Epilogue

R. A. Marcus

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125

THE FIELD OF ELECTRON-TRANSFER REACTIONS has expanded dramatically since the early days in the late 1940s and the 1950s when the rates of many such reactions (isotopic-exchange reactions) were studied by using isotopic labeling techniques. The chapters in this volume demonstrate some of the more recent developments. They speak eloquently for themselves, and my summary will be relatively brief.

The excellent prefactory chapters by Bolton et al. and by Bolton and Archer introduce the electron-transfer field. The latter surveys key concepts underlying the theory for these reactions, together with relevant equations used in comparisons with experimental results.

Among the topics treated in some detail in the symposium and in this volume are

1. factors influencing the effect of donor–acceptor separation distance on electron transfer (ET) reaction rates, the distance influencing the rate constant via both electronic and reorganizational factors,
2. electron transfers in proteins, including photosynthetic systems,
3. the "inverted effect" for ET rates,
4. comparisons of photoinduced charge separation and charge recombination,
5. solvent and/or temperature and molecular bridge effects on ET rates,
6. charge-transfer states in porphyrin–chlorophyll systems and their enhancement of the quenching of locally excited states in polar solvent by mixing with CT states, the role of perpendicularity in favoring the CT state,

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7. solvent dynamics and intramolecular ET,
8. the effect of applied electric fields on the long-range $BChl_2^+ Q^-$ recombination in a photosynthetic system, and
9. intramolecular transfers involving triplets.

This volume thus embraces a broad range of topics in the electron-transfer field. It is, of course, not possible to be all-inclusive in a relatively small publication. There are a number of other active areas in the electron-transfer field: electron transfers at metal–liquid, semiconductor–liquid, and liquid–liquid interfaces; ET on semiconductor colloidal particles, micelles, and at modified metal electrodes; ET with bond rupture; salt effects on ET rates; computer simulations of reorganizational and dynamical aspects of electron transfers; and the detailed relation to charge transfer and photoelectric emission spectra. Several recent results from our laboratory on electron transfer in liquid–liquid and semiconductor–liquid systems and on electronic matrix elements in donor–acceptor rigid molecular bridge and protein systems are described elsewhere (*1*, *2*).

The widespread growth into new areas may strike many observers of the electron-transfer field. New problems, new questions, and challenges continue to arise and are being addressed, both experimentally and theoretically. Systems of increasing complexity, or systems at a greater level of molecular detail, are being examined.

In the early days of modern electron-transfer study (namely, in the few decades after 1945) a primary focus was delineation of the main features of simple inorganic electron transfers, the impact of the standard free energy of reaction on their rate, and the effect of an "intrinsic reorganizational parameter" related to bond-length changes and to molecular size. Such concepts as the extent of adiabaticity vs. nonadiabaticity were also important, as was the relationship between homogeneous and heterogeneous electron-transfer rates. Now, with the aid of the information and methodology derived in these earlier studies, many areas are being explored, including those at various other interfaces and in biological systems. Computer simulations provide a useful added supplement to the earlier analytical-type (equations) development, and recent calculations of electronic effects have supplemented current experimental work on long-range electron transfer.

Further communication among researchers working in rather different aspects of the ET field continues to be desirable. Some may not be familiar, for example, with the relatively recent work by Iwasita et al. (*3*) showing adiabaticity for electron transfer between $Ru(NH_3)_6^{+2,+3}$ and metal electrodes. They showed that the electron-transfer rate between ion and electrode (the "exchange current") was constant for metals having widely different density of electronic states. This example may also serve to show

how information can be readily obtained in one area, whereas comparable information for homogeneous bimolecular ETs is less readily derived.

References

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