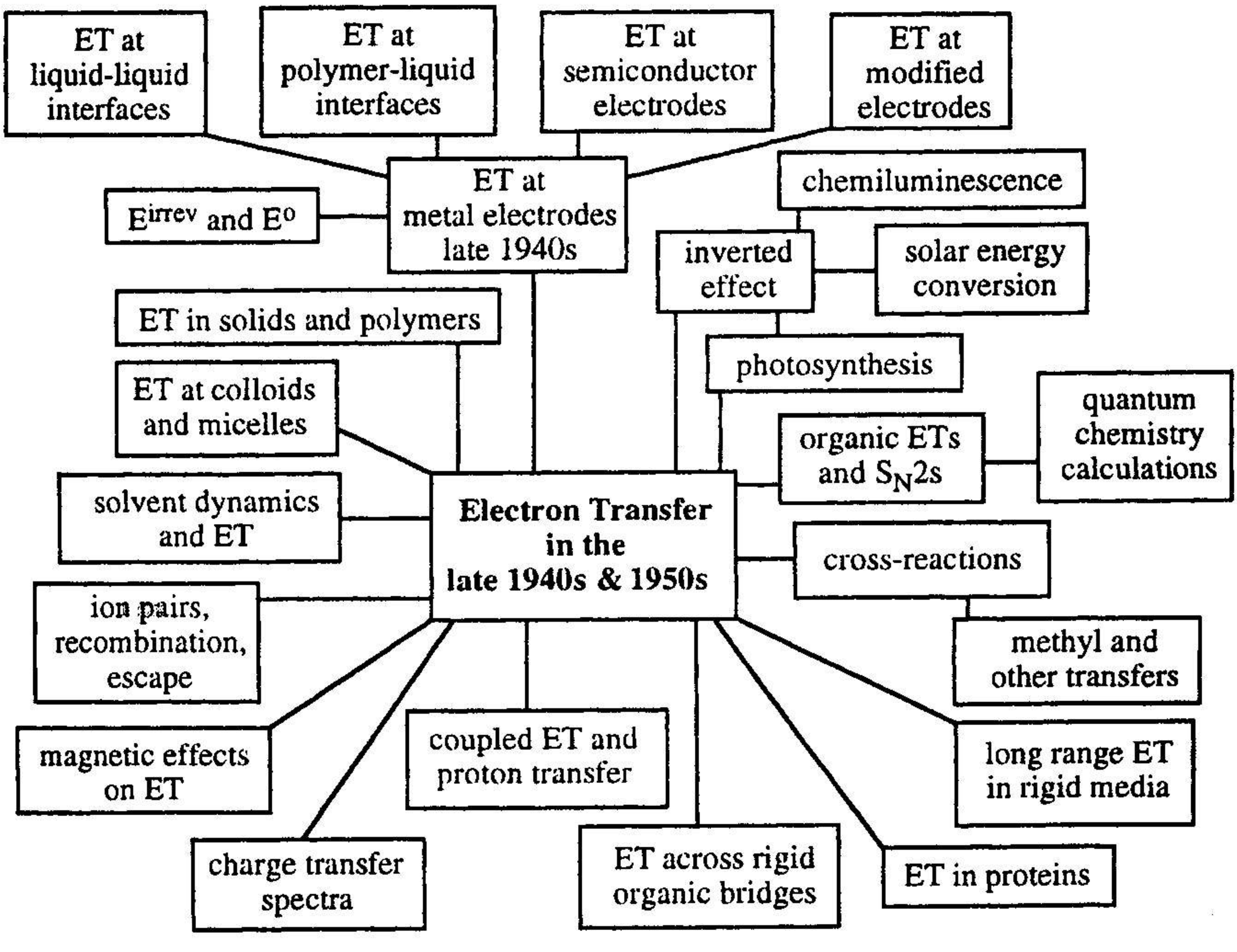

Figure 1. Developments in the electron transfer field after the 1940s.

predicted in 1960, was not confirmed by experiments until the mid 1980s and awaited the construction of these rigid compounds. (It was subsequently confirmed in many nonrigid systems.)

While proteins were of course known, the structure of redox proteins in the 1940s was not, and while oxidation–reduction reactions in biological systems had been studied, the techniques for studying and perhaps even the idea of measuring long-range ET in proteins were a subject for the future. Electrodes with self-assembled monolayers were quite unknown until recently, and other ways of systematically modifying electrodes were also not known. While fireflies have been around for quite some time, chemical "lightsticks" were not yet available, and the relation of these forms of chemiluminescence to several chemical reaction steps, of which one is an ET, was still in the future. ET chemiluminescence was to first appear in the 1960s.

In fact, I think it is fair to say on reflection that very few of the developments in the chart in Figure 1 were anticipated when this era of modern electron transfer research began in the late 1940s. The developments that did occur were, in part, consequences of the newly available technology, such as

electronics, flow systems, and lasers, and in part to ideas generated by the comparative simplicity of the systems that were being studied. The extensive interaction between simple theory and experiments undoubtedly played a major role. The added excitement that accompanies that kind of interaction has added so much to the enjoyment and stimulation in the field.

