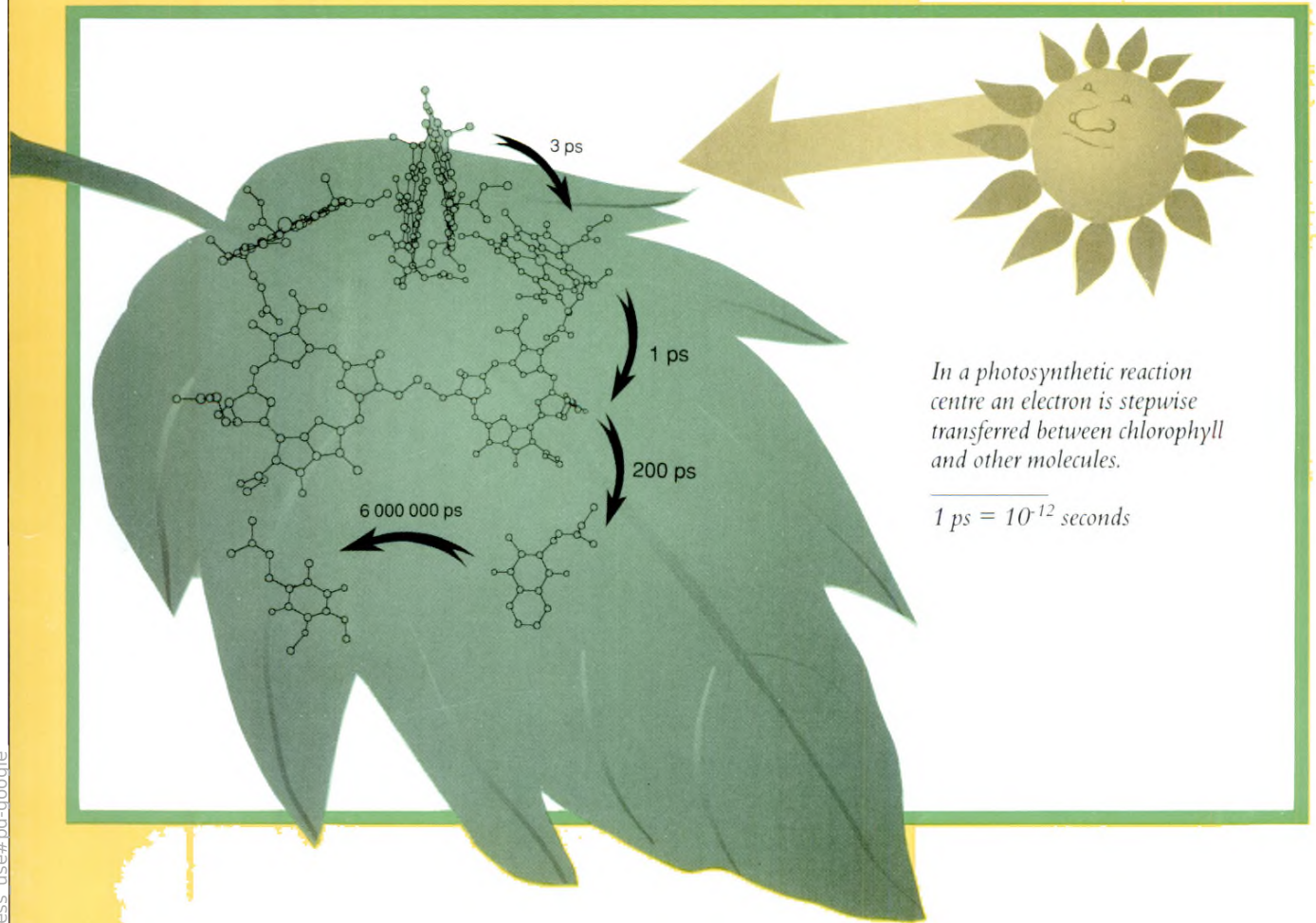


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In a photosynthetic reaction centre an electron is stepwise transferred between chlorophyll and other molecules.

$1 \text{ ps} = 10^{-12} \text{ seconds}$

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Marcus Joins the Nobel Ranks



Professor Rudolph A. Marcus receiving the 1992 Nobel Prize in chemistry from King Carl Gustaf of Sweden for his pioneering research which has led to a better understanding of what happens when atoms join to make new molecules. He is the Arthur A. Noyes Professor of Chemistry at the California Institute of Technology and for 40 years has been a principal investigator for the Office of Naval Research. Under the sponsorship of ONR, Marcus published between 1956 and 1964 his theory of electron-transfer in a series of now classic papers in the scientific literature. The concepts and equations, which Marcus developed, he has since expanded and refined into what is known today as the Marcus Theory.

Currently with the support of ONR, Marcus and his research associates are delving into new aspects of electron transfer. A current focus, says Marcus, is on reactions in which electron transfer occurs over distances of a billionth of a meter or so -- quite long in the molecular world -- in cytochrome C and other proteins important in photosynthesis and cellular respiration. Such studies should reveal how energy flows through these large molecules and perhaps point toward possible spinoffs, such as improved devices for tapping solar energy. (Photo is reproduced through the courtesy of Tobbe Gustavsson, Reportagebild, Stockholm, Sweden)

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About the Cover

In photosynthesis plants use light to form energy-rich compounds from water and carbon dioxide from the air. The decisive reactions occur in a reaction center in the cell. The incoming light is caught in an antenna system and finds its way to a pair of chlorophyll molecules. Within these molecules an electron is lifted to a higher energy level and is then transferred stepwise (follow the arrows) in a well-defined manner. It is important that the first leaps are very fast as otherwise the electron has time to return to the ground state. The Marcus model may explain the speed of these leaps. Finally the electron finds itself in a relatively stable state and still has enough energy to carry out the chemical work necessary for the organism. See article on page 9

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1

Introduction

*Peter Schmidt, Guest Editor
Chemistry and Materials Divisions
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Being invited to participate in the activities during the week of the award of the Nobel Prizes is both an honor and a thrill that is hard to put exactly in words. Anticipation and excitement are words that capture, in part, feelings I had before the week of events. The week itself had a dream-like quality that, in retrospect, makes it difficult to believe I actually was in Stockholm. The thrill of being there was greatly enhanced by the fact that someone I have known for more than twenty years, Professor R. A. Marcus, was to receive the Nobel Prize in Chemistry. It is therefore an equally great honor for me to act as a guest editor of this edition of *Naval Research Reviews* that honors Rudy's accomplishment by reprinting his Nobel address as well as publishing articles that reflect the influence of his contribution to electron transfer theory, the work for which he received the Prize. It is a proud moment for the Navy to acknowledge its contribution to Marcus's work through the support provided by ONR to the original research on which the award was based.

In the following few paragraphs I want to do three things. I want first to try to give you an idea of the singular importance of Marcus's research to the general understanding we now have of chemical processes. I then want to indicate briefly how the following articles in this issue of *Naval Research Reviews* build on and reflect the strength of Marcus's original contribution. And, finally, I want to end with a personal note, a short chronology, as I experienced it, of the events that took place during the week of the award of the Nobel Prizes.

For more than thirty years now, scientists in a number of disciplines that have connections to chemistry – for example, chemistry itself, biochemistry, solid state chemistry, and materials science – have been using Marcus's name to refer to the only successful theory of electron transfer. Marcus theory has come simply to mean the fundamental theory of oxidation and reduction processes. Let me take a minute to explain what this means. Readers familiar with chemistry will recall that very early in the study of the subject, one is introduced to chemical reactions that involve the gain or loss of charge in individual reactants and products. We have known for some time now that the charged particle involved is primarily the electron; although in a few cases the proton figures in the charge transfer. The electron can be exchanged either between chemical species in solution or between species in solution at the boundary with a metal, an electrochemical charge transfer. In many cases, it is possible to harness the potential for electron transfer stored in chemical species to produce electricity: thus, the battery. It may seem hard to believe, but before 1956 there was no complete understanding at the molecular level, even at



Dr. Peter Schmidt (left) of the Office of Naval Research and long time friend of Dr. Marcus congratulates him at the Nobel Ceremonies. Beside Schmidt is his son Nicholas.

the simplest level of approximation, of how these chemical processes take place.

Marcus's great contribution built on his understanding of chemical reactions in general (he had been involved with O. K. Rice in the development of unimolecular reaction rate theory in what is now referred to as the RRKM theory – the last M being Marcus) and on insight into the way in which solvent can play a role in activating the electron transfer. He details all of this in his Nobel address and there is no need for me to repeat it here. What I want to point out, however, is the fact that Marcus's theory, and his approach to the electron transfer theory in particular, was far more general than the title electron transfer theory would imply. Imitation – whether intentional or not – is surely the finest form of flattery. And, Marcus's fundamental theoretical approach was imitated.

In 1964 Marcus published several papers in which he generalized reaction rate theory and the electron transfer theory in particular. A crucial point in this generalization was the conceptual recognition that in a reacting chemical system, which can only be described by a countless number (at least Avogadro's number) of coordinates and momenta, the dynamics of the system along only one coordinate is important. One can imagine a surface in a many-dimensional space to which this one important coordinate is perpendicular. The particular surface represents the condition for which the initial and final state energies of the reacting system are the same. In more concise terms, at this special surface, energy is conserved for a reaction that proceeds from a reactant to a product state. But, any point on this surface is not necessarily the optimal point for reaction. Marcus was perhaps the first to recognize that the optimal point is found through a saddle point; there are well-established methods to find this point. It is interesting to note that this method yields a functional form generally referred to

as "Gaussian" for the dependence of the reaction on various energy quantities. The appearance of this functional form led Marcus to predict unusual behavior for chemiluminescent electron transfer reactions [R. A. Marcus, *J. Chem. Phys.*, **43**, 2654 (1965)]. The verification of the Gaussian dependence of the rate constant on free energy has been verified.

Several years later, a very nice paper by Glyde appeared in the *Reviews of Modern Physics* [*Rev. Mod. Phys.*, **39**, 373 (1967)] concerning a conundrum of the time – the temperature dependence of the self-diffusion coefficient for fluoride in an FCC lattice. The analysis is virtually the same as Marcus originally provided. And, although Marcus's work was apparently not known to Glyde, the omission is understandable [Glyde was working in a separate area] and must not be held against him. Glyde provides a convincing independent verification of the solidity of Marcus's pioneered approach.

There are other areas of investigation of phenomena that overlap the Marcus theory. One notable area is that of the mobility of the small polaron. This particular work, given a beautiful treatment by Holstein in 1959 [T. Holstein, *Ann. Phys. (NY)*, **8**, 325 (1959)], derives expressions for the mobility of a local excess charge in weakly polar lattice that are very much the same as the expressions derived by Marcus. It should be noted, however, that Marcus used a dielectric response method developed by Pekar to handle the effect of a polar environment on a transferring electron. It is natural, therefore, to expect that theory developing in the areas of polar solids and polar liquids might share some similarities. The similarities are indeed remarkable.

An additional facet of Marcus's research that is known perhaps to fewer people than it should be has to do with the effect of polar solvents on spectral properties. The Marcus theory was cast into a different form in 1959-60 by the late V. G. Levich and R. R. Dogonadze [V. G. Levich and R. R. Dogonadze, *Doklady Akad. Nauk, SSSR*, **124**, 123 (1959); *Coll. Czech. Chem. Comm.*, **26**, 293 (1961)]. Beginning with a Born-Oppenheimer representation of the electron transfer/solvent system, they were able to use time-dependent perturbation theory to derive an expression for the electron transfer rate constant. Much of the expression they derived was the same as that found by Marcus, and they noted the similarities. The frequency factor was in fact the same as derived by Marcus using the Landau-Zener theory for what is called the "non-adiabatic limit"; this is a limit in which there is very weak interaction between the reactant and product states of a reaction. A number of subsequent papers by a variety of authors during the next fifteen years built on various aspects of the Marcus and Levich-Dogonadze approaches to electron transfer. But, the interesting aspect of this work was the fact that the quantum mechanical treatment to obtain spectral line shapes (giving the shape of an absorption band as a function of frequency) was formally very similar to the quantum mechanical treatment of the electron transfer reaction. Indeed, the

similarity between the use of the polar solvent modes in the electron transfer reaction and their role in determining spectral properties was not lost originally on Marcus. A paper [R. A. Marcus, *J. Chem. Phys.*, **24**, 979, (1956)] that accompanies his Nobel Prize-winning paper of 1956 deals with general polar solvent effects that, in the work of others, eventually grew into the first account of polar solvent effects on spectra [E. G. McRay, *J. Phys. Chem.*, **61**, 562 (1957)]. The connection between spectral shape functions and chemical reactivity is now well established and is much more than a theoretical chemistry cottage industry; it is the foundation of many recent advances in chemical reaction rate theory.

Thus, the influence of Marcus's theoretical contributions is great. The theory has survived the test of time. There is firm experimental corroboration now that did not exist twenty years ago. We are indeed now in possession of a much greater and more sophisticated understanding of electron transfer reactions and chemical reactions in general.

I turn now to introduce the papers that follow Marcus's Nobel address. The research described by these authors builds on or corroborates Marcus theory. We have selected a variety to reflect some of the exciting recent developments in electron transfer. Although not represented fully here, I want to note that one of the most exciting new areas of investigation for the electron transfer reaction is in the biological area. Electron transfer, it seems obvious to say, has to be an important part of many processes in living organisms. Uncovering these processes alone has to be a difficult experimental challenge. Unravelling the electron transfer pathways is being aided directly by the unifying conceptual approach provided by Marcus theory. That aspects of the theory need to be modified to apply to the complexity of a biological system is a change in degree, not substance.

In recent years, drawing on the wealth of formalism offered by correlation function theory, it has been possible to incorporate Feynman path integral methods into Marcus theory. At first sight, the proof that Feynman's methods work may not seem to add more than the effort is worth, but this is an illusion. Greg Voth provides us with an account that shows nicely how the added sophistication of the Feynman path integral approach yields much greater insight than would have been possible plodding along using methods that many (including me) have used for years. Moreover, the path integral approach may indeed bring closer to fruition the hope (long held by me) that a computational theory of electron transfer, similar to the currently available quantum chemical programs, might be available to all.

Mark Ratner provides a wealth of experience and knowledge of chemical reactivity. His interest in the basic theory of chemical reactivity is long standing. Mark has had a continuing interest in electron transfer and some of his interest focuses on the use density functional formalism. In addition, over the years he has tackled a number of physically interesting and

important issues such as the mobility of charged ions in random (often polymeric) networks. Much of that work has enhanced our current understanding of the operation of a number of new high energy density polymer film battery systems. Some of this work has been carried out with ONR participation.

Professors Weaver and Hupp make contact with experimental reality. I have known Mike Weaver for a number of years now and I am always impressed by his enthusiastic and constant probing the limits of applicability of all aspects of the electron transfer theory. His, and Joe Hupp's, relentless investigations have provided us with a valuable body of valuable information concerning the role of the polar solvent in oxidation-reduction reactions. They occupy, therefore, a commanding vantage from which to survey the match of theory to experiment.

Finally, Michael Zerner provides us with an account of his recent successful work to improve the incorporation of polar solvent effects into quantum chemical calculations. One of the great difficulties encountered in the past few years in accounting for polar solvent effects particularly in calculations of biochemical and biophysical importance has been the fact that all too often simple dielectric models do not work. In a review I wrote about twenty years ago [P. P. Schmidt, *Specialist Periodical Reports* (The Chemical Society, London), *Electrochemistry*, 5, 21-131 (1975)], I concluded that the polar solvent model embodied in the dielectric continuum approximation would serve for some time to come. This prediction has proved accurate. The seminal contributions to this approximation are, one, Marcus's original recognition that the polar continuum could be incorporated properly into theories of chemical reactivity and spectroscopy in solution, and, now, two, Zerner's methods to incorporate dielectric continuum manipulations properly into quantum chemical calculations. There is a thread that begins with Marcus's work and continues to present-day applications.

To close this introduction, I thought it would be of interest to some readers to have a brief account of the activities that take place during the week of the Nobel Ceremonies.

The prizes in physics, chemistry, physiology or medicine, and literature and a prize in economics in the name of Nobel are awarded in Stockholm on the anniversary of the death of Alfred Nobel, December 10. The Peace Prize is awarded in Oslo, Norway at the same time. In the time leading up to the actual awards, each of the prize winners gives a Nobel address, of which Marcus's is reprinted here.

Because of the way I scheduled travel, I unfortunately missed being able to attend Professor Walcott's address on literature on Monday of the week of the awards. I arrived with my family Monday morning in time to get a little rest before the reception for the chemistry, physics, and economics prize-winners at the Academy of Sciences that evening. This reception is one of the first of many that the prize-winners attend

and it was an opportunity for each of us to meet the recipients and give them our congratulations. For me, it was pure pleasure to be able to see Rudy receiving the recognition for his work that I have admired so long. It was also a fitting recognition for a fine human being.

The main events of the next day were the lectures given by Professors Marcus and Charpak in chemistry and physics and by Professors Fischer and Krebs for physiology and medicine. The lectures in physics and chemistry were held at the Academy of Sciences and those in physiology at the Karolinska Institute. Because of the distance between these two institutions, it proved not possible to attend all lectures and also attend the Nobelkonsert (concert) at Concert Hall Tuesday evening.

Although it would seem that with only a few lectures during each day there would be plenty of time to go sightseeing, we found this difficult. The bus ride from the Grand Hotel to the Academy of Science was sufficiently long that trips back and forth – to get lunch or to prepare for the next event – took more time than anticipated. Of course, there were ample opportunities to converse with other attendees, among whom were Harrison Shull, Provost of the Naval Postgraduate School, and his wife.

The main address Wednesday was in Economics by Professor Becker. This was also one of the days for some sightseeing. The award-winners, their families and dignitaries were feted at various embassies. We used the time to tour the old city of Stockholm.

Thursday was the jewel of the week because of the award ceremony and banquet afterward. It can only be said that these two events are magic. The Concert Hall where the awards were presented was filled with men and women in formal attire. White tie and tails for men and formal gowns for women were required. We were given seats with the diplomatic corps with a fine view of the stage. This is an event for which those entitled to wear them display all their medals. Green, blue or crimson ribbons supporting prominent distinctions abounded. It was truly a glittering occasion.

The stage was occupied by the Royal Family, members of the Academy of Science and the Karolinska Institute, and the winners of the Nobel Prizes. The symphony orchestra, under Valdimir Ashkenazy, provided music. Each prize winner was introduced to King Carl XVI Gustav and his accomplishments noted in Swedish. Following this introduction, the King awarded the prize-winner with the gold Nobel medal and diploma. Each diploma was individually crafted by an artist to capture the essence of the work for which the prize was given.

If the awarding of the prizes was glittering, the Award Banquet that followed was spectacular. It was a splendid celebration of human excellence and accomplishment attended by approximately 1,500 people, some of whom had received the Nobel Prize in earlier years. It is almost impossible for the common mortal in this century to imagine state

dinners if one is not part of the diplomatic service or attached at a high level to a government office. The Nobel Award banquet has its own service that is used only for that occasion. The City Hall, in which the banquet is held, literally sparkles. Nothing is left to chance. The dinner is a lavish affair with each course introduced by music or music and dance. In a touch that I found appealing, Swedish university students serve as ushers and guides. They were easily identified by their characteristic student caps and sashes with emblems that indicated the particular "Student Nations" (fraternities or sororities) to which they belonged.

Each of us was assigned a place at the banquet. Our seat assignments were listed in a program that contained all of our names, including the names of the Royal Family. My wife and I found ourselves with friends and the friends and acquaintances of Professor Marcus. Even though the food was delightful, and memorable, the conversation with those at our table was equally enjoyable. And, even though the meal, with its many courses, took hours to complete, the time passed all too quickly. At the end of the banquet, we were ushered to a hall upstairs in which the Ball took place. There were two dance bands that entertained well into the night. The students, we understand, generally celebrate until dawn. Being somewhat past that age, and relying at that hour, on bus transportation back to the Grand Hotel, most of the rest of us reluctantly ended the evening with a trip home around midnight.

For the prize winners, the ceremonies did not end with the banquet. They then moved on throughout Sweden to present their Nobel Addresses at several universities. For us, it was a time to wonder if it all really happened, visit one more sight, and to see friends and colleagues before boarding the plane for the trip home.

Electron Transfer: Simple Model, Successful Theory

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Although many people have a basic knowledge of chemistry, the somewhat sanitized-sounding title "Electron Transfer Reaction" masks a well-known process. It is the familiar *oxidation-reduction* reaction. While there are many examples of *homogeneous* oxidation-reduction reactions that take place in solution, electrochemical reactions that take place at solid surfaces also belong. Oxidation and reduction involve the loss and gain of charge, generally electronic charge, in chemical species that undergo reaction. An interesting feature of some of these reactions is the fact that charge can transfer without the formation or destruction of distinct chemical bonds. This fact made it possible for Marcus to construct a theory for the reaction that has since been verified. My purpose is to discuss the model of these reactions in a simple costume, in much the same way as Marcus originally did.

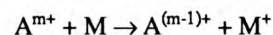
There has been an increasing effort during the past decade or so to extend the electron transfer theory; yet there has been no modification of the foundation of the theory. It is noteworthy that with the use of the clearly understandable arguments based in electrostatics and statistical mechanics, Marcus was able to provide a clear understanding of how these reactions occur¹. His original equations are accurate in the adiabatic limit for the model of the solvent as a polar continuum. There has been no subsequent contribution to the body of theory to contravene this discovery. Indeed, when the theory is developed beginning with the quantum mechanical expression for the transition probability², the same expression emerges that Marcus derived making additional use of the Landau-Zener³

theory to describe weak overlap, or non-adiabatic, reactions. It is useful, therefore, to examine the model of the electron transfer and its interpretation that leads to the Marcus theory.

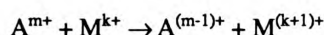
A system in which simultaneous oxidation and reduction occurs is the following. Two charged, spherical species, A^{m+} and B^{n+} , dissolved in a polar solvent come into proximity and exchange charge according to the following reaction:



The available electronic charge on one species, A, migrates to the second species, B. In the process, energy contained in the whole system must localize in the region of the individual molecular reacting species to provide the driving force to activate the transfer. The transition state is higher in energy than either the initial or final state. Thus the energy needed to activate the reaction passes back to the surroundings after the system moves through the transition to the final state. As long as the system is free of external sources of additional energy – unconnected to a battery, for example – there is no net gain or loss of energy over time. But, energy within the system can redistribute itself, and is therefore available to activate chemical reactions. If, for example, one of the reactants, B, is replaced by a metal surface, M, the reaction with an individual state of the metal surface can be written in essentially the same form:



¹ Although this short article reviews the basic notions of the Marcus theory, it is not intended as any kind of exhaustive review. As a result, I do not provide a large list of references. References to some of the earlier reviews are given. The articles to follow in this issue of the *Naval Research Reviews* will contain additional references to current work.

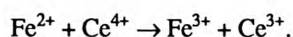


but now, as indicated, there are many of these reactions to consider, k of them. The index k also labels a level within a band of energy levels at the metal surface. An electrochemical electron transfer is therefore a sum of all the possible surface reactions. Because the energy of a metal surface state can be changed with the imposition of an external potential, the expressions for the electrochemical electron transfer rate constant will differ from the homogeneous case by terms that reflect the effect of the external potential.

As is customary with the thermodynamic analyses of chemical systems, we imagine the system composed of two main parts: (1) the individual reactants, the A and B-species, and (2) the solvent. The model is further refined by considering the fact that, because of the great difference between the mass of the electron and the masses of the other atomic and molecular species in the system, the motion of the electron to a first approximation can be referred to the remainder of the heavier species held *at rest*. In molecular quantum mechanics this assumption is referred to as the *Born-Oppenheimer adiabatic approximation*. It is essential here^{4,5}.

With this subdivision of the system into local reactants and the larger surroundings, it is now possible to account for a reaction as follows⁵. Given a solution in which oxidation and reduction takes place, the migrating electronic charge marks this change and moves in response to the *fluctuations* of all the other atomic and molecular species. Even in a system that is in a state of thermodynamic equilibrium, with overall total energy a constant quantity, local energy within the system is continually redistributed. It is therefore possible that sufficient energy can collect at the point of reaction for an instant in time to activate the process.

It is simpler first to consider the case in which two species A and B exchange charge and both species are chemically different: for example, the reaction



The (thermodynamic) energy of the system described by the reactants on the left of the equation is clearly different from the products on the right. When an electron migrates, the transfer takes place at a point in the many-dimensional phase space where the energy of the initial matches the energy of the final state. There are many places where this condition is satisfied but are not transition states. One of the states is the transition state and eventually will be identified^{6,7}.

Marcus has shown that the free energy of charging two ions, labelled 1 and 2, in solution is^{1,8,9}

$$\Delta G = \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \left(\frac{\Delta e_1^2}{2a_1} + \frac{\Delta e_2^2}{2a_2} + \frac{\Delta e_1 \Delta e_2}{R} \right)$$

The dielectric constant ϵ_{op} is associated with the optical modes and is generally equal to the square of the index of refraction. The second dielectric constant, ϵ_s , is the static constant for the solvent – for water it is about 78. The charge difference Δe is $e^* - e$ where one has taken the system from a charge state e to a new state e^* and back.

The optimum free energy of activation, ΔG^T , is determined through the requirement that (1) the energies of the initial and final states be equal at the transition state, and (2), that the point at which the energies are equal be the lowest possible transition state energy. This condition is ensured through the requirement that the variation of the free energy of formation for the overall reaction be zero: $\delta \Delta G_0 = 0$. Together with the requirement for the conservation of charge, one can take the variation of ΔG to find the free energy of formation of the transition state⁹:

$$\Delta G^T = \frac{(\lambda_0 + \Delta G_0)^2}{\lambda_0}$$

where

$$\lambda_0 = \Delta e^2 \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_0} \right) \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right)$$

and now Δe is the quantity of charge transferred in the reaction. ΔG^T is the famous Marcus expression for the free energy of activation of an electron transfer reaction. The expression for the rate constant is then¹

$$k = Z \exp(-\Delta G^T/RT)$$

and Z is the "collision" number. The unusual feature, for the time, was the quadratic dependence of the free energy of activation on the square of the free energy of reaction. It is just this dependence that has been demonstrated to hold for reactions in the extremely endo- and exothermal regions, the so-called abnormal reactions.

It seems evident that the simple model of a simple electron transfer reactions is indeed too simple. The modes of the dielectric continuum alone do not account for all of the process of activation. Nevertheless, consideration of classical polarization does account for much of the activation even though more sophistication seems warranted. Marcus, in his early electron transfer work, improved the original theory by accounting for discrete vibrations of solvent and ligand in the *immediate vicinity* of the reactive species¹¹. This adds a term for the *inner sphere* contribution, in effect a Stokes energy. There are in addition many systems within which electronic charge transfers but which are not well represented as dielectric systems. The vast collection of biological electron transfer systems fall largely into this class¹². In these systems, charge migrates over great distances. It is generally believed that

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superexchange mechanisms are involved. The migratory electron makes use of intervening molecular species as bridges between donor and acceptor. The polarization of the system still figures in the calculations, but must be handled carefully.

One of the more interesting developments over the past two decades has been, I believe, the realization that the process of electron transfer resembles to a significant degree radiationless transitions in molecules suspended in condensed phases¹³. The understanding that one could cast the rate constant into a dependence on a time-dependent correlation function opened the analysis of, first, the electron transfer reaction, and then the remainder of reactions to useful quantum mechanical treatment. It is also interesting to note that many of the individuals involved in the development of radiationless transition theory branched into the development of the electron transfer reaction as a natural outlet¹⁴. This process continues. One of the main difficulties in both the radiationless transition theory in spectroscopy and electron transfer theory has to do with the problem of bond break that accompanies charge transfer. Bond break in general is a process that begs to go beyond the harmonic limit of analysis. The harmonic limit is generally the savior of the electron transfer and radiationless transition theory. Some attempts have been made to try to incorporate adequate account of anharmonic effects. This has not been done to my satisfaction, but the continuing effort is well worth the price. What continues to be noteworthy, however, is the simple fact that the harmonic limit of analysis of the contribution of molecular vibrational modes to the activation of any process seems to give us the majority of the energy we expect. Were this not the case, Marcus's analysis never would have been possible. With the polaron type of analysis of the polar mode representation – as was originally done by Levich and Dogonadze² – however, one immediately sees that it is the representation of *energy states of the polarization* that admit the harmonic representation for two reasons: (1) the energy of the polarization field depends on $\int \mathbf{P} \cdot \mathbf{P} \, dV$, and (2) boson quantization. This is of course implicit in Marcus's original analysis¹ because it is a basic part of (linear) electrostatics. Non-linear polarization effects might play some role, but one can anticipate that they would be very small.

Where are the uncharted regions of the electron transfer theory now? I think there are a few. The important development for the near term, I believe, will continue to be with the construction of an adequate model and analysis of the contribution of discrete molecular vibrations to the activation process. For, while these modes may not dominate the activation in comparison to the polar continuum, they do nevertheless manifest subtle effects that may be very important in our efforts to interpret important biological and materials science applications. Finally, there has been, and continues to be, a desire among many to move well past the continuum representation of the solvent. Efforts have been made¹⁵ to formalize a theoretical dependence on various better-defined, more rig-

orous models of polar solutions, *e.g.*, the mean spherical approximation. There need to be reasonable computational algorithms that allow one to use effectively Monte Carlo or molecular dynamics routines to find rate parameters. Some of this effort is discussed in this issue of the Reviews.

The Marcus theory is elegant in its design, its execution, and its apparent simplicity of expression. The evolution of the theory will add texture to a strong foundation. Chemistry is now richer for the greater understanding of nature that Marcus theory has helped us to attain.

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Electron Transfer Reactions In Chemistry Theory And Experiment*

(Nobel Lecture in Chemistry presented in
Stockholm, Sweden December 8, 1992)

by
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Looking Back

My first encounters with McGill University came when I was still in a baby carriage. My mother used to wheel me about the campus when we lived in that neighborhood and, as she recounted years later, she would tell me that I would go to McGill. There was some precedent for my going there, since two of my father's brothers received their M.D.'s at McGill.

I have always loved going to school. Since neither of my parents had a higher education, my academic "idols" were these two paternal uncles and one of their uncles, my great-uncle, Henrik Steen (ne Markus). My admiration for him, living in faraway Sweden, was not because of a dr.telol. (which he received from the University of Uppsala in 1915) nor because of the many books he wrote – I knew nothing of that – but rather because he was reputed to speak 13 languages. I learned decades later that the number was only 9! Growing up, mostly in Montreal, I was an only child of loving parents. I admired my father's athletic prowess – he excelled in several sports – and my mother's expressive singing and piano playing.

My interest in the sciences started with mathematics in the very beginning, and later with chemistry in early high school and the proverbial home chemistry set. My education

at Baron Byng High School was excellent, with dedicated masters (boys and girls were separate). I spent the next years at McGill University, for both undergraduate and, as was the custom of the time, graduate study. Our graduate supervisor, Carl A. Winkler, specialized in rates of chemical reactions. He himself had received his Ph.D. as a student of Cyril Hinshelwood at Oxford. Hinshelwood was later the recipient of the Nobel Prize for his work on chemical kinetics. Winkler brought to his laboratory an enthusiastic joyousness in research and was much loved by his students.

