

Offprints From
YEAGER, TRANSACTIONS OF THE
SYMPOSIUM ON ELECTRODE PROCESSES

Published by
John Wiley & Sons, Inc., 1961

A Theory of Electron Transfer Processes at Electrodes*

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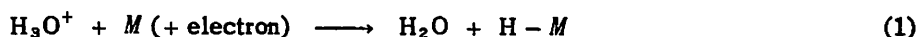
INTRODUCTION

Chemical and electrochemical redox reactions have many characteristics in common from the point of view of the experimental results and theory. A quantitative theory of the rates of electron transfer reactions in solution has been formulated (1) and related concepts used to develop an analogous treatment of electrode processes (2). In this chapter we consider the foundations of this theory, their relation to quantum mechanical principles, and the relation between the electron transfer mechanism and other mechanisms of electrode processes. The quantitative development has been presented elsewhere (2). The theoretical equations themselves have been used to interpret some of the data (3). In the interpretation, the relation to chemical electron transfers has been emphasized.

Some electrochemical processes are known to consist of only one elementary reaction, the redox step. In other electrochemical processes this step may be preceded or followed by various chemical reactions and equilibria involving the electrochemically active species. Naturally, it is essential in any careful interpretation that the data be previously analyzed in sufficient detail so that the current is known as a function of the *overpotential of the redox step*, rather than simply of the more usual overpotential of the over-all reaction sequence. When such an analysis has been performed for a complicated electrode reaction, attention can then be focused on the actual redox step itself.

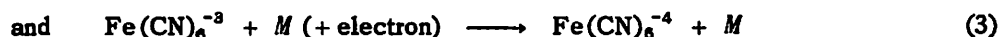
Like any other elementary reaction, this redox step can be visualized as occurring in a way now familiar in reaction-rate theory. A suitable atomic motion of the system occurs on some potential energy surface. This surface is a function of the coordinates of all the atoms of the entire system — those of the solvent, the solute, the double layer ions, and the electrode. By a suitably concerted motion of the atoms — to be discussed in more detail — the system moves from a region of this many-dimensional space where the electrochemically active species exists in one valence state to a region where it exists in the other valence state, the electrode having undergone a corresponding change.

These changes of atomic configuration are considerable. In some cases chemical bonds are known to be broken:



*Supported by the Office of Naval Research under Project NR-051-400.

where M is the electrode. At other times no chemical bonds are broken:



In reactions 2 and 3 the change of atomic configuration consists primarily of a large re-orientation of the solvent molecules about the species. This re-orientation, which arises because of the change in ionic charge, naturally occurs in reaction 1 as well.

In still other reactions, bonds are considerably stretched (4) but not broken, such as the Co-N bond, for example, in



and the solvent molecules again undergo a re-orientation.

In each system the change in ionic charge also causes a change in the ionic atmosphere about ion and electrode as well. At the same time this ion approaches the electrode closely enough to effect the necessary interaction with the electrode and then recedes.

Although these various mechanisms all involve atomic motion on a potential energy surface, it is convenient to classify them according to whether:*

- (a) chemical bonds are broken or formed during the electron transfer,
- (b) no bond rupture or formation occurs, but merely an electron transfer.

An example of group *a* is reaction 1. Another example would be deposition of a cation on a metal if bonding to the metal occurs during the charge transfer. Examples of group *b* are reactions 2, 3, and 4.

In both groups, a theory of the electrode process involves some estimate of the solvent reorganization required for formation of the activated complex. Group *a* has the additional difficulty associated with the present lack of an adequate theoretical knowledge of the electronic energy of a system in which chemical bonds are in the process of being formed and old ones broken. For this reason, as in the case of chemical reactions, it has been necessary to introduce various parameters and *ad hoc* assumptions in theories of group *a*. These same theories have, incidentally, treated the solvent reorganization in a rather similar way.

Previously, only group *a* processes have been treated theoretically in quantitative detail. In this chapter we shall present a theory of group *b* processes, a theory which is free from the arbitrary character of those theories describing group *a*.

