Quantum Chemistry of Electrode Processes.* I. General Relations for Electron Exchange between Electrode and Electroactive Species under Equilibrium and Nonequilibrium Conditions

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It is assumed in this paper that at the electrode–solution interface there is molecular order of the electroactive species resembling solid-state order. Specifically, it is assumed that next to the electrode is a layer of adsorbed neutral solvent molecules which are also ligands coordinated to the ions found in the interface. The mechanism of electron transfer from the electrode to the ion or the reverse from the ion to the electrode is assumed initially to involve a transition from either the electrode or the ion to the solvent molecule. This is followed by a transition of the electron from the solvent molecule to either the ion or the electrode. The two transitions involved in the net transfer of an electron across the interface are considered analogous to the charge-transfer mechanism of spectroscopy. The wavefunctions representing the system at the interface are then of the same form as the charge-transfer wavefunctions given by Mulliken.

By considering the radiationless transition probabilities for the electron transitions in the interface system at the electrode, it is found that the usual current expressions result. By imposing the condition of zero net current at equilibrium the Nernst equation results. By further considering the polarization of the electrode under nonequilibrium conditions as a perturbation of the energy levels of the system, it is found that with the proper identification of terms the current expression for the polarized electrode results.

I. INTRODUCTION

THE presence of an electrode in a solution of an electrolyte which is a redox system allows for the possibility of heterogeneous electron exchange between the two phases. The condition of thermodynamic equilibrium requires that there be no excess charge in the interface, that there be equality of the chemical potential in both phases, and that the current in one direction equals the current in the reverse direction (exchange current). Within the interface there exists a potential gradient which is a result of the electrical potential difference between the two phases. This potential difference presents a potential barrier through which, or over which, the electron must pass in getting from one phase to the other.[1]

The presently accepted model of the electrical double layer formed at the interface of the electrode and the solution consists in part of an oriented neutral adsorbed layer of solvent molecules which is at least one monolayer thick (in the absence of specific adsorption of the ions of the electrolyte).[2] The distance of closest approach of a charged ionic species to the electrode is at the plane of the adsorbed neutral monolayer. The Gouy–Chapman theory, with modifications due to Stern, Frumkin, and others, predicts the potential and the differential capacitance in the double layer as a function of the distance from the electrode plane.[2] The expression for the current passing from one phase to the other is derived on the basis of a kinetic treatment of the reacting species at the electrode.[3] As this model is statistical in nature it does not consider the microscopic ordering of the molecules and ions at the interface and cannot explain the mechanism of electron transfer between the electrode and ion on a molecular scale.

Previously Gurney[4] has treated the passage of the electron from one phase to the other through the potential barrier on the basis of a tunnel effect. Gerischer[1] has extended the treatment and presented current expressions for the simple reaction of the type

$$M^{(z+1)+}\cdot\text{solv.}+e^-_{\text{metal}}=M^{z+}\cdot\text{solv.}$$

From the above reaction the density of states of the occupied and unoccupied levels in the solvated ions can be determined by the work involved in converting one form to the other. The work needed to bring an electron from infinity and place it in solution to occupy the lowest state without change in the solvate structure defines the energy of the unoccupied states. The requirement that the solvent structure does not change is a result of the Franck–Condon principle. The energy levels of the occupied states are defined by the reverse process: that being the work needed to remove an electron from the solvated ion, without change in the solvate structure, and the subsequent removal of the electron to infinity.

Each ion in solution is surrounded by solvent molecules which are associated with the ion through ion–

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[1] H. Gerischer, Z. Physik. Chem. (Frankfurt) **26**, 223 (1960); **27**, 48 (1961).

[2] See, for example, R. Parsons, in *Modern Aspects of Electrochemistry*, edited by J. O'M. Bockris (Butterworths Scientific Publications Ltd., London, 1954), Vol. 1.

[3] See, for example, J. O'M. Bockris, in *Modern Aspects of Electrochemistry*, edited by J. O'M. Bockris (Butterworths Scientific Publications Ltd., London, 1954), Vol. 1.

[4] R. W. Gurney, Proc. Roy. Soc. (London) **A134**, 137 (1931).

dipole and other interactions. Due to thermal agitation the solvation structure can fluctuate, and the distribution of solvate structures can be represented by a Boltzmann distribution. With each structure of the solvated ion there is a corresponding energy state in the redox system, and, hence, the density-of-states functions for the redox system.