During my McGill years, I took a number of math courses, more than other students in chemistry. Upon receiving a Ph.D. from McGill University in 1946, I joined the new post-doctoral program at the National Research Council of Canada in Ottawa. This program at NRC later became famous but at the time it was still in its infancy and our titles were Junior Research Officers. The photochemistry group was headed by E.W.R. Steacie, an international figure in the study of free-radical reactions and a major force in the development of the basic research program at NRC. I benefitted from the quality of his research on gas phase reaction rates. Like my research on chemical reaction rates in solution at McGill (kinetics of nitration), it was experimental in nature. There were no theo-

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retical chemists in Canada at the time, and as students I don't think we ever considered how or where theories were conceived.

About 1948 a fellow post-doctoral at NRC, Walter Trost, and I formed a two-man seminar to study theoretical papers related to our experimental work. This adventure led me to explore the possibility of going on a second post-doctoral, but in theoretical work, which seemed like a radical step at the time. I had a tendency to break the glass vacuum apparatus, due to a still present impetuous haste, with time-consuming consequences. Nevertheless, the realization that breaking a pencil point would have far less disastrous consequences played little or no role, I believe, in this decision to explore theory!

I applied in 1948 to six well-known theoreticians in the U.S. for a postdoctoral research fellowship. The possibility that one of them might take on an untested applicant, an applicant hardly qualified for theoretical research, was probably too much to hope for. Oscar K. Rice at the University of North Carolina alone responded favorably, subject to the success of an application he would make to the Office of Naval Research for this purpose. It was, and in February 1949 I took the train south, heading for the University of North Carolina in Chapel Hill. I was impressed on arrival there by the red clay, the sandy walks, and the graciousness of the people.

After that, I never looked back. Being exposed to theory, stimulated by a basic love of concepts and mathematics, was a marvelous experience. During the first three months I read everything I could lay my hands on regarding reaction rate theory, including Marcellin's classic 1915 theory which came within one small step of the Transition State Theory of 1935. I read numerous theoretical papers in German, a primary language for the "chemical dynamics" field in the 1920s and 1930s, attended my first formal course in quantum mechanics, given by Nathan Rosen in the Physics Department, and was guided by Oscar in a two-man weekly seminar in which I described a paper I had read and he pointed out assumptions in it that I had overlooked. My life as a working theorist began three months after this preliminary study and background reading, when Oscar gently nudged me toward working on a particular problem.

Fortunately for me, Oscar's gamble paid off. Some three months later, I had formulated a particular case of what was later entitled by B. Seymour Rabinovitch, RRKM theory ("Rice-Ramsperger-Kassel-Marcus"). In it, I blended statistical ideas from the RRK theory of the 1920s with those of the transition state theory of the mid-1930s. The work was published in 1951. In 1952 I wrote the generalization of it for other reactions. In addition, six months after arrival in Chapel Hill, I was also blessed by marriage to Laura Hearne, an attractive graduate student in sociology at UNC. She is here with me at this ceremony. Our three sons, Alan, Kenneth and Raymond, and two daughters-in-law are also present today.

In 1951, I attempted to secure a faculty position. This effort met with little success (35 letters did not yield 35 no's, since not everyone replied!). Very fortunately, that spring I met Dean Raymond Kirk of the Polytechnic Institute of Brooklyn at an American Chemical Society meeting in Cleveland, which I was attending primarily to seek a faculty position. This meeting with Dean Kirk, so vital for my subsequent career, was arranged by Seymour Yolles, a graduate student at UNC in a course I taught during Rice's illness. Seymour had been a student at Brooklyn Poly and learned, upon accidentally encountering Dr. Kirk, that Kirk was seeking new faculty. After a subsequent interview at Brooklyn Poly, I was hired, and life as a fully independent researcher began.

I undertook an experimental research program on both gas phase and solution reaction rates, wrote the 1952 RRKM papers, and wondered what to do next in theoretical research. I felt at the time that it was pointless to continue with RRKM since few experimental data were available. Some of our experiments were intended to produce more.

After some minor pieces of theoretical study that I worked on, a student in my statistical mechanics class brought to my attention a problem in polyelectrolytes. Reading everything I could about electrostatics, I wrote two papers on that topic in 1954/55. This electrostatics background made me fully ready in 1955 to treat a problem I had just read about on electron transfers. I comment on this next period on electron transfer research in my Nobel Lecture. About 1960, it became clear that it was best for me to bring the experimental part of my research program to a close – there was too much to do on the theoretical aspects – and I began the process of winding down the experiments. I spent a year and a half during 1960-61 at the Courant Mathematical Institute at New York University, auditing many courses which were, in part, beyond me, but which were, nevertheless, highly instructive.

In 1964, I joined the faculty of the University of Illinois in Urbana-Champaign and I never undertook any further experiments there. At Illinois, my interests in electron transfer continued, together with interests in other aspects of reaction dynamics, including designing "natural collision coordinates", learning about action-angle variables, introducing the latter into molecular collisions, reaction dynamics, and later into semiclassical theories of collisions and of bound states, and spending much of my free time in the astronomy library learning more about classical mechanics, celestial mechanics, quasiperiodic motion, and chaos. I spent the academic year of 1975-76 in Europe, first as Visiting Professor at the University of Oxford and later as a Humboldt Awardee at the Technical University of Munich, where I was first exposed to the problem of electron transfer in photosynthesis.

In 1978, I accepted an offer from the California Institute of Technology to come there as the Arthur Amos Noyes Professor of Chemistry. My semiclassical interlude of 1970-80 was intellectually a very stimulating one, but it involved for

me less interaction with experiments than had my earlier work on unimolecular reaction rates or on electron transfers. According, prompted by the extensive experimental work of my colleagues at Caltech in these fields of unimolecular reactions, intramolecular dynamics and of electron transfer processes, as well as by the rapidly growing experimental work in both broad areas world-wide, I turned once again to those particular topics and to the many new types of studies that were being made. Their scope and challenge continues to grow to this day in both fields. Life would be indeed easier if the experimentalists would only pause for a little while!

There was a time when I had wondered about how much time and energy had been lost doing experiments during most of my stay at Brooklyn Poly – experiments on gas phase reactions, flash photolysis, isotopic exchange electron transfer, bipolar electrolytes, nitration, and photoelectrochemistry, among other – and during all of my stay at NRC and at McGill. In retrospect, I realized that this experimental background heavily flavored my attitude and interests in theoretical research. In the latter I drew, in most but not all cases, upon experimental findings or puzzles for theoretical problems to study. The growth of experiments in these fields has served as a continually rejuvenating influence. This interaction of experiment and theory, each stimulating the other, has been and continues to be one of the joys of my experience.

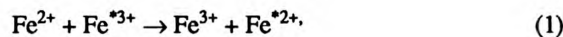
Honors received for the theoretical work include the Irving Langmuir and the Peter Debye Awards of the American Chemical Society (1978, 1988), the Willard Gibbs, Theodore William Richards, and Pauling medals, and the Remsen and

Edgar Fahs Smith Awards, from various sections of the ACS, (1988, 1990, 1991, 1991, 1991), the Robinson and the Centenary Medals of the Faraday Division of the Royal Society of Chemistry (1982, 1988), Columbia University's Chandler Medal (1983) and Ohio State's William Lloyd Evans Award (1990), a Professorial Fellowship at University College, Oxford (1975 to 1976) and a Visiting Professorship in Theoretical Chemistry at Oxford during that period, the Wolf Prize in Chemistry (1985), the National Medal of Science (1989), the Hirschfelder Prize in Theoretical Chemistry (1993), election to the National Academy of Sciences (1970), the American Academy of Arts and Sciences (1973), the American Philosophical Society (1990), honorary membership in the Royal Society of Chemistry (1991), and foreign membership in the Royal Society (London) (1987) and in the Royal Society of Canada (1993). Honorary degrees were conferred by the University of Chicago and by Goteborg, Polytechnic, McGill, and Queen's Universities and by the University of New Brunswick (1983, 1986, 1987, 1988, 1993, 1993). A commemorative issue of the Journal of Physical Chemistry was published in 1986.

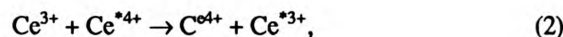
Electron Transfer Experiments Since The Late 1940s

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, represents 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.

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, such as



and

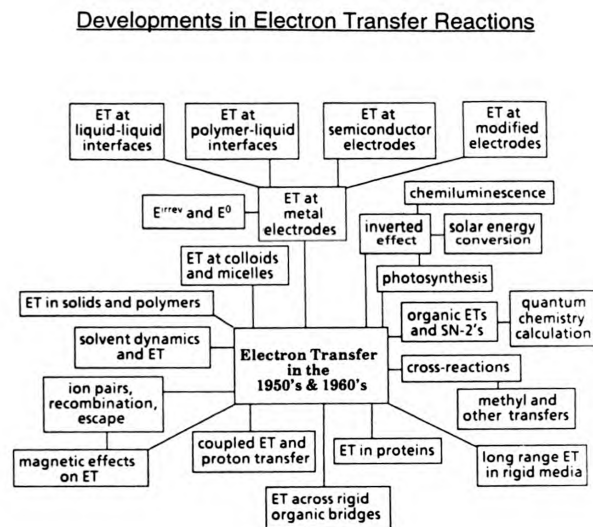


in aqueous solution, where the asterisk denotes a radioactive isotope.

There is a two-fold simplicity in typical self-exchange electron transfer reactions (so-called since other methods besides isotopic exchange were later used to study some of them): (1) the reaction products are identical with the reactants, thus eliminating one factor which usually influences the rate of a chemical reaction in a major way, namely the relative

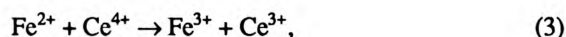
Figure 1.

Examples of topics in the electron transfer field (Marcus and Siddarth, ref. 2).



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 reactions 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 (cf Shaik *et al.*, ref. 2).

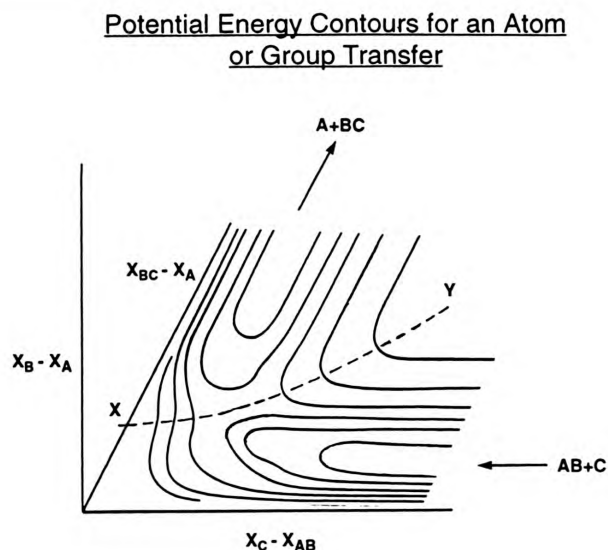
A second factor in the growth of the electron transfer field was the introduction of new instrumentation, which permitted the study of the rates of rapid chemical reactions. Electron transfers are frequently rather fast, compared with many reactions which undergo, instead, a breaking of chemical bonds and a 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 of the latter 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 "cross reactions," i.e., electron transfer reactions between two different redox systems, as in



which supplemented the earlier studies of the self-exchange electron transfer reactions. A comparative study of these two

Figure 2.

Potential energy contours for reaction (4), $\text{AB} + \text{C} \rightarrow \text{A} + \text{BC}$,



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 which 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 depicted in Figure 1. Some of these investigations were made possible by a newer technology, lasers particularly, and now include studies in the picosecond and subpicosecond time regimes. Just recently, (non-laser) nanometer-sized electrodes have 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 various effects, such as varying the metal-solution potential difference on the electrochemical electron transfer rate.

In some studies of electron transfer reactions in solution there has also been a skillful blending of these measurements of chemical reaction rates with various organic or inorganic synthetic methods, as well as with site-directed mutagenesis, to obtain still further hitherto unavailable information. The use of chemically modified proteins to study the distance dependence of electron transfer, notably by Gray and coworkers, 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. The present lecture addresses the underlying theory and this interaction.

The Early Experience

My own involvement in the electron transfer field began in a rather circuitous way. In an accompanying biographical note I have commented on my earlier background, which was in experimental measurements of reaction rates as a chemistry graduate student at McGill University (1943-46) and as a post-doctoral associate at the National Research Council of Canada (1946-49). A subsequent post-doctoral study at the University of North Carolina (1949-51) on the theory of reaction rates resulted in what is now known in the literature as RRKM theory (Rice, Ramsperger, Kassel, Marcus).

This unimolecular reaction field reflects another long and extensive interaction between theory and experiment. RRKM theory enjoys widespread use and is now usually referred to

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in the literature only by its acronym (or by the texts written about it, ref. 4), instead of by citation of the original articles.

After the theoretical post-doctoral 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 (1951-52). I remember vividly how a friend of mine, a colleague at Brooklyn Poly, Frank Collins, came down to my office every day with a new idea on the liquid state transport theory which he was developing, while I, for theoretical research, had none. Perhaps this gap in not doing anything immediately in the field of theory 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.

In the biographical note I have also recalled 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 (1954-55), one of which required a considerable expansion in my background in electrostatics, so as to analyze different methods for calculating the free energy of these systems: In polyelectrolyte molecules, it may be recalled, 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 to me on electrostatics (Caltech's Mason and Weaver's 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 which lay ahead.

Developing An Electron Transfer Theory

Introduction

My first contact with electron transfers 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 which 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 $\text{Fe}(\text{CN})_6^{3-} - \text{Fe}(\text{CN})_6^{4-}$ and $\text{MnO}_4^- - \text{MnO}_4^{2-}$, are relatively fast.

Libby explained this observation in terms of the Franck-Condon principle, as discussed below. 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 solvation energy barrier which 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.

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 electronic energy of the entire system, plotted versus the positions of all the atoms. A very common example is the transfer of an atom or a group B from AB to form BC



An example of reaction (4) is the transfer of an H, such as in $\text{IH} + \text{Br} \rightarrow \text{I} + \text{HBr}$, 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, this potential energy function is

Figure 3.

Typical nuclear configurations for reactants, products, and surrounding solvent molecules in reaction (1). The longer $\text{M}-\text{OH}_2$ bond length in the +2 state is indicated schematically by the larger ionic radius. (Sutin, ref. 2)

Electron Transfer in Solution

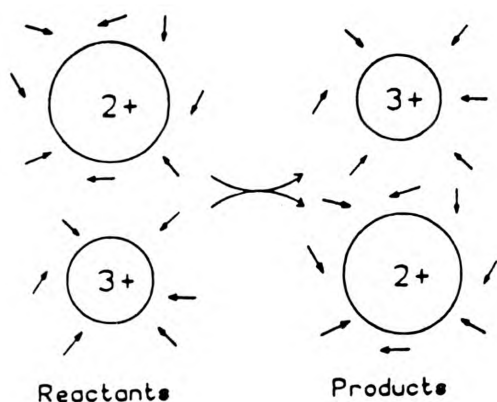
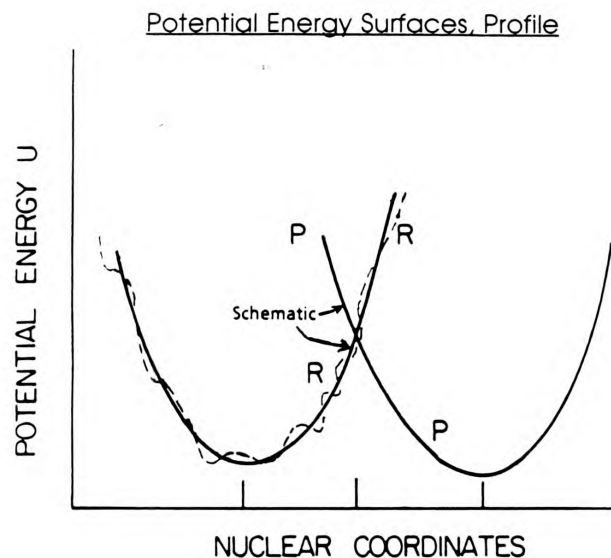


Figure 4.

Profile of potential energy surfaces for reactants plus environment, R , and for products plus environment, P . Solid curves: schematic. Dashed curves: schematic but slightly more realistic. The typical splitting at the intersection of U_r and U_p is not shown in the Figure (Marcus and Siddarth, ref. 2).



frequently plotted as constant energy contours in a space whose axes are chosen to be two important relative coordinates such as, in reaction (4), 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 this reacting system begins its trajectory in the lower right region of the figure in a valley in this plot of contours, the "valley of the reactants." 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, and so form the reaction products. There is a line in the figure, XY, analogous to the "continental divide" in the Rocky Mountains in the U.S., which separates systems which could spontaneously flow into the reactants' valley from those which could flow into the products' one. In chemists' terminology this line represents the "transition state" of the reaction.

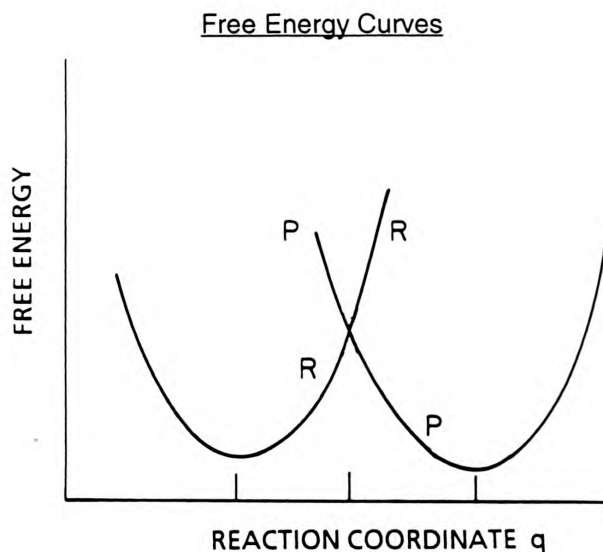
In transition state theory a quasi-equilibrium between the transition state and the reactant is frequently postulated, and the reaction rate is then calculated using equilibrium statistical mechanics. A fundamental dynamical basis, which replaces this apparently *ad hoc* but common assumption of transition state theory and which is perhaps not as well known in the chemical literature as it deserves to be, was given many years

ago by the physicist and one-time chemical engineer, Eugene Wigner (1938). 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 one in classical mechanical trajectory studies of chemical reactions. Usually, recrossings are relatively minor, except in nonadiabatic reactions, where they are readily treated (cf discussion, later).

In practice, transition state theory is generalized, so as 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.)

Figure 5.

Free energy of reactants plus environment vs. the reaction coordinate Q (R curve), and free energy of products plus environment vs. reaction coordinate Q (P curve). The three vertical lines on the abscissa denote, from left to right, the value for the reactants, for the transition state, and for the products. (Marcus and Siddarth, ref. 2).



Electron Transfer Theory. Formulation

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 for the electron transfer reaction.

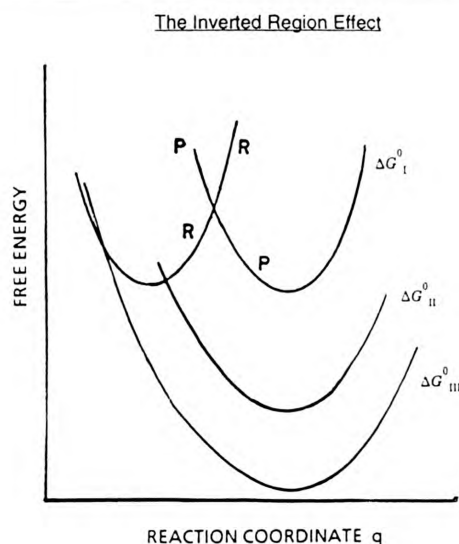
In his 1952 symposium paper, Libby noted that when an electron is transferred from one reacting ion or molecule to another, the two new molecules or ions formed are in the wrong environment of the solvent molecules, since the nuclei do not have time to move during the rapid electron jump: in reaction (1) a 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 $\text{Fe}(\text{CN})_6^{-3}$ – $\text{Fe}(\text{CN})_6^{-4}$ and MnO_4^{2-} – 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 $\text{Co}(\text{NH}_3)_6^{3+}$ – $\text{Co}(\text{NH}_3)_6^{2+}$ reaction is very slow, and it was pointed out that there was a large difference in the equilibrium CoN bond lengths in the 3+ and the 2+ ions, and so 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 which 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 system behave in the dark so as to satisfy 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.

Figure 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 indicated in Figure 8 (Marcus and Sridhar, ref. 2).



For a reaction such as reaction (1), an example of an initial and final configuration of the solvent molecules 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.

The theory then proceeded as follows. The potential energy U , 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. (E.g., the inner coordination shell of an ion such as Fe^{2+} or Fe^{3+} in water is known from EXAFS 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.)

Due to the effect of the previously neglected electronic coupling and the coupling between the electronic motion and to 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, and so 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, 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 the electron donor and acceptor is large enough at the intersection, a system crossing S from the lower surface on the reactants' side of S continues onto the lower surface on the products' side, and so 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 using quantum mechanical perturbation theory, for example, 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.

Electron transfer theory. Treatment

In the initial paper (1956) I formulated the above picture of the mechanism of electron transfer and, to make the calculation of the reaction rate tractable, treated the solvent as a dielectric continuum. In the transition state the position-dependent dielectric polarization $P_u(r)$ of the solvent, due to the orientation and vibrations of the solvent molecules, 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 for the solvent molecules, on the other hand, can rapidly respond to any such fluctuations and so is that which is 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 with 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 the G for the transition state. That G was then introduced into transition state theory and the reaction rate calculated.

In 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 month 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 was also able to obtain 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

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

where ΔG^* , in turn, is given by

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2, \quad (5b)$$

The A in Eq. (5a) is a term depending 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), λ is a "reorganization term," composed of solvational (λ_0) and vibrational (λ_i) components.

$$\lambda = \lambda_0 + \lambda_i \quad (6)$$

In a two-sphere model of the reactants, λ_0 was expressed in terms of the two ionic radii a_1 and a_2 (including in the radius 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:

$$\lambda_0 = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (7)$$

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 Eq. (5) for notational brevity. The expression for the vibrational term λ_i is given by

$$\lambda_i = \frac{1}{2} \sum_j k_j (Q_j^r - Q_j^p)^2 \quad (8)$$

where Q_j^r and Q_j^p are equilibrium values for the j th normal mode coordinate Q_j and k_j is a reduced force constant $2k_j^r k_j^p / (k_j^r + k_j^p) k_j^r$ being the force constant for the reactants and k_j^p being that for the products. (I introduced a "symmetrization" approximation for the vibrational part of the potential energy surface, to obtain this simple form of Eqs. (5) to (8), and tested it numerically.)

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 using chemical bond length coordinates and neglecting bond-bond correlation had already been published for self-exchange reactions by George and Griffiths in 1956.

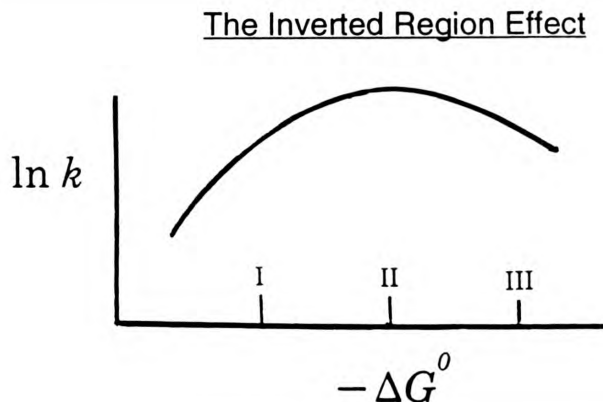
I also extended the theory to treat electron transfers at electrodes, and distributed it as an Office of Naval Research Report in 1957, the equations being published later in a journal paper in 1959. I had little prior knowledge of the subject, and my work on electrochemical electron transfers was facilitated 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 was again given by Eqs. (5)-(8), but with A now having a value appropriate to the different "geometry" of the encounter of the participants in the reaction. The $1/2a_2$ in Eq. (7) was now absent (there is only one reacting ion) and R now denotes twice the distance from the center of the reactant's charge to the electrode (it equals the ion-image distance). A term $e\eta$ replaced the ΔG^0 in Eq.(5b), where e is the charge transferred between the ion and the electrode, and η is the activation overpotential, namely the metal-solution potential difference, 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 G curves in Figure 5 have the same height.

When $|\eta| < \lambda$, 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 was now predicted to be absent for this process, i.e., the counterpart of Eq. (5) is applicable only in the region $|\eta| < \lambda$: 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

Figure 7.

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

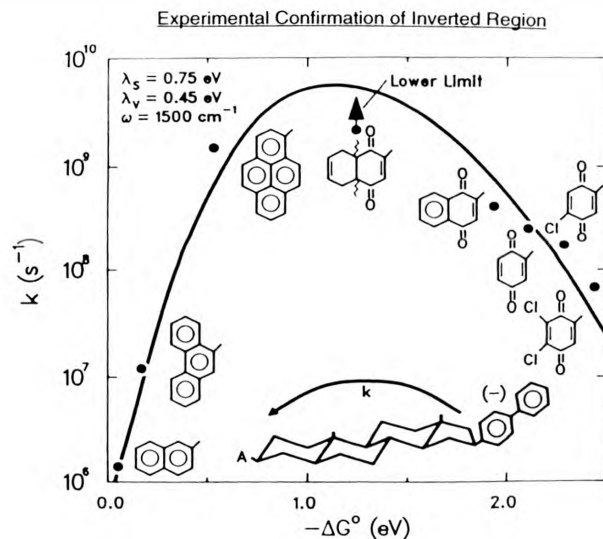


unoccupied quantum state of the metal, or (if leaving) departing from a low occupied quantum state, each far removed from the Fermi level. (The inverted region effect should, however, occur for the electron transfer when the electrode is a narrow band semiconductor.)

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 intro-

Figure 8.

Inverted region effect in chemical electron transfer reactions. (Miller, et al, ref. 3).



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duced a purely molecular treatment of the reacting system. Using statistical mechanics, the solvent was treated as a collection of dipoles in the 1960 paper, and later in 1965 a general charge distribution was used for the solvent molecules and for 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) (cf A. Warshel, 1987). It was, thereby, a coordinate 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. (In contrast, in reactions such as that depicted by Figure 2, it is customary, instead, to define a reaction coordinate locally, namely, 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 are 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 approxi-

mation," 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 beyond 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. This picture permitted a depiction of the reaction in terms of parabolic free energy plots in simple and readily visualized terms, as in Figure 5. With them 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, due to changes in strong ion-polar solvent interactions. (The free energy plot is legitimately a one-coordinate plot while the potential energy plot is at most a profile of the complicated U_r and U_p 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 (4), (5) and (initially via (7) and (8)) on the approximate relation

$$\lambda_{12} \approx \frac{1}{2} (\lambda_{11} + \lambda_{22}) \quad (9)$$

where λ_{12} is the λ for the cross-reaction and the λ_{11} and λ_{22} are those of the self-exchange reactions.

Predictions

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 these predictions. Among the latter was one which became one of the most widely tested aspects of the theory, namely, the "cross-relation." This expression, which follows from Eqs. (5) and (9), 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.

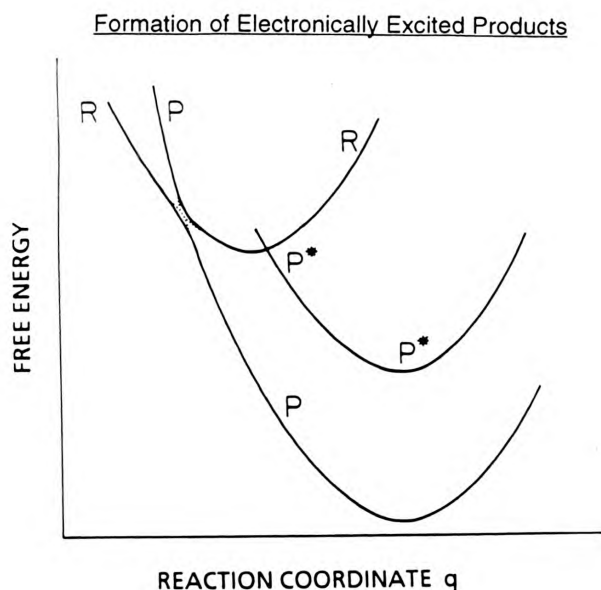
$$k_{12} \approx (k_{11} k_{22} K_{12} f_{12})^{1/2} \quad (10)$$

where f_{12} is a known function of k_{11} , k_{22} and K_{12} and is usually close to unity.

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

Figure 9.

A favored formation of an electronically excited state of the products (Marcus and Siddarth, ref. 2).



free energy ΔG^* vs. ΔG^0 is seen from Eq.(5) to first decrease as ΔG^0 is varied from 0 to some negative value, vanish at $\Delta G^0 = \lambda$, and then increase when ΔG^0 is made still more negative. This initial decrease of ΔG^* with increasingly negative ΔG^0 is the expected trend in chemical reactions and is similar to the usual trend in "Bronsted plots" of acid or base catalyzed reactions 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 using 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 non-specific solvent effects, the dependence of the reaction rate on solvent dielectric properties. The testing of some of the predictions was delayed by an extended sabbatical in 1960-61, which I spent auditing courses and attending seminars at the nearby Courant Mathematical Institute.

Comparisons 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 via his stopped-flow apparatus or otherwise knew rate constants and equilibrium constants which permitted the cross-relation Eq. (10) to be tested. There were about six such sets of data which he had available. I remember vividly the growing sense of excitement we both felt as, one by one, the observed k_{12} 's 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-relation and of the other predictions. A few examples of the cross-relation test are given in Table I.

The encouraging success of the experimental tests given in the 1963 paper suggested that the theory itself was more general than the approximations (e.g., solvent dipoles, 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 transfers in solution and at metal electrodes, and served, thereby, to generalize my earlier (1957) treatment of the electrochemical electron transfers.

Table 1.

Comparison of Calculated and Experimental k_{12} Values

Reaction	$k_{12} (M^{-1} sec^{-1})$	
	Observed	Calculated
$IrCl_6^{2-} + W(CN)_8^{4-}$	6.1×10^7	6.1×10^7
$IrCl_6^{2-} + Fe(CN)_6^{4-}$	3.8×10^5	7×10^5
$IrCl_6^{2-} + Mo(CN)_8^{4-}$	1.9×10^6	9×10^5
$Mo(CN)_8^{3-} + W(CN)_8^{4-}$	5.0×10^6	4.8×10^6
$Mo(CN)_8^{3-} + Fe(CN)_6^{4-}$	3.0×10^4	2.9×10^4
$Fe(CN)_6^{3-} + W(CN)_8^{4-}$	4.3×10^4	6.3×10^4
$Ce^{IV} + W(CN)_8^{4-}$	$> 10^8$	4×10^8
$Ce^{IV} + Fe(CN)_6^{4-}$	1.9×10^6	8×10^6
$Ce^{IV} + Mo(CN)_8^{4-}$	1.4×10^7	1.3×10^7
$L-Co[(-)PDTA]^{2-} + Fe(bipy)_3^{3+}$	8.1×10^4	$\geq 10^5$
$L-Fe[(-)PDTA]^{2-} + Co(EDTA)^-$	1.3×10^1	1.3×10^1
$L-Fe[(-)PDTA]^{2-} + Co(ox)_3^{3-}$	2.2×10^2	1.0×10^3
$Cr(EDTA)^{2-} + Fe(EDTA)^-$	$\geq 10^6$	10^9
$Cr(EDTA)^{2-} + Co(EDTA)^-$	$\approx 3 \times 10^5$	4×10^7
$Fe(EDTA)^{2-} + Mn(CyDTA)^-$	$\approx 4 \times 10^5$	6×10^6
$Co(EDTA)^{2-} + Mn(CyDTA)^-$	9×10^{-1}	2.1
$Fe(PDTA)^{2-} + Co(CyDTA)^-$	1.2×10^1	1.8×10^1
$Co(terpy)_2^{2+} + Co(bipy)_3^{3+}$	6.4×10	3.2×10
$Co(terpy)_2^{2+} + Co(phen)_3^{3+}$	2.8×10^2	1.1×10^2
$Co(terpy)_2^{2+} + Co(bipy)(H_2O)_4^{3+}$	6.8×10^2	6.4×10^4
$Co(terpy)_2^{2+} + Co(phen)(H_2O)_4^{3+}$	1.4×10^3	6.4×10^4
$Co(terpy)_2^{2+} + Co(H_2O)_6^{3+}$	7.4×10^4	2×10^{10}
$Fe(phen)_3^{2+} + MnO_4^-$	6×10^3	4×10^3
$Fe(CN)_6^{4-} + MnO_4^-$	1.3×10^4	5×10^3
$V(H_2O)_6^{2+} + Ru(NH_3)_6^{3+}$	1.5×10^3	4.2×10^3
$Ru(en)_3^{2+} + Fe(H_2O)_6^{3+}$	8.4×10^4	4.2×10^5
$Ru(NH_3)_6^{2+} + Fe(H_2O)_6^{3+}$	3.4×10^5	7.5×10^6
$Fe(H_2O)_6^{2+} + Mn(H_2O)_6^{3+}$	1.5×10^4	3×10^4

*Bennett, Ref. 3.