GENERAL THEORY OF ELECTRODE PROCESSES

The potential energy of the system is a function of all the atomic coordinates. Plotted in a many-dimensional space consisting of these coordinates, this energy surface has valleys corresponding to the stabler atomic configurations of the reactants and valleys corresponding to those of products. These two sets of valleys are separated by regions of high potential energy. A reaction then can occur only when the system moves through a "pass" (saddle point) connecting the valleys. The surface itself changes shape when the metal-solution potential difference is changed.

The rate of the reaction, that is, the electric current, equals the total probability of being in these "passes" multiplied by an appropriate frequency factor for passage through them and by the concentration of the active ions in the body of the solution. This probability is usually calculated by means of equilibrium statistical mechanics from a knowledge of the potential energy surface at the passes and in the valleys of the reactants. The assumption normally made for this purpose is that the reaction hardly disturbs the equilibrium between systems in these two regions.

*There is a third, intermediate class conceivable in which bonds between ions and the electrode surface are formed to facilitate electron transfer and then broken. Such a class of "bridged activated complexes" occurs in certain electron transfers in solution, an anion forming a bridging species between two cations (5). For the electrode reactions, it is possible that some anions adsorbed on the electrode could form a bridge between the metal electrode and the cation about to undergo electron transfer.

We shall first examine how the mechanism of an electron transfer process can be discussed in terms of an atomic motion on a potential energy surface.

The Theory

Usually in a chemical reaction there is considerable electronic interaction between the two reactants in order to effect the necessary breakage of old bonds and formation of new ones. In a simple electron transfer, on the other hand, it may often be sufficient to have merely a weak electronic interaction instead. This interaction would serve to couple the two reactants – here, the ion and the electrode. We shall assume a weak electronic interaction in the quantitative description given later.

Let us first examine the hypothetical case of zero electronic interaction. There are two important electronic states to consider, each having its own many-dimensional potential energy surface. In the first of these states, the ion is in an oxidized form and the electrode has the electronic charge distribution appropriate to the given metal-solution potential difference. In the second state, the ion is in a reduced form; the electrode has lost to it the corresponding number of electrons and again has a charge distribution appropriate to the same potential difference.

The valleys of one surface are centered at quite different atomic coordinates from those of the other surface. The difference in ionic charge, for example, results in a difference in the average stable orientations of the solvent molecules outside the coordination shell and in the ionic atmosphere about the ion and electrode. The difference in electronic configuration of the ion in the two valence states also leads to somewhat different interatomic instances inside this shell.

If these surfaces are plotted vs. N atomic coordinates, they will intersect on some $(N-1)$ -dimensional "line" or surface. At the intersection surface, the atomic coordinates have values which represent a compromise configuration of solvent molecules, atmospheric ions, and coordination shell. The compromise is between the stabler atomic configurations of the reactants and those of the products.

A profile of the two surfaces and of their intersection is indicated in Fig. 1. The height of one valley relative to the other, and hence the height of the intersection surface relative to any valley, depends of course on the metal-solution potential difference.

Because of the assumed absence of electronic interaction between the ion and the electrode, there will be no electron transfer if a system moving on one potential energy surface reaches the intersection region. The system merely stays on the surface appropriate to this electronic configuration. During the reverse fluctuation, the system again passes through this intersection region, always staying on the initial potential energy surface, and reverts to the stable atomic configurations of the latter.

Let us consider next the case of a weak electronic interaction between an ion and electrode. Such a weak interaction hardly affects the two potential energy surfaces. In the usual quantum mechanical fashion* this interaction does remove the degeneracy at the intersection of the two surfaces as indicated in Fig. 1, so that we no longer have an intersection. The lower of the two new surfaces at this region has a potential energy less than that of the intersection surface at the same atomic coordinates. It is less by the resonance energy. The behavior of the system on passing through this region of atomic coordinates, that is, on passing through this $(N-1)$ -fold dimensional surface, will depend on the magnitude of this resonance energy. If it is sufficiently large (about 1 kcal/mole), a system passing through this region and initial residing on the lower surface to the left in Fig. 1 will remain throughout on the lowest surface and end up on the lowest surface to the right. We see from Fig. 1 that an electron transfer has been effected because of this atomic motion in much the same way as the usual chemical reactions occur.