As the electron-transfer process at the electrode is radiationless, the condition for tunneling is that the electron makes transitions between equi-energetic states in the electrode interface. If the density-of-states functions for the redox system are signified by $D_{ox}(E)$, $D_{red}(E)$, and the density-of-states functions for the metal electrode by $N_0(E)$, $N_u(E)$ for the occupied and unoccupied levels, respectively, the expressions for the total cathodic and anodic currents are given by[1]

$$j^- = e_0 \int_{-\infty}^{\infty} \nu^-(E) N_0(E) D_{ox}(E) dE$$

and

$$j^+ = e_0 \int_{-\infty}^{\infty} \nu^+(E) N_u(E) D_{red}(E) dE,$$

where $\nu^-(E)$ and $\nu^+(E)$ are the penetration coefficients in the anodic and cathodic directions, and e_0 is the electronic charge. By using the density-of-states functions for the redox electrolyte defined above, Gerischer has shown that an electron in that system obeys the Fermi–Dirac statistics, and further that the Fermi level of the redox system is defined as[1]

$$E_{F,redox} = {}^0E_{F,redox} + kT \ln(c_{red}/c_{ox}),$$

where ${}^0E_{F,redox}$ is defined as the energy difference between the ground-state vibrational reduced ion level and the ground-state vibrational oxidized ion level.

Although the barrier penetration model predicts the mode of the over-all electron transfer, it does not account explicitly for the effect of the geometry of the solvate molecules about the ion, nor does it account explicitly for the individual effect of the energy levels within the solvent upon the magnitude of electron transfer across the interface. In the following sections the nature of the solvate structure and the solvate energy levels is discussed, and a simple model proposed which focuses upon the effects of these individual properties on the process of electron transfer at the electrode.

II. SYSTEM

In constructing a molecular model for the electrode interface which will explain the mechanism of electron transfer, it is assumed that there is molecular order resembling solid-state order in the neutral solvate species which, in the absence of other more preferentially adsorbed substances, makes up the neutral adsorbed layer. This molecular order is assumed to extend several monolayers out into the bulk of the solution. The matrix of ordered solvate molecules at the electrode makes up the basis of a semiconductor material with the associated formation of conduction and valence states in the matrix. The ions to be reduced or oxidized occupy sites in the ordered matrix and behave as impurity sites.

The semiconductor analogy is limited, however, because the dimensions of the ordered system extending out from the electrode are small. The order which is assumed to exist at the electrode will vanish rapidly as one moves away from the electrode. Thus, the direct application of the current expressions for the solid-state situation to electrode phenomena will break down and one must resort to a more limited approach to the problem. The approach to be taken in this paper is to consider the detailed order of the solvent molecules and ions at the electrode surface and then to consider the stepwise transference of the electron through the regions in the interface which presently is defined.

Considering the detailed arrangement of the species in the ordered layer making up the interface, the assumption is made that the nature of the order is determined as a result of the combination of three factors. These three factors are (i) the adsorptive and (ii) electrostatic fields in the interface, and (iii) the geometry or coordination of the solvate molecules around the ions in the bulk of the solution. In the interface the order assumed by the solvate molecules and the ions is that order which minimizes the lattice energy under the equilibrium concentration conditions dictated by the Nernst equation. The geometry of the solvate spheres about the ions in the bulk of the solution is in effect an initial condition in determining the type of order of the species at the electrode. It is reasonable to assume that the coordination of the solvate sphere of the ion in excess under an equilibrium concentration for the entire system exerts the greatest influence upon the order of species in the interface. For the special equilibrium condition of equal concentrations of all ionic species, the order assumed at the interface is dependent upon the relative coordination energies of the ionic species. The coordination of that species having the lowest bulk-solution–solvate-sphere coordination energy predominates. Although the same for both ionic species, the coordination of solvate spheres at the electrode is not the same as the coordination found in the bulk of the solution, due to the combined effect of the adsorptive and electrostatic fields.

The process of forming the interface requires that the solvation spheres about the ions must change, as indicated, in order that the ions be incorporated into the ordered layer. The change in energy needed to accomplish this process can either be given up by, or to, the bulk of the solution. Under nonequilibrium conditions the formation of an excess of either the oxidized or reduced species in the ordered layer creates a condition whereby an attempt is made by the system to

regain the equilibrium distribution. Thermal energy from the bulk of the solution can be exchanged with the ordered layer to change the solvate structure of the product species, which has just gained or lost an electron. This causes layer breakdown with subsequent departure of the product ion surrounded by solvate molecules with the coordination characteristic of that ion in the bulk of the solution. Once a product ion—with its new solvate structure—leaves the electrode, another reactant ion can move in and change its solvation sphere to assume the equilibrium coordination found at the electrode.