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 several-fold and have been discussed elsewhere.

Previously, indirect evidence for the inverted region had been obtained by observing that electron transfer reactions with a very negative ΔG^* may result in chemiluminescence: when the G_r and G_p curves intersect at a high ΔG^* because of the inverted region effect, there may be an electron transfer to a more easily accessible G_p curve, one in which one of the products is electronically excited and which intersects the G_r curve in the normal region at a low ΔG^* , as in Figure 9. Indeed, experimentally in some reactions 100% formation of an elec-

tronically excited state of a reaction product has been observed by Bard and coworkers, and results in chemiluminescence.

Another consequence of Eq. (5) is the linear dependence of $k_B T \ln k$ on λ with a slope of 1/2, when $|\Delta G^0/\lambda|$ is small, and a similar behavior at electrodes, with ΔG^0 replaced by $e\eta$, 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.

Comparison of experiment and theory has also included that of the absolute reaction rates of the self-exchange reactions, the effect on the rate of varying the solvent, an effect sometimes complicated by ion pairing in the low dielectric constant media involved, and studies of the related problem of charge transfer spectra, such as



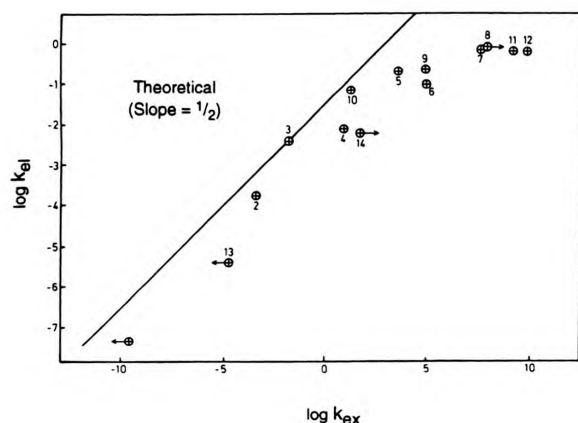
Here, the frequency of the spectral absorption maximum is given by

$$h\nu_{\max} = \lambda + \Delta G^0. \quad (12)$$

Figure 10.

Comparison of isotopic exchange electron transfer rates in solution, covering 20 orders of magnitude, with rates of corresponding electron transfers at metal electrodes. (Cannon, ref. 2).

Electrochemical vs Self-Exchange Rate Constants



Comparisons with Eq. (12), using Eq.(7) for λ , have included those of the effects of separation distance and of the 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 rates are seen to vary by some twenty orders of magnitude. The discrepancy at high k 's 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.)

Other Applications and Extensions

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, where the protein framework holding fast the constituents in this reaction center is not shown.

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 picoseconds) and from it to a quinone Q_A in 200 psec and thence to the other quinone Q_B . (Other chemical reactions then occur with these separated charges at each side of the membrane, bridged by this photosynthetic reaction center.)

To avoid wasting the excitation energy of the $BChl_2^*$ unduly it is necessary that the 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 for that first electron transfer step be small and hence, by Eq. (5), that the λ be small. The size of the reactants is large, and the immediate protein environment is largely nonpolar, so leading to a small λ (cf Eq.(7)). Nature appears, indeed, to have constructed a system with this desirable property.

Furthermore, to avoid another form of wasting the energy, 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 ($\sim 1.1\text{eV}$). It has been suggested that the small λ ($\sim 0.25\text{eV}$) 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 which can mimic the behavior of nature's photosynthetic systems, and so offer other routes for the harnessing of solar energy. The current understanding of how nature works has served to provide some guidelines. In this context, as well as that of electron transfer in other proteins, there are also relevant experiments in long range electron transfer. Originally the studies were of electron transfer in rigid glasses and were due to Miller and coworkers. More recently the studies have involved a donor and receptor held together by synthetically made rigid molecular bridges. The effect of varying the bridge length has been studied in the various systems. A theoretical estimate of the distance dependence of electron transfers in a photosynthetic system was first made by Hopfield, who used a square barrier model and an approximate molecular estimate of the barrier height.

Recently, in their studies of long range electron transfer in chemically modified proteins, Gray and coworkers 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 chosen should be such that $-\Delta G^0 \approx \lambda$, i.e., which has a k at the maximum of the $\ln k$ vs. $-\Delta G^0$ curve (cf Eqs. (4) -(5)). The value of k then no longer depends on a ΔG^* . Since ΔG^* is distance-dependent (cf Eq.(7)), it is particularly desirable to make $\Delta G^* \approx 0$, so that the relative k 's at the various sites now reflect only the electronic factor. Dutton and coworkers 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 Ebersson (ref. 2), in the light of current electron transfer theory. Other organic reactions have been explored by Shaik and Pross, in their analysis of a possible electron transfer mechanism vs. a conventional mechanism, and by Shaik *et al* (ref.2).

Theoretical calculations of the donor-acceptor electronic interactions, initially by McConnell and by Larsson, and later

by others, our 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.

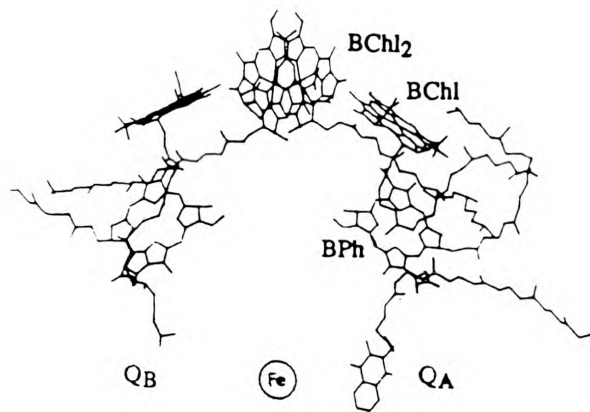
Another area of much current activity in electron transfers is that of solvent dynamics, following the pioneering treatment for general reactions by Kramers (1940). Important later developments for electron transfer were made by many contributors. Solvent dynamics affects the electron transfer reaction 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_v) contribution to λ .

Computational studies, such as the insightful one of David Chandler and coworkers on the $\text{Fe}^{2+} + \text{Fe}^{3+}$ self-exchange reaction, have also been employed recently. Using computer simulations they obtained a verification of the parabolic G curves, even for surprisingly high values of the fluctuation in G. They also extended their studies to dynamical and quantum mechanical effects of the nuclear motion. Studies of the quantum mechanical effects on 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).

There were important subsequent developments by various authors on these quantum effects, including the first dis-

Figure 11.

*Redox-active species involved in the initial charge separation for a photosynthetic bacterium (cf Deisenhofer *et al*, ref. 3; and Yeates *et al*, ref. 3), with labels added, to conform to the present text; they include a missing Q_B .*



cussion of quantum effects for the vibrations of the reactants by Sutin in 1962 and the important work of Jortner and coworkers in 1974-75, who combined a Levich and Dogonadze type approach to treat the high frequency vibrations of the reactants with the classical expression which 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 Eq.(5) to reactions which involved the rupture of a chemical bond by electron transfer and 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 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 vs 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 Eqs. (5) and (9), but 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 so a different theoretical approach was needed. For this purpose I adapted (1968) a "bond-energy-bond-order" model of H. Johnston, in order to treat the problem for a reaction of the type given by Eq.(4). The resulting simple expression for is similar to Eq.(5), when $|\Delta G^0/\lambda|$ is not large ($1/2$), but differs from it in not having any inverted region. It has the same property as that given by Eq.(9), and has resulted in a cross-relation analogous to Eq. (10). The cross-relation has been tested experimentally for the transfer of methyl groups by E. Lewis, and the vs relation has been used or tested for other transfers by Alberty and by Kreevoy and their coworkers, 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 (ref. 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.

Acknowledgments

My acknowledgments are to 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 this 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 University 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. Coming here, 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.

References

Some of my relevant articles, largely from the 1956-65 period, are listed in ref.1 below, and some general references which review the overall literature are listed in ref. 2. Several additional references for the Table and for the Figures are given in ref. 3. Classic texts on unimolecular reactions are given in ref. 4.

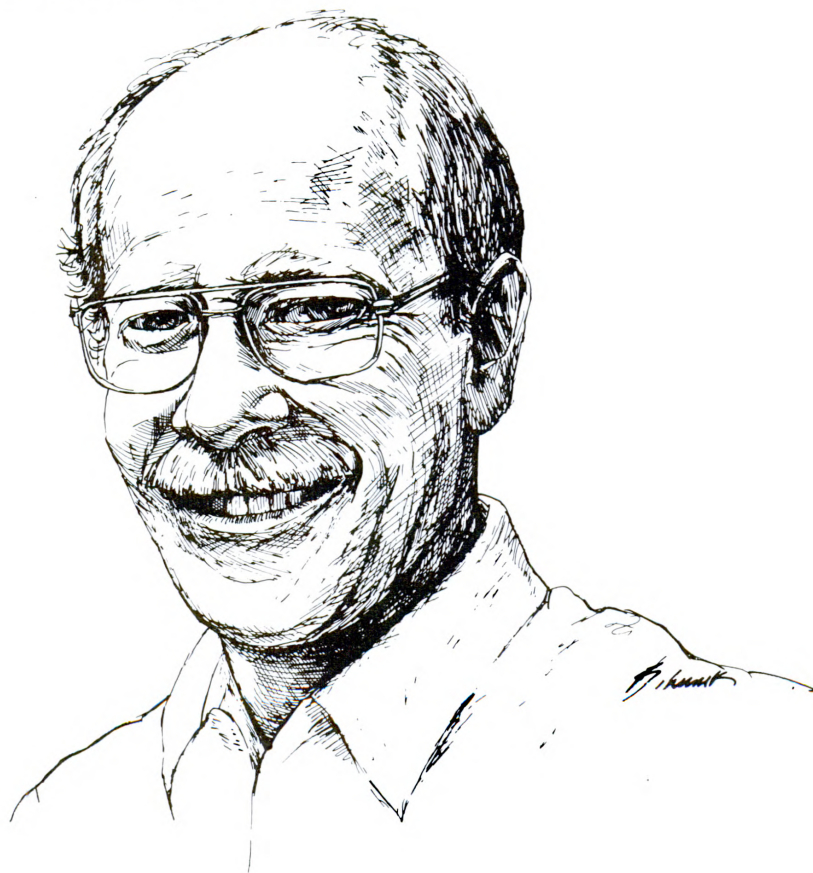
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Profiles in Science



Royce W. Murray

Professor Royce W. Murray is Kenan Professor of Chemistry at the University of North Carolina, Chapel Hill, where he has been a faculty member for 33 years. For many years, he has been a principal investigator for the Office of Naval Research.

Professor Murray's research interests include electroanalytical methods, the molecular design of electrode surfaces, electrochemically reactive polymers, mass electron transport in thin films, electrocatalysis, macromolecular electronics and polymer film microstructures, solid state voltammetry, and electrochemistry. In these areas, he has been responsible for inventing measurement tools and strategies that give access to previously inaccessible chemical phenomena.

Professor Murray has been colleague to over 70 Ph.D and post-graduate students, with whom he has published about 240 papers. Among his many honors and awards for contributions to science are: Sloan and Guggenheim Fellowships, the Carl Wagner Memorial Award (Electrochemical Society), the Charles N. Reilley Award (Society for Electroanalytical Chemistry), the Electrochemistry Group Medal of the Royal Society of Chemistry. He is a member of the National Academy of Sciences and a Fellow of the American Academy of Arts and Sciences.

Computer Simulation Methods for Electron Transfer and Other Quantum Rate Phenomena

Gregory A. Voth
University of Pennsylvania

Introduction

During the past decade, the uses of computer simulation and modeling techniques in scientific research have grown enormously. The remarkable power of the computer, when harnessed through intelligent and efficient simulation methodologies, has led in many instances to a modification of the scientific method. In particular, modern scientific research often involves a dynamic interplay between theory, experiment, and computer simulation. This "triad", when properly balanced, can offer a considerable advantage over the more traditional interplay between theory and experiment alone.

The exciting field of electron transfer (ET) has also begun to be influenced by computer simulation. Most of these simulations have focused on classical calculations of the famous Marcus free energy curves¹ for realistic models of several ET systems.² While these realistic classical calculations have confirmed the validity of the linear response assumptions employed by Marcus in his original theory,¹ a first principles computational treatment of electron transfer requires a method which can *directly and simultaneously* address both the influ-

ence of medium/vibronic effects and the quantum mechanical character of the electron being transferred between donor and acceptor. (A similar statement also holds true for the study of other quantum rate phenomena such as condensed phase proton and hydride transfer reactions, hydrogen diffusion in and on materials, etc.) For kinetic processes involving heavier particles (e.g., most chemical reactions), such a computational method has existed for many years in the form of the well known classical transition state theory (TST).³ Only recently, however, has the formulation of a quantum mechanical TST (QTST) been proposed⁴⁻⁶ which provides a consistent and computationally powerful generalization of the classical TST. This quantum theory, which is based on Feynman path integrals,⁷ will be briefly described below and representative applications to computer simulation discussed.

Classical Rate Theory

To begin, it is useful to first review the structure of classical TST which provides a basis for understanding the attributes of a more general quantum theory.⁴⁻⁶ The TST ap-

proximation to the classical rate constant k_{cl} is often expressed as

$$k_{cl}^{TST} = \frac{k_B T}{h Q_{R,cl}} \exp(-\beta F_{cl}^*), \quad (1)$$

where $Q_{R,cl}$ is the classical partition function of the total system in the reactant state, and the excess classical free energy at the dividing surface, F_{cl}^* , is given by

$$F_{cl}^* = -k_B T \ln [Q_{cl}^* / (m/2\pi\hbar^2 \beta)^{1/2}] \quad (2)$$

where m is the effective mass of the reaction coordinate motion and β equals $(k_B T)^{-1}$. In Eq. (2), Q_{cl}^* is the classical phase space density at the position of the dividing surface along the reaction coordinate q , given by

$$Q_{cl}^* = \frac{1}{(2\pi\hbar)^N} \int dp_q \int dp_x \int dq \int dx \delta(q^* - q) \exp(-\beta H), \quad (3)$$

In the above equations, q^* is the transition state value of the reaction coordinate, N is the number of degrees-of-freedom of the entire system, and H is the classical Hamiltonian. The coordinates x and their conjugate momenta p_x are for all degrees-of-freedom other than the reaction coordinate. The key factor in Eq. (1) is the dimensionless classical excess free energy factor $\exp(-\beta F_{cl}^*)$ which, in relation to the reactant state partition function, leads to the *activation factor* in TST. The latter factor dominates the temperature dependence of the rate constant. The pre-exponential factor in Eq. (1) is the mathematical result of the TST assumption³ (i.e., all trajectories which reach the transition state configuration from the reactants will continue onward to the products). Marcus was able to employ classical TST in his original formulation of the theory of adiabatic electron transfer by choosing the collective solvation variable as the reaction coordinate.¹ Not surprisingly, the theoretical basis for classical computer simulations of ET reactions² has been the classical TST perspective (i.e., these simulations focus on the classical solvent activation free energy for ET).

The most important feature of the path integral formulation of quantum TST is that it specifies both a quantum activation factor and a TST prefactor,⁴⁻⁶ both of which are the analogs to the classical TST quantities in Eqs. (1)-(3). As in classical TST, the activation factor is the most important feature of the quantum theory since it dominates the temperature dependence of the rate constant and can be determined *without any dynamical information* (i.e., by using statistical mechanics). The quantum activation factor also captures any tunneling and zero-point energy effects which can give rise to substantial deviations from the classical TST rate constant.

Feynman Path Integrals

The approach to a quantum mechanical TST described in the following section⁴⁻⁶ draws heavily on Feynman's path integral formulation of quantum statistical mechanics.⁷ The path integral formalism is, in fact, the essential basis for the conceptual and *computational* power of the quantum TST. The Feynman path integral for, e.g., the partition function of the system is derived by first expressing the trace of the Boltzmann operator in the coordinate representation, i.e., as

$$Q = \text{Tr} e^{-\beta H} = \int dq \langle q | e^{-\beta H} | q \rangle. \quad (4)$$

It should be noted here that for simplicity Eq. (4) has been written for a single degree-of-freedom, but an extension to multiple dimensions and/or particles is straightforward. The Boltzmann operator can now be written as a product of P components such that

$$e^{-\beta H} = (e^{-\epsilon H})^P, \quad (5)$$

where ϵ equals β / P . The partition function is then rewritten exactly as

$$Q = \int dq \langle q | e^{-\epsilon H} e^{-\epsilon H} \dots e^{-\epsilon H} | q \rangle. \quad (6)$$

It is now possible to insert P complete sets of coordinate space states, each given formally by

$$\int dq | q \rangle \langle q | = 1 \quad (7)$$

between the individual pieces of the Boltzmann operator. The partition function is then given by

$$Q = \int dq_1 \int dq_2 \dots \int dq_P \langle q_1 | e^{-\epsilon H} | q_2 \rangle \langle q_2 | e^{-\epsilon H} | q_3 \rangle \dots \langle q_P | e^{-\epsilon H} | q_1 \rangle, \quad (8)$$

where a numbering scheme from 1 to P has been adopted to keep track of the different integrations over complete sets of coordinate states. For large values of P , the expressions for the matrix elements $\langle q_i | e^{-\epsilon H} | q_{i+1} \rangle$ are known⁷ since the Boltzmann operator $\exp(-\epsilon H) = \exp(-H/k_B T_p)$, with $T_p \equiv T \times P$, is equivalent to one for a very high temperature system. Upon substitution of these expressions for each matrix element in Eq. (8), the partition function is given by the classical-like expression

$$Q = \lim_{P \rightarrow \infty} (m/2\pi\hbar^2 \epsilon)^{P/2} \int dq_1 \dots \int dq_P \exp[-\beta V_{eff}(q_1, \dots, q_P)] \quad (9)$$

where the effective potential is given by

$$V_{\text{eff}}(q_1, \dots, q_P) = \sum_{i=1}^P \left[\frac{mP}{2\hbar^2} \beta^2 (q_i - q_{i+1})^2 + \frac{1}{P} V(q_i) \right] \quad (10)$$

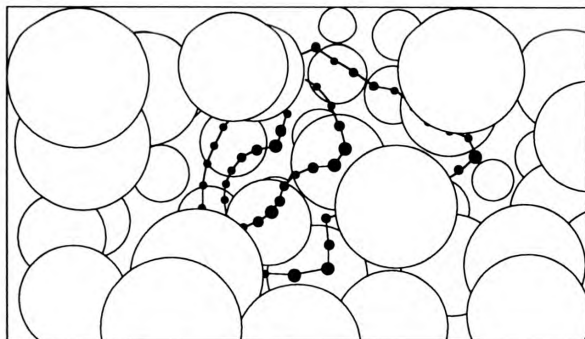
Remarkably, the seemingly daunting quantum expression in Eq. (8) is now reduced to an effective classical partition function similar to a “polymer” consisting of P quasiparticles located at the coordinates $\{q_i\}$.⁸ The quasiparticles interact with each other through nearest-neighbor harmonic potentials, and each quasiparticle feels the potential energy function via the term $V(q_i)/P$. In addition, the quasiparticle coordinates are cyclic so that q_i equals q_{i+P} . Figure 1 schematically depicts the discretized path integral representation of an electron solvated in a heavy classical fluid such as argon.

The path integral “isomorphism” between a single quantum mechanical particle and a polymer of effective classical quasiparticles is the centerpiece of modern computational path integral techniques.^{8,9} If one chooses a large enough value of P in Eq. (8) to insure convergence, the evaluation of quantum equilibrium quantities is simply mapped onto an isomorphic classical calculation. Such calculations can be readily performed on a computer using Monte Carlo or Molecular Dynamics techniques. Many studies have now appeared in the literature in which path integral Monte Carlo has been employed to simulate a quantum particle (or particles) in very complex environments involving hundreds of atoms and/or molecules.⁹

The level of abstraction in the path integral theory increases when one takes the formally exact $P \rightarrow \infty$ limit in Eq. (8). In that case, the path integral for the partition function becomes a true functional integral,⁷ i.e.,

Figure 1.

A schematic diagram of the isomorphic path integral “polymer” for an electron in a condensed phase environment of heavy classical particles. Equilibrium properties are calculated by performing an appropriate Boltzmann-weighted sum over all possible configurations of the path integral polymer and bath particles.



$$Q = \int \dots \int Dq(\tau) \exp\{-S[q(\tau)]/\hbar\}, \quad (11)$$

where $q(\tau)$ is the path of the quantum particle in imaginary time and $S[q(\tau), x(\tau)]$ is the imaginary time action functional⁷

$$S[q(\tau)] = \int_0^{\hbar\beta} d\tau \left\{ \frac{m}{2} \dot{q}(\tau)^2 + V[q(\tau)] \right\} \quad (12)$$

The above exact path integral representation is necessary when one develops new formalism or analytic theory, but the discrete “polymer” picture embodied in Eq. (9) and Fig. 1 is all this is required for one to understand and visualize the path integral perspective.⁸

Quantum Rate Theory

In general terms, the calculation of the quantum activated rate constant can be accomplished with a general TST-like theory if such a theory provides expressions for *both* the quantum activation free energy *and* the prefactor as in the classical theory [cf. Eqs. (1)-(3)]. The latter factor must be the QTST equivalent to the classical pre-exponential factor in Eq. (1). Such a theory has been under development during the past few years.⁴⁻⁶

The progress towards a path integral quantum TST is partly due to the importance of the path “centroid” variable $\tilde{q}_0$ in path integration.⁴⁻⁶ This variable is defined along the q direction, for example, by the expression

$$\tilde{q} = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} d\tau q(\tau) \quad (13)$$

or, in the discretized path integral notation,⁸ by

$$\tilde{q}_0 = \frac{1}{P} \sum_{i=1}^P q_i \quad (14)$$

The centroid variable is seen from Eq. (13) to be the imaginary time average of the quantum path $q(\tau)$ or, in the discretized path integral expression in Eq. (14), to be the center-of-mass of the discretized “polymer” of classical quasiparticles having coordinates $\{q_i\}$.

The path integral quantum TST rate constant is given by⁴⁻⁶

$$k_{\text{QTST}} = \frac{k_B T}{h Q_R} \exp(-\beta F_c^*) \quad (15)$$

where the excess path integral centroid free energy at the dividing surface is defined as

$$F_c^* = -k_B T \ln [Q_c^*/(m/2\pi\hbar^2\beta)^{1/2}] \quad (16)$$

The reduced centroid density Q_c^* at the dividing surface along the reaction coordinate q is the central quantity in determining the value of the rate constant. The latter quantity is given by⁴⁻⁶

$$Q_c^* = \int \dots \int Dq(\tau) D\mathbf{x}(\tau) \delta(q^* - \tilde{q}_0) \exp \left\{ -S[q(\tau), \mathbf{x}(\tau)] / \hbar \right\} \quad (17)$$

The above formula may be readily applied to a variety of problems because, in the spirit of classical transition state theory,³ *no explicit quantum dynamical information is required* to estimate the rate constant. Additionally, the activation free energy in Eq. (15) can be calculated with discretized path integral Monte Carlo or Molecular Dynamics techniques⁹ for highly complex systems.

Representative Applications

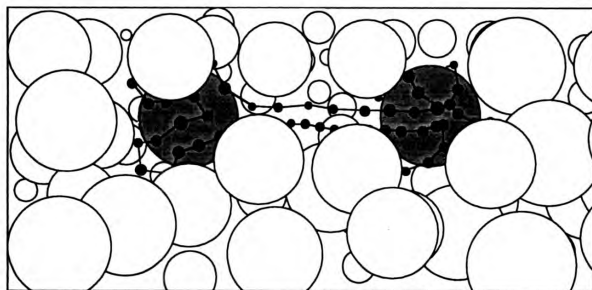
In this section, two applications of the path integral QTST are described. The interested reader is referred to papers containing other applications path integral QTST, including homogeneous electron transfer theory^{10,11} and simulation,^{10,12} proton transfer theory¹³ and simulation,¹³⁻¹⁵ hydrogen diffusion metal surfaces,¹⁶ molecular diffusion on metals,¹⁷ and the theory of condensed phase effects in quantum activated dynamics.^{4,5,11,18}

Proton Transfer Reactions in Polar Solvents

Proton transfer reactions in condensed phases are of considerable importance in chemistry. Since proton transfer involves a redistribution of solute electronic charge density, a substantial contribution to the activation free energy may

Figure 2.

A graphical depiction of the discretized Feynman path integral representation of a quantum particle being transferred between two heavy classical-like particles. The reacting system is immersed in a simple classical fluid. The centroid of the quantum electron paths is constrained to be at the transition state in order to calculate the relevant quantum activation free energy.



come from solvent reorganization effects just as in electron transfer¹ (i.e., solvent fluctuations are necessary to create a degeneracy between the two proton binding states so that the proton can transfer). In some ways, however, proton transfer is even more complicated than ET, since intramolecular vibrations may also play a central role in modulating the proton transfer process.^{13,19} At the very least, proton transfer reactions in polar solvents provide fascinating systems through which to study the interplay between solvent activation dynamics, intramolecular mode coupling, and quantum tunneling effects. Not surprisingly, they have attracted a considerable degree of experimental and theoretical attention in recent years.

In this section, the application of path integral QTST to proton transfer reactions described in Refs. 13 and 14 is reviewed. The benefit of this approach is that it includes both the solvent and intramolecular contributions to the proton transfer activation free energy while treating any number of particles in the system quantum mechanically (including, of course, the proton). The method also bridges the adiabatic and nonadiabatic limits of the activation factor and is applicable to situations where the proton itself becomes thermally activated. In this implementation of path integral QTST, the actual *proton transfer coordinate* is treated as the reaction coordinate (e.g., a proton asymmetric stretch mode),¹³ rather than the collective solvent polarization coordinate as in a Marcus-like approach.¹⁹ This formulation of the problem allows the quantum tunneling of the proton to be explicitly treated on the same footing as the solvent activation free energetics. It also facilitates detailed examination of specific intramolecular interactions between the proton transfer coordinate and other molecular modes in the charge transfer complex.¹³

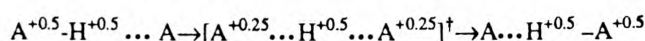
According to the path integral QTST equation, the central quantity in any quantum activated rate process in the quantum activation free energy. This quantity can be cast into a form particularly well suited for computer simulation,¹⁴ i.e.,

$$\Delta F_c^* = -k_B T \ln [P_c(q_r \rightarrow q^*)] \quad (18)$$

where $P_c(q_r \rightarrow q^*)$ is the quantum probability to move the reaction coordinate centroid variable from the reactant configuration to the transition state. This probability is readily calculated¹⁴ by path integral Monte Carlo techniques⁹ combined with umbrella sampling.²⁰ In the latter computational technique, a number of "windows" are set up which confine the path centroid variable of the reaction coordinate to different regions.¹⁴ These windows connect in a piecewise fashion the possible centroid positions in going from the reactant state to the transition state. A series of Monte Carlo calculations are then performed, one for each window, and the centroid probability distribution in each window is determined. These individual window distributions are then smoothly joined to calculate the overall probability function $P_c(q_r \rightarrow q^*)$ in Eq. (18). Alternatively, the mean force on the path integral centroid reaction coordinate could be calculated in the simulation and

then integrated from q_r to q^* to give the activation free energy. In Fig. 2, a schematic picture depicts the path integral QTST representation of a quantum particle (e.g., an electron or proton) at the transition state between the donor and acceptor species in a classical fluid. The centroid of the path integral “polymer” for the quantum particle [cf. Eq. (9)] is constrained to be halfway between the donor and acceptor (i.e., at its transition state). The function $P_c(q_r \rightarrow q^*)$ in Eq. (18) is the probability for the path integral of the quantum particle to achieve the transition state configuration relative to the reactant state.

By using path integral QTST approach, one can directly study the solvent contribution to a proton or an electron transfer reaction without making any classical assumptions. As an example, consider the model proton transfer reaction



where “A” denotes some heavy atom. In Ref. 14, the path integral QTST was used to calculate the total quantum activation free energy for the model three-body proton transfer complex solvated in the SPC/E model²¹ for water. Changes in the total activation free energy, and hence the reaction probability, due to the proton tunneling were also a focus of the study. For more details of the model or the path integral Monte Carlo calculations, the reader is referred to Ref. 14.

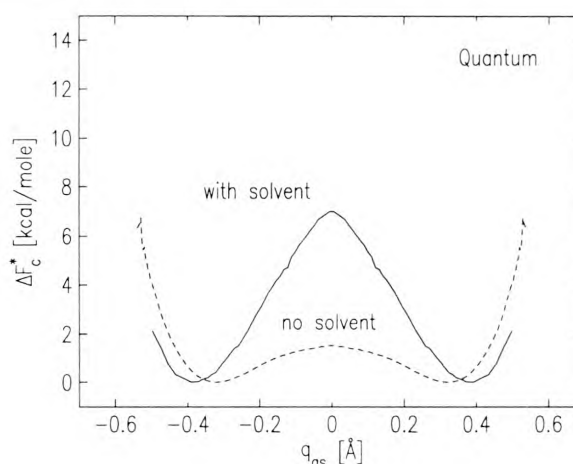
For the system studied in Ref. 14, the total quantum activation free energy curves as a function of the proton asymmetric stretch coordinate are depicted in Fig. 3. Shown are the activation curves for the complex in isolation and for the complex in the water solvent. The effect of the solvent in the total activation process is obvious, contributing ~5 kcal/mole to the overall activation free energy.¹⁴ In fact, the solvent activation is apparently the rate determining step for this proton transfer system just as in many ET reactions. The activation free energy curves were also calculated in the classical limit of the proton transfer reaction. By comparison with the fully quantum result, the effect of the proton tunneling on the total activation free energy was found to be large (~5 kcal/mole), increasing the total reaction probability over the classical case by roughly a factor of 2400. A similar path integral calculation has been performed¹⁰ for the Fe^{2+}/Fe^{3+} ET reaction in water using a simplified, but accurate, tight-binding model for the electron. Interestingly, the water librational modes were found to exhibit a large degree of tunneling, leading to an unexpected quantum enhancement of the ET rate by a factor of 40 over the classical Marcus theory prediction.

Heterogeneous Electron Transfer at Electrodes

While path integral QTST allows one to directly simulate many outer-sphere homogeneous electron transfer reactions,

Figure 3.

Quantum activation free energy curves for the model proton transfer described in the text and Ref. 14. The free energy is calculated by virtue of Eq. (18). The solid line is for the solute immersed in the water solvent, while the dashed line is for the solute in isolation.



the simulation of heterogeneous ET at electrodes represents an even greater challenge due to the many-electron nature of the problem, as well as the increased complexity of the molecular interactions in such systems. As a first step, electron transfer between an ion in solution and a metal electrode can be described^{22,23} using a version of a Hamiltonian referred to in the literature as the Anderson-Newns Hamiltonian.²⁴⁻²⁷ This Hamiltonian can be written as

$$H = H_{\text{sol}} + H_{\text{el}} \quad (19)$$

where H_{sol} is the Hamiltonian for the electrolyte solution (including solution-metal interactions) and H_{el} is the “electron transfer” part of the Hamiltonian, given by

$$H_{\text{el}} = (\epsilon_a + \Delta E) n_a + \sum_k \left(\epsilon_k n_k + V_{ak} c_a^\dagger c_k + V_{ka} c_k^\dagger c_a \right) \quad (20)$$

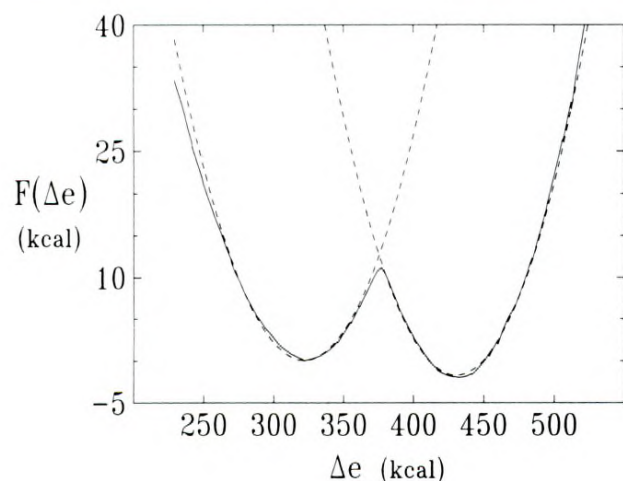
Here, ϵ_a is the vacuum energy level of the ion electron orbital which is involved in the electron transfer (orbital “a”) and an infinitely dilute solution is assumed for simplicity, though not necessary. This acceptor orbital has an occupancy number n_a equal to either 0 or 1, depending on whether or not it is empty, and ΔE is the instantaneous energy shift of the ion electron state $|a\rangle$ due to the interaction with the fluctuating solvent (i.e., the Marcus solvation variable¹ or “coordinate”). The sum over k in Eq. (20) represents the electronic states in the semi-infinite metal electrode. The latter term clearly includes contributions arising from both the occupancy of the metal

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Figure 4.

Adiabatic free energy curves for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ heterogeneous electron transfer reaction between an ion and a Pt electrode. The parabolic fits to the Marcus diabatic curves are shown by the dashed lines.



electron states as well as a piece which is a “transfer” interaction leading to the charge transfer between the metal states and the ion orbital (i.e., $c_i^\dagger$ and c_i are electron creation and annihilation operators, respectively, and V_{ij} are the matrix elements which couple the relevant states).

The quantum mechanical Hamiltonian of Eq. (19) is not yet in a useful form for the purpose of simulating heterogeneous electron transfer. Following the work of Grimley,²⁴ and Muscat and Newns,²⁵ as well as invoking the physically reasonable assumption that the solvent and electronic degrees of freedom are separable due to different timescales, one must first concentrate on the electronic Hamiltonian H_a in Eq. (20). After a series of mathematical manipulations involving the resolvent operator for this Hamiltonian, the ground state electronic energy $E_0(\Delta E)$ can be analytically obtained as a function of four quantities: (1) the Fermi level of the metal electrode ϵ_F , (2) the vacuum energy level ϵ_a of the ion, (3) the Marcus solvation variable ΔE , and (4) the vacuum broadening of the ion orbital $|a\rangle$ due to the interaction with the metal electronic states. The latter parameter Δ is given by the expression

$$\Delta(\epsilon) = \pi \sum_k |V_{ak}|^2 \delta(\epsilon - \epsilon_k) \quad (21)$$

and is evaluated at $\epsilon = \epsilon_F$. Because one can relate the Marcus solvation variable ΔE to the nuclear configurations of the solvent molecules, one can use the overall adiabatic ground state Hamiltonian function $H_0 = H_a + E_0(\Delta E)$ to describe the forces on the solvent molecules.^{22,23}

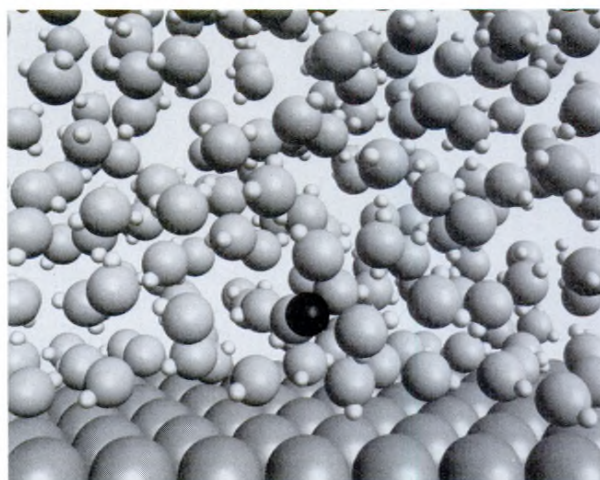
At this point, simulations of heterogeneous electron transfer at metal electrodes can now be designed.²⁸ One needs to first construct a realistic microscopic potential which describes the interactions between the solvent molecules, the solvent and the electrode, the donor/acceptor and the solvent, and the donor/acceptor and the electrode.²⁹ Once completed, umbrella sampling techniques can then be applied to calculate the adiabatic Marcus free energy curve as a function of ΔE and thus find the classical solvent activation free energy barrier to the charge transfer reaction involving the ionic orbital $|a\rangle$. The first such curves to ever be calculated²⁸ are depicted in Fig. 4 for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction near a Pt(111) electrode. Shown by the dashed lines are the parabolic Marcus-like curves²⁹ which best fit the diabatic product and reactant states. In Fig. 5, a “snapshot” is shown from the classical simulations²⁸ which produced Fig. 4. The next step in this research will be to employ the path integral QTST along with a quantized version of the water solvent to search for any quantum solvent effects such as those found in the homogeneous $\text{Fe}^{2+}/\text{Fe}^{3+}$ ET simulations.¹⁰

Outlook for the Future

The path integral QTST formulation⁴⁻⁶ reviewed in the present article represents one way to introduce the considerable advantages of computer simulation into the study of electron transfer reactions and other quantum rate phenomena. Such simulations have helped to confirm many of the theoretic

Figure 5.

A snapshot from the simulation of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ heterogeneous electron transfer reaction between an ion and a Pt electrode. The single iron ion is the dark sphere, surrounded by water molecules, and is at a distance of 5 Å from the Pt electrode surface.



cal ideas developed by Marcus 40 years ago¹ and may indeed help to uncover some unexpected effects in the field of electron transfer. One real challenge for the future will be to simulate, on a very large scale, increasingly complex systems such as those found in heterogeneous ET reactions.^{28,29} If these efforts are to be truly influential, however, new "first principles" simulation methods will need to be developed which, for example, unify path integral QTST with novel methods³⁰ to calculate the electronic structure of materials. Given the current rapid development of computer simulation techniques for homogeneous electron transfer and other quantum rate processes, as well as the advances in the fundamental theory underlying those techniques, the outlook seems bright for the role of computer simulation in field of heterogeneous electron transfer.

Biography

Gregory Voth received his Ph.D. in 1987 from the California Institute of Technology where he was a graduate student of R. A. Marcus. At Caltech, he was awarded the Clauser Doctoral Prize for the most original doctoral thesis and the H. N. McCoy Award for excellence in research. After postdoctoral study as an IBM Postdoctoral Fellow at the University of California, Berkeley, Dr. Voth became a faculty member in the Department of Chemistry at the University of Pennsylvania in 1989. He is a recipient of an Alfred P. Sloan Research Fellowship, a National Science Foundation Presidential Young Investigator Award, a David and Lucile Packard Fellowship in Science and Engineering, a Camille and Henry Dreyfus Foundation New Faculty Award, and a Proctor and Gamble Award in Physical Chemistry from the American Chemical Society.

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Some Perspectives on Solution-Phase Electron-Transfer Processes

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Introduction

The kinetics of electron-transfer (ET) processes is a subject graced by a remarkable diversity as well as importance in chemistry and biology. Of the manifold types of chemical ET reactions, those occurring in solution and at electrode-solution interfaces have been the subject of a notably concerted and fruitful research effort. This activity was in large part spawned, and subsequently spurred, by the development of the theoretical treatments by Rudy Marcus and others, now broadly known as "Marcus theory."¹⁻⁶ The happy circumstances that enabled the formulation of such quantitative theoretical relationships for solution-phase ET kinetics having true predictive and interpretative value have acted as a considerable impetus to the development of an increasingly diverse and impressive range of experimental activities. These now encompass thermal and photoinduced charge transfers for inorganic, organic, and biological systems in homogeneous solution, ET at metal-solution interfaces, and ET and photo-ET at semiconductor-solution interfaces. Indeed, the ability of the Marcus theoretical framework to interrelate, interpret, and predict ET rates and other dynamical phenomena across such diverse classes of reactions constitutes a major achievement in contemporary physical chemistry, and was undoubtedly responsible in part for the award of the 1992 Nobel Prize in Chemistry to Rudy Marcus.

Along with numerous other experimentalists, our research into electron transfer has been influenced centrally, persistently, and encouragingly not only by Marcus theory, but also by Rudy Marcus himself. In this article we outline some pertinent issues and experimental inquiries into solution-phase ET phenomena, illustrated in part by findings from our laboratories. Some emphasis is placed on solvent effects, for which the interaction between experiment and theory has been particularly lively and beneficial. For the benefit of the more general reader, we preface this discussion with a short summary of some relevant conceptual and theoretical material. The article also in this issue by Ratner contains further detailed information along these lines.

Some Conceptual Background

The central challenge, met so ably by Marcus theory, is to rationalize, interpret, and predict the seemingly dazzling array of rates observed for solution-phase ET reactions, corresponding to reaction half lives ranging from picoseconds to many months or years! A generalized expression for bimolecular or electrochemical rate constants based on activated-complex theory is¹

$$k = Z \exp (-\Delta G^*/RT) \quad (1)$$

where Z is the prefactor and ΔG^* is the overall free energy of activation. The original Marcus formulations focussed attention on the latter component, understandably so since one expects that the very wide range of observed rate constants can often be attributed primarily to differences in the activation energetics. The framework of Marcus theory provides an extremely useful way in which the various factors which influence ΔG^* can be separated, identified, and understood.

Particularly useful is the distinction between “intrinsic” and “extrinsic” (or thermodynamic) components, denoting contributions to ΔG^* arising from factors present in the absence, and additional presence, of the free-energy driving force, ΔG^0 . With the presumption of parabolic free-energy surfaces, the following well-known relation is obtained:⁵

$$\Delta G^* = (\lambda + \Delta G^0)^2 / 4\lambda \quad (2)$$

In eq. 2, λ is the so-called “reorganization energy”, equal to four times the “intrinsic barrier”, ΔG_{int}^* , the component of ΔG^* which remains in the absence of a driving force (see Figure 1). Kinetic-based tests of Eq. 2 have attracted much attention, formerly concerning the predicted quadratic $\log k - \Delta G^0$ dependence in the “normal” driving-force region (where $-\Delta G^0 < \lambda$)⁷, and latterly the *diminishing* rates anticipated with *increasing* driving force in the “inverted” region (where $-\Delta G^0 > \lambda$) (see below)⁸. While Eq. 2 has limitations under some conditions, the reasonable concordance often observed with experiment, especially in the “normal” free-energy region, is a notable feature of ET phenomena.

Another central aspect of Marcus theory concerns the nature of the intrinsic barrier, ΔG_{int}^* . The Marcus treatment of the outer-shell (solvent) contribution, ΔG_{os}^* , to the intrinsic barrier, based on a nonequilibrium dielectric-continuum model, has proven remarkably resilient; representative experimental tests based on the energetics of optical ET transitions are discussed below.

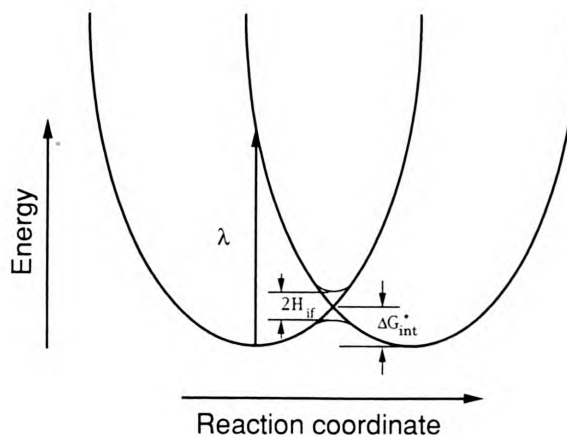
Among the more significant consequences of the theoretical treatments emphasized originally by Marcus, are the interrelationships predicted between rate constants for different outer-sphere reactions featuring common redox couples.^{4,5} Probably the best known is a connection between the rate constants for homogeneous-phase cross reactions and for the pair of constituent self-exchange processes. Also significant, however, is the relation predicted between the rate constants for corresponding self-exchange (k_{ex}^e) and electrochemical exchange (k_{ex}^e) reactions:⁴

$$k_{\text{ex}}^e / A^e \leq (k_{\text{ex}}^h / A^h)^{1/2} \quad (3)$$

where A^e and A^h are the relevant prefactors (*vide infra*). In eq. 3, the extent of the predicted inequality depends on the extent of image stabilization of the electrochemical transition state. Another prediction that has proven useful in mapping reactiv-

Figure 1.

Schematic representation of energy relationships for activated electron transfer.



ity trends in related homogeneous-phase and electrochemical processes is⁴

$$(k_1^e / k_2^e)_E = (k_1^h / k_2^h)_R \quad (4)$$

referring to electrochemical rate constants for a pair of redox couples at a fixed electrode potential, E , in comparison with homogeneous-phase rate constants involving the same pair of couples reacting with a common reagent (oxidant or reductant), R .

It is instructive to consider further the appropriate form of the prefactor terms appearing, for example, in Eqs. 1 and 3. Presumably for simplicity as well as convenience, such terms for outer-sphere ET reactions were initially formulated on the basis of collision-theory expressions. More recently, it was recognized by Sutin,⁹ Marcus,¹⁰ and ourselves¹¹ that an alternative “encounter preequilibrium” treatment can provide a more useful description of the preexponential factors in both outer- and inner-sphere ET processes.

A general expression for the overall preexponential factor on this basis is¹¹

$$A = K_p K_{el} v_n \quad (5)$$

where K_p is an equilibrium constant (statistical factor) for forming the precursor state (i.e. with appropriate geometry for ET but prior to nuclear activation). The remaining pair of terms in Eq. 5 refers to the ET activation step itself: the nuclear frequency factor v_n (s^{-1}) describes the net dynamics of approaching the transition state (associated with nuclear reor-

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ganization), and the electronic transmission coefficient κ_{el} denotes the fractional probability with which electron tunneling (so to consummate the reaction) takes place once the transition state is formed. The magnitude of K_p for inner-sphere reactions is clearly governed by the bonding established between the redox centers. For outer-sphere processes, simple statistical expressions can be deduced, depending on the reaction geometry. Thus for homogeneous-phase processes between spherical reactants in the absence of electrostatic work terms:

$$K_p = 4\pi N r^2 \delta r \quad (6)$$

where N is Avogadro's number, r is the reactant separation in the transition state, and δr is a "reaction-zone thickness" denoting the range of internuclear separations over which electron transfer primarily takes place. A related expression applies to outer-sphere electrochemical reactions, only now $K_p = \delta r$ since the "coreactant" is a planar interface. The values of δr are anticipated typically to be around $1 \text{ \AA}$, enabling at least approximate estimates of the statistical factor K_p to be obtained.

Another useful outcome of this "encounter preequilibrium" treatment is that it enables the reactivities of related homogeneous-phase and electrochemical processes to be compared in an especially direct fashion.¹² Specifically, the rate constant for a homogeneous reaction involving a pair of redox couples, k_{12}^h , is usefully compared with the electrochemical rate constant involving one of the reactants, k_1^e , measured at an electrode potential equal to the formal potential for the coreactant redox couple. In view of Eq. 6, the homogeneous-phase and electrochemical reactivities can be evaluated on a common basis by multiplying the latter by $4\pi N r^2$. This yields an "equivalent second-order" rate constant,

$4\pi N r^2 k_1^e = k_{12}^e$, having the same units as k_{12}^h and equalling the electrochemical reactivity in the (hypothetical) circumstance where the electrode "coreactant" offers the same reaction geometry as the homogeneous coreactant. Comparison between the values of k_{12}^e and k_{12}^h can provide straightforward insight into the differing environmental factors that influence electrochemical and homogeneous-phase reactivities. This procedure is most useful if the latter rate constants are corrected for the inner-shell (vibrational) activation associated with the homogeneous-phase coreactant. For the resulting k_{cor}^h values, any differences in comparison to k_{12}^e values will reflect only differences in the outer-shell (solvent) reorganization and/or electronic overlap factors between the two reaction environments.

An extensive comparison recently undertaken for inorganic reactions shows that k_{12}^e typically exceeds k_{cor}^h , the former quantities commonly being as much as 10^2 - 10^4 fold larger than the latter.¹² Some illustrative rate data of this type are given in Table I. These substantial rate differences, illustrating the often markedly more facile nature of electrochemical outer-sphere processes, most likely reflect the greater efficiency of electron tunneling (i.e. larger κ_{el}) and possibly smaller outer-shell reorganization energy prevalent at metal-solution interfaces.

The physical factors that control the preexponential factor, and especially the nuclear reaction dynamics as reflected in ν_n (Eq. 5), have been the subject of considerable recent interest, particularly with regard to the role of solvation dynamics.¹³ In spite of the apparent form of Eq. 5, the nuclear dynamics will only influence the ET rate significantly when the donor-acceptor electronic coupling is sufficiently strong so that $\kappa_{el} \rightarrow 1$ (so-called "adiabatic pathway"). For weaker coupling (such that $\kappa_{el} \ll 1$) the reaction dynamics will be determined instead by electron tunneling. (In other words, $\kappa_{el} \nu_n (= \nu_{el})$ will be proportional to $(H_{if})^2$, where H_{if} is the

Table I. Comparison Of "second-order Equivalent" Electroreduction Rates For Selected Reactions At Mercury Surface With Corresponding Homogeneous-phase Rates

Oxidant	Reductant	Solvent	k_1^a cm s^{-1}	k_{12}^b $\text{M}^{-1} \text{s}^{-1}$	k_{12}^c $\text{M}^{-1} \text{s}^{-1}$
$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	H_2O	4×10^{-5}	1.3×10^3	0.45
$\text{Ru}(\text{NH}_3)_6^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	H_2O	2.5	8.5×10^3	3.5×10^5
$\text{Fe}(\text{OH}_2)_6^{3+}$	$\text{Ru}(\text{NH}_3)_6^{2+}$	H_2O	-5	-2×10^8	2.5×10^7
O_2	$\text{Ru}(\text{NH}_3)_6^{2+}$	H_2O	0.06	2×10^6	1.1×10^2
Cp_2Co^+	Cp_2Co	DMF	2.0	9×10^7	7×10^7
Cp_2Co^+	Cp_2Co	TMU	0.35	1.5×10^7	3.5×10^7

See ref. 12 for details.

a. Work-corrected electrochemical rate constant for reduction of oxidant measured at formal potential of reductant redox couple.

b. "Equivalent second-order" rate constant for electroreduction, derived from k_1^e (see text and ref. 12).

c. Second-order rate constant for homogeneous reaction.

electronic coupling matrix element.) Nonetheless, there are many experimental ET systems (including outer-sphere systems), where reaction adiabaticity is achieved (or approached). Consequently, the dynamics of activated nuclear barrier crossing, as denoted by v_n , should often hold sway over the preexponential factor.

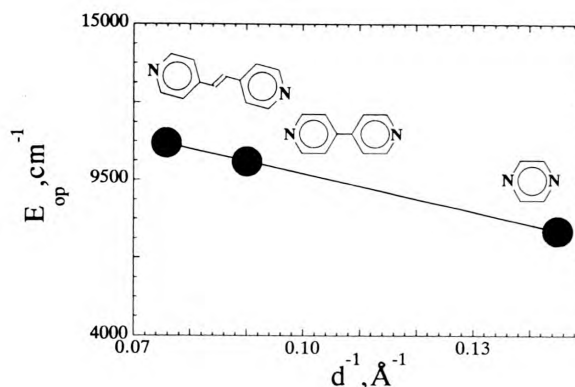
Generally speaking, the overall nuclear frequency factor v_n will be determined by the dynamics of both the reactant vibrational (inner-shell) and solvation (outer-shell) components of the activation barrier. In the transition-state theory (TST) limit, v_n is usually predicted to be governed chiefly by the fastest dynamics (usually reactant vibrations). The role of solvation dynamics, therefore, was originally thought to be unimportant. Recently, however, it has become apparent that significant or even substantial deviations from TST may occur as a consequence of so-called "solvent friction", whereby the dynamics of collective solvent motion (restricted rotations, etc.) required to surmount the ET transition state fall below the dynamics for the rotation of *individual* solvent dipoles (solvent inertial TST limit). Unlike the TST case, the frictional solvent motion is predicted to exert an important or even dominant influence upon v_n even in the face of considerably more rapid inner-shell dynamics.¹⁴⁻¹⁶ Interestingly, the frictional dynamics can be sensitive to the nature of the solvating medium, so that distinctly different solvent-dependent ET kinetics are anticipated depending on whether the activation energetics, or additionally the solvent dynamics, influences the reaction rate.¹³ This issue is considered further below.

Solvent Barriers

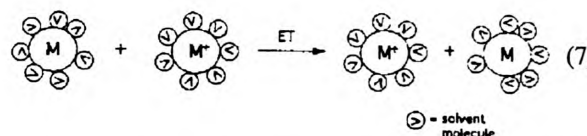
One of the earliest features of the theoretical treatments now collectively known as "Marcus theory" was a unique description

Figure 2.

Plot of E_{op} vs $1/d$ for the mixed-valence dimers $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$, where L = pyrazine, 4,4'-bipyridine, trans-1,2-bis(4-pyridyl)ethylene (data from ref. 17).



of condensed-phase ET activation barriers as nonequilibrium solvent polarization barriers.¹⁻⁵ A schematic representation of the barrier effect is shown below. A more quantitative



representation followed from the recognition by Marcus that a transferring charge (electron) would essentially instantaneously perturb the bound electrons associated with the surrounding medium (i.e. polar solvent), but would only slowly

Table II. Spectroscopic, Structural and Reorganizational Parameters for Electron Transfer from $Fe(CN)_6^{4-}$ to Colloidal

Mode	Relative Intensity	Δ^2	$ \Delta a $	λ_1	Assignment
2118 cm ⁻¹	20.0	0.95	0.048 Å	1000 cm ⁻¹	VC-N bridge
2072	6.61	0.33	0.014	340	VC-N radial
2058	5.44	0.27	0.026	280	VC-N terminal
720	0.27	.11	?	40	?
598	1.00	0.59	0.026*	180	VFe-C
540	0.33	0.24	0.039	60	VFe-C bridge
516	1.12	0.89	**	230	VTi-O
484	0.90	0.82	**	200	VTi-O
418	0.56	0.69	**	140	VTi-O
364	0.27	0.43	0.059	80	VTi-N

* Taken from (or taken as) the crystallographically determined value for $Fe(CN)_6^{4-}$.

**Value not determined, since the measured normal coordinate displacement (Δ) may entail more than one type of bond length displacement (i.e., local-mode approximation may not be appropriate).

(in comparison to the timescale for an electronic transition) perturb the solvent nuclei. The relatively slow nuclear response was expected to create an intrinsic barrier to ET that could be surmounted by random solvent polarization fluctuations. The barrier was theoretically characterized, therefore, by both high frequency (ϵ_{op}) and low frequency (ϵ_s) dielectric components (corresponding to fast (electronic) and slow (nuclear) polarization responses). Further consideration of the electrostatic consequences of finite molecular reactant size (radius, r) and finite reactant separation distance or image distance (d) led to the following barrier expressions:

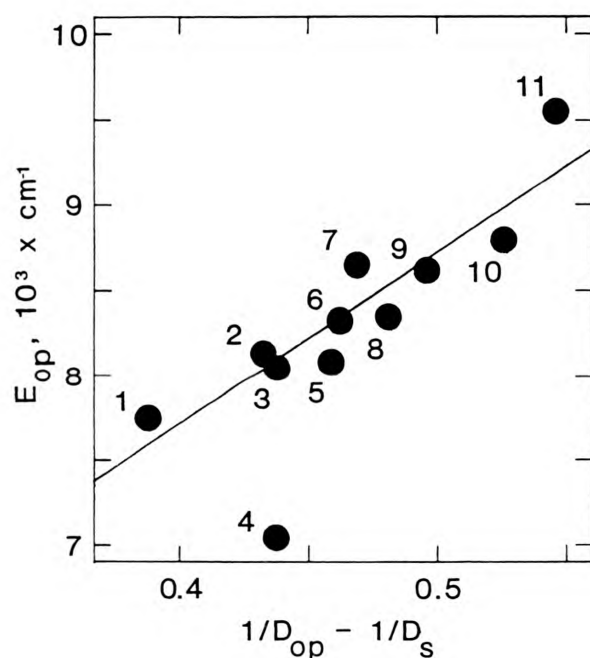
$$\Delta G^* = (e^2/4)\{(1/2r_1) + (1/2r_2) - 1/d\} (1/\epsilon_{op} - 1/\epsilon_s) \quad (8a)$$

$$\Delta G^* = (e^2/8)(1/r - 1/d)(1/\epsilon_{op} - 1/\epsilon_s) \quad (8b)$$

where Eq. 8a is applicable to homogeneous solution-phase reactions, Eq. 8b to interfacial electrochemical processes, and e in both equations is the unit electronic charge. As suggested by Eq. 8, the polarization analysis offers some remarkably

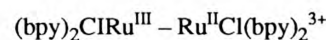
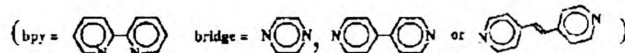
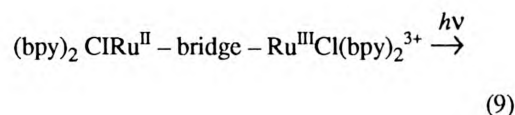
Figure 3.

Intervalence transfer band energies vs $1/\epsilon_{op} - 1/\epsilon_s$. Key to solvents: (1) nitrobenzene, (2) dimethyl sulfoxide, (3) 1-methyl-2-pyrrolidone, (4) hexamethylphosphoramide, (5) dimethylacetamide, (6) dimethylformamide, (7) formamide, (8) propylene carbonate, (9) acetone, (10) acetonitrile, and (11) deuterium oxide.



simple predictions as to how barriers and, therefore rates, for electron transfer should depend on macroscopic solvent properties, as well as molecular reactant size and geometry. Nevertheless, compelling experimental evidence in support of the solvent barrier theory was lacking for a number of years, despite several seemingly straightforward kinetics investigations (such as rate studies as a function of the solvent, etc). In retrospect, many of these studies were bound to fail in this context because of the existence of other important solvent-variable kinetic factors, most notably: 1) electrostatic work terms (including interfacial adsorption and solution-phase ion pairing), and 2) dynamics effects (see below). In addition, at least some of the systems chosen for evaluation at *electrochemical* interfaces (for example, reduction of protons to dihydrogen) were inappropriate because they involved extensive bond creation or annihilation.

Given these circumstances, a key experimental development was the design and synthesis (largely by the Meyer^{17,18} and Taube^{19,20} groups) of molecular donor-acceptor (D-A) systems featuring well-resolved charge-transfer absorption bands.^{21,22} When these systems are symmetrical (i.e. when the donor and acceptor sites are chemically identical as in Eq. 9), the absorption energy (E_{op})

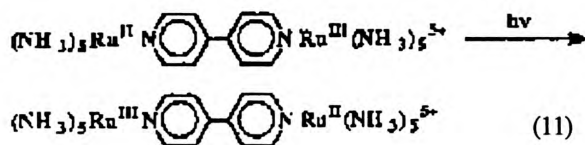


for the lowest charge-transfer transition can be identified directly with the (vertical) Marcus reorganization energy, λ .^{23,24} As already noted (Fig. 1), the reorganizational parameter, in turn, can easily be related to the expected thermal ET activation energy, ΔG^* . For parabolic energy surfaces (i.e. those derived from displacement of harmonic oscillators) the energy relationship is simply:

$$\Delta G^* = \lambda/4 (= E_{op}/4) \quad (10)$$

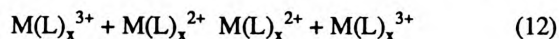
Shortly after the appearance of the first valence-localized D-A studies,^{18,21} systematic variations in bridge length were examined,¹⁷ leading to a verification of the predicted dependence (Eq. 8a) of the solvent reorganization energy on D-A separation distance d (Fig. 2).

A central aspect of the optical ET strategy as exemplified by the system illustrated in Fig. 3 (Eq. 11) is the evaluation of the reorganization energy (or



optical ET barrier) as a function of the solvent dielectric properties. The dependence found in this example,^{25,26} and in several others, clearly is consistent with the qualitative predictions of the polarization theory (Eq. 8). We – along with the Brookhaven group²⁷ – have noted, however, that quantitative agreement is lacking: the extent of variation of λ with solvent is (in this instance) markedly less than anticipated from theory. A clue to the origin of this disparate behavior is provided by the ET distance-dependent study in Fig. 2. The nominal charge-transfer distance in reaction 11 (i.e. the ruthenium-to-ruthenium distance) is 11.3 Å. The detailed chemistry, however, is such that the pertinent $d\pi$ metal orbitals mix (selectively) with bridging ligand orbitals of the same symmetry (both π and π^*) and become significantly polarized along the charge-transfer axis. The effective ET distance, as recently determined by electronic Stark-effect spectroscopy,²⁸ is closer to 6 Å. A shorter charge-transfer distance should lead to correspondingly less polarization of solvent and smaller reorganization energies (again, note Fig. 2). With the experimentally determined distance modification, we find that agreement with the dielectric-continuum theory now becomes essentially quantitative.²⁵

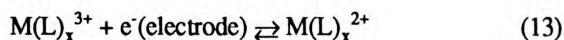
Related work on the solvent barrier/ET reactivity problem – in this case by the Brookhaven group²⁹ – has revealed the spectacular consequences of simple variations in molecular size. This group showed, for example, that systematically increasing the average molecular radii of pairs of simple transition-metal complexes (from 7 Å to 14 Å) could increase bimolecular (homogeneous) electron-exchange rates (Eq. 12) by over five orders of magnitude!²⁹ The observed



reactivity variations are almost undoubtedly solvational in origin, as the redox pairs were carefully chosen so as to minimize reactant vibrational barriers (see below) as well as nonadiabaticity (κ_{el}) effects. Interpretation of the experiments in terms of nonequilibrium solvent-polarization phenomena provides a quantitative explanation for the reactivity pattern once the secondary influence of reactant size on separation distance (d ; Eq. 2) is also taken into account. From a primitive physical perspective, the size dependence arises, then, from two sources: 1) a diminution of the effective charge density on the surfaces of the reacting molecular spheres (and therefore a decrease in surrounding solvent polarization) with increasing

sphere size, and 2) a diminution of partially compensating image-charge interactions as the center-to-center distance (d) for each reacting pair is likewise increased.