*If ψ_I denotes the electronic wave function for one of the two electronic states in the hypothetical zero-interaction case of Fig. 1, and if ψ_{II} denotes the other, ψ_I and ψ_{II} are functions of the atomic coordinates. They describe not only the motion of the electrons of the central ion but also those in the molecules outside this ion. For example, they describe the electronic polarization of the solvent by a central ion in each of the two valence states. Because of the ionic charge difference in the two states, this electronic polarization is quite different.

The weak interaction can be shown from quantum mechanics to produce two new wave functions. In the quantum mechanical adiabatic case, which is the major subject of this paper, these two wave functions are essentially $\psi_I + \psi_{II}$ and $\psi_I - \psi_{II}$ for atomic coordinates on intersection surface. Because of the weak interaction, these wave functions have energies slightly different from those of ψ_I and ψ_{II} , as indicated in Fig. 1. Since the wave functions $\psi_I \pm \psi_{II}$ describe the state of such a system better than ψ_I or ψ_{II} alone, one will have a lower energy than either ψ_I or ψ_{II} – lower by the resonance energy in the usual manner, as indicated in Fig. 1.

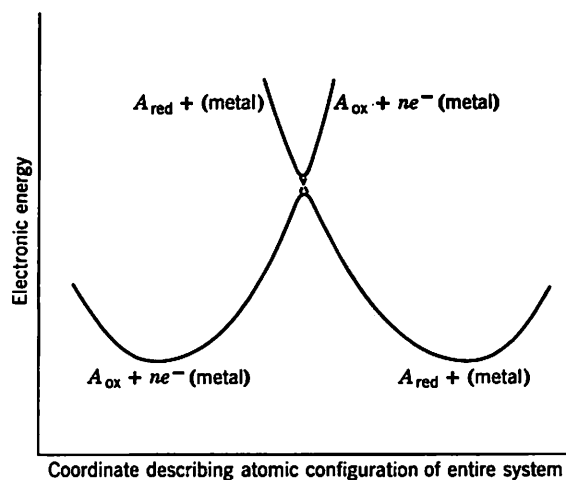


Fig. 1. Cross-section of two intersecting electronic energy surfaces in N -dimensional atomic configuration space. Electrochemical process: $A_{ox} + ne^{-}(\text{metal}) \longrightarrow A_{red}(\text{metal})$. The intersecting dashed lines indicate zero overlap of the electronic orbitals of A and metal.

Consider next the case of extremely small resonance energy, that is, extremely small electronic interaction between ion and electrode. Such interaction is only slightly different from the zero electronic interaction. On passing through the intersection region, the system would tend to stay on the same surface that it stays on in the zero interaction. That is, if the system is started on the lower surface in the left of Fig. 1, this atomic motion would tend to carry it to the upper surface on the right and conversely during the return fluctuation. We see that when the interaction is extremely weak, the system "jumps" from the lower surface to the upper one at the intersection. Actually, in the intersection region, the concept of potential energy surfaces and the adiabatic Born-Oppenheimer approximation on which it is based break down to this extent when the interaction is so extremely weak. During a passage through this region there is, however, a certain probability that the system will not "jump" and hence a certain probability that the system will end up on the lower surface to the right in Fig. 1 and so have effected an electron transfer.

In accordance with the customary terminology, we may call these electron transfer mechanisms involving *weak* interaction and *extremely weak* interaction the quantum mechanically adiabatic and non-adiabatic mechanisms, respectively. The practical quantitative treatment will naturally employ a somewhat different approximation for each case: At present, the few existing data on pre-exponential factors in rate constants for electron transfer tend to favor the adiabatic mechanism.

We next consider how to formulate this qualitative discussion of electron transfer mechanisms in a quantitative way. As mentioned earlier, the quantitative details themselves are described elsewhere(2).

Quantitative Formulation

As previously observed, the intersection surface in the zero-interaction case is a $(N-1)$ -dimensional surface. From Fig. 1, we see that it is essentially the same surface that in the weak interaction case defines a potential energy maximum along the reaction path separating valleys of stable configurations of the reactants from those of products. To obtain an equation defining the atomic coordinates on the latter surface, it is sufficient, therefore, to consider the case of zero interaction.