So in inquiring with the editors about the future now, in 1997, perhaps we might first look to the new technology. In the field of gas-phase reactions, for example (typically not electron transfer!), the technology of molecular beams and of ultrafast lasers is having a dramatic effect. They permit a more detailed and specific study of molecular reaction mechanisms. Lasers have already been applied to ETs, but the application of the combination of lasers, molecular beams, and computer technology to ETs, in clusters, for example, is only in its infancy.

A piece of technology that is older, but considerably helped by the application of computers, is X-ray crystallography. Since the 1980s it has been used in the study of proteins important in biological electron transfers. More recently it has been supplemented by the application of two-dimensional NMR to the study of protein structures in solution. The crystallographic techniques have already had a signification impact on one area of election transfer research, namely, photosynthesis, where it has been used to obtain the structure of the relevant membrane-bound protein. Given its current application to cytochrome oxidase and to the ATPase involved in the formation of ATP from ADP and inorganic phosphate, and in the associated proton and other ion pumping across membranes, major developments in the understanding of ion pumps and their connection with ET can be anticipated. In general, a detailed molecular structure is needed for understanding a chemical reaction, in the present case an electron transfer. So it is an obvious prediction to anticipate that one area of active research in ET will occur in the concerted electron transfer/ion transfer field.

Coherence phenomena in electron transfer, initiated in the photosynthetic reaction center, can be expected to be explored further and extended to other systems. Site-directed mutagenesis in various proteins is now playing a significant role in electron transfer research. Organic synthesis also is proving to be helpful in constructing various bridged compounds for the study of specific effects—its use to confirm the inverted effect was a particularly striking example—and it can be expected to provide a useful tool in research.

Another topic that has been of recent interest in the literature is the possibility of a material such as DNA serving as a "molecular wire." There is currently some difference of opinion in the interpretation of the data, but time-resolved ultrafast studies in molecular beam systems, perhaps

in solvent clusters to stabilize the ionic charges, will no doubt be used in an effort to resolve this problem.

Another active area of research has been that of solvent dynamics, in which ultrafast lasers were used to study the relaxation of photoinduced charge transfer systems. At present, because of the technique that was used (an up-conversion method to study the fluorescence, instead of pump–probe optical absorption, the latter apparently encountering an obscuring optical interference in the system studied), events in the first 50 fs could not be time resolved. Yet according to the theory [we used the dielectric dispersion function $\varepsilon(\omega)$, to calculate the spectral relaxation], interesting results also happen at times shorter than 50 fs. One can certainly anticipate that these short-time investigations will be undertaken.

There are other biological systems involving electron transfer, in addition to those mentioned earlier. There as been a trend in chemical research toward a better understanding of the mechanisms of various processes in biology or biochemistry, and we can expect in general an increased emphasis on the study of complex phenomena and systems by those with expertise in electron transfer. Similarly, applications of electron transfer to electronic and other processes in complex materials and to electronic devices can be anticipated. Techniques involving nanotechnology, single molecule spectroscopy, and perhaps those involving scanning near-field optical microscopy, can be expected to be influential.

The introduction of scanning tunneling microscopy, a form of electron transfer, was a considerable surprise to most of us chemists, and some of the experimental results are puzzles yet to be solved. For example, the apparent observation of STM currents in relatively thick nonconducting samples, and the similarly low-energy barriers of organic monolayers (inferred from the dependence of tunneling current on STM tip–sample distance at a given potential difference) for STM currents remain to be explained. Making similar studies in vacuum (and hence using cleaner metal tip conditions), and perhaps at low temperatures, may provide some resolution of the puzzles.

The harnessing of solar energy will no doubt continue to be of both practical and theoretical interest. A key aspect of photosynthesis and its synthetic analogs is the charge separation and the subsequent chemical reactions of the separated charges. In synthetic systems used to mimic the initial steps in photosynthesis, and in photosynthesis itself, the first forward step after the photoexcitation is very rapid (picoseconds), and the wasteful back-reaction to reform the unexcited state is very slow (nanoseconds). Both aspects are essential for the successful conversion of solar energy to chemical energy. The relative slowness of the back reaction has several possible origins—in some cases the systems may have to go initially slightly uphill,

via an intermediate, before going greatly downhill to reform the unexcited reactant. However, there are two other factors that may play a major role: The forward reaction involves an excited electronic orbital of the photo-excited reactant, while the back reaction involves reversion to the reactant's ground-electronic-state orbital. The latter is probably less extended in space than the former (and the former may even be extended to occupy somewhat the nearby intermediate). Again, the back reaction is very downhill and in a region of the protein (in the photosynthetic system) that is relatively non-polar. The latter factor results in only a small "reorganization energy," and so, in conjunction with the large negative ΔG^0, this back reaction may be in the "inverted region," and hence be slow. How to utilize the charge separation in these systems so as to then harness it remains yet another major goal in application via synthesized systems.

Perhaps we could summarize the preceding discussion by stating how much the present knowledge has laid the groundwork for future developments. The technology necessary to address some of these questions is here. Nonetheless, just as so many of the post-1940 developments were, to our knowledge, not foreseen in the late 1940s, it would be surprising if today our vision had undergone any dramatic improvement! That electron transfer continues to be an exciting area for study, and that problems of interest continue to reveal themselves, also seem to be very clear and encouraging.

ACKNOWLEDGMENTS

It is a pleasure for me to acknowledge the support of my electron transfer research during these many years by the National Science Foundation and by the Office of Naval Research.

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