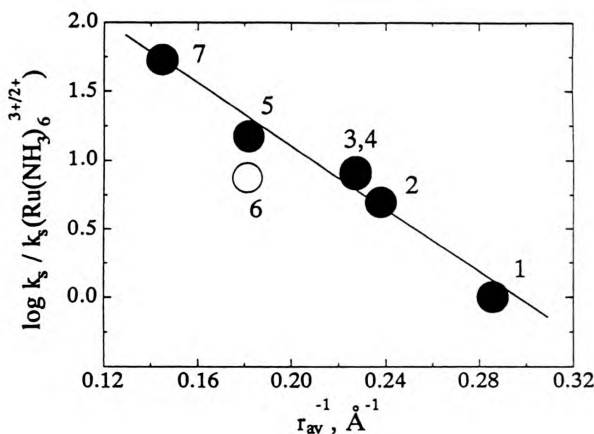
Surprisingly, only recently have the corresponding effects of reactant size on electrochemical reactivity been explored. As Figure 4 illustrates, rates for



interfacial ET (Eq. 13) have been observed to increase exponentially with decreasing effective reactant radius.³⁰ This observation is broadly consistent, of course, with a Marcus-type solvent barrier effect. Two additional points, however, are worth noting. First, the magnitude of the kinetic size effect (spanning roughly two orders of magnitude in ET rate, and corresponding to ca. 3 kcal mol⁻¹ in barrier height) is considerably less than found in the study of homogeneous bimolecular reactivity noted above. The most important difference chemically between the two studies is the involvement of only a single molecular reactant in each of the electrochemical processes, versus two reactants in the solution-phase processes. At a crude intuitive level one would expect, therefore, roughly half the extent of solvent repolarization in the former as the latter. Indeed, this notion – expressed more rigorously by Marcus²⁻⁵ – underlies the so-called homogeneous/hetero-

Figure 4.

Log of k_s for the indicated ET reaction (eq. 13; normalized to k_s for Ru(NH₃)₆3+/2+) versus the inverse radius of the reactant. The electrode material is low-defect-density HOPG; the electrolyte is 1 M aq. KCl. Line drawn is a best-fit line for all points except point 6 (open circle). Key to data points: (1) Ru(NH₃)₆3+/2+, (2) Ru(NH₃)₅(pyridine)3+/2+, (3) (NH₃)₅Ru(pyrazine)Ru(NH₃)₅5+/4+ (4) (NH₃)₅Ru(pyrazine)Ru(NH₃)₅6+/5+, (5) t-(pyridine)(NH₃)₄Ru(pyrazine)Ru(NH₃)₄(pyrazine)5+/4+, (6) t-(pyridine) (NH₃)₄Ru(pyrazine)Ru(NH₃)₄(pyrazine)6+/5+, and (7) Fe(phenanthroline)33+/2+.



geneous cross relationship (see Eq. 3) that permits solution-phase reactivities to be predicted from electrochemical kinetics data and vice versa. The second point is that two of the reactants in the electrochemical study are actually small diameter reactants whose effective sizes have been increased by covalently linking them to an additional reactant and then delocalizing the associated charges over the resulting "super molecule". We suggest that this could prove to be a more generally effective strategy for accelerating outer-sphere electron-transfer reactivity. In any case, it provides a simple illustration of the experimental exploitation of basic barrier concepts to manipulate reactivity.

As perhaps suggested by the preceding discussion, one of the active areas of current research is the synthetic manipulation of specific chemical systems to provide detailed control of solvent-based barrier effects. Several reports from Curtis and co-workers have illustrated how control can be exerted via a clever combination of mixed solvation and selective reactant/solvent hydrogen bond formation.^{31,32} Related studies at Northwestern have illustrated how local solvation can be manipulated to: a) trigger kinetically observable intramolecular ET events,³³ b) create barriers and induce valence localization (or partial localization) in otherwise delocalized, multi-site systems,³⁴ and c) significantly modulate superexchange-based electronic coupling effects.³⁵

Another important focus of contemporary research is solvent "molecularity". The nonequilibrium solvent polarization theory of Marcus achieves its simplicity and broad applicability, in part, by representing the solvent as a structureless, polarizable medium, i.e. "molecularity" is intentionally neglected. Nevertheless, molecules – including solvent molecules – are obviously of intrinsic interest to chemists! Recent attempts to gain a more molecular-level understanding of solvent reorganization effects have proceeded along at least four different lines. One involves the introduction of a mean spherical approximation (MSA) for individual solvent molecules, within the context of a broader electrostatic representation of medium repolarization effects. An interesting MSA-based model due to Wolynes treated the nonequilibrium solvation problem in terms of a frequency-dependent Gurney cosphere engendered by the solvent molecular size.³⁶ This approach, along with other MSA treatments, usually yields reorganization energies that are somewhat (say 15-25%) smaller than obtained from the conventional continuum estimates. A numerical comparison with solvent-dependent E_{op} values for ferrocene species indicates a rough concordance in several aprotic solvents, although not in hydrogen-bound media.³⁷ A more recent MSA treatment by Blum and Fawcett for equilibrium solvation (i.e. the zero-frequency part of the solvent reorganization energy) emphasizes anticipated differences between the solvation of cations and anions.³⁸ This model has also been applied to an analysis of the solvent-dependent electrode kinetics of $Cp_2Co^{+/0}$ versus $Cp_2Co^{0/-}$ ($Cp =$

cyclopentadienyl).³⁹ Interestingly, the MSA model can account for the observed more sluggish kinetics of the latter couple, from the predicted higher solvent activation barrier, although other factors (inner-shell barriers, specific double-layer effects, ion-pairing, solvation dynamics, etc.) perhaps also play a role. The evaluation of E_{op} data for differently charged mixed-valence systems in this context would be worthwhile.

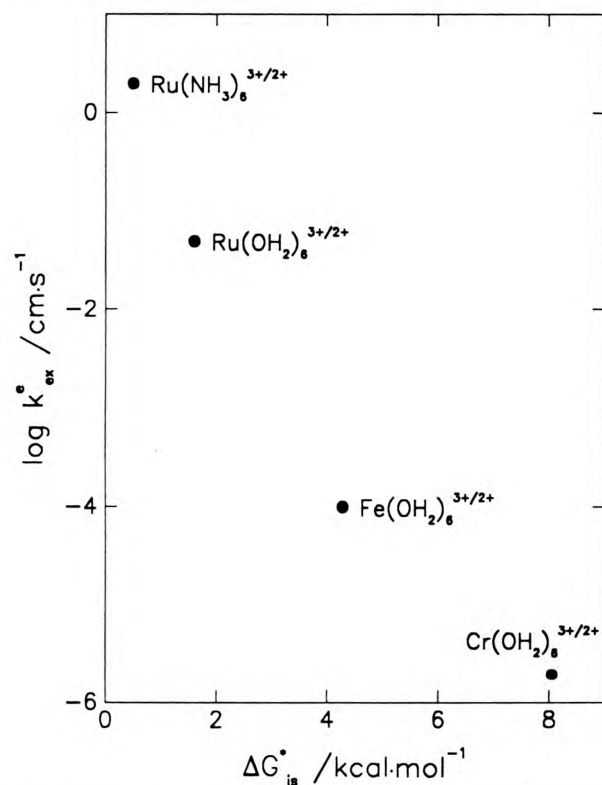
An alternative, perhaps complementary, semi-empirical approach to estimating ΔG^* is the so-called "nonlocal" electronic treatment due to Kornyshev and Ulstrup,⁴⁰ which considers the effects of spatial correlation on the wavevector-dependent solvent dielectric properties. One worthwhile facet of this model is that it can provide a viable rationalization of some deviations from the continuum predictions observed for metallocenes in hydrogen-bound media.^{37,41}

A second, fundamentally different, approach to molecular solvent reorganization makes use of molecular-dynamics (MD) simulations and carefully chosen potentials for solvent interactions. Some encouraging results based on this strategy have emerged from Chandler and coworkers⁴² (see also the article in this issue by G. Voth). This group has successfully simulated the redox activation behavior of the well-known hexaquo iron(III/II) system in water as solvent, and has derived important new insights regarding the role of nuclear tunneling.⁴² Most notably, they found a remarkable concordance with the Marcus prediction of parabolic potential-energy surfaces for solvent reorganization, even though complex short-range interactions abound in this highly charged/hydrogen-bonded system. On the other hand, model MD simulations for both dipole creation/annihilation⁴³ and ET⁴⁴ in methanol show clear evidence for non-linear polarization effects, that is, significant deviations from parabolic free-energy surfaces. The latter simulations also yield higher activation barriers for anion-neutral than for cation-neutral reactant pairs (*vide supra*) attributable to short-range solvation, although the effect is small for reactant radii approaching those prevalent in ET phenomena.⁴⁴ Overall, while such MD simulations can be complex and time consuming, they are beginning to add a new molecular-level dimension to our understanding of the energetics of nonequilibrium solvation. The associated dynamical aspects are discussed briefly below.

A third approach is largely experimental and focuses on the controlled assembly of orientationally constrained, local solvent environments (for example, large "encapsulating" crown ethers, semi-rigid hemicarcerands, etc.). Such assemblies may be amenable to detailed *in situ* (multidimensional NMR) and/or *ex situ* (crystallographic) structural characterization as a function of encapsulated reactant or product oxidation state. Initial studies have shown that the overall solvent reorganizational energetics for such systems can readily be monitored by optical ET methods (cf. Eq. 12).⁴⁵ Finally,

Figure 5.

Plot of logarithm of work-corrected standard electrochemical rate constants k_{ex}° at mercury-aqueous interface versus calculated inner-shell activation barrier ΔG_{is}° . Data taken from J.T. Hupp and M.J. Weaver, *Inorg. Chem.*, 22, 2557 (1983); T. Gennett and M.J. Weaver, *Anal. Chem.*, 56, 1444 (1984).



a fourth approach – pioneered by Hendrickson and co-workers – involves solid-state electron transfer.⁴⁶ Single crystals of various molecular mixed-valency species are prepared with zero, one, or two solvent molecules of co-crystallization. Coupling of isolated solvent motions to ET can then be examined via a combination of X-ray and variable-temperature Mossbauer spectroscopy techniques.

The presence of such a myriad of molecular solvent reorganization treatments notwithstanding, it is worth reiterating that the Marcus dielectric-continuum approach remains a generally useful, and in most cases, a semiquantitatively (or even quantitatively) reliable means of estimating total ET solvent reorganization energies. That this should be the case even though the relevant physics contains a common element with the Born solvation model – well known to be much less reliable – lies partly in the usual dominance (at least in polar media) of the optical frequency component (ϵ_{op}^{-1}) with respect to the Born term (ϵ_s^{-1}) in Eq. 8. Indeed, quite marked deviations between the equilibrium solvation energies and the Born pre-

dictions can occur without influencing substantially the *non-equilibrium* solvation energy (λ or ΔG°). We discussed this point some time ago in an analysis that harnesses experimental solvation energies for redox couples (i.e. differential solvation energies) in place of the Born term in Eq. 8.⁴⁷

Other solvent related issues of current interest and importance include: 1) “solvent” reorganization in protein environments (where again, additional molecular-level theory development would be invaluable), 2) solvent reorganization at *nonmetal/solution* interfaces – for example, liquid/liquid interfaces, semiconductor/solution interfaces, and membrane/solution interfaces, and 3) solvent reorganization at mesoscopic and nanoscopic particle(or electrode)/solution interfaces. Some insightful theoretical work on liquid/liquid and semiconductor/liquid interfaces has appeared recently from Marcus⁴⁸ and from Smith and Koval.⁴⁹ Experiments capable of testing these theories would be most useful. Finally, in the mesoscopic chemistry field, a number of exciting experimental developments relating to interfacial ET and energy conversion have emerged in the last three years, in particular.⁵⁰⁻⁵² Fundamental studies of barrier phenomena here could provide a rational basis for further advances and could help to explain some of the more provocative existing results.

Vibrational Barriers

A second major component of most ET reaction barriers is vibrational reorganization. This component arises because of the oxidation-state dependence of the normal coordinates or internal bond lengths. Interconversion of oxidation states (electron transfer) therefore requires the displacement of coordinates (bond compression or bond stretching) and is accomplished, in the Marcus classical limit, by vibrational activation.^{3,5,53} The combination of net coordinate displacement and transient vibrational excitation leads to an energy barrier shaped much like the one in Figure 1. In this picture, the actual charge transfer occurs at the top of the barrier (the transition state) where the best compromise, in terms of bond lengths, has been achieved between the redox reactant and product. According to Marcus, the vibrational activation barrier (ΔG_{vib}°) or reorganization energy (λ_{vib}) for an electron exchange reaction (homogeneous or electrochemical) can be estimated simply from known bond length changes (Δa) and associated force constants (f):

$$\Delta G_{vib}^{\circ} = \frac{1}{8} \sum_j b(\Delta a_j)^2 f_j \quad (14)$$

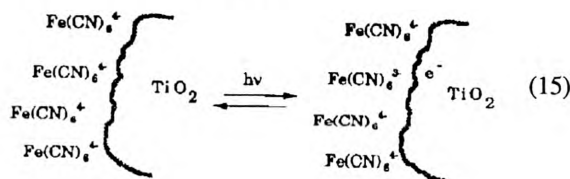
In Eq. 14, b is the number of equivalent bonds displaced, and the summation (j) is over all bonds displaced.

The importance of vibrational reorganizational effects can hardly be overstated. For example, Brunschwig et al.,⁵⁴ in a study of about a dozen transition-metal redox couples, found that bimolecular self-exchange rate variations over some 15

orders of magnitude could be explained almost entirely on the basis of classical vibrational activation effects. We showed in a related study that similar effects can also control reactivity for cross reactions and at electrochemical interfaces.⁵⁵ Figure 5, for example, shows a plot of standard double-layer corrected electrochemical rate constants for four transition-metal complexes of similar size versus independently estimated vibrational activation energies. As in the Brunshwig study, a reasonable correlation exists.

In both the examples above, vibrational barriers were derived from X-ray measurements (EXAFS or crystallography) of metal-ligand bond lengths in oxidized and reduced states, with the bond length differences then incorporated into Eq. 14. This strategy is useful when: a) normal coordinate displacements can be approximated by local coordinate (i.e. bond length) displacements, b) the number of coordinates or types of bonds displaced is small, c) both redox states are chemically stable and long lived, and d) the available crystalline or solution X-ray measurement environment is sufficiently similar to the redox reaction environment to yield kinetically meaningful structural data. In many cases, however, one or more of these conditions is not fulfilled, and alternative routes to structural data are required. Viable routes include: 1) Franck-Condon analysis of structured emission (fluorescence or phosphorescence) from photo excited electronic states,⁵⁶ 2) empirical correlations (e.g. Badger's rules, etc.) of redox-induced vibrational frequency shifts with normal or local coordinate displacements,⁵⁷ and 3) time-dependent analysis of resonance Raman scattering intensities.⁵⁸

Over the past few years the Northwestern group⁵⁹⁻⁶², and the Myers group at Rochester,⁶³ have made extensive use of the third strategy and have found it to be extremely powerful. To implement the strategy, it is necessary to identify electronic absorption bands corresponding to the thermal electron transfer reaction of interest. This is reasonably straightforward for homogeneous solution-phase reactions. We find, however,⁶¹ that the Raman method can also be applied to interfacial reactions such as reaction 15:



Visible region excitation of an intense ferrocyanide to titanium dioxide (particle or electrode) charge transfer band leads, in this case, to enhanced Raman scattering from nearly a dozen vibrational modes. Observation of enhancement implies vibronic coupling of these modes to the transition of interest, i.e. Eq. 15 or the reverse. Time-dependent theory then permits one to connect the observed scattering intensities quantitatively to normal coordinate displacements (Δ) – which, in turn, may be

transformed into bond length changes. Table II summarizes the results of such an experiment. A number of points are worth noting. First, the symmetry of the molecular system is clearly reduced by surface binding, resulting in activation of several vibrational modes which are completely undetectable in solution or single crystal environments (i.e. X-ray measurement environments). Second, the electrode (i.e. TiO₂) lattice itself is activated by interfacial ET. Third, the overall vibrational barrier can be partitioned into high- and low-frequency components. This then permits important tunneling corrections to the classical Marcus vibrational analysis to be applied in a mode-specific fashion. Finally it is worth noting that this particular system would be very difficult to examine by conventional structural methods because the redox form on the right hand side of Eq. 15 returns to the initial form in less than 400 ns.⁶⁴ The Raman method overcomes this problem by interacting with the short-lived state only in a resonance fashion; significant real lifetimes, therefore, are not required.

It is appropriate to conclude this section by outlining some of the current issues and problems in this area of redox chemistry. One of these concerns bridged systems where coupling of bridge-localized vibrations to intramolecular ET is of appreciable theoretical, as well as experimental, interest. Also currently being investigated – primarily by resonance Raman in the extended near infrared – is the question of how specific vibrational modes conspire to cause electronic localization versus delocalization in more strongly electronically coupled systems.⁶⁵ Conceptually related to the Raman studies, and especially the time-dependent scattering studies, are new theoretical studies involving wave packet propagation methods. These studies, being carried out primarily by Nitzan and Ratner⁶⁶ (see accompanying article), may offer significant insights into the real-time progress of ultrafast ET reactions. The increasing *experimental* availability of ultrafast techniques (i.e. laser-based techniques which can probe reactions in the 15 to 50 femtosecond time regime) should soon permit some very exciting issues in rapid-reaction chemistry to be examined. One of these concerns coherence effects, where extremely fast reverse ET might, in fact, provide a fundamental dephasing mechanism for rapidly created states. On a slightly longer timescale (i.e. 0.5 to 5 picoseconds) the availability of tunable transient infrared spectrometers may permit one to understand how ET product states dispose of excess vibrational energy and reconfigure themselves for further reaction. Indeed, preliminary studies along these lines (by Doorn, Dyer, Woodruff and Stoutland at Los Alamos⁶⁷) appear promising. Transient IR methods should also permit chemists to examine how photochemically generated, vibrationally hot systems behave in redox transformations. This problem could be of particular importance in molecule-based studies of solar energy conversion. Emerging work from Spears and co-workers⁶⁸ suggests that highly unusual reactivity patterns will be seen. Other solution-phase work of interest concerns reactions

where the formation of one or more bonds directly accompanies the transfer of a single electron. A specific example, from the Barbara group, involves charge transfer between a halogen atom and a dimeric (van der Waals) benzene cation.⁶⁹ Here two bonds appear to be formed. Interestingly, adequate understanding of the problem – in both a dynamic and a vibronic sense – would appear to lie beyond the realm of current theory.

Returning to surfaces or interfaces, the unexpected observation of electrode lattice activation during electron transfer (Eq. 15) merits further investigation. Is the phenomenon restricted to semiconductor materials, or might it also be significant at metal surfaces? For either class of material or surface, are there vibrational activation consequences for quantum confinement, i.e. for geometrically constraining the transferred electron or hole within an electrode or particle of smaller size than the characteristic e^- or h^+ radius? Both questions could be of importance in emerging redox-based applications of colloidal particle dispersions. We further suggest that both may be amenable to investigation by systematic electrochemical, spectral and theoretical studies of cluster systems. Finally, one may ask whether there are likely to be unusual local, or collective, vibrational effects in reactions involving self-assembled monolayers. Preliminary studies by Abruna and co-workers, based on an unusual X-ray standing wave method, indicate that there are.⁷⁰ In the X-ray study clear evidence is found for coupling of an “accordion” type bridge compression motion to ET between an electrode and a tethered transition-metal reactant. Also of interest is a very recent observation by Bedzyk and Mirkin of long range two-dimensional ordering in a redox-active monolayer (again via standing-wave techniques).⁷¹ These new experiments should open up the possibility of detecting and evaluating collective coordinate displacement effects in interfacial ET processes. Interestingly, collective – or at least correlated – coordinate displacements appear to play a very important role in the kinetics of ET in solid-state environments (i.e. three-dimensional crystalline environments), as demonstrated by Hendrickson and co-workers.⁴⁶

Driving Force Effects

Just as important (in a kinetic sense) as solvational and vibrational reorganization energies are the effects of thermodynamic driving forces (reaction free energies). As suggested by eqs. 1 and 2, the way in which driving forces affect ET rates is primarily through classical barrier height manipulation (although other effects, such as electronic tuning, are known). For small changes in driving force (ΔG°) a linear variation in $\Delta G^\ddagger$ is predicted by Marcus theory; for larger changes the expected variation is quadratic. In other words, an exponential, or nearly exponential, increase in ET rate with increasingly favorable driving force is predicted – much as in other transi-

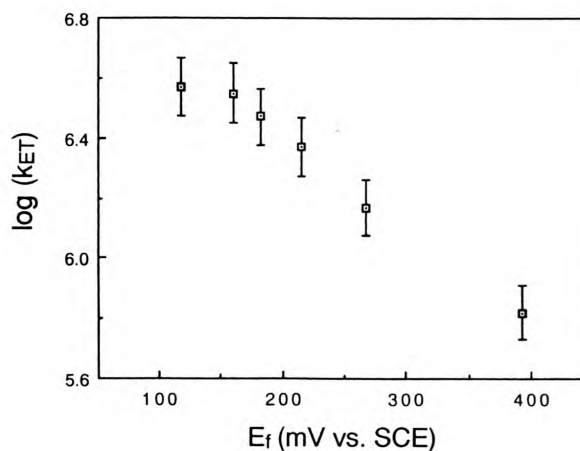
tion-state theories. A very large number of examples of this type of behavior have been described experimentally.

More unusual is the prediction, already noted, that for very large driving forces ($-\Delta G^\circ > \lambda$), electron-transfer rates should *decrease* with increasing exoergicity, i.e. “inverted” rate versus driving force behavior should be seen. This well-known prediction proved quite resistant to verification, leading many to conclude that the underlying theory was not fully correct. In 1979, however, inverted rate behavior – consistent with Marcus theory – was finally observed by Beitz and Miller for a series of bimolecular ET reactions in low-temperature glasses.⁷² Nevertheless, because of the exotic medium, many researchers were skeptical. Ultimately, in 1984 – nearly 30 years after the initial theoretical proposal – Miller, Calcaterra, and Closs provided an even more convincing demonstration of rate inversion.⁷³ These experiments involved intramolecular ET and were based on a clever application of pulsed radiolysis methods to solution-phase kinetics. In retrospect, the functional equivalent of inverted ET was, in fact, seen some time before in various studies of nonradiative decay with organic⁷⁴ (and later inorganic⁷⁵) chromophores as both Marcus⁷⁶ and Meyer⁷⁷ have noted. It is now generally appreciated that the so-called “energy-gap law”, often used to characterize these experiments, can be obtained from a low-temperature quantum version of Marcus’ classical inverted-region analysis.

Since 1984, more than two dozen additional examples have appeared, encompassing a variety of chemical contexts. For illustrative purposes we will focus on two of the more

Figure 6.

Plot of $\log k_{ET} (s^{-1})$ at colloidal TiO_2 versus reduction potentials (solution phase) for $Fe^{III}(CN)_5L^n$ species.



recent. The first is represented schematically by the photo-redox sequence shown below (where Ir_2 is $[\text{Ir}(\text{1,5-cyclooctadiene})(\mu\text{-pyrazolyl})_2]$ and py^+ is any of several alkyl pyridinium ions):⁷⁸



Note that ET is bimolecular and that it can occur in two directions. Furthermore, Gray and co-workers have shown that the driving force can be made to exceed λ in both.⁷⁸ Surprisingly, however, rate inversion occurs only in the reverse direction (i.e. diiridium cation reduction, eq. 16c). In the forward direction, rates increase to a diffusion-limited value with increasing $-\Delta G^\circ$, but are then unresponsive to further increases in driving force. Several explanations have been devised. But, as yet, none have been confirmed. The second example is shown in Figure 6 and comes from Northwestern.⁶⁴ The reaction involved is Eq. 15, where the driving force has been varied by replacing one of the six available CN^- ligands of the parent compound with any one of several pyridyl ligands. The absolute driving forces are unknown at present, but clearly they will scale as the formal potentials (E_f) of the molecular reactants in solution. In this case it also has been possible to calculate the slope of the rate vs. driving-force plot by using Raman-derived displacement and force-constant data (Table II) and low-temperature theory. The calculated slope (roughly a factor of ten decrease in rate for a 300 mV increase in driving force) is in good agreement with experiment. Perhaps surprisingly, the experiment represents the first in which rate inversion has been observed at an interface.

Among other important current issues and problems relating to driving-force phenomena are: 1) "gating" effects (see article by Ratner) which may decouple ET from very slow nuclear coordinates and make certain ET processes driving-force independent,⁷⁹⁻⁸² 2) exploitation of rate inversion to inhibit reverse ET – and enhance efficiency – in artificial, molecule-based solar energy conversion devices,⁸³ and 3) adaptation of Marcus-type analyses to atom and ion transfer reactions.^{84,85}

Reaction Dynamics

We have so far focussed attention primarily on the energetic aspects of ET chemistry, that is the factors and strategies utilized to understand and evaluate energy barriers. A complete description of ET kinetics, however, also necessarily involves evaluation of the reaction dynamics, that is, the rapidity by which the system is able to move along the reaction

coordinate so to yield products from reactants. As already noted, several factors may influence the reaction dynamics, and hence the preexponential factor for activated ET processes, not the least of which is the electron-tunneling probability for nonadiabatic processes. Much experimental information on the kinetic consequences of electronic coupling in nonadiabatic ET has been gained from intramolecular D-A systems where the donor and acceptor sites are separated by extended and/or saturated organic linkages. These include deliberately synthesized systems,^{73,86} as well as modified biological systems such as metalloproteins,⁸⁷ both of which also have been featured prominently in tests of driving-force effects (see above). In the context of electronic coupling effects, primary tactics involve discerning the kinetic response to alterations in the spatial and/or structural D-A separation. Besides homogeneous-phase intramolecular ET, substantial advances have been made along these lines for structurally well-defined films at electrochemical surfaces.^{88,89}

We confine our comments here primarily to the reaction dynamics anticipated for adiabatic processes, where nuclear (especially solvational) rather than electronic factors should prevail. Up to the late 1970's, theoretical treatments of solvent effects, including Marcus theory, focussed on activation energetic aspects. Beginning around 1980, and continuing to the present, substantial research effort has been invested in understanding the *dynamical* roles of reactant solvation.⁹¹⁻⁹⁹ Progress has been driven, in particular, by the recognition of "solvent-friction" effects in chemical kinetics (which, as mentioned above, constitute an interesting deviation from the usual TST approach). While the precise physical meaning and interpretation of solvent-friction effects depend somewhat on the type of reaction being considered, the usual notion is that an impediment exists to net progress along the reaction coordinate, because of irreversible energy dissipation from the "reactive" (possibly solvent molecular rotation) modes to the surrounding solvent "bath". The reaction coordinate motion is then no longer smooth and unidirectional (as in TST) but is characterized instead by "fits and starts", commonly termed "overdamped motion", perhaps even involving several recrossings within the barrier-top region before the reaction is finally consummated.

While ET was historically not the first class of reactions for which the notion of solvent friction was considered in dynamical descriptions, the central role of solvation in the ET reaction coordinate attracted attention in this context by theoreticians by the early 1980's.⁹¹⁻⁹³ Since then, the literature has expanded enormously. Most of this work emphasizes the idea that "dielectric friction", associated physically with collective rotations (and related motions) of solvent dipoles that necessarily attend solution ET processes, should exert significant or even substantial influences upon the net barrier-crossing dynamics, and hence the ET reaction rate.

The emergence of this theoretical framework has inspired a large number of experimental studies aimed variously at probing the nature of, and the extent to which, collective solvent polarization can influence the dynamics of ET and related processes. Broadly speaking, the experimental inquiries fall into four categories. The first (type I) involves the evaluation of time-dependent fluorescence Stokes shifts (TDFS) for solute chromophores forming suitable charge-transfer excited states.^{100,101} In optimal cases, these ultrafast (≥ 50 ps) laser-induced measurements can probe directly the real-time dynamics of polar solvent relaxation around a newly formed solute dipole, and have yielded some fascinating information of relevance to ET kinetics. The second type concerns a related use of ultrafast pulse lasers to follow intramolecular ET processes emanating from phototexcited states.¹⁰¹ So far, however, almost all of the

ET reactions studied in this fashion have evolved only small free-energy barriers, $\Delta G^* \geq k_B T$ (k_B is Boltzmann's constant).^{101,102} (The additional role of *inertial* solvent motions, therefore, can probably not be overlooked.)

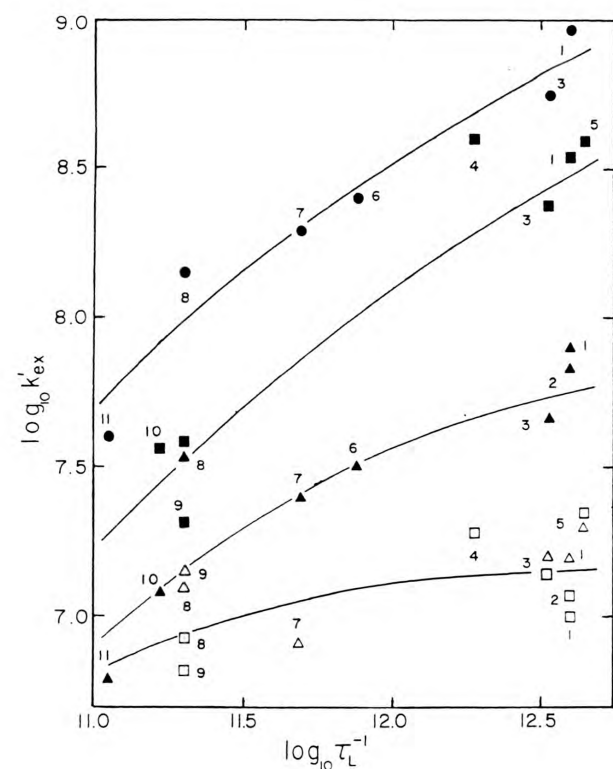
The remaining two experimental categories constitute attempts to extract information concerning dynamical solvent effects for *activated* ET processes (say, for $\Delta G^* \geq 5k_B T$). The most common approach (type III) involves the acquisition of solvent-dependent kinetic data for bimolecular outer-sphere electron-exchange reactions, especially symmetrical self-exchange, and for related reactions at electrode surfaces.¹³ The kinetics of the former are most commonly evaluated by means of magnetic resonance (nmr, epr) line-broadening methods. These reaction systems feature significant (commonly 5–10 $k_B T$) solvent reorganization barriers (i.e., they truly are activated processes). In addition, these systems provide opportunities to examine the dynamical consequences of systematically altering solute-solvent interactions, reactant electronic structure, vibrational barriers, etc. Despite the clear fundamental importance of activated ET processes, however, the experimental extraction of information on barrier-crossing dynamics is somewhat problematic. The core of the problem concerns the need to separate the dynamical (preexponential factor) and energetic (barrier height, ΔG^*) contributions to the measured solvent-dependent rate constants. In most cases, the extraction of the desired dynamical information from rate data requires one to use theoretical estimates for ΔG^* . An additional problem in these conventional analyses is that the geometry as well as stability of the precursor complexes for bimolecular (or electrochemical) outer-sphere processes is often unknown.

The conclusions regarding the role of solvent dynamics reached in this fashion are therefore often critically dependent on the validity of the theoretical models utilized to separate the dynamical and energetic factors. These type III tactics have consequently tended to be regarded as a "poor cousin" in comparison with the more direct (and sophisticated-looking) insight into real-time dynamics obtained from approaches I and II. Most of the uncertainties faced with such dynamical analyses for activated ET reactions could be circumvented by evaluating solvent-dependent rate data for intramolecular (preferably symmetric) ET reactions (labelled here as type IV). The evaluation of both the unimolecular ET rates and the barrier heights (the latter from optical ET energies) would provide the preferred route to the separation of dynamical and energetic factors. Unfortunately, however, relatively few type IV systems have been scrutinized in the context of solvent dynamics.¹⁰³

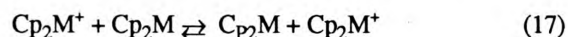
Despite the complications, sufficient information on barrier height and related factors can be obtained for certain *bimolecular* ET reactions to allow reliable, and even quantitative, deductions to be made regarding solvent-dependent barrier-crossing dynamics. The specifics have been reviewed in some detail recently.^{13,102} Broadly speaking, the extant experimental information lends support to the earlier theoretical

Figure 7.

Logarithmic plots of "barrier-corrected" rate constants ($M^{-1} s^{-1}$, extracted from rate and optical barrier data) versus inverse longitudinal relaxation time (s^{-1}) for five metallocene self-exchange reactions in 11 solvents, taken from ref. 29. See Table I of ref. 107 for key to solvents. Key to redox couples: filled circles, $Cp_2^+Co^{+/0}$ (Cp = pentamethylcyclopentadienyl); filled squares, $Cp_2^eCo^{+/0}$ [Cp^e = (carboxymethyl) cyclopentadienyl]; filled triangles, $Cp_2Co^{+/0}$; open triangles, $Cp_2Fe^{+/0}$; open squares, (hydroxymethyl) ferrocenium-/ferrocene.



predictions that overdamped solvent motion ("solvent friction") can often influence and even control the ET barrier-crossing dynamics, as prescribed most simply by the longitudinal solvent relaxation time, τ_L . While a large number of type III reactions (both homogeneous and electrochemical) have now been examined, one series of systems studied by the Purdue group a few years ago provides an interesting example of what may be discerned experimentally in optimal cases. The series consists of metallocenium-metalloocene self-exchanges:



where Cp is a cyclopentadienyl ligand (or derivative), and M is iron or cobalt.^{13,104-107} The reactions were selected for several reasons, including the dominance of outer-shell (solvent) reorganization in the activation energetics, and the opportunity to modulate the relevant electronic properties via both metal and ligand alterations.

Figure 7 shows a logarithmic plot of the self-exchange rate constant $k_{\text{ex}}^{\text{M}} (M^{-1}s^{-1})$ for five metallocene couples versus the inverse longitudinal relaxation time for a range of solvents (see caption and ref. 107 for details). The rate constants k_{ex}^{M} were corrected in an approximate way for solvent-induced variations in barrier height via comparisons to optical ET data for a related mixed-valence ferrocenium-ferrocene system; solvent-induced variations in k_{ex}^{M} for a pair of given self-exchange reactions, therefore, should reflect only differences in the reaction dynamics (i.e. $\kappa_{\text{el}}v_n$ in Eq. 5). The τ_L^{-1} parameter, extracted from dielectric loss spectra, provides an approximate assay of the overdamped solvent dynamics in so-called "Debye" media (those characterized by only a single relaxation time). While the solvents selected for Fig. 7 generally exhibit only approximate Debye behavior, the solvent friction dynamics (i.e. the τ_L^{-1} values) are seen to span a substantial numerical range (ca. $1 \times 10^{11} s^{-1}$ to $4 \times 10^{12} s^{-1}$).

Interestingly, the sensitivity of the ET rates to the solvation dynamics varies systematically with the nature of the metallocene: The slowest reactions (ferrocenium/ferrocene) are insensitive to the solvent dynamics, while the fastest (cobaltocenium/cobaltocene) vary almost proportionally with τ_L^{-1} – with intermediate behavior seen for others. This spectrum of reactivity can be rationalized on the basis of a transition from nonadiabatic to adiabatic behavior (see Background section above). The slowest reactions follow largely nonadiabatic ET pathways, so that the barrier-crossing probability is essentially proportional to $(H_{\text{if}})^2$ and independent of the solvation dynamics. For reactions featuring larger D-A electronic coupling (larger H_{if}), reaction adiabaticity is approached or reached, and the reaction dynamics become highly sensitive to the nuclear dynamics (in this case, solvent friction).

The observation ultimately of almost pure solvent dynamical control (cobaltocene reactions; see figure) also allows approximate estimates of H_{if} to be obtained for the entire series of metallocenes.¹⁰⁷ The resulting H_{if} estimates, varying from

about 0.075 to 1 kcal mol⁻¹, are in reasonable agreement with theoretical predictions by Newton and coworkers,^{111,112} and can be understood qualitatively in terms of the primarily metal- and ligand-centered nature of the redox orbitals in the ferrocene and cobaltocene couples, respectively. The observation of clearly solvent-controlled adiabatic ET rates also enables the detailed nature of the solvation dynamics for activated ET processes to be explored. One aspect of this latter endeavor concerns the extent to which faster solvent dynamical components can accelerate the reaction rate beyond that prescribed by more overdamped motions. Comparisons between such kinetic data and subpicosecond TDFS measurements in non-Debye media (such as methanol) have demonstrated the importance of such effects.^{108,109}

Prompted by theoretical work by Marcus and coworkers,^{14,15} an important issue also receiving attention is the extent to which solvent dynamics can limit ET reaction rates even in the face of faster (and inherently underdamped) reactant vibrational components of the activation barrier. Experimental data has so far provided at least qualitative support to the theoretical predictions.^{16,110}

Concluding Remarks

Although the foregoing is only an incomplete (and subjectively selective) survey of some experimental aspects of fundamental research in solution-phase ET processes, it is evident that much has been learned concerning the physical and chemical factors that control activation energetics and dynamics, especially for small molecule reactions. In particular, the interplay between theory and experiment, initiated almost forty years ago by Marcus, is now stronger and more diverse than ever. This situation reflects not only the present buoyancy and health of the subject, but bodes well for the rapid development of our understanding of ET processes in much more complex systems. The future promises to be an exciting one!

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Biographies

Joseph Hupp received a Ph.D. degree in chemistry in 1983 from Michigan State University where he studied with M. J. Weaver. After postdoctoral studies with T. J. Meyer at the University of North Carolina (1984-86) he joined the faculty at Northwestern University where he is currently a professor in the Department of Chemistry and a member of the Materials Research Center. His present interests include interfacial electrochemistry, photo-redox and mixed-valence chemistry, quantum confinement phenomena and mesoscopic chemistry,

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Michael Weaver received his Ph.D. in 1972 from Imperial College, London. Following postdoctoral research under Fred Anson at Caltech from 1972-75, he was a faculty member at Michigan State University, moving to Purdue University in 1982, where he has been Professor of Chemistry since 1985. His current research interests span electrochemistry, electron-transfer chemistry, electrochemical applications of surface vibrational spectroscopies and scanning probe microscopies, and electrochemical surface science.

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Electron Transfer Rate Theory, and Control of Electron Transfer Processes

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Introduction

The process of electron transfer is one of the most important and fundamental in all of chemistry¹⁻⁹. It occurs over a very broad range of time scales (from subpicoseconds to many seconds), and in a bewildering variety of natural and synthetic systems ranging from bacteria to biosensors, from photosynthesis to photomultipliers. The fundamental understanding of rates of the electron transfer process, and what microscopic parameters and behaviors control the rate of electron transfer, has been the focus of Rudy Marcus' work for nearly forty years, and is the basis for his having been awarded the 1992 Nobel Prize in Chemistry. Despite Rudy's enormous contributions,¹⁰⁻¹⁹ and important early work on electron transfer rates by Noel Hush,²⁰ and by Levich and his school,²¹⁻²⁴ and a number of other workers, many important issues of understanding electron transfer reactions still remain to be clarified.

One of the great strengths of chemistry is that, based on increased understanding, chemists can create and design new molecules, new structures, and new processes. In electron transfer, we are only beginning to see *designed* molecular systems whose electron transfer rates can be controlled. These designed electron transfer systems, one component of an area often referred to as molecular electronics,²⁵⁻³⁰ may lead to important advances in energy transduction, in information

storage and retrieval, in chemical sensing and in integrated molecular electronic devices.

In this article, I will discuss the understandings of electron transfer rates that have been developed in the past four decades, and the beginnings of molecular system design to control electron transfer rates and processes.

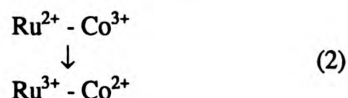
The Beginnings: Activated Complex Theory and Solvent Polarization

Modern experimental studies of electron transfer began after World War II, when the availability of separated isotopes made it possible to measure experimentally the rates of electron transfer exchange reactions between metal complexes.³¹ As such measurements became available, chemists searched for a simple rate theory to describe electron transfer. Generically, one can write an electron transfer reaction as in equation 1,



where A and D denote acceptor and donor, respectively. In fact, as Marcus realized, for separated species in solution the rate of electron transfer will depend upon the distance and orien-

tations of the donor and acceptor species. For this reason, it is often simpler to study intra-molecular electron transfer reactions, whose experimental investigation was pioneered by Taube and his students. A characteristic intra-molecular transfer system³² is that indicated by equation 2,



in which electrons move from the stable Ru^{2+} to form the labile Co^{2+} . In such intra-molecular transfer reactions, there is no work term to assemble the reactants into a configuration appropriate for electron transfer.

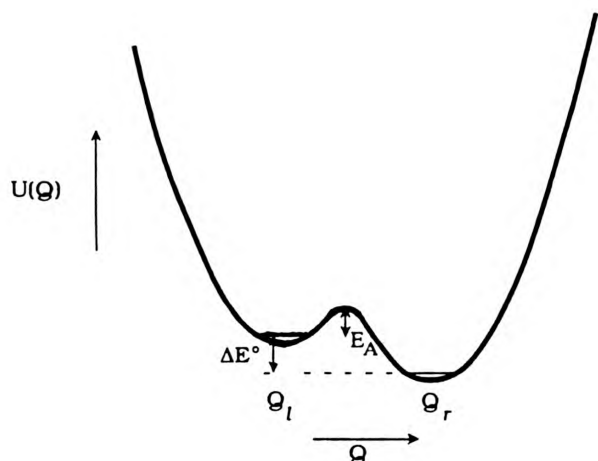
Marcus' original formulation of the electron transfer rate problem was based on activated complex theory. That is, he wrote the electron transfer rate as:

$$k_{\text{et}} = Z \exp [-E_a / RT] \quad (3)$$

a typical Arrhenius expression. Here the prefactor Z is the molecular collision rate, generally taken as $10^{13}/\text{sec}$, while E_a is the activation energy for electron transfer. Marcus' critical realization was that when electrons move, the changing multipole charge distribution is coupled to polarization fluctuations in the solvent. Indeed, the activated complex state is that in which the polarization for the reactant and the product are the same. This is shown schematically in figures 1 and 2, which show the reactant well, the product well, the activated complex, and the energy quantities $\Delta E^0 = \Delta$ (reaction exoergicity)

Figure 1.

Ground state potential energy surface, in one schematic dimension Q , for electron transfer. The activation barrier and overall exoergicity, ΔE^0 , are defined. The minima corresponding to reactant and product are denoted Q_l and Q_r respectively.



and λ (reorganization energy). Marcus realized, in 1956, that the polarization energy in both reactant and product states is a quadratic function of the polarization coordinate. Given this, it is a simple matter of high school algebra (equating reactant and product parabolic energy surfaces) to derive the important result for the activation energy,

$$E_a = (\Delta + \lambda)^2 / 4\lambda \quad (4)$$

Thus the three quantities activation energy, exoergicity and reorganization energy are clearly related, and knowledge of any two will yield the third. Two important early contributions led to increased understanding of the reorganization energies. Marcus used continuum dielectric theory to derive the result, for geometric models of precursor complexes for electron transfer, that

$$\lambda_0 = \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty} \right) (\Delta n)^2 F(R) \quad (5)$$

Here, ϵ_∞ and ϵ_0 are the optical and static dielectric constants of the solvent, Δn is the amount of charge transferred, and $F(R)$ is the geometric factor depending on the relative sizes of reactants and products. This form gives the solvent contribution (often referred to as the outer sphere contribution, hence λ_o) to the reorganization energy. Noel Hush pointed out³³ that optical excitation from the reactant well yields an excitation whose frequency is $\lambda/4\hbar$ for exchange reactions; this leads to a direct experimental estimate of the reorganization energy.

These early understandings form the basis for all of modern electron transfer theory. Nevertheless, there clearly were some difficulties and inadequacies of these early formulations; since the electron transfer reactions occur over such broad times and in such widely differing systems, it is not surprising that different control mechanisms are relevant.

Tunneling Behavior: Non-adiabatic Transfer, Electron Tunneling, and Nuclear Tunneling

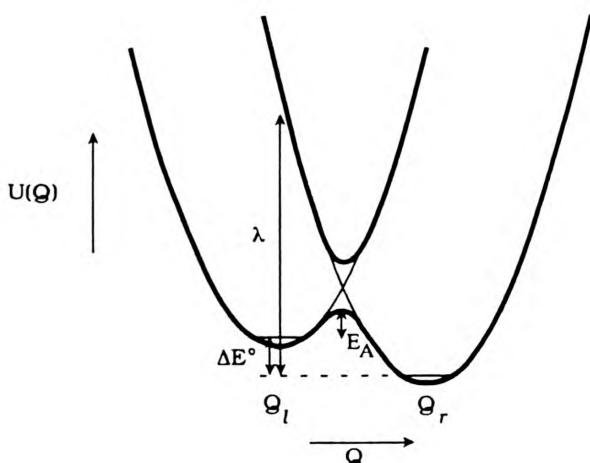
The conceptual underpinning of equation 3 is that once the solvent has rearranged itself to attain the top of the activation barrier in figure 1, the reaction will proceed. The number of times per second that the system attempts to cross the barrier is given by the prefactor Z , and the value $10^{13}/\text{sec}$, generally assumed for Z , is a characteristic nuclear vibrational frequency. In a number of electron transfer systems, however, the system does not simply cross from the reactant side to the product side once the barrier top is attained. It was realized in the 1960's that electron transfers resemble other sorts of curve crossing phenomena - that is, there is an excited state curve

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Figure 2.

Same as figure 1, but showing the excited state potential surface also. The diabatic surfaces are defined by the light lines, the adiabatic ones by the heavy lines. The exoergicity ΔE^0 is roughly equal to the free-energy change ΔG^0 ; they differ by small entropic terms. The distance between the ground and excited state surfaces at the crossing point is $2H_{rp}$.



that "goes with" the ground state curve figure 1. Figure 2 sketches the more general situation; note here that half the splitting between the two curves is given by H_{rp} , an electronic tunneling matrix element. Landau and Zener, in the 1930's, had analyzed this sort of curve crossing process.³⁴ Under reasonable conditions, the rate of crossing from reactant to product on the lower potential surface will depend on H_{rp} , for small enough H_{rp} . For very large H_{rp} (as is generally assumed in activated complex theory), the rates are independent of this electronic tunneling. On the other hand, for small H_{rp} (such as are found in long distance electron transfers), the rate becomes proportional to the square of this electronic mixing matrix element. This sort of result is characteristic of quantum mechanical perturbation theory, in which the rates are given by how strongly mixed the reactant and product are, times the density of product states, averaged over all of the reactant states. The generalization of the simple Marcus formula of equation 3 to the non-adiabatic regime is simply given by

$$k_{et} = \frac{(H_{rp})^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp(-E_a/RT) \quad (6)$$

This rate law takes into account the electron tunneling, through the presence of the mixing element H_{rp} . Generally,¹⁻⁹ one distinguishes electron transfer rates of eq. 6 as non-adiabatic transfer, as compared to adiabatic transfer, described by eq. 3.

At very low temperatures, it was observed that many electron transfer rates are not activated – for example, figure 3 shows the historical observation³⁵ by Chance and DeVault of electron transfer process in chromatium; note that, though activated at high temperatures, the rate is essentially temperature independent at low temperatures. To explain this, it is necessary to invoke quantum mechanical tunneling at low temperatures. Although classical chemical kinetics, as expressed in equation 3, is based on the idea that this system will overcome the activation barrier in equation 1, quantum mechanically the system can also tunnel through the barrier. While such tunneling contributions to chemical reactions have been known since Wigner's work in the 1930's, the understanding of the role of nuclear tunneling in chemical reactions of electron transfer type is much newer. Vibronic models of electron transfer, that give nuclear tunneling contributions at low temperatures and go over to the appropriate Marcus-like form at high temperatures, were given in the 1970's by a number of investigators, including Jortner,³⁶ Fischer and Van Duyne,³⁷⁻³⁸ Schmidt³⁹ and (of course!) Marcus.¹⁵ These polaron-type models^{40,41,42} are based on an assumed linear coupling between the electron population density and all the vibrations of the system, including solvent polarization (λ_o) and intra-molecular vibrations (λ_i , or inner-shell reorganization energy). The formulas for non-adiabatic electron transfer rates that take nuclear tunneling into account properly, based on this polaron model, do not yield results that are simple as equations 6 or 3, though they go over to 6 in the appropriate high temperature limit. They do, however, correctly characterize the low temperature, non-activated rate seen in many non-adiabatic electron transfers.¹⁻⁹

Solvent Dynamics, and Dynamic Gating

Like activated complex theory itself, all of the preceding discussion has been based on relating the rate of a chemical reaction (in this case electron transfer) to the energetics involved in that chemical reaction. Both the original Marcus formulation and the polaron vibronic theory use parameters such as reorganization energy, exoergicity, and electronic tunneling matrix elements that characterize the equilibrium properties of the reactant or product species. A bit of reflection, however, suggests that if the rates at which the nuclear motions, especially solvent rotations, explore their potential surfaces are slow enough then the rates of such relaxation processes might dominate the overall electron transfer rate. In the Soviet Union, Burshtein and his students, especially Zusman,⁴³ pointed out the role that solvent dynamics might play in reducing the rates of electron transfer: naively, one can simply imagine that, in the case of adiabatic electron transfer, when the system reaches the top of the barrier in figure 1, the solvent may not relax to the appropriate geometry to trap the

product on a rapid enough time scale. Under these conditions, the entire reaction dynamics can be dominated not by electron tunneling or nuclear attempt frequencies, but simply by how rapidly the solvent can relax into the geometry appropriate to the product state.^{16,17} An approximate equation for this limit is given by⁴⁴

$$k_{et} = \frac{k_{na}}{1 + 4\pi (H_{rp})^2 \tau / \hbar \lambda} \quad (7)$$

where k_{na} is the nonadiabatic rate of eq.(6), and τ is a characteristic relaxation time. Thus when the relaxation time is very rapid, and the equilibrium state indeed always prevails, one retains the standard non-adiabatic rate expression as given, say, by vibronic theory; alternatively, when the solvent relaxation rate is slow compared to the non-adiabatic reaction rate, the rate constant is given simply by the rate of solvent relaxation.⁴⁵

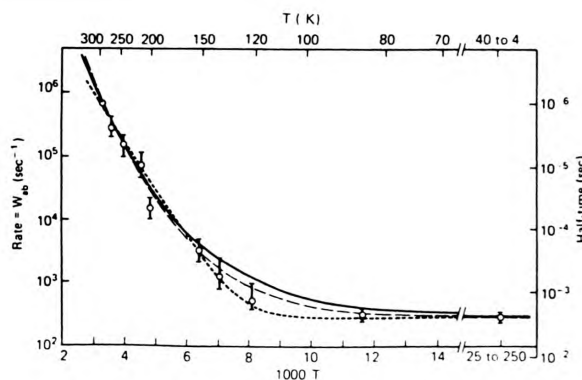
Experimentally, different fluids have different relaxation rates. Lovely picosecond and subpicosecond experiments by Fleming,⁴⁶ Barbara,⁴⁷ Simon,⁴⁸ Weaver⁴⁹ and others have demonstrated quite clearly the substantial regime in which solvent dynamics controls the rate of electron transfer.

The Many Dimensions of Electron Transfer–Solvent Gating

Figures 1 and 2 are highly schematic, in that the reaction coordinate is indicated as being unidimensional – in Marcus' original work, it was a solvent polarization coordinate. The vibronic models, and the experimental realization that there were inner and outer sphere contributions to the reorganization energy, focused specific attention on the fact that many vibrational modes of the molecules, as well as polarization modes of the solvent, contributed to the reorganization energies and might contribute nuclear tunneling terms. Agmon and Hopfield⁵⁰ suggested that differential friction, corresponding to diffusion rates along different nuclear distortion directions, might give highly complex chemical kinetics, such as is seen in, for example, ligand rebinding to myoglobin. In the simplest model for processes of this kind, one can envision two nuclear displacement coordinates coupled to the electron transfer reaction. For instance, figure 4 shows a schematic potential surface with the abscissa a fast, intra-molecular vibrational coordinate and the ordinate a slow, solvent conformational coordinate. If the rates of relaxation, or of diffusion, along these two coordinates are substantially different then the system point may not simply cross over the saddle point, or mini-max, on the potential surface – rather, it can cross the ridge line between reactant and product many times along the fast coordinate while slowly diffusing along the slow. Such behavior, whose theory has been extensively explored by a number of groups,^{51,52,53} would among other things result in non-exponential rates of reaction. There are a number of other

Figure 3.

Temperature dependence of the electron transfer in *C. vinosum* cytochrome oxidase, along with theoretical fits. The dashed line is the experimental data from the original work of DeVault and Chance. Taken from reference 1, page 72.



situations in which reaction rates are also non-exponential, and some experimental evidence has indeed been found (again, often in biological systems) for such non-exponentiality.

There is a second situation in which multi-dimensional behavior can yield surprises in the overall electron transfer rate. It was pointed out by groups at Northwestern⁵⁴ and at Brookhaven⁵⁵ that subsidiary minima on the potential surface may permit the system to avoid what appears to be the saddle point, and, instead, to proceed from reactants to products by the motions that first move along one reaction coordinate and subsequently along another. This is indicated schematically in figure 5, and, indeed, such processes are well known in electrochemistry, where the kinetics that proceeds via the indicated subsidiary minima, rather than crossing over the global saddle point at the center of the diagram, is referred to as a square scheme⁵⁶ process (perhaps because the system point motion looks like part of a square dance or a box step).

Golden Rules and Correlation Functions - A General Dynamical Model

The several stages of improved understanding that have been recounted so far lead to a contemporary view of electron transfer reactions that is both physically appropriate and computationally accurate. Still, however, several crucial aspects are missing. Perhaps the most important of these are that for dissociative electron transfer reactions, like that of equation 2, the potential surfaces are certainly not in any sense harmonic; the polaron model,³⁶⁻⁴¹ which is the basis for the most sophisticated of the theories described thus far, assumes harmonic

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vibrations. Second, the electronic tunneling matrix element may well depend on the particular nuclear configuration - for instance, early work^{14,57} on electron transfer between planar entities such as phthalocyanines indicates an important dependence of the electron transfer tunneling on the relative geometries, especially rotational geometries, of the two phthalocyanine units. Third, general solvent behaviors should include both homogeneous and inhomogeneous broadening, arising from solvent motions on the one hand, and from differing solvation energetics on the other.⁵⁸ All of these can be included,^{59,60,61} within a general golden rule rate formulation, by replacing the energy conserving delta function that appears in Fermi's golden rule for the rate constant by its time equivalent, and recasting the entire expression in terms of correlation function. This treatment was first done for spectroscopy by Lax⁶² in the early 1950's, and applied, very effectively, in a chemical context first by Gordon⁶³ and later (using a particularly elegant wavepacket formulation) by Heller.^{64,65} The generalization from spectroscopy to electron transfer has been recently given by cooperative efforts of groups from Evanston and Tel Aviv.⁵⁹⁻⁶¹

The rate constant expression in the time-dependent correlation function context is quite simple, and is given by equation 8.

$$k_{et} = \int_0^\infty dt e^{i\Delta(t)/\hbar} \langle H_{rp} e^{-iH_i t/\hbar} H_{rp} e^{-iH_f t/\hbar} \rangle \quad (8)$$

There are several aspects of this expression that are quite remarkable. First, notice that the gap parameter Δ is now given as an explicitly time-dependent function; this permits information on correlations within the solvent, including inhomogeneous and homogeneous broadening, dephasing, and slow dynamics, to be included directly. Second, the tunneling matrix element appears in the correlation function - that is, when the averaging is performed it can be performed over whatever dynamical variables may affect the tunneling (that is, the Condon approximation is not invoked). Third, the hamiltonians H_i and H_f of the initial and final states enter directly into the propagator - that is, one explicitly considers the time evolution of the initial and final states. If the potential surface is harmonic, this evolution is essentially trivial; on the other hand, generalization to anharmonic behaviors, to multiple tunneling events, to superexchange, to dissociative electron transfer, and even to multiple minima is relatively straightforwardly handled within the time domain.⁵⁹⁻⁶¹

Rate Control: Insights from Theory

Nearly four decades of electron transfer theory have resulted in a clear picture of electron transfer rates at a number of different levels depending on the conditions of the actual

Figure 4.

A schematic sketch of the potential surface for ligand protein rebinding. R denotes the ridge, and S the saddlepoint. Stable reactant and product configurations are noted by a and b , respectively. Note that the shapes and orientations of the ridge are schematic, but also that the contour lines for diffusion are quite different in reactant and product states. From reference 51.

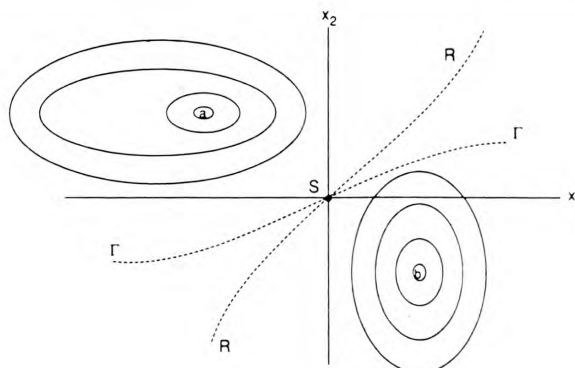


Figure 5.

Schematic potential energy surface for electron transfer with conformational equilibrium. The abscissa and ordinate are, respectively, internal motion and configurational motion. The reaction goes from the reactant in the upper left to the product in the lower right; note the presence of the saddlepoint in the middle of the diagram, but also the two subsidiary minima in the upper right and lower left. Transfer from the precursor state in the upper left to the successor in the lower right can occur by a two step process, either across and down or down and across, rather than the direct path over the saddlepoint. From reference 54.

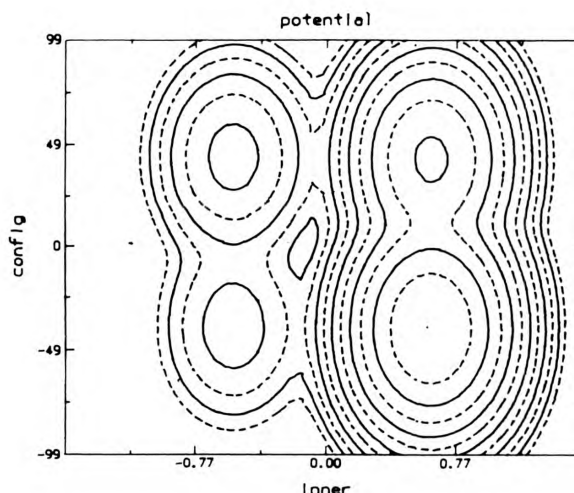
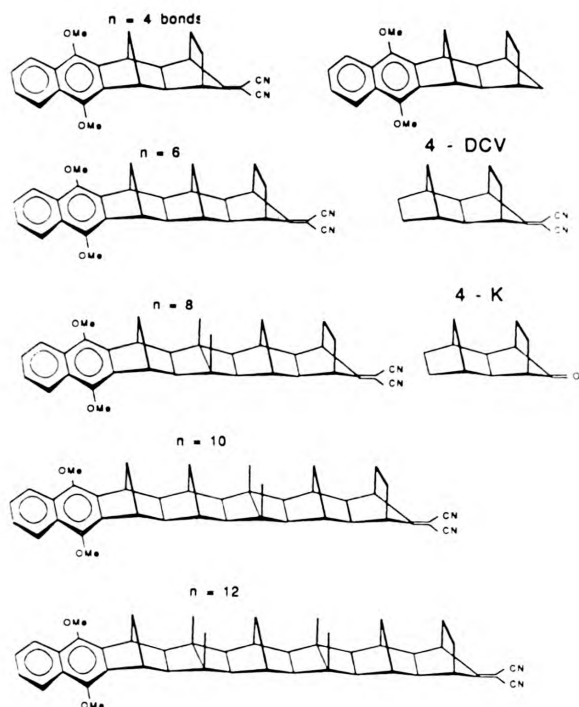


Figure 6.

A series of synthetic intra-molecular electron transfer systems, containing rigid sigma bridges between donor and acceptor groups. From reference 68.



experiment. With respect to the traditional chemical view of rate determining steps, this theoretical picture permits us to characterize conditions under which particular physical effects may control the rate of electron transfer. These control processes include:

- 1) Franck-Condon factors, that limit the acceptance of the exoergicity by the vibrational modes of molecules and the solvents. This was the motivation for the gap law and the so-called Marcus inverted regime behavior, that reflect the counter-intuitive notion that under particular conditions increasing exoergicity results in decreasing rate.⁶⁶
- 2) Solvent relaxation dynamics, that can slow down an electron transfer rate due to the inability of the solvent slow modes to follow the equilibrium evolution predicted on the basis of the potential surface. These may be particularly important in polymeric, glassy, or protein systems.
- 3) In non-adiabatic electron transfers, the electron transfer tunneling matrix element H_{TP} (whether direct or assisted by bridging groups) will limit how effectively the sys-

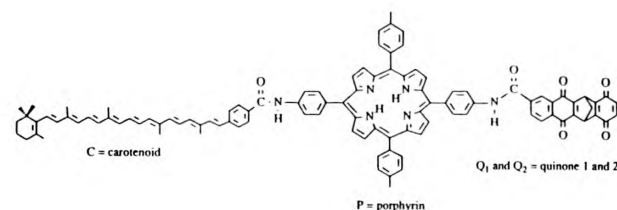
tem passes over the barrier top. Synthetic engineering based on the size of H_{TP} permits fairly precise control of electron transfer rates.

- 4) Gating effects are a particular manifestation of solvent dynamics, in which motion along one coordinate is so slow that it essentially determines the overall rate behavior. Gating conditions are, again, expected in glass-forming materials. In particular, one strongly over-damped, slowly diffusing coordinate may completely dominate the overall reaction, resulting in non-exponential behavior and very slow electron transfer.
- 5) The presence of subsidiary minima on the potential surface can result in a completely different set of reaction pathways, leading to so-called "square scheme" dynamics. This can lead to the system completely avoiding the global saddle point, and, as a function of variables such as solvation or energy, evolving either through the subsidiary minima or over the saddle point. Thus by emplacing subsidiary minima, the entire reaction mechanism can be changed.
- 6) Energetic control. The overall exoergicity, Δ , is a critical factor in electron transfer reactions. Changing exoergicity can either increase (in the normal regime) or decrease (in the abnormal regime) the transfer rate. Both chemical synthesis and such weak effects as hydrogen bonding, selective solvation or ion pairing can substantially change the overall exoergicity, and therefore the rate of the reaction. One interesting form of energetic control involves shifts of local energy levels either by selective complexation^{66a} or by ionic Coulomb interaction^{66b} ("ion gated electron transfer").

Given these elements of rate control, it becomes a fascinating and promising synthetic target to design electron transfer reactions whose rates can be varied by the experimenter, either statically (particular design structures), or even dynamically (particular design structures whose behavior can be changed by controls such as photon switching, ion switching or voltage switching).

Figure 7.

A tetrad molecule, containing a carotenoid, a porphyrin, and a diquinone, synthesized to provide artificial photosynthesis – that is, long-life separation of an excited state into isolated cationic and anionic structures. From reference 30.



Controlled Electron Transfer Structures – Experimental Molecular Electronics

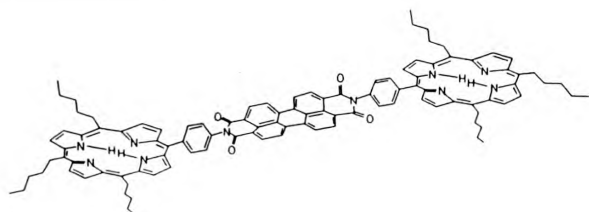
By controlling the relative magnitudes of the six possibly rate controlling steps just discussed, it should be possible to prepare systems whose electron transfer rates can be controlled. The solid state analogs of such molecular systems have been known for a long time; indeed, transistor-based technology essentially arises from controlling directional electron flow across p/n junctions, analogous to electron donor/acceptor interfaces. The first steps in attaining molecular devices based on controlled electron transfer entail demonstration of controlled electron transfer as an elementary process, in synthetic structures. In the remainder of this article, we will mention both completed experimental work on controlled electron transfer, and current investigations on application of controlled electron transfer rate processes to the understanding and preparation of molecule based devices.

Controlled Single Step Electron Transfer

Both intra and inter-molecular transfers have been studied in which rates can be changed, often by many orders of magnitude, by control of the exoergicity parameter. More recently, an elegant series of synthetic methods has culminated in the preparation of a number of species (figure 6) in which changing the nature of the bridge between donor and acceptor sites changes the efficiency of intra-molecular electron transfer.⁶⁶⁻⁶⁹ Finally, it has been shown that dropping the environmental temperature such that the solvent becomes glassy limits the available outer sphere reorganization energy, and can essentially turn off electron transfer processes.⁷⁰

Figure 8.

A bridged diporphyrinic system that constitutes a light-intensity dependent optical switch. This molecule switches its transient absorption frequency with the intensity of the applied light field; after absorption that photon, an ion pair located on the left porphyrin and the bridge becomes stable, following which the second electron absorbs at the bluer wavelength. From reference 76.



Electronic Shuttles, and Molecular Wires

Covalent structures to provide facilitated electron transfer between particular donor and acceptor sites has been used in the preparation of biosensor devices.^{30,71,72,73} Here, modified electrodes are attached to immobilized electron transfer enzymes, by means of a molecular wire feature, that facilitates electron transfer between the sensing electrode and the redox enzyme. More generally, Lehn and co-workers⁷⁴ have investigated conjugated systems for facilitating very long-range electron transfer, by what they call a "molecular wire."

Charge Separation and Storage

The natural photosynthetic apparatus leads to separated electrical charges following the absorption of a photon. A number of artificial systems have now been prepared,^{30,75} in which charge separation is induced by controlled electron transfer and trapping, subsequent to initial excitation by photons at a particular chosen wavelength. Obvious applications of such structures to energy transduction and solar energy capture are under intensive investigation, using such species such as that shown in figure 7.

Molecular Switches, Based on Two-Step Electron Transfer

Wasielwski and collaborators⁷⁶ have designed an electron donor/acceptor/donor molecule, in figure 8, which exhibits optical switching based on two ultrafast electron transfer reactions. The molecule absorbs light strongly at two different frequencies, 713 nm and 546 nm, in the singly and doubly reduced states of the electron acceptor end. This photophysical behavior is the basis for a light intensity dependent optical switch. As the light intensity increases, the molecule switches from being a strong transient absorber at 713 nm to a strong

Figure 9.

The pi donor-sigma bridge-pi acceptor structure first proposed as a molecular rectifier. The acceptor on the left end has a lower unoccupied first level than the donor on the right so that current would pass in a more facile fashion from left to right than vice versa. From reference 77.

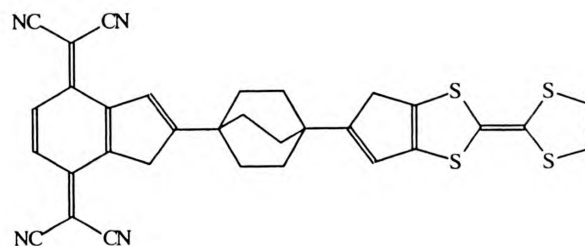
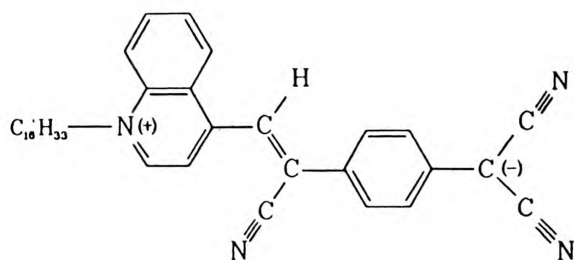


Figure 10.

The zwitterionic species recently demonstrated to provide molecular rectification. Except for the nature of the bridging structure, it bears a remarkable similarity to the species of figure 8. From reference 78.



absorber at 546 nm. The molecule can then be used to modulate two beams of light at different colors on the picosecond time scale and even to perform logic operations. This stands as an interesting prototype of integrated molecular opto-electronic devices, that would be both very small in size and very fast in performance.

Molecular Rectification

It was proposed twenty years ago⁷⁷ that use of an intramolecular donor/acceptor structure with a bridge that permits only weak mixing of donor/acceptor levels could result in rectification of applied current. The first proposed structure is shown in figure 9: the forward bias would result in oxidation of the donor and reduction of the acceptor, but on reverse bias the more energetically demanding processes of reduction of the donor and oxidation of the acceptor would not be observed until a much higher driving field is applied. Very recently, the structure shown in figure 10 has been prepared,⁷⁸ and apparently demonstrated to act, indeed, as a molecular rectifier (figure 11). If verified, this would be an important advance in the understanding and preparation of single molecule electronics.

Macroscopic and Microscopic Coupling – Scanning Tunneling Microscopy and Electron Transfer

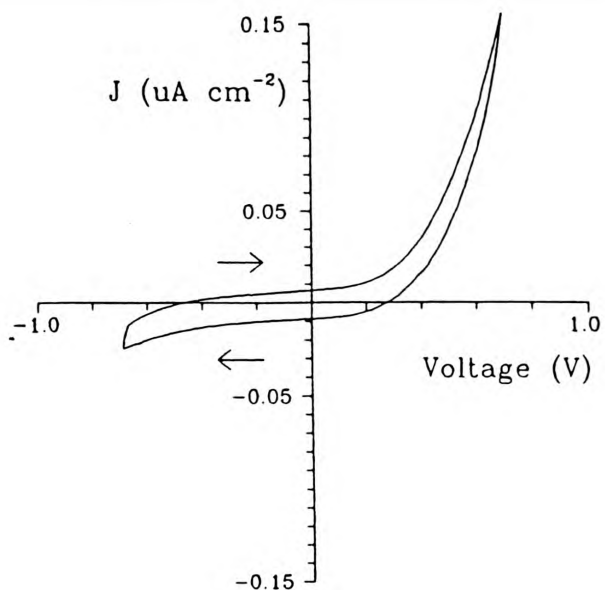
Single molecule electronics has as one goal the preparation of molecular circuits that operate in a fashion similar to those of macroscopic solid state circuits. A close analogy between electron flow in engineered molecular structures and in solid state device applications is strikingly indicated by consideration of scanning tunneling microscopy.^{79,80} In this technique, electrical currents pass between an electrode and a

metallic or semi-conductive tip; the intervening structures facilitate the electron transfer process, and study of the currents as a function of applied voltage, or of tip to electrode distance, provides information (in the form of images) on the dimension and nature of the intervening material. In the very weak perturbation limit,⁸¹ the STM current is proportional to the density of electronic states on the electrode/overlayer structure, evaluated at the position of the tip and the energy of the applied voltage. If, however, the tip is brought closer to the surface, simple perturbation analysis fails and one must consider the direct calculation of the tunneling current.⁸²

A simple and effective picture for discussing the STM experiment, in the limit of small applied voltage, involves transport through an overlayer consisting of discrete local electronic levels (such as atomic orbitals) coupled by usual, extended Huckel-type tunneling matrix elements. At the electrode end and the tip, these local sites are coupled to continua, corresponding to the conduction bands biased by the applied potential. Under these conditions, the rate can be described⁸³ in terms of an effective scattering matrix element that acts between an initial state on the electrode and a final state that has traversed from electrode through overlayer to tip. Development of such a formalism, based⁸⁴ on applications of formal scattering theory, is in fact fairly straightforward.⁸³

Figure 11.

The measured current voltage curve from a structure consisting of a silver surface, several monolayers of the molecule in figure 10, and a magnesium junction. The voltage sweep was set at 44mV/s. Note the obvious rectification behavior, with forward bias providing much larger current. From reference 78.



The striking resemblance between STM and non-adiabatic electron transfer, at a molecular level, is that in the electron transfer process one again deals with a series of tunneling matrix elements between local atomic orbital sites. In place of the electronic continuum, however, these electronic structures are coupled to a quasi-continuum of vibrational energy states, and the Franck-Condon weighted density of states structures replace the continua arising, in the STM experiment, from the metal bands. This analogy suggests not only that similar formalisms can be used, but that the distinguishing hallmarks of the electron transfer process (inverted region slow down, and the other rate-controlling steps mentioned above), can be observed, appropriately, in STM measurements. Conversely, it also appears that some of the characteristic behavior of mesoscopic structures, in particular formally negative resistances, coulomb blockades, and resonance assisted tunneling processes should be observed in electron transfer phenomena. These lead to an additional level of control, and may well provide a very rich area for real molecular electronics.

Electron transfer or, more generally, the flow of electrical charge in designed structures, lies at the very heart of current research and applications in chemistry, materials science, biochemistry and solid state physics. Exploration of the commonalities of these processes, and possible control mechanisms and design structures, makes electron transfer research one of the most exciting, forefront topics in each of these fields.

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Biography

Mark Ratner is a Professor of Chemistry at Northwestern University. His academic background stated in Ohio, followed by undergraduate, graduate and postdoctoral work at Harvard, Northwestern and Aarhus (Denmark), respectively. He has been on the Northwestern faculty since 1975. His major research interests are in electron transfer, ion transfer, molecular electronic applications, and self-consistent field models of relaxation, charge transfer and energy transfer processes.

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Solvent Effects in Quantum Chemistry: The Self-Consistent Reaction Field Model

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Nearly all of quantum chemistry relates directly to the chemistry of isolated molecules in the gas phase at absolute zero temperature. In spite of the fact that quantum chemistry and quantum chemical concepts now permeate the chemical literature, most everyday chemistry takes place in solution, where it is influenced, sometimes considerably, by the surrounding solvent. This article presents some simple concepts that help to bridge the gap between quantum chemistry and the chemistry that most of our colleagues examine experimentally. We examine here the *reaction field model*, and show the impact these considerations have on structure, thermochemistry, and on electronic spectroscopy. Examples range from simple equilibria to the photochemistry involved in the initial photochemical event in photosynthesis.

Introduction.

Solvent effects.

Now this seems at first glance a subject far from the heart of most quantum chemists, and I am a Quantum Chemist. By-and-large quantum chemistry refers to isolated molecules in the gas phase. And the history of modern physical chemistry focuses around isolating systems – low pressures, molecular beams, matrix isolation. Everything possible is being done by modern physical chemists to uncover the “basic” nature of a molecule or a pair of molecules reacting in isolation – free from complicating

environmental factors that make these studies complex. It is these “modern” physical chemists that most of my crowd want to talk to. These 200 or so scientists are creating the data where we can test our “fundamental” theories. Unfortunately, most of chemistry simply isn’t like this. It is messy. Molecules are generally surrounded by many others, in “solution”, and they react with others also in solution. For every low pressure gas phase physical chemist, there are hundreds of bench chemists happily creating things, and their results are not directly predicted by modern quantum chemistry if solvent effects are ignored. Quite the contrary. There are now many examples of state-of-the-art quantum chemistry yielding incorrect results. Not necessarily incorrect results for the gas phase experiment, which usually has not been done, but incorrect when compared to the only experiments that have been done – in solution, or surrounded by protein material, or on surfaces. These environmental effects are not necessarily small.

That these effects are not small is hardly news to biochemists or to anyone interested in charge or electron transfer. Fundamental processes that occur in biology or in solution often do not occur in the gas phase. Certainly solvent participation, or more precisely dielectric relaxation of a solution or surrounding protein materials is at the heart of the theories developed by Rudy Marcus for charge transfer¹, our unusual colleague to which this article is devoted.

That solvent effects are not necessarily small may not be news to the biochemist, or the statistical mechanician or Rudy

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Marcus. It should not even have been news to me, as I follow much of the statistical mechanical literature. But it was. It was a surprise to me when some of the things I was doing didn't turn out as expected. I will write briefly about two of these below: merostabilization of dyes, and the initial photochemical event in photosynthesis. Both depend crucially on the surrounding media.

Now what are these solvent effects? Below is a useful classification, although it is certainly ordered in a way useful for a quantum chemist.

None.

Then, of course, this paper need not be written! There is a chemistry at low pressure with but small environmental effects, the experiments we alluded to above. Also solvent effects on non-polar systems MIGHT have only a slight effect on structure or reactivity, and even vibrational spectroscopy. But as more careful experiments are done, we notice that even systems in "matrix isolation" are not as isolated as one might hope.

Weak.

By weak we usually refer to binding energies between solute and solvent below thermal energies, below " kT ", the Boltzman constant time temperature. Since liquids generally have binding energies also of the order of kT (or they would be solids or gases at room temperature), they are influenced by the field of the solute, but continue to maintain to good degree of approximation

the properties of the pure solvent. From the quantum mechanical point of view we want to be able to consider the solvent and solute as separable. This implies no charge transfer and no exchange between solvent and solute.

Strong.

Here strong refers to interactions greater than kT . In such a case the nearest neighbor solvent molecules have a relatively fixed geometric relationship with the solute. The solute is best considered as the dissolved molecule and its strongly bound neighbors. The binding between this super-molecule and the rest of the solvent is then weak.

Reaction.

The reacting species must all be considered as a super-molecule, and the rest weakly interacting. The reacting species may include the solvent directly, or as a catalyst. For example, many proton transfer reaction exchange protons with water when it is present ².

Mechanical.

Two species can be trapped in a solvent cage and forced to influence one-another, or even react with one another, as they are in proximity for a longer time than they would be in the gas phase. For example, they collide with one another, and would bounce apart if it were not for the fact that they collide with the solvent and bounce together again.

Figure 1.

Three regions to be considered in simulating solvent effects.

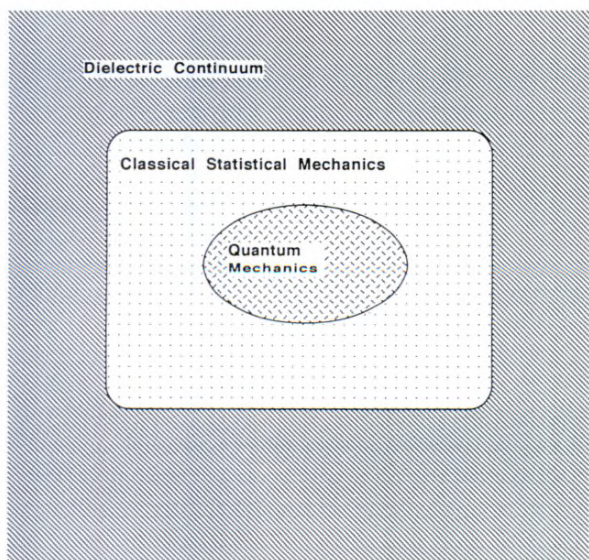
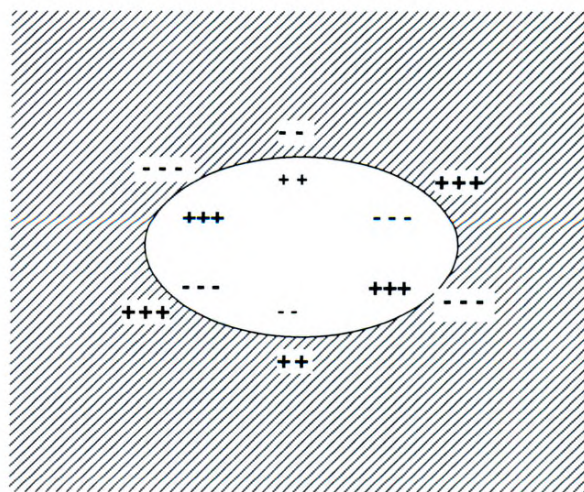


Figure 2.

A hypothetical charge distribution of a molecule in a cavity, and the image charges generated from in a dielectric continuum.



There is an important operational difference between weakly and strongly interacting species. In the former the changing orientation between solute and solvent, and solvent and solvent, is important, and effects the properties of the solute. This is correctly modeled only through a careful statistical mechanical averaging of all possible orientations. In the latter, a fixed geometric relationship generally pertains, and this is the usual domain of quantum chemistry.

Much can happen to a molecule as it dissolves in solution. It can dissociate, react, complex, form associations or dimers, etc. Still all species present can be treated as weakly or strongly binding with the solvent, if the reaction is slow, or if it is fast. This becomes more difficult if what happens happens on the same time scale as do the thermal motions of the solvent itself.

How does one treat a "solution?"

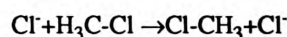
In principle, we should perform:

1. A Monte-Carlo or molecular dynamics study of the solute and solvent using potentials derived from quantum mechanics. In general, we cannot perform a study of this nature on Avogadro's number of molecules to mimic systems of macroscopic size (we would need 6×10^{23} molecules, and just keeping track of so many coordinates exceeds the memory of any computer). Generally a solvent and, say, 200 solute molecules with the appropriate boundary conditions that mimic the remaining solution is sufficient to accurately represent the thermodynamics^{3,4}. But now the quantum chemistry becomes a problem. The thermodynamics requires that one study millions of spatial configurations in order to calculate the average macroscopic property. Since there are about 31 million seconds in the year, if we could perform each calculation

in 30 seconds this becomes feasible if we had a computer dedicated to this task. Hartree-Fock Molecular-orbital independent-electron calculations using semi-empirical quantum chemistry can perform in this time frame on these big systems on today's largest computers. But the interactions in the system are weak, and it is dubious if independent-particle calculations are of any value as they do not correctly yield weak interactions. What will be needed are "correlated" theories, those that take more specific care of electrons that then yield correct weak interactions. Considering the problems that then arise with basis sets, basis set errors and corrections, correlation^{-5,6} this is not possible today and not in the near future.

2. Monte-Carlo or molecular dynamic studies with classical potentials. This is a well established branch of theoretical chemistry, and has been used to yield a great wealth of information on solvation and on biological interesting systems^{3,4}. The accuracy of these results rely on the accuracy of the potentials assumed, and these potentials are generally selected to reproduce a set of well known properties. These potentials are relatively simple, treating atoms as balls, and bonds as springs. This is a technique generally for weak interactions. Classical mechanics can not be used to correctly describe reactions or electronic spectroscopy, for examples, as these phenomena are electronic in nature. Atoms are not balls, and bonds are not springs: molecules are made of electrons and nuclei.

There is a middle ground here, and one that is beginning to be successfully exploited. Here one obtains the potential for isolated pairs (or even triplets) of molecules, and then fits these potentials, without necessarily recourse to ball and spring models. This was shown very successfully in modeling the famous SN2 reaction⁸



which reacts 20 orders of magnitude more rapidly in water than in the gas phase. The water-water potential was treated from a fit classical potential, while the potential for the reaction itself came from quantum mechanics.

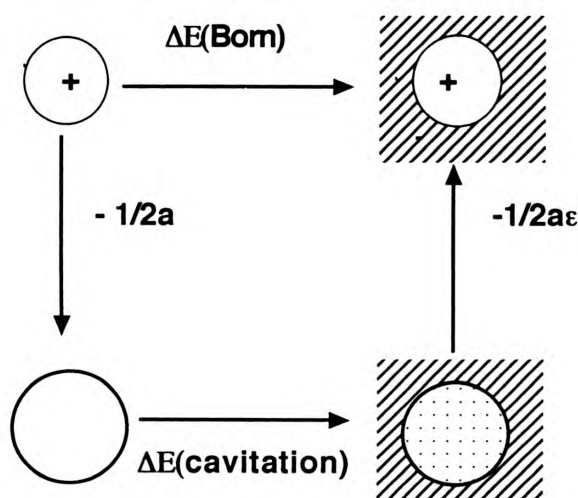
3. Cluster models. Here one surrounds the solute molecule with an ever increasing number of solute molecules and treats the system using quantum mechanical potentials and statistical averaging. One then watches for the convergence of calculated properties with cluster size.

This is a very difficult approach, and is fraught with the very many pitfalls that have accompanied similar studies on solids: how many atoms or molecules make a solid? This is still an unanswered (unanswerable?) question, and the far greater thermal motion of a solution will make the answer to this question even more difficult. Most likely we will not like the answer.

4. Perturbative models. A picture is given in Figure 1. A quantum mechanical supermolecule is surrounded by a region

Figure 3.

The Born model of solvation for an ion, see text.



of solvent molecules treated by classical potentials, and the entire system placed in a dielectric continuum.

Examining the utility of the dielectric continuum model will form the bulk of this manuscript. The energy (Hamiltonian) of this system can be written as the sum of its parts plus the pairwise interactions between parts.

$$H = H(\text{QM}) + H(\text{Classical}) + H(\text{QM-Classical}) + H(\text{QM-Dielectric}) + H(\text{Classical-Dielectric}) \quad (1)$$

This is a particularly easy way to describe the problem of solvation and to decompose the problem into more manageable pieces. In some sense, it has no content, for it clearly includes case 1., above, if the QM-supermolecule is made big enough, case 2. if the QM moiety is dropped completely, case 3 if the QM-supermolecule is developed as an isolated cluster.

In this work we will focus mostly on the quantum mechanical supermolecule within the dielectric continuum. This is the easiest to describe, and already yields interesting results. In the final section we will describe calculations for spectroscopy that contain all three moieties.

The Dielectric Model for Ground State Properties

When a molecule is dissolved in a dielectric material, the electric field it establishes sets up a reaction field, one that counters it, and stabilizes it. Figure 2 pictorially represents this. Figure 3 presents the Born model⁹ for the solvation of an ion. The ion and atom are assumed to be spherical. The net energy for the Born-Habor cycle is then given by

$$\Delta H(\text{sol}) = \Delta H(\text{gas}) + \Delta H(\text{cavitation}) + \Delta H(\text{solvent}) \quad (2)$$

$$\approx -Q^2/2a + 0.0 + Q^2/2\epsilon a$$

where a is the radius of the ionic sphere, Q is the charge of the ion, and the cavitation energy, a few kcal/mol., is forgotten for the moment when examined in the context of these other larger numbers. $\Delta H(\text{gas})$ and $\Delta H(\text{sol})$ are the energies required to charge a sphere of radius a reversibly, i.e.

$$\Delta H = -\int_0^Q q \, dq \quad (3)$$

where ϵ is the dielectric constant of the medium, unity for the gas phase, 80 for water at room temperature, 2.2 for a non-polar solvent like cyclohexane.

Assuming a simple ion, the radius of the largest orbital can be estimated from

$$\langle r \rangle = (2n+1)/2 \, \xi \quad (4)$$

where n is the principle quantum number ($n=1$ for Li^+) and ξ is the orbital exponent for this orbital, which can be, for illustrative purposes, taken from the Zener-Slater screening rules ($\xi = Z-0.3$ for 1s orbital, 2.7 for Li^+)^{10,11}. This yields for Li^+ a solvation energy of 13.1 eV (1 eV = 23 kcal/mol.). An experimental value of 15.1 is reported for Li. This is remarkably close for such a simple theory. On the other hand, 2 eV = 46 kcal/mol., a large error for some purposes! Such a simple and appealing theory has, as might be expected, led to tables of effective radii for atoms, ions and molecular groups fit to reproduce experimental heats of solution¹².

This theory can, and has been generalized by Kirkwood¹³. The interaction between a molecule and its environment is given by¹⁴.

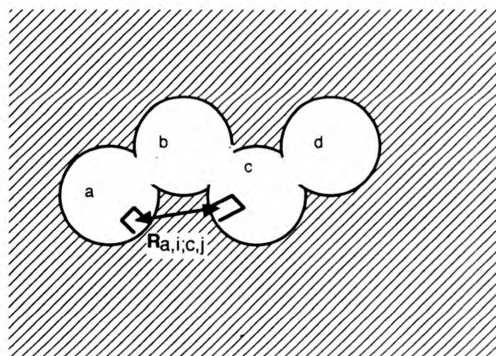
$$E = -1/2 \int p(r) U_p(r) \, dV \quad (5)$$

where $p(r)$ is the electronic density of the molecule (or supermolecule) and U_p is the reaction potential that this charge distribution generates within the medium. Assuming the solute is embedded in a sphere of radius a , and expanding the field generated by the molecular density in terms of electric moments yields the expression¹³

$$E = -1/2 \sum_l g_l \sum_{m=-l}^l M_{lm} M_{lm} \quad (6a)$$

Figure 4.

A more realistic model for the shape of a molecule in a solvent is generated from surrounding each atom by a sphere, rather than the entire molecule by a sphere or an ellipse. The external surface of each sphere is then divided into patches in which the surface charge density is estimated, and the boundary equation 9 is solved.



In the above, $M_{1,m}$ are the moments and g_1 are the reaction "tensor" given by

$$g_1 = 2 [(1+1)(\epsilon-1)] / [(1+1)\epsilon+1] \quad (6b)$$

The first term is simply the Born charge term. The second term, the dipolar term, was first explored by Onsager¹⁵.

$$E = 1/2 Q^2/a - 1/2 g_1(\epsilon) \mu \cdot \mu / a^3 \quad (7)$$

where μ is the molecular dipole with components $M_{1,1} = \mu_x$, $M_{1,-1} = \mu_y$ and $M_{1,0} = \mu_z$, etc., and, from the above equation,

$$g_1(\epsilon) = 2(\epsilon-1) / (2\epsilon+1) \quad (8)$$

Analytical expressions analogous to those above can also be derived for an ellipsoid^{14, 16, 17}. More general shapes can be generated also, as depicted in Figure 4, in which each molecular group is surrounded by a sphere of a given size (either a Van Der Waal radius or a radius fit to reproduce experimental values^{18, 19}). In this case, the electrostatic potential must be generated on each surface point, and the reaction charge "facing" it generated by the continuity equation.

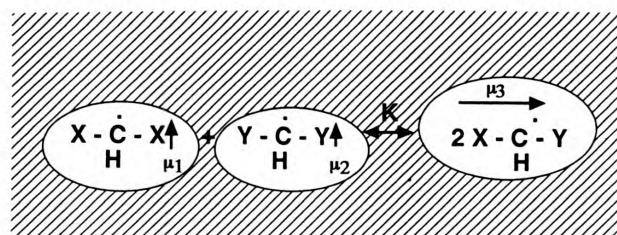
$$\epsilon(\text{internal})(\delta V/\delta v)_{\text{internal}} = \epsilon(\text{external})(\delta V/\delta n)_{\text{external}} \quad (9)$$

In equation 9, the derivatives represent the electrostatic potentials normal to the surface, internal to the sphere, with usually equal to unity, and external to the sphere, with $\epsilon(\text{external})$ usually equal to the bulk dielectric constant.

Generally this is done using finite element procedures¹⁸. The generation of the electrostatic potential at the surface is difficult, and has been approximated often just from atomic charges¹⁹, and the number of surfaces patches often suffi-

Figure 5.

A pictorial representation of mero-stability. Molecules 1 and 2, symmetrically substituted, have small dipole moments along the symmetry axis, here "z". The asymmetric molecule 3 has a much larger dipole moment. Since the stabilization in a dielectric medium is roughly proportional to the dipole moment squared, molecule 3 is stabilized more than 1 or 2.



$$\mu_1 \text{ and } \mu_2 < \mu_3$$

Table I:

A Study of Merostability in the Gas Phase ($\epsilon=1$) and in "Water"

Molecule	$\epsilon=1$ kcal/mol	$\epsilon=80$ kcal/mol
CH(CN)OH		
INDO	3.1	-24.4
4-31G	3.3	-22.2
CH(CN)OCH ₃		
INDO	1.2	-28.8
CH(CN)NH ₂		
INDO	5.7	-7.3
4-31G	5.8	-7.0

ciently large as to suggest further tricks to cause more rapid convergence.

Another criticism of this approach, in addition to attempts to describe the shape of wiggling solute molecules in a solvent, is that the dielectric strength passes directly from that of the gas phase to that of bulk dielectric. One correction is to create two spheres (or ellipsoids) and more gradually pass from dielectric constant 1 to ϵ' to ϵ (bulk)²⁰. This is somewhat more successful, but involves two additional parameters, ϵ' and the corresponding a' . A more realistic approach would be to model the dielectric as a value that smoothly went from 1 to bulk as a function of r . This has also been developed successfully²¹ but has not yet been systematically examined.

One can establish in the context of quantum mechanics the equivalent Hamiltonian (Schrodinger equation), and solve the equation

$$H\psi = E\psi \quad (10a)$$

$$H = H_0 - 1/2 g(\epsilon) / \langle \mu \rangle \cdot \mu / a^3 \quad (10b)$$

in which H_0 is the gas phase super-molecular Hamiltonian operator, and the remaining terms mimic the effects of solvation. ψ is the many electron wave function. The charge term is classical, and can be added to the energy at the end of the calculation (i.e., the net charge on the supermolecule does not depend on the quantum mechanics). If the arbitrary shape of Figure 4 is used, then

$$H = H_0 - 1/2 \sum_a \sum_{i \in a} q(i,a) / r(i,a) \quad (10c)$$

is used, where $q(i,a)$ are the surface charges established through solving the continuum equation 9, and the sum is over all point "i" generated on the patches "a" on the surface.

Equations 10 are iterative in nature, as we do not know the charge distribution of the molecule that generates the

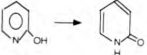
moment expansion of equation 10b when we begin, nor do we know the electrostatic potential needed for equation 10c. But this is not a real concern, as the solution of Ho, itself, is also iterative in nature. This includes (along with the sum of the momentum of the electrons, the electron nuclear electrostatic attraction, and the additive nuclear-nuclear repulsion) electron-electron repulsion, and this also can not be established without the electron distribution.

This is a brief introduction to the major ideas behind the quantum mechanical description of the "self consistent reaction field model, SCRF.

Some Examples of the Simple SCRF Theory for Ground states:

Table II:

Reaction Field Effects on LogK from AM1 Calculations. Experimental values are in parentheses^a.

Equilibrium	$\epsilon = 1$ (gas)	$\epsilon = 78$ ("water")
	0.4 (0.4)	-2.8 (-3.1)
	1.7	-4.7 (-4.7)
	6.0	-3.0 (-3.0)
	6.5	-7.3 (-4.6)

a. From reference 26. In this reference 12 systems are examined, of which the above are typical. The experimental values are from A.R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York (1985) pp. 47-50.

Table III.

An Estimate of Boiling Temperatures from Cavitation Energy (Scaled Particle Theory) and Calculated Dispersion Energies.^a

	calc. (K)	obs. (K)
CH ₄	123	113
C ₂ H ₆	177	188
Benzene	327	353
Naphthalene	520	491

^a From M. Karelson and M. C. Zerner, work in progress.

There are many examples obtained from SCRF theory²², but I first got "hooked" while trying to examine a phenomena called mero-stability²³. This has to do with the stability of a series of dyes with general formula X(CH)Y. Merostability is then defined as

$$E(\text{mero}) = E(\text{XCY}) - [E(\text{XCX}) + E(\text{YCY})] / 2 \quad (11)$$

This is a quantum mechanician dream system! All systematic errors should cancel (at least hopefully) in the subtraction. This is borne out. *Ab-initio* calculations of nearly any quality yield nearly the same results as do semi-empirical calculations-and ALL of these calculations showed that E(mero) is clearly positive. There is less of the mixed species present than the symmetrically substituted ones. By now my poor colleague Alan Katrisky²⁴, was having his experiments attacked "left and right" by knowledgeable theorists. But now we are prepared to worry about the solvent. Table 1 shows a few examples from our study²⁵. Figure 5 shows our explanation for these results. The asymmetric substitution in these systems generates a large charge asymmetry, and this receives considerable stabilization in water. The symmetrically substituted compounds have only relatively small dipole moments along their

Figure 6.

A comparison of the free energy of solvation with ΔE_{aq} calculated from $\Delta H(\epsilon=80) - \Delta H(\epsilon=1)$ using the AM1 model and the multi-cavity self consistent reaction field model; from reference 26. Molecules range from CH₄, point 2 and CH₃CONH₂, point 11.

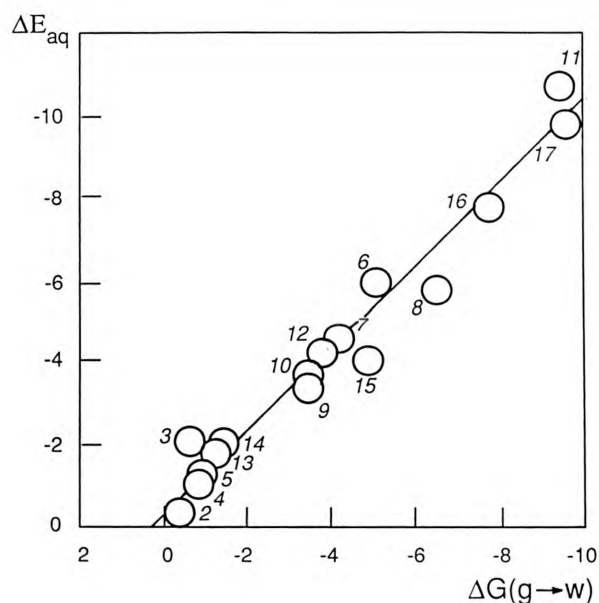


Figure 7.

The influence of a dielectric medium on absorption spectroscopy. The ground state of the chromophore is assumed to be in equilibrium with the solvent. The absorption process is assumed so fast that only the electronic polarization of the solvent can adjust. The image dipole only partially rotates in this short time. Complete rotation requires the nuclei of the solvent to translate and rotate, a process much slower than the absorption process.

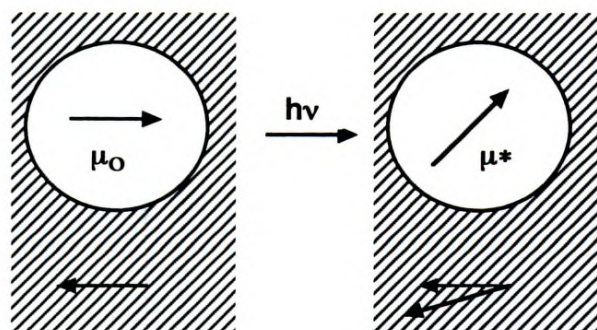
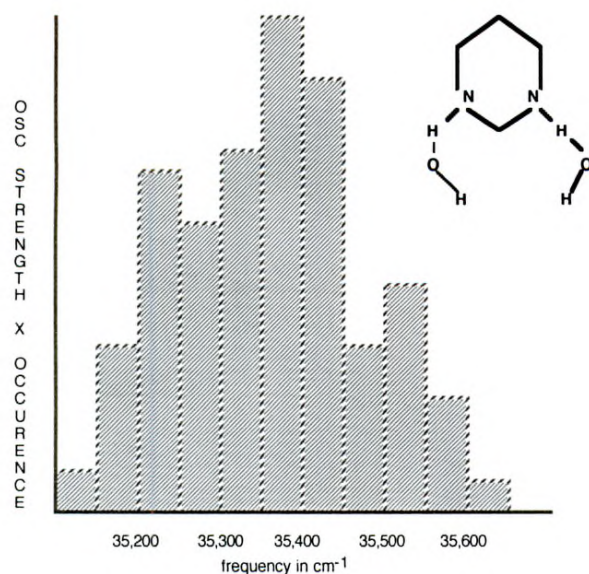


Figure 8.

A simulated spectrum of pyrimidine in water. The spectrum is calculated using the INDO/S model (J. E. Ridley and M. C. Zerner, *Theoretica Chimica Acta* (1973) 32, 111) and includes pyrimidine and two water molecules all embedded in a reaction field simulating bulk water. The geometric conformations were generated using the water-shell option of QUIPU (from George Purvis III).



axis of symmetry and receive a relatively small amount of stabilization.

Table 2 shows a study of the relative stabilities of the tautomers of hydroxy-pyridine-pyridone systems²⁶. These systems are of importance in biology and many studies have been made of them, some with the best of quantum mechanical technology. These studies yielded incorrect results. Again, as shown in this table, solvation favors the largest electrical asymmetry and yields quantitative results for the Log(K), with K the equilibrium constant, the ratio of product to reactant. A negative Log(K) means that the molecule on the right (reactant) side of the equilibrium dominates, a positive value that the molecule on the left (product) side dominates.

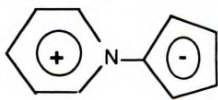
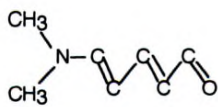
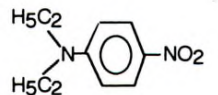
A final example for ground state properties examines the use of a multi-cavity SCRF, MCa-SCRF, scheme for solvation²⁷. In this,

$$\Delta G(\text{sol}) = \Delta G(\text{es}) + \Delta G(\text{pol}) + \Delta G(\text{cav}) + \Delta G(\text{disp}) + \Delta G(\text{S}) \quad (12)$$

$\Delta G(\text{es})$ from the pure electrostatics will come from our self-consistent reaction field calculations. $\Delta G(\text{pol})$ refers to polarization effects—changes in the electronic distribution due to the presence of the solvent, and this is also included (this is the

Table IV:

Some Calculated Spectroscopic Shifts in $\pi - \pi^*$ Transitions, in 1000cm^{-1} . The quantum chemistry is from ZINDO, reference 42. See also Reference 32.

Molecule		Calc	Obs
	1. Gas	20.1	
	2. CHCl_3	21.8	19.6 ^a
	3. water	24.6	22.1
	$\omega(3) - \omega(2)$	2.8	2.5
	1. Gas	32.0	
	2. C_6H_{14}	32.8	30.1 ^b
	3. water	29.1	26.1
	$w(3) - \omega(2)$	-3.7	-4.0
	1. Gas	29.7	
	2. C_6H_{12}	26.3	27.4 ^c
	3. water	22.3	23.3
	$w(3) - \omega(2)$	-4.0	-4.1

a. Daehne, S.; Schob, F.; Nolte, K.-D. *Z. Chem.* 1973, 13,471

b. Kosower, E.M.; Ramsey, B.G. *J. Am. Chem. Soc.* 1959, 81,856

c. Brooker, L.G.S.; Craig, A.C.; Haseltine, D.W.; Jenkins, P.W.; Lincoln, L.L. *J. Am. Chem. Soc.* 1965, 87,2443

Table V:

INDO/S SCRF CI Calculated and Experimental $n \rightarrow \pi^*$ Transition Energies of Some Heterocycles in Different Media (from Reference 34).

Molecule	Solvent	ϵ	n_D	$\nu_{calc} (cm^{-1})$	$\nu_{exp} (cm^{-1})$
1. Pyrimidine	Gas Phase	1.000	1.0000	32966	
	Isooctane	1.940	1.3915	33559	34200
	Diethyl Ether	4.355	1.3527	34127	34400
	Acetonitrile	37.50	1.3416	34697	34800
	Water	80.10	1.3330	34743	36900
	2H ₂ O	1.000	1.0000	30982	36900
	Water + 2H ₂ O ¹	80.10	1.3330	36572	36900
2. Pyridazine	Gas Phase	1.000	1.0000	28329	
	Isooctane	1.940	1.3915	29460	29740
	Diethyl Ether	4.355	1.3527	30382	30150
	Acetonitrile	37.50	1.3416	31296	31080
	Water	80.10	1.3330	31368	33570
	2H ₂ O	1.000	1.0000	26490	33570
	Water + 2H ₂ O	80.10	1.3330	33927	33570
3. Pyrazine	Gas Phase	1.000	1.0000	30387	
	Isooctane	1.940	1.3915	30387	31610
	Diethyl Ether	4.355	1.3527	30387	31610
	Acetonitrile	37.50	1.3416	30387	31740
	Water	80.10	1.3330	30387	33160
	2H ₂ O ²	1.000	1.0000	32900	33160
	Water + 2H ₂ O ³	80.10	1.3330	33301	33160

¹The calculation gives two close transitions at 35465 and 37678 cm⁻¹ of equal oscillator strength. In the table the mean value of transition energy is given.

²The calculation gives two close transitions at 30505 and 33562 cm⁻¹ of unequal oscillator strength. In the table the weighted mean value of transition energy is given.

Table VI:

Calculated Absorption Spectra of the Reaction Center of *R. Viridis*, See Figure 9.

State	Isolated - Molecule,		Solvent - Simulated	
	$\Delta\nu(cm^{-1})$	$\Delta\nu(Debye)$	$\Delta\nu(cm^{-1})$	$\Delta\nu(Debye)$
P*	11,600	4.6	11,400	4.6
(P*H) _L	19,700	78.9	12,600	75.0
(P*B) _L	19,800	49.9	16,600	46.1
(P*H) _M	20,600	76.9	13,500	74.8
(P*B) _M	20,200	55.5	16,700	48.4

“self consistent” part. A non-iterative solution of equations 10 would not include this term). When a cavity is made in the solvent, this requires energy, represented by $\Delta G(\text{cav})^{28}$. Finally, $\Delta G(S)$ is a term representing changes in the solvent structure due to the presence of the solute.

Experimental $\Delta G(\text{sol})$ are plotted against the results from the MCa-SCRF approach calculated as $\Delta E(\text{sol}) = \Delta H_{\text{fo}}(\epsilon=80) - \Delta H_{\text{fo}}(\epsilon=1)$ in Figure 6. The cavities surround each rotationally independent moiety of the molecule: for example, CH_3F is one cavity, $\text{CH}_3\text{-CH}_3$ two cavities and the $\text{CH}_3\text{-CO-CH}_3$ three cavities. The total volume of each molecule is determined from mass density and the volume of a CH_3 group determined as half that of $\text{CH}_3\text{-CH}_3$, etc. Such a plot assumes that the cavitation energy and the dispersion contributions are roughly the same and of opposite sign, which they are, and cancel, and that the entropy term is similar for all these similar molecules. The linearity of this NO FREE PARAMETER plot is remarkable.

The single cavity SCRF model gives about the same result for all of these systems (at least up to the dipole term), demonstrating that it is important to identify rotationally free sections of a molecular system that have orientation times of the order of the orientation times of the solvent itself. They establish independent “reaction fields”.

Recently we have established a theory to calculate the dispersion energies for a molecule in a reaction field^{29, 30}. Using these values, and cavitation energies from scaled particle theory²⁸, we can estimate heats of vaporization for a pure solvent. If there is little polarity, then equation 12 becomes

$$\Delta G(\text{sol}) = \Delta G(\text{cav}) = \Delta G(\text{disp}) \quad (13)$$

as the $\Delta G(S)$ term is zero. We are examining this equation now, but an interesting sideline is, that at the boiling temperature,

$$\Delta G(\text{cav}) = -\Delta G(\text{disp})$$

again for a non-polar solvent. Since $\Delta G(\text{cav})$ at most temperatures is a linear function of T from scaled particle theory, we

can estimate the boiling points of some pure solvents. Boiling point must be considered one of the most colligative of all properties, and this can be estimated from a single QM calculation! Preliminary results appear in Table 3. Mati Karelson and I stress preliminary, for we have not had time for a careful examination of these results, nor what is behind the choice of a number density that is required in scaled particle theory^{28, 31}.

The Dielectric Model for Excited State Properties:

It is well known that the spectrum (color) of a molecule is different in the gas phase than in solution. Solution spectroscopy is everyday business in any experimental lab: vapor phase spectroscopy is already a specialized topic. Can we predict the spectrum of a molecule, or, at least, what size “solvent shift” to expect?

A molecule can absorb light, and then re-admit light. Absorption spectra is generally estimated using the Franck-Condon principle that states that the nuclei do not move during the absorption process. Absorption of light is general of the order of 10^{-18} seconds, much more rapid than the molecular vibrations required to move nuclei relative to one-another, generally of the order of 10^{-13} seconds, or 100,000 times slower. Once excited, however, the excited state can often live from seconds to, perhaps, 10^{-8} seconds, and this is enough time for the molecule to assume the geometry of the excited state. For this reason, emission spectroscopy is calculated from the geometry of the excited state. This idea of relative time scales becomes important when considering the effects on solvation on absorption or emission. The model we will assume for absorption is that the solute molecule (the chromophore) is in equilibrium with the solvent before it absorbs radiation. The absorption process is then assumed so rapid that the solvent molecules cannot rotate or translate during the absorption process. The orientation and translational degrees of freedom of the solvent that make up the dielectric response of the

Table VII:

Simulated Spectra of CH_2O in Water, Shift in cm^{-1} .

Supermolecule, $\text{CH}_2\text{O} \dots \text{H}_2\text{O}^a$	385
Supermolecule in SCRF $\text{CH}_2\text{O} \dots \text{H}_2\text{O}^a$	1130
Simulation	
Scaled Changes ^{b)}	1200
Unscaled Changes	1900

^{a)} An average of the ten lowest lying conformations, see text. Only one H_2O is kept from the simulation

^{b)} The scaling is simply to set $\epsilon(R)=R$. The charges are chosen to reproduce the dipole moment of water in water.

solvent are frozen. However, the electronic response of the solvent is considered instantaneous, and we assume that the electrons do follow the chromophore excitation: i.e., part of the solvent responds to the excitation during the absorption process—the electronic polarization, another part is too slow—the orientation and translational polarization.

The dielectric constant consists of components of different frequencies. Here we need consider only two—that slow relative to the excitation lifetime and that rapid relative to it. This can be expressed as^{14, 32}

$$g(\epsilon) = g(D) + g(n(D)^2) \quad (14)$$

where D is the component of the dielectric response that is slow, rotations, vibrations and translations, and $g(n(D)^2)$ is the part that is rapid. Here $n(D)$ is the index of refraction, and $n(D)^2$ approximates the instantaneous dielectric response of the solvent^{14, 32}.

Proceeding with this model, we solve the many electron problem as before in the presence of the SCRF. We then must correct the energy of the excited state (to first order) by subtracting the electronic polarization contribution that is proportional to the charge distribution of the ground state, and that is automatically incorporated in solving a Schrodinger equation having a Hamiltonian of the form of Equation 10, and then adding back that part of the solvent electronic polarization that senses the excited state charge distribution.

$$\Delta E(\text{absorption}) = \Delta E(\text{SCRF}) - 1/2 g_1(n(D)^2) \langle \mu^* \rangle \cdot \langle \mu \rangle \quad (15a)$$

where $\langle \mu^* \rangle$ is the dipole moment of the excited state, etc. This of the ground process is shown schematically in Figure 7.

This is not the only way in which we can view the absorption process. For example, we could also view this process as if the electrons of the solute are always in equilibrium with those of the solvent. This leads to a somewhat different results than that above³³.

$$\Delta E(\text{absorption}) = \Delta E(\text{SCRF}) - 1/4 g_1(n(D)^2) \langle \mu^* \rangle \cdot \langle \mu \rangle^2 \quad (15b)$$

and suggests that the electron of the solvent sense both the ground state and excited state charge distribution in an average way. As the terms that we add in either 15a or 15b are similar in most cases, and small relative to the shifts already included in $\Delta E(\text{SCRF})$ it is difficult to decide between these two models³³.

Using the model suggested by equation 15a., we reported the spectra of some $\pi \rightarrow \pi^*$ excitations that appear in Table 4 that show unusually large solvent shifts³³. The results are remarkably good for such a simple straight-forward model, and we must assume that many of the errors inherent in such an approach must cancel when we subtract excited state energies from those of the ground state. This would include errors in molecule shape (these molecules are certainly not spherical), errors in the simple time development assumed, and errors from

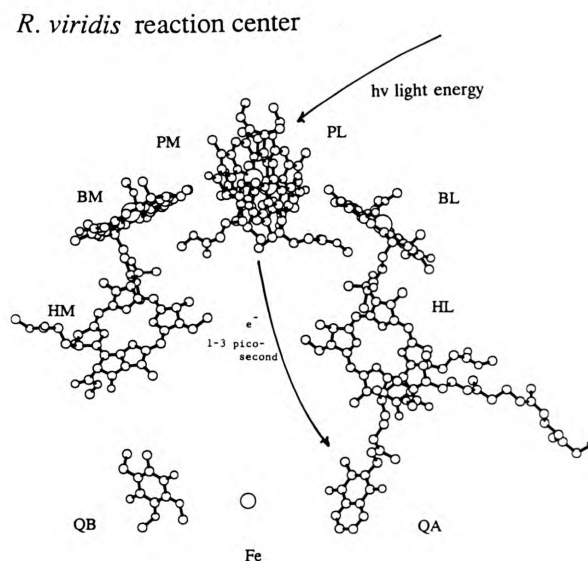
omission of the cavitation and entropic terms of equation 12. The dispersion energy is not constant, and so the shifts we compare are between two different solvents, and not between solvent and the gas phase. In general dispersion effects “red” shift (a shift to lower energies) higher excited states more than lower one when compared to gas phase spectra, but are reasonably constant for different solvents^{29, 30, 34}.

In Table 5 we report the shifts in some $n \rightarrow \pi^*$ states of diazabenzenes³⁵. The calculated shifts nicely reflect the experimental observations. But we note that the shifts calculated for these systems in acetonitrile and water are very similar, for example, 31,296cm⁻¹ and 31,368cm⁻¹ for pyridazine respectively. Experimentally the difference is nearly 2500cm⁻¹.

The line “2H₂O” designates a supermolecule of two waters hydrogen bonded to each of the lone pairs of the basic nitrogens of the azabenzenes, as would be expected on chemical grounds. These hydrogen bonds are of the “strong” nature discussed previously and cannot be expected to be accurately represented by a dielectric continuum model which assumes thermal averaging of orientations of the solvent in the field of the solute. Interestingly enough, this would lead to the prediction of a red shift (to lower energy) of these systems in a supermolecule. But note that when the entire super-molecule is embedded in the reaction field, nearly quantitative results are obtained. For example, in the pyridazine case discussed above a shift of 2630cm⁻¹ is observed between water and acetonitrile, compared to the experimental value of 2490cm⁻¹.

Figure 9.

The structure of the reaction center of *R. Viridis*, from reference 35.



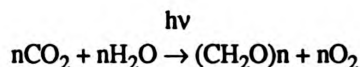
A question naturally arises from these results. How sensitive is the calculated spectra of these compounds in water to the relative positions of the bound waters? This is the type of question that can be answered in a combined classical QM approach. Considering a Monte-Carlo calculation on the super-molecule in the presence of a dielectric continuum yield for pyrimidine a shift of 2600cm⁻¹ relative to iso-octane as a solvent (experiment is about 2700 cm⁻¹) and a width of the band of about 1300cm⁻¹. This width comes from sampling the different possible conformations of the two waters bound to pyrimidine. No doubt the presence of more water molecules treated explicitly, either quantum mechanically or through classical force field, would yield a greater width. The results we obtain for this initial study are shown as a histogram in Figure 8.

Photosynthesis:

I mentioned two problems that propelled me from a naive quantum chemist, to one that was forced to acknowledge that many interesting problems simply do not occur in the gas phase. The first of these was the mero-stability problem described above. The second had to do with our studies on the initial photo-chemical event in photosynthesis.

To say that photosynthesis is an interesting reaction (or series of reactions) is an understatement. Nearly all of the biomass on earth is the result of photosynthesis. This reaction is the major one-almost unique-for fixing carbon atoms in arrangements more suitable for life as we know it. To accomplish this, photosynthesis must destroy the strong bonds found

in the carbon dioxide that is found in the atmosphere. The energy to do this comes from the sun. Light is absorbed, and produces sugars and starches from water and carbon dioxide. The overall stoichiometry for plant photosynthesis is given below:



A lot of wonderful problems are associated with this reaction, and much is known about the chemistry that follows the initial photochemical event. What is uncertain is what happens during the first second after the absorption of a photon. This is an unlikely problem to be tackled by quantum chemistry until recently, when the structure of a photosynthetic bacteria, *R. viridis*, was obtained by Huber, Deissenhofer and Michel³⁶. The essential part of the "reaction center" RC, is given in Figure 9. Experiments indicate that within 1 to 3 picoseconds after the energy is received in the RC, in a dimer of chlorophyll, Figure 10, an electron is transferred from this "special pair" to bacterio-pheophytin, a magnesium free bacterio-chlorophyll.

So we^{37,38}, as well as others^{39,40}, embarked on applying quantum chemistry to this structure of over 500 atoms and 1500 electrons, to examine the nature of the ground states, and the various excited states. These calculations clearly indicated that the lowest excited state of the system was one localized to the special pair, P*, and that the formation of the dimer itself was sufficient to insure this³⁸. The charge transfer states, however, were calculated to lie some 8000cm⁻¹ (1eV or about 23kcal/mol.) higher in energy than the absorbing state of the dimer. It thus is difficult to understand how to transfer energy from P* to P*H⁺, the state in which the pair has surrendered an electron (P[→]P⁺) and the bacterio-pheophytin (H[→]H⁺) has accepted it.

But there is some 17 Ångstroms from the center of the pair to the distant pheophytin. The transfer of an electron this distance generates a dipole moment of nearly 82 Debye (the dipole moment of water, for example, is 1.8 Debye). It is naive to expect that the protein material that surrounds the RC does not notice this large electric moment and respond to it! Using the SCRF theory for excited states as described above suggests that the largest term for the stabilization of this charge separated state is proportional to the dipole moment squared.

SCRF calculations yield the results given in Table 6. The P* state shifts to slightly lower energies, while the P*H⁺ state "red" shifts some 7000cm⁻¹, and now lies but 1200 cm⁻¹ above P*. The crossing from P* into the important P*H⁺ state, the precursor to all this chemistry, could easily occur through relaxation of the geometries of the 6 chromophores that make up the RC, or through further relaxation of the dielectric media through positional changers (rotations, translations and vibrations, see above). An important observation in this studies is that excited charge-transfer states from the pair to the auxiliary

Figure 10.

The structure of an idealized dimer of *R. Viridis*, see reference 37. The large central balls represent magnesium atoms. The light smaller balls represent nitrogen atoms, and the darker ones carbon atoms. The hydrogen atoms are not shown.

PAIR3

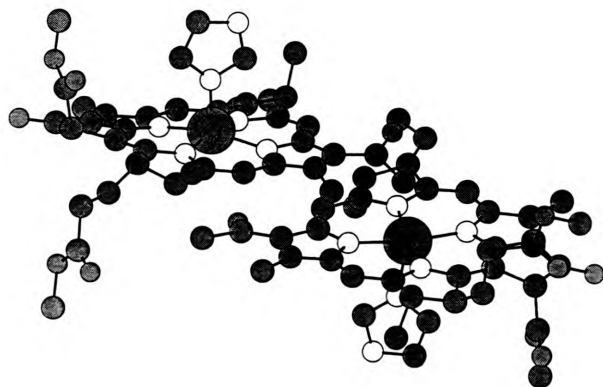
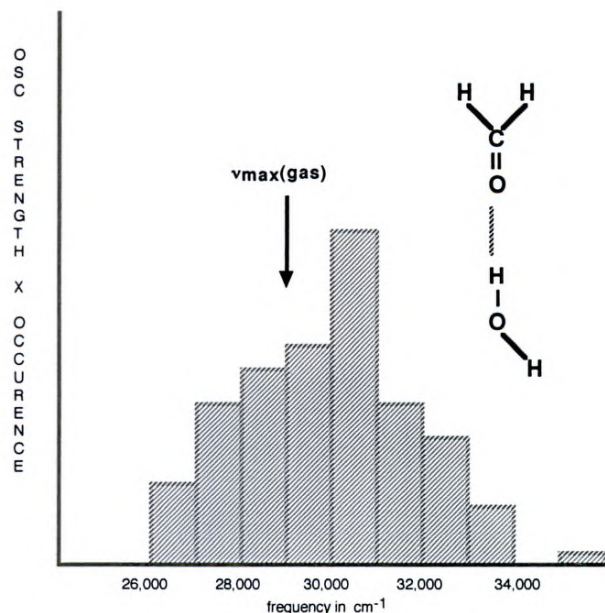


Figure 11.

The simulated spectrum of CH_2O in water. The quantum mechanics is from ZINDO and includes only the atoms of CH_2O in the presence of 99 water molecules, treated as scaled point charges, see text. The conformations were generated by the Mobi program, reference ⁴¹.



bacterio-chlorophyll's, B, and from B to H that are near in energy to the P^+H^- state *before* application of the reaction field, are considerably higher in energy after, and are too high in energy to take part in the electron transfer process itself, a matter of some controversy in the past. This observation is easy to understand: the dipole moments generated by the states P^+B^- and B^+H^- are much smaller than that of P^+H^- (about half as large) and the stabilization is roughly proportional to the dipole moment squared. the actual calculations show P^+H^- stabilized by 7100cm^{-1} , P^+B^- by only 3200cm^{-1} .

Now the RC is not surrounded by a homogeneous dielectric material. It is surrounded by real atoms in reasonably fixed positions. We have modeled all these atoms and their structure with cyclohexane treated as a dielectric continuum! We have tried to examine this crude model by adding more and more of the molecules present until we have run out of reasonable computing resources: i.e., extended the supermolecule of Figure 1. The results we obtained from the simple cyclohexane model have not changed.

More recently, Marchi, Gehlen, and Newton⁴¹ have performed statistical mechanical calculations on the RC and much of its surrounding proteins using our gas phase computed values to align the excited states correctly. The "solvent

effect" is then generated through examining the motions of the various atoms included in the simulation. Their results are very similar-although more detailed-to those we obtained for the energetics. Their results, however, also include the dynamics necessary to show that our results can actually lead to the observed electron transfer in under 3 picoseconds, and in particular that the P^+B^- and B^+H^- states are not needed for the observed dynamics^{37, 41}.

Preliminary Results from Combined Models:

In this section I would like to compare results obtained from the SCRF model with those obtained from a model in which a solute is embedded in a solvent and then the spectroscopy of this model examined using a molecular Monte-Carlo method. This model should, as discussed above, approach the correct answer if we could treat the ensemble quantum mechanically. We cannot do this. The system examined is formaldehyde in water. The potentials and the calculated relative orientations of the 99 water molecules and formaldehyde come from the Mobi program⁴² utilizing box boundary conditions. At every tenth geometry that we obtain from the simulation consistent with room temperature (298K) we calculate the spectroscopy of formaldehyde in the presence of 99 waters. The spectroscopy is calculated treating formaldehyde quantum mechanically and treating the waters as point charges that reproduce the dipole of water in water using the ZINDO program⁴³. The screening of the waters is checked by including more and more of the waters that surround the acetone in the quantum mechanics for several test conformations. A histogram of results occur in Figure 11. The average shift from the gas phase spectra of acetone is 1200cm^{-1} . This might be compared with a 1900cm^{-1} shift calculated by Blair, Levy, and Krogh-Jespersen^{44, 45}. We believe the differences have to do with different charge scaling schemes.

In Table 7 we present the results we obtain for a formaldehyde-water super-molecule in the reaction field of water. Two observations are very interesting! The first is that these far simpler calculations yield the same average shift, 1200cm^{-1} . The second is that the bound water molecule is responsible for about 1/3 of the average shift. This is also the conclusion that we reach in the full Monte-Carlo calculation if we include only one (or even two) of the nearest neighbor water(s)⁴⁴⁻⁴⁶.

Conclusions:

This paper is long enough! Hopefully what is portrayed is the wealth of information that can be obtained from a relatively simple model-the self consistent reaction field model. There is now little question that this model bridges most of the gap between gas phase quantum chemistry, and what is observed in solution. By its very nature, however, we

model reality. This SCRF model is unlikely ever to be truly quantitative. More accurate models are available, such as Monte-Carlo or molecular dynamics models using classical potentials that can be used together with quantum chemistry as discussed briefly in this manuscript. This model should be quite accurate for examining situations in which the coupling between solute and solvent is weak, and the "solute" is defined as containing all the parts that *must* be treated quantum mechanically—parts reacting, parts absorbing light, parts containing strong interactions as described previously. A fully quantum mechanical Monte-Carlo or molecular dynamics model is not available today, nor likely in the near future. But I am hopeful that many of the interesting chemistry and physics questions that arise will find their solutions in these simpler models.

Acknowledgements

Much of these studies have been done in collaboration with terrific colleagues: Dr. Mati Karelson, Tartu University, Dr. Notker Rosch, Technical University, Munich, and Dr. Mark Thompson, now at PNL, Washington. Much of the financing for these studies has come from the Office of Naval Research.

Biography

Michael Zerner is a Professor of Chemistry and Physics and Chairman of Chemistry at the University of Florida. He received his BS from Carnegie-Mellon University in 1961 and his PhD from Harvard University in 1966. Following two years in the United States Army where he served to Captain, he spent two years at the Quantum Chemistry Group at the University of Uppsala in Sweden before he accepted an academic appointment at the University of Guelph, Ontario, Canada. In 1982, he joined the Quantum Theory Project at the University of Florida. Professor Zerner's interests span nearly all areas of theoretical chemistry, and, especially of late, he has focused on the effects condensed phases have on the predictions made by quantum chemistry.

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