With zero interaction, along the intersection surface the potential energy of the electronic state having the electronic configuration of the reactants equals that of the state having one electronic configuration of the products. The potential energy of either state relative to its minimum can be expressed, in principle at least, in terms of displacements of atomic coordinates from those at its energy minimum. The potential energy difference of the two minima can, in turn, be written in terms of the activation overpotential and the average energy (really free energy) of each state above its potential energy minimum (2). By combining these relations we obtain an equation that must be satisfied by the atomic coordinates along the intersection surface.

Having found an equation defining the intersection surface, we can then calculate properties such as the free energy of a system whose atomic coordinates lie on the intersection surface. By computing

also the free energy of the reactants and treating the atomic motion through the intersection surface as simple translation, we can use the absolute reaction rate method to calculate the current and its dependence on activation overpotential.

Such a formulation would assume a comparatively simple form if only simple harmonic forces were involved. While this force law might be approximately true for changes in atomic configuration in the coordination shell of the ion, it is clearly inadequate to describe the complicated atomic motions occurring in the surrounding solvent.

There is, however, another approximate way of estimating the latter interactions. Accompanying the change of ionic and electrode charges there is a reorganization of the nearby solvent molecules and ion atmosphere. Commonly, the free energy of these microscopic ion-solvent ionic interactions has been computed (relative to the free energy of the system when the charge on the control ion is zero) by employing the usual macroscopic electrostatic equations for a dielectric. The use of these equations can be shown to assume, however, that only the stabler atomic configurations contribute to the macroscopic functions. (The charge on the central ion and the electrode is tacitly assumed in these equations to dictate a certain dielectric polarization, ion atmosphere, and electrostatic potential at each point of the medium. This assumption is appropriate only when the stabler atomic configurations are involved.) Accordingly, these electrostatic equations cannot be used to compute the properties of a system existing on some region in the upper reaches of the potential surface of this electronic state, but only those of a system near its minimum. In particular, they cannot be used in the intersection region.

In an arbitrary upper region (particularly near the potential energy minimum of the intersection surface), however, the average behavior of the atomic configurations in a particular electronic state will be assumed to give rise to an arbitrary dielectric polarization function and ion atmosphere. Only in the vicinity of the potential energy minimum of this electronic state (i.e., far below the intersection surface) does this polarization function and atmosphere take on the "equilibrium" values dictated by the charges on the central ion and on the electrode. Equations describing the free energy of a system having an arbitrary polarization function and ion atmosphere have been derived earlier (6) and applied to the present problem (1, 2).

Along the intersection surface of the zero-interaction case, the two electronic states have the same atomic coordinates and therefore the same atomic plus orientation dielectric polarization function. Again, the free energy associated with these atomic configurations on this surface is the same for each of the two electronic states. A system in either electronic state, constrained to move on this surface, has the same potential energy function in each electronic state and hence the same average total energy as well as the same entropy.

Using the usual electrostatics, we next compute the free energy (relative to zero charge on the central ion) of each electronic state. The average behavior of each state naturally arises from the stable atomic configurations of that electronic state. The free energy difference of these two electronic states can next be expressed in terms of the activation overpotential. From all of these results, an equation for the dielectric polarization and ionic atmosphere of a system residing on the intersection surface was obtained (2).

The values of these functions on the upper reaches of this intersection surface differ from those on its lower reaches. We are naturally interested in the latter. By a procedure involving a minimization of the free energy of a system on the intersection surface, subject to the above equation of restraint, unique values were found for the dielectric polarization and ion atmosphere at each point of the medium. Substitution of these values into the appropriate expression resulted in an equation for the free energy of formation, from the reactants, of a system existing on the intersection surface. We have seen earlier that this term must be equal to that for formation of a system existing on the potential energy maximum in the weak interaction case.

Incorporation of these results into an absolute rate theory led to the deduction (2) of an equation for the current density i as a function of the activation overpotential η_a and various properties.

$$i = neF A' \exp (-\Delta F^*/kT) \quad (5)$$

$$\text{where } \Delta F^* = w^* + m^2 \lambda/2 \quad (6)$$

$$-(2m+1) \lambda/2 = -ne\eta_a + w - w^* \quad (7)$$

$$\lambda = n^2 e^2 [(1/a) - (1/r)] [(1/D_{op}) - (1/D_s)] \quad (8)$$

In these equations w^* and w are the work required to bring the reactant and the product to the electrode, respectively; m and λ are defined by eq. 7 and 8; n is the number of electrons transferred; e is the unit of electronic charge; F is the Faraday; a is the ionic radius (including the region occupied by the coordinate shell); r is twice the distance between the electrode and the center of the ion; D_{op} is the square of the refractive index of the solvent and D_s is the static dielectric constant; A' is of the order of $1 \cdot 10^4$ to $5 \cdot 10^4$ cm/sec². We note that the activation overpotential η_a used here is one which is zero for equilibrium at the given salt concentration.

When the activation overpotential is small in relation to the free energy barrier prevailing at zero overpotential, m^2 in eq. 6 can be expanded about its value at $\eta_a = 0$, and we obtain a linear dependence of ΔF^* on η_a :

$$\Delta F^* \approx \frac{w + w^*}{2} + \frac{\lambda}{8} + \frac{(w - w^*)^2}{2\lambda} - \frac{ne\eta_a}{2} \left[1 + \frac{2(w - w^*)}{\lambda} \right] \quad (9)$$

We see from this equation that if the salt concentration is sufficiently large for w and w^* to be small, the transfer coefficient should equal 0.5.

Additions in Progress

At present, work is in progress to treat the kinetic energy of the polarization vectors of the medium in a somewhat more detailed fashion and so to obtain a more detailed quantitative description of passage through the energy intersection surface. Further extensions include incorporating into the formalism the configurational changes involving any bond stretching or compressing in the coordination shell, and a treatment of the nonadiabatic case. As a first approximation, the current in the nonadiabatic case would be expected to be approximately the value deduced earlier multiplied by a factor less than unity describing the probability of change of electronic configuration per passage through the intersection surface.

The Theory and Franck-Condon Applications

The Franck-Condon principle has been applied in qualitative discussions of electron transfers in solution and at electrodes in a variety of ways. In this concluding section we examine these applications and their relation to the theory outlined previously.

According to the Franck-Condon principle, one valence state can be formed from another (in the present case by electron transfer with the electrode) only as a result of a vertical transition, that is, one occurring without change of the positions and momenta of the atoms. From Fig. 1 we see that for any of the *probable* atomic configurations of a given valence state this can only occur through the absorption of radiation, such as light. Certain applications of the principle to the nonradiative electron transfer mechanism have ignored this requirement and have failed, thereby, to recognize the need for the reorganization of atomic configuration described earlier.

We also see from Fig. 1 that the only region where a nonradiative electron transfer becomes possible with comparatively little or no change in atomic configuration and momenta is at the intersection region. Thus, when more correctly applied in this way, the Franck-Condon principle points up the need for the reorganization of atomic configuration prior to electron transfer and indicates the region of atomic configurations where a transfer can occur. On the other hand, since the principle emphasizes electron transfer at fixed configuration and momenta, it does gloss over the role played by the atomic motion itself in effecting an electron transfer when the mechanism is an adiabatic one.

There is another type of application of this principle which has occasionally appeared in the literature of electron transfers and which has some resemblance to the second application, but which is incorrect. In this third application, potential energy curves are plotted as a function of the distance between the two species, but they are plotted in such a way that in every other respect the atomic configuration of each state is one of the "equilibrium" or probable configurations for that state. Since the probable configurations for one electronic state are quite different from those of the other, such a plot compares the electron energy of two electronic states at two entirely different atomic configurations. Any application of the Franck-Condon principle to this plot, therefore, is not meaningful.

CONCLUSIONS

In conclusion, we have attempted to show in this chapter how the adiabatic electron transfer mechanism can be formulated qualitatively in a way which is intimately related to the common mechanism of chemical reactions and of other types of electrochemical processes. Because of the absence of bond ruptures, this mechanism is unique at the present time, however, in that a quantitative treatment can be offered which is rather free from arbitrary parameters normally needed to treat bond rupture mechanisms.

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DISCUSSION

Dr. R. Marcus: It would be desirable to have more data comparing the exchange currents of simple electron transfers with rate constants of the corresponding chemical electron transfer rate constants (the latter normally determined by isotopic exchange and spin resonance techniques). Some parallelism would be expected between these two sets of rate constants, particularly if any necessary corrections are made for ionic repulsions or attractions.¹ For example, the electron transfer rate of $\text{Fe}(\text{CN})_6^{-3} - \text{Fe}(\text{CN})_6^{-4}$ is faster than $\text{Fe}^{+2} - \text{Fe}^{+3}$ electrochemically and chemically. The rate of $\text{Co}(\text{NH}_3)_6^{+2} - \text{Co}(\text{NH}_3)_6^{+3}$ is slower than that of $\text{Co}(\text{en})_3^{+2} - \text{Co}(\text{en})_3^{+3}$ in both cases. Since the rate of $\text{MnO}_4^{-1} - \text{MnO}_4^{-2}$ is fast chemically, we might expect it to be fast electrochemically also.

¹ cf. similarity of the theoretical equations derived for these processes: R. Marcus, *Can. J. Chem.*, **37**, 155 (1959).

Dr. R. Parsons: I have several brief points to make. First, since you mentioned the permanganate-manganate reaction, you may be interested to know that we have recently done some preliminary experiments on this reaction at a rotating disc electrode of platinum. It does appear to be a fast reaction, although there are complications such as the deposition of manganese dioxide.

Second, is it possible to calculate from your theory a limiting rate constant to compare with the kinetic theory value that was calculated a few years ago by Randles?¹ In other words, can you put the heat of activation equal to zero and calculate a minimum entropy of activation?

Third, do you, in general, predict that α will vary with the overpotential?

Finally, would you like to comment on the recent paper by Hush² in relation to your work?

¹ J. Randles, *Trans. Faraday Soc.*, **48**, 828 (1952).

² N. Hush, *J. Chem. Phys.*, **28**, 962 (1958).

Dr. R. Marcus: At sufficiently high overpotentials, ΔF^* becomes zero and the limiting rate constant of an adiabatic mechanism becomes essentially that computed by Randles. Incidentally, eq. 5 applies only for $\Delta F^* \leq 0$. For $\Delta F^* > 0$, the rate constant equals A' (i.e., $i = neFA'$).

When an ion-electrode repulsion predominates, we can conceive of a case of essentially zero activation energy and large negative entropy of activation (see my discussion of Dr. Randles' remarks, to follow). Sufficiently high overpotentials would produce the limiting rate constant here as well, by making ΔF^* zero.

At low overpotentials, there would be essentially no variation of α with overpotential, except insofar as a change in metal-solution potential difference can effect the work required to transport each valence state of the ion to the electrode (see eq. 9).

Both Hush and I have concentrated on the adiabatic mechanism for electron transfer. However, certain aspects of Hush's very interesting treatment are not consistent with the quantum mechanical implications of the weak electronic interaction assumptions — implications described in detail in this chapter.

Professor J. Randles: There are two questions that I would like to ask you. The first probably stems from a misunderstanding on my part. The overvoltage enters in eq. 6 through the term m , and m appears squared in the expression for the free energy of activation. I do not quite understand this because the overvoltage would be expected to be to the first power in the energy of activation. Secondly, I was very interested in the point about the entropy of activation. You implied that the lowering of the reaction rates because of repulsion of the reactant from the electrode can be interpreted as an adverse entropy of activation. Since repulsion results from the interaction of an electrode with ions of like charge, we might expect the solvent molecules at the interface to be more disordered than when the charge of the electrode and ions are similar. With like charges, the solvent molecules do not know which way to turn. I would expect that this would represent an increase in entropy, and therefore, not a negative entropy of activation which is what is required.

Dr. R. Marcus: The m^2 term in eq. 6 can, for low overpotentials, be expanded about its value at zero overpotential. We then obtain a linear dependence of ΔF^* on m and hence on overpotential (see eq. 9 of text).

In reactions between ions of like sign, the enhanced local electric field causes an ordering of the solvent molecules and so produces the large negative entropy of activation observed experimentally for such reactions. (The free energy of coulombic repulsion, $\Delta F = q^2/Dr$ is, for water, largely a $T\Delta S$ term. The ratio of this $T\Delta S$ to $-\Delta F$ is $T\left(\frac{\partial \ln D}{\partial T}\right)$, which for water at room temperature is 1.1.) We would expect a similar situation to prevail in ion-electrode repulsions.

Dr. B. Conway: I would just like to make two comments on Dr. Marcus' interesting paper. First, with regard to the question of the layer of water molecules at the interface, I think that for a positive ion at a negative electrode or a negative ion at a positive electrode, any water layer adsorbed at the electrode can be shared in the solvation sheath of other ions which are near to the electrode in the double layer. (The situation is analogous to that involved in ion-pair formation with an hydrated anion and cation.) If you have a positive ion near a positive electrode, you may really have a barrier. We considered this problem first in trying to think about ion-transfer steps in metal deposition¹ where we have a somewhat similar situation and want to know what happens as the ion is transferred out of its solvation sheath into some position on a metallic surface. What is your opinion concerning this situation?

The second point is more in the nature of a comment, and that is with regard to what actually constitutes the change of energy in the potential energy curves. In the calculations on hydrogen evolution kinetics and in our calculations on metal deposition,¹ we have attributed the change of potential energy largely to contributions from the change of energy of the solvation complex as we pull the ion out from it. One interesting point which I want to make in this connection is that we have found that there are important differences in the shape of the potential energy curve if we calculate it by reference to a detailed electrostatic model of the solvation shell of the ion or if we just take the total solvation energy and introduce it into a Morse function. The latter procedure appears to be more or less correct for a proton-transfer step where a proton is just pulled out from a single entity, H_3O^+ , the secondary solvation energy of this entity being relatively small compared with the "proton affinity" of water. With regard to ion-transfer in metal deposition, the calculations based on the detailed electrostatic interaction between the ion and solvent molecules yield a much flatter curve¹ than the curve based on a simple Morse function.

We have been puzzled a little about the role of primary solvation energy in this kind of problem. As you know, Hush² has regarded this as relatively unimportant in determining the activation energy of adiabatic charge transfer processes. To what extent do you have to consider it in your calculations?

¹ B. Conway and J. Bockris, *Proc. Roy. Soc. (London)*, A 248, 394 (1958).

² N. Hush, *J. Chem. Phys.*, 28, 962 (1958).

Dr. R. Marcus (partially communicated): It would seem reasonable to assume that such water molecule bridges could form, and that they could act as intermediate states, at least in some high activation energy reactions. Incidentally, there is some kinetic evidence for water molecule bridges in some special cation-cation reactions.¹

In regard to the desolvation problem in cation deposition and hydrogen overvoltage, the basic ideas described in this paper would have some applicability, although the specific model would naturally differ in detail from that of the simple electron transfer discussed here. If, for example, the valence-bond method were used to calculate potential energies in these "bond rupture" examples, we might at

first neglect the "resonance energy" of the (usually two) bond structures and compute the potential energy of each, recognizing that the usual electrostatics could not be used reliably to estimate approximately some of the interactions for reasons discussed in the text. Modifications such as those referred to there would be needed.

We could next determine the region where the intersection of these two potential curves has a minimum and then compute the "resonance energy" in this vicinity. I have not examined how we would take the preceding precautions into account in the calculation of such a "resonance energy," but they may perhaps have a less serious effect on this quantity.

In an electron transfer where the two valence states of an ion have essentially the same values of corresponding interatomic distances in their coordination shells, I believe that the re-orientation of the solvent molecules becomes of major importance (see text and Fig. 1). The solvation of the two ionic charges is quite different, and a corresponding re-orientation must occur, partly before and partly after electron transfer.

¹ H. Taube, *Can. J. Chem.*, 37, 155 (1959).

Professor J. Bockris (communicated): The construction of potential energy surfaces, in preference to profile diagrams, is clearly desirable, and Conway and I once entered such an investigation. However, the numerical uncertainties are greater than in the profile method and it seems questionable whether the realism and accuracy with which surfaces can be constructed justifies the labor.

Dr. Marcus has discussed the potential energy functions for several electron transfer reactions. Increased difficulty in this calculation arises if the ion transfer reaction is considered, and this appears to be the appropriate one in consideration of the transfer of a hydrated ion to the adionic state on the surface of the electrode.^{1,2}

¹ B. Conway and J. Bockris, *Proc. Roy. Soc. (London)*, A 248, 394 (1958).

² H. Gerischer, *Z. Elektrochem.*, 62, 256 (1958).

Dr. R. Marcus (communicated): In the difficult case of "bond rupture" electrode processes such as hydrogen overvoltage and cation deposition, the uncertainties in present knowledge hardly justify, as you say, the labor involved in a very detailed calculation. However, some minimization procedure is necessary, even in these cases, to locate the saddle point on the energy surface, taking into consideration some factors mentioned in my answer to Dr. Conway's query.

In simple electron transfer, on the other hand, many atomic coordinates contribute importantly to the reaction and have to be taken into consideration. Fortunately, because of the use of the simple harmonic force law inside a coordination shell and because of the use of "nonequilibrium macroscopic functions" for computing the effect of interactions outside this shell, simple expressions are obtained for the final answer (e.g., eq. 5-8 of text).

Dr. E. Nightingale: On previous occasions, Dr. R. J. Marcus and several others have suggested the possibility of electron tunneling in electrode processes. Do you now feel that this is a probable mechanism?

Dr. R. A. Marcus: There are perhaps two types of experimental data which bear on the electron tunneling problem of R. J. Marcus, Zwolinski, and Eyring.

The first of these lies in the pre-exponential factors in the Arrhenius expression for chemical and electrochemical electron transfer rate constants. This factor differs from the kinetic theory value by a factor approximately equal to some tunneling probability per collision, multiplied by $\exp(\Delta S^*/R)$, where ΔS^* is an activation entropy largely associated with ion-ion and ion-electrode coulombic attractions or repulsions. For electron transfer between ions of low ionic charge, ΔS^* is relatively small and becomes increasingly so at high salt concentration. The data for $\text{MnO}_4^- - \text{MnO}_4^{2-}$ indicate a tunneling factor of the order of unity. The data for $\text{Fe}(\text{CN})_6^{3-} - \text{Fe}(\text{CN})_6^{4-}$, corrected approximately for this ΔS^* , indicate that the factor lies between 0.01 and 1. The electrochemical rate constants at high salt concentration suggest a value perhaps of the order of 0.1 or 1.

A second type of information may perhaps be inferred from spin-spin interactions between adjacent hydrated cations in crystals. This interaction may be in part a rough measure of how much the electronic orbital of the cation hydrate tends to spread itself outside the hydrate and hence would bear

some relationship to the "tunneling." The magnitude of the interaction would appear to suggest a factor of the order of 0.1, but a detailed analysis of this interpretation is probably needed before such a conclusion can be drawn.

Dr. E. Nightingale: It does appear that the role of electron tunneling is still open to question.

(Communicated): We recently have calculated the probability of electron exchange between two hydrated ions such as Fe^{+2} and Fe^{+3} using the simple hydrogen molecular ion model and a generalized 3d wave function. These data indicate a finite probability for electron transfer which suggests that the energy barrier may not be so large as to require electron tunneling. The reorganization energy for the hydration spheres, however, was not included in the calculation.¹ It should be emphasized, however, that the energy barrier or reaction rate for the most probable mechanism for exchange between hydrated ions, namely hydrogen atom transfer, cannot be calculated *a priori*.

¹ See W. Reynolds, *J. Chem. Phys.*, 29, 851 (1958).

Dr. R. Brodd: In your electrostatic calculations, you indicate that these calculations are not always valid. Does this mean that you do not use a Lorentz field in applying your equations? I note that you did use the optical dielectric constant.

Dr. R. Marcus: The limitation of electrostatic calculations which assume a dielectric continuum lies in their macroscopic nature; they are rigorously true when we are describing the behavior of a medium in which the electric field varies slowly with position (as for example when describing the interionic interactions of the Debye-Huckel theory in extremely dilute solutions where the ions are far apart). In the immediate vicinity of an ion, the field varies quite rapidly with distance, and it is interesting that the macroscopic equations still appear to provide a "reasonable" approximation to such charge-solvent interactions.

The Lorentz field (which is used in relating the dielectric constants of a medium to the microscopic properties of its molecules) does not enter the present calculation in a significant way. Here, we treat the dielectric as forming a continuum of arbitrary to-be-determined polarization, and do not have to treat in this approximation its relation to its microscopic properties. While the dielectric does exert a field on the ion-electrode system and does polarize the ion somewhat, this polarizing effect on the energy appears to be relatively small.