As it has been assumed that the ionic species at the electrode–solution interface preserve a solvation environment, it is reasonable to expect that the neutral adsorbed layer of solvent molecules next to the electrode corresponds to a part of the solvation structure around the ions in the interface. It is further assumed in the treatment that metal–metal-ion association—which would be the case if the ions reacted directly at the metal surface of the electrode—does not take place. Establishing these conditions leads to a model for the electron transfer across the interface which can best be represented by analogy to the charge-transfer mechanism in spectroscopy. With such a model two charge-transfer transitions need to be considered. The first takes the electron from the electrode to the solvent sphere of the ion, and the second, from the solvent sphere of the ion to the ion itself. Under most circumstances the transitions are radiationless.

III. ELECTRONIC STATES

It is known from kinetic studies of reactions at the electrode that, in most instances, the barrier to electron transfer across the electrode interface is very low. It is reasonable that, for a low barrier, the associations between substituents in the interface are strong and that a mechanism analogous to the spectroscopic charge-transfer mechanism is justified. The choice of wavefunctions for the low-barrier case is then

$$\psi_{\mathrm{I}}=a\phi(\mathrm{el})\phi(\mathrm{s})+b\phi(\mathrm{el}^{+}\leftrightarrow\mathrm{s}^{-}),$$

$$\psi_{\mathrm{II}}=a'\phi(\mathrm{el}^{+}\leftrightarrow\mathrm{s}^{-})-b'\phi(\mathrm{el})\phi(\mathrm{s}),$$

$$\psi_{\mathrm{III}}=c'\phi(\mathrm{i}^{(z+1)+}\leftrightarrow\mathrm{s}^{-})-d'\phi(\mathrm{i}^{z+})\phi(\mathrm{s}),$$

$$\psi_{\mathrm{IV}}=c\phi(\mathrm{i}^{z+})\phi(\mathrm{s})+d\phi(\mathrm{i}^{(z+1)+}\leftrightarrow\mathrm{s}^{-}). \quad \text{(III.1)}$$

These wavefunctions are of the form used by Mulliken in his treatment of charge-transfer spectra.[5] The basis functions for the above charge-transfer functions (perturbation corrected) are $\phi(\mathrm{el})$, the surface-state metal wavefunction for the electrode; $\phi(\mathrm{s})$, the lowest unfilled molecular orbital (MO) of the solvent; $\phi(\mathrm{i}^{(z+1)+})$ and $\phi(\mathrm{i}^{z+})$, the crystal-field orbitals of the oxidized and reduced states of the ion; and $\phi(\mathrm{i}^{(z+1)+}\leftrightarrow\mathrm{s}^{-})$ is the charge-transfer complex wavefunction. The functions ψ_{II} and ψ_{III} are both excited-state wavefunctions, the former constructed with respect to the electrode, and the latter with respect to the ion. The reason for this particular choice of wavefunctions is seen as follows. Moving an electron from the ion or the electrode to the solvent molecule involves an expenditure of energy. The reverse movement of the electron from the solvent to the ion or the electrode results in the regaining of energy. The existence of an electron in the solvent molecule as a result of a transition from either starting point—the electrode or the ion—constitutes a metastable state. Furthermore, the continuity condition imposed by the choice of model requires that the link between the two transitions involved be through the excited state.

The wavefunctions, $\phi(\mathrm{el})$, $\phi(\mathrm{s})$, $\phi(\mathrm{i}^{z+})$, $\phi(\mathrm{i}^{(z+1)+})$ and $\phi(\mathrm{i}^{(z+1)+}\leftrightarrow\mathrm{s}^{-})$, which are used as basis functions in the charge-transfer wavefunctions [Eq. (III.1)], are perturbation corrected. The electrode wavefunctions are eigenfunctions of the Hamiltonian

$$\mathcal{H}=H_{\mathrm{el}}^{0}+V_{\mathrm{i}}+V_{\mathrm{ads}}, \quad \text{(III.2)}$$

where H_{el}^{0} is the Hamiltonian of the unperturbed surface-state wavefunctions of the metal electrode. V_{i} is the electrostatic potential due to the ions at the electrode and is given by $\sum_j(z_j e_0/r_{\mathrm{el},j})$, where z is the charge on Ion j, and $r_{\mathrm{el},j}$ is the ion–electrode distance. Finally, the perturbation due to the adsorption of the solvent (or any other substance) on the electrode is given by V_{ads}. Likewise, the Hamiltonian for the solvent layer molecules is

$$\mathcal{H}=H_{\mathrm{s}}^{0}+V_{\mathrm{i}}+V_{\mathrm{el}}+V_{\mathrm{ads}}, \quad \text{(III.3)}$$

where H_{s}^{0} is the Hamiltonian of the free solvent molecule the eigenfunction for which is the lowest unfilled MO of the solvent. The effect of the electrostatic potential of the electrode is given by V_{el} which is due only to the metal atoms on the surface of the electrode in the absence of external polarization of the electrode. Finally, the crystal-field orbitals are perturbed by the electrostatic potential of the metal ions on the surface of the electrode and the Hamiltonian is

$$\mathcal{H}=H_{\mathrm{i}}^{0}+V_{\mathrm{el}},$$

where H_{i}^{0} is the Hamiltonian for the free coordinated ion.

IV. ELECTRON TRANSFER—DETAILED MECHANISM

The magnitude of the current passed in either direction (anodic or cathodic) at the electrode depends upon the transition probability per second for the charge transfer from the solvent to the ion or the electrode. The probability that an electron occupies a MO of the solvent molecule as a result of a transition from the

[5] R. S. Mulliken, J. Am. Chem. Soc. 74, 811 (1953).

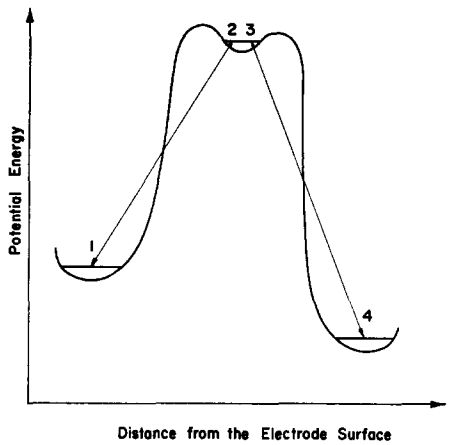

FIG. 1. The potential function at the electrode in the absence of an external electric field.

electrode is P_{I}. The probability per second that the electron is then transferred to the ion is P_{II}. The probability that a solvent MO is occupied by an electron as a result of a transition from the ion is P_{III}, and the probability per second of a transition of that electron to the electrode is P_{IV}. The net transition probability per second is given by

$$P(\mathrm{el}\rightarrow\mathrm{ion})=P_{\mathrm{I}}P_{\mathrm{II}}=P_f \tag{IV.1}$$

and

$$P(\mathrm{ion}\rightarrow\mathrm{el})=P_{\mathrm{III}}P_{\mathrm{IV}}=P_r. \tag{IV.2}$$

The total number of electrons making transitions in either direction is given by

$$w_n(\mathrm{el}\rightarrow\mathrm{ion})=N_{\mathrm{ox}}P_{\mathrm{I}}P_{\mathrm{II}} \tag{IV.3}$$

and

$$w_r(\mathrm{ion}\rightarrow\mathrm{el})=N_{\mathrm{red}}P_{\mathrm{III}}P_{\mathrm{IV}}, \tag{IV.4}$$

where N_{ox} is the number of ions in the oxidized state and N_{red} is the number of ions in the reduced state. It is more convenient for the purposes of studying electrode processes to express these total transition probabilities in terms of concentrations; thus

$$W_n=c_{\mathrm{ox}}P_{\mathrm{I}}P_{\mathrm{II}} \tag{IV.5}$$

and

$$W_r=c_{\mathrm{red}}P_{\mathrm{III}}P_{\mathrm{IV}}, \tag{IV.6}$$

where c_{ox} and c_{red} are the concentrations of the oxidized and reduced species in moles per liter. The current, then, in either direction is given by

$$j_f=A\mathfrak{F}W_f \tag{IV.7}$$

and

$$j_r=-A\mathfrak{F}W_r, \tag{IV.8}$$

where A is the area of the electrode surface in square decimeters and $\mathfrak{F}$ is the Faraday constant. The total current is

$$j=j_f+j_r. \tag{IV.9}$$

The exact nature of the transition probabilities P_f and P_r depends upon the particular set of wavefunctions used. In general, however, the forward and reverse transition probabilities can be expressed in terms of the Einstein transition coefficients and the Boltzmann equation for the population of a particular state. The various probabilities can be written

$$\begin{aligned}P_{\mathrm{I}}&=\exp(-\hbar\omega_{12}/kT),\\ P_{\mathrm{II}}&=B_{34}\rho(\omega_{43})+A_{34},\\ P_{\mathrm{II}}&=\exp(-\hbar\omega_{43}/kT),\\ P_{\mathrm{IV}}&=B_{21}\rho(\omega_{12})+A_{21}.\end{aligned} \tag{IV.10}$$

These relations hold for either photon- or phonon-induced transitions. The current expressions can now be written

$$j_n=c_{\mathrm{ox}}A\mathfrak{F}\{\exp(-\hbar\omega_{12}/kT)[B_{34}\rho(\omega_{43})+A_{34}]\}, \tag{IV.11}$$

$$j_r=-c_{\mathrm{red}}A\mathfrak{F}\{\exp(-\hbar\omega_{43}/kT)[B_{21}\rho(\omega_{12})+A_{21}]\}. \tag{IV.12}$$

In order to evaluate these expressions it is necessary to evaluate the Einstein transition coefficients for either the photon- or phonon-induced transitions. In this paper, though, we concern ourselves only with the phonon-induced transitions, leaving the discussion of photon-induced transitions for a future paper.

In general, the term which links the vibrational and electronic motion is given by[6]

$$\begin{aligned}&H'_{\mathrm{int}}\psi(x_\alpha)\psi(r_1)\\ &\quad=-\sum_\alpha(\hbar^2/m_\alpha)\partial\psi(x_\alpha)/\partial x_\alpha\partial\psi(r_1)/\partial x_\alpha,\end{aligned} \tag{IV.13}$$

where x_α is the nuclear coordinant and r_1 the electronic coordinate of the particle α. From this interaction term one can construct the matrix elements of interest in the transition probabilities. These matrix elements are given by

$$\begin{aligned}&(r,\,l/H'_{\mathrm{int}}/s,\,j)\\ &\quad=-\sum_\alpha\int dx_\alpha(\hbar^2/m_\alpha)\psi_r(x_\alpha)\psi_i(r_l)\\ &\qquad\times\partial\psi_s(x_\alpha)/\partial x_\alpha\partial\psi_j(r_l)/\partial x_\alpha.\end{aligned} \tag{IV.14}$$

It is found that in practice matrix elements of the type given by Eq. (IV.14) are difficult to evaluate. Ziman[6] has introduced a treatment, based on an intuitive approach, in which it is assumed the lattice vibrations move the molecules making up the lattice and hence change the lattice potential U by an amount δU. It is possible then to write the change in the lattice

[6] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962), Chap. 5.

potential as

$$\delta U=\sum_{l,b}\eta_{l,b}\partial U(r_i)/\partial\eta_{l,b}, \qquad \text{(IV.15)}$$

where $\eta_{l,b}$ is the displacement of the ion and (l, b) is its position. The variation in the potential is now treated as a perturbation equivalent to the perturbation caused by the interaction operator Eq. (IV.13). Gouterman[7] makes use of the perturbation

$$H'_{\text{int}}=\sum_{\alpha}\eta_\alpha x_\alpha F_\alpha\cos(\omega t+\mathbf{K}\cdot\mathbf{r}_\alpha), \qquad \text{(IV.16)}$$

where η_α is the coupling constant with the phonon field, x_α is the displacement of Particle α, F_α is the force analogous to eE in the electric case, the cosine term gives the interaction in terms of a phonon plane wave polarized along the unit vector $\hat{\imath}$. The relation between ω and K is given by $\omega=c_s\mid\mathbf{K}\mid$, where c_s is the speed of sound. Gouterman's perturbation term corresponds to an explicit statement of the interaction δU. The total Hamiltonian is now

$$H=H_0+H'_{\text{int}}, \qquad \text{(IV.17)}$$

where H_0 is the total Hamiltonian for the free molecule. Using the semiclassical treatment of radiation Gouterman gives the probability of the excitation to a state m from a state n as

$$c_m{}^*c_m=[F_x{}^2\sin^2\tfrac{1}{2}(\omega_{mn}-\omega)t/\hbar^2(\omega_{mn}-\omega)]\times\left|\int dx\psi_m\sum\eta_\alpha x_\alpha\exp(-i\mathbf{K}\cdot\mathbf{r}_\alpha)\psi_n\right|^2,$$

$$\omega_{mn}=\omega_m-\omega_n. \qquad \text{(IV.18)}$$

The energy density of the phonon field is given by $F_x{}^2/4\pi$, and in analogy to the photon case one can write

$$F_x{}^2\rightarrow\tfrac{1}{3}(8\pi)\tfrac{2}{3}e^2\int d\omega\rho_s(\omega), \qquad \text{(IV.19)}$$

where the factor $\frac{2}{3}$ arises due to longitudinally polarized phonons and e^2 is inserted to make the units work out correctly. The Einstein coefficient B_{nm} is found to be

$$B_{nm}=(4\pi^2/3\hbar^2)\tfrac{2}{3}\mid\mathfrak{y}_{mn}{}^s\mid^2, \qquad \text{(IV.20)}$$

where $\mathfrak{y}_{mn}{}^s$ is given by

$$\mathfrak{y}_{mn}{}^s=e\int dx\psi_m{}^*[\sum_\alpha\eta_\alpha\mathbf{r}_\alpha\exp(-i\mathbf{K}\cdot\mathbf{r}_\alpha)\psi_n]. \qquad \text{(IV.21)}$$

The analogy to the Planck formula for the energy density of a phonon field is found in the Debye theory for the determination of the specific heat, and is given by

$$\rho_s(\omega)=\tfrac{3}{2}(\hbar\omega^3/\pi^2c_s{}^3)[\exp(\hbar\omega/kT)-1]^{-1} \quad \text{for } \omega<\omega_{\max} \qquad \text{(IV.22)}$$

and

$$\rho_s(\omega)=0 \quad \text{for } \omega>\omega_{\max}, \qquad \text{(IV.23)}$$

where $\omega_{\max}$ is the cutoff frequency for phonon radiation. The number of states making the transition from m to n (where $E_m<E_n$) is equal to the number of states making the reverse transition at equilibrium and

$$N_n[B_{nm}\rho_s(\omega)+A_{nm}]=N_mB_{mn}\rho_s(\omega). \qquad \text{(IV.24)}$$

From the Boltzmann distribution law

$$N_n/N_m=\exp(-\hbar\omega/kT), \qquad \text{(IV.25)}$$

and from Eq. (IV.24) one finds

$$\rho_s(\omega)=A_{nm}/B_{nm}[\exp(\hbar\omega/kT)-1]^{-1}. \qquad \text{(IV.26)}$$

From Eqs. (IV.20), (IV.22), and (IV.26) the Einstein spontaneous emission coefficient is

$$A_{nm}=\tfrac{3}{2}(\hbar\omega^3/\pi^2c_s{}^3)B_{nm} \quad \text{for } \omega<\omega_{\max}$$
$$=(4\omega^3/3\hbar c_s{}^3)\mid\mathfrak{y}_{mn}{}^s\mid^2$$
$$=0 \quad \text{for } \omega>\omega_{\max}. \qquad \text{(IV.27)}$$

Substituting the values of the Einstein coefficients [Eqs. IV.20), (IV.27)] into the expressions for the currents [Eqs. (IV.11), (IV.12)] one finds

$$j_f=c_{\text{ox}}A\mathfrak{F}(4\omega_{43}{}^3/3\hbar c_s{}^3)\mid\mathfrak{y}_{43}{}^s\mid^2$$
$$\times\exp(-\hbar\omega_{12}/kT)\{[\exp(\hbar\omega_{43}/kT)-1]^{-1}+1\} \qquad \text{(IV.28)}$$

and

$$j_r=-c_{\text{red}}A\mathfrak{F}(4\omega_{12}{}^3/3\hbar c_s{}^3)\mid\mathfrak{y}_{12}{}^s\mid^2$$
$$\times\exp(-\hbar\omega_{3}/kT)\{[\exp(\hbar\omega_{12}/kT)-1]^{-1}+1\}. \qquad \text{(IV.29)}$$

Making use of the approximation for high temperatures ($\hbar\omega<kT$) of

$$[\exp(\hbar\omega/kT)-1]^{-1}\cong kT/\hbar\omega$$

one gets

$$j_f=c_{\text{ox}}A\mathfrak{F}(4\omega_{43}{}^2/3\hbar^2c_s{}^3)\mid\mathfrak{y}_{43}{}^s\mid^2(kT)$$
$$\times\exp[\hbar(\omega_{43}-\omega_{12})/kT] \qquad \text{(IV.30)}$$

and

$$j_r=-c_{\text{red}}A\mathfrak{F}(4\omega_{12}{}^2/3\hbar^2c_s{}^3)\mid\mathfrak{y}_{12}{}^s\mid^2(kT)$$
$$\times\exp[\hbar(\omega_{43}-\omega_{12})kT]. \qquad \text{(IV.31)}$$

The net current is given by the sum of the forward and reverse currents and is

$$j=(4A\mathfrak{F}/3\hbar^2c_s{}^3)(kT)\{\omega_{43}{}^2\mid\mathfrak{y}_{43}{}^s\mid^2c_{\text{ox}}$$
$$\times\exp[\hbar(\omega_{43}-\omega_{12})/kT]-\omega_{12}{}^2\mid\mathfrak{y}_{12}{}^s\mid^2c_{\text{red}}$$
$$\times\exp[-\hbar(\omega_{43}-\omega_{12})/kT]\}, \qquad \text{(IV.32)}$$

[7] M. Gouterman, J. Chem. Phys. **36**, 2846 (1962).

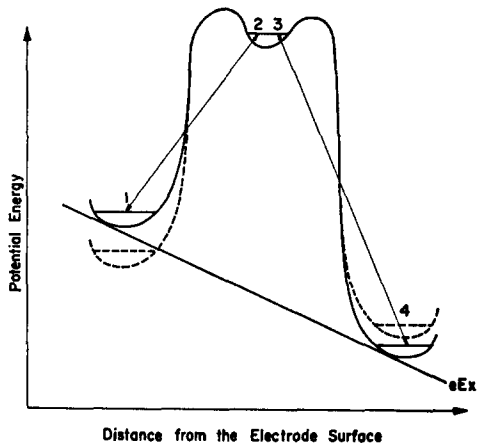

FIG. 2. The potential function at the electrode in the presence of an external electric field which is a result of the polarization of the electrode.

where

$$[4(kT)/3\hbar^2 c_s^3]\omega_{43}^2 \mid \mu_{43}^e \mid^2$$

and

$$[4(kT)/3\hbar^2 c_s^3]\omega_{12}^2 \mid \mu_{12}^e \mid^2$$

are equivalent to the forward and reverse rate constants.

V. ELECTROCHEMICAL EQUILIBRIUM

Electrochemical equilibrium is realized when the sum of the two currents is zero. Equating the two currents, as the equilibrium condition implies, gives from Eq. (IV.32)

$$c_{ox}\omega_{43}^2 \mid \mu_{43}^e \mid^2 \exp[\hbar(\omega_{43}-\omega_{12})/kT] = c_{red}\omega_{12}^2 \mid \mu_{12}^e \mid^2 \exp[-\hbar(\omega_{43}-\omega_{12})/kT]. \quad (V.1)$$

Rearranging and identifying $2N\hbar(\omega_{43}-\omega_{12})$, where N is the Avogadro number, with the free energy of activation, and, from the fact that $-\Delta F^0 = n\mathfrak{F}\mathcal{E}^0$, one gets

$$\mathcal{E}^0 = \frac{RT}{n\mathfrak{F}} \ln \frac{\omega_{43}^2}{\omega_{12}^2} \left| \frac{\mu_{43}^e}{\mu_{12}^e} \right|^2 + \frac{RT}{n\mathfrak{F}} \ln \frac{c_{ox}}{c_{red}}, \quad (V.2)$$

which is precisely the Nernst equilibrium condition.

VI. EFFECT OF EXTERNALLY APPLIED ELECTRIC FIELDS

The application of an electric field at the electrode other than the fields which exist under equilibrium conditions results in the net flow of current in either the anodic or cathodic direction, providing the equilibrium concentration ratio at the electrode c_{ox}/c_{red}, as defined by the Nernst equation, remains the same. Under the effect of an externally applied field at the electrode the bulk concentration of ion species changes after a long enough period of time. This change in concentration is in the direction of the equilibrium concentration ratio given by the Nernst equation with an equilibrium potential equal to the applied potential. When the new equilibrium is attained the current will once again become zero. The tendency of the system to move to an equilibrium situation is the essence of the diffusion-controlled kinetic treatment of electrode processes given by many authors.[8]

In Fig. 2 the distribution of the potential function at the electrode in an applied electric field is shown. In comparison with Fig. 1 it is seen that the external field decreases the energy separation between States 1 and 2 and increases the separation between States 3 and 4. If the biasing, given by eE in Fig. 2, were reversed the energy separation between States 3 and 4 would be decreased and between States 1 and 2 increased.

We can rewrite Eq. (IV.32) in terms of the energy separations between levels in the system for any situation:

$$j = (4A/3\hbar^2 c_s^3)(kT)\{\omega_{43}^2 \mid \mu_{43}^e \mid^2 c_{ox} \exp[(E_{43}-E_{12})/kT] - \omega_{12}^2 \mid \mu_{12}^e \mid^2 c_{red} \exp[-(E_{43}-E_{12})/kT]\}, \quad (VI.1)$$

where $E_{mn} = E_{mn}^0 + E'$, and E' is the correction to the unperturbed energy. The externally applied field will introduce correction terms of the form $-\mu_{12}^e \cdot \mathbf{E}$ and $\mu_{43}^e \cdot \mathbf{E}$, where μ^e is the electric transition dipole moment and $\mathbf{E}$ the electric field. The external field will not be of a magnitude to force corrections to be added to the ω_{mn} terms in the pre-exponential factor which then remains the same. The current expression, including the external field, is

$$J = (4A/3\hbar^2 c_s^3)(kT)(\omega_{43}^2 \mid \mu_{43}^e \mid^2 c_{ox} \exp\{[(E_{43}^0-E_{12}^0)+(\mu_{43}^e+\mu_{12}^e)\cdot\mathbf{E}]/kT\} - \omega_{12}^2 \mid \mu_{12}^e \mid^2 c_{red} \exp\{-[(E_{43}-E_{12}^0)+(\mu_{43}^e+\mu_{12}^e)\cdot\mathbf{E}]/kT\}). \quad (VI.2)$$

The cathodic free energy of activation under a potential change of $\Delta\mathcal{E}$ is[9]

$$\Delta F_c^\ddagger = \Delta F_0^\ddagger - \alpha n\mathfrak{F}\Delta\mathcal{E} \quad (VI.3)$$

and the anodic free energy is

$$\Delta F_a^\ddagger = \Delta F_0^\ddagger + (1-\alpha)n\mathfrak{F}\Delta\mathcal{E}. \quad (VI.4)$$

[8] See, for example, P. Delahay, *New Instrumental Methods in Electrochemistry* (Interscience Publishers, Inc., New York, 1954).
[9] H. A. Laitinen, *Chemical Analysis* (McGraw-Hill Book Company, Inc., New York, 1960), p. 306.

We can identify $\Delta F_c^{\ddagger}$ with

$$N[(E_{43}^0 - E_{12}^0) + (\mathfrak{y}_{43}^e + \mathfrak{y}_{12}^e)\cdot\mathbf{E}],$$

and $\Delta F_a^{\ddagger}$ with

$$-N[(E_{43}^0 - E_{12}^0) + (\mathfrak{y}_{43}^e + \mathfrak{y}_{12}^e)\cdot\mathbf{E}].$$

This leads to

$$j = (4A/3\hbar^2 c_s^3)(kT)\{\omega_{43}^2 \mid \mathfrak{y}_{43}^e \mid^2 c_{ox} \exp[(\Delta F_0^{\ddagger} - \alpha n\mathfrak{F}\Delta\mathcal{E})/RT] - \omega_{12}^2 \mid \mathfrak{y}_{12}^e \mid^2 c_{red} \exp[\Delta F_0^{\ddagger} + (1-\alpha)n\mathfrak{F}\Delta\mathcal{E}/RT]\}$$

$$= (4A/3\hbar^2 c_s^3)(kT)\{\omega_{43}^2 \mid \mathfrak{y}_{43}^e \mid^2 c_{ox} \exp[-\alpha n\mathfrak{F}(\mathcal{E} - \mathcal{E}^{\iota})/RT] - \omega_{12}^2 \mid \mathfrak{y}_{12}^e \mid^2 c_{red} \exp[(1-\alpha)n\mathfrak{F}(\mathcal{E} - \mathcal{E}^0)/RT]\}. \quad \text{(VI.5)}$$

We can solve Eqs. (VI.3) and (VI.4) for α giving

$$\alpha = (\Delta F_0^{\ddagger} - \Delta F_c^{\ddagger})/n\mathfrak{F}\Delta\mathcal{E}. \quad \text{(VI.6)}$$

Substituting the values for $\Delta F_0^{\ddagger}$ and $\Delta F_c^{\ddagger}$ into (VI.6) leads to

$$\alpha = [N(E_{12}^0 - E_{43}^0) + N(\mathfrak{y}_{43}^e + \mathfrak{y}_{12}^e)\cdot\mathbf{E}]/n\mathfrak{F}\Delta\mathcal{E}. \quad \text{(VI.7)}$$

VII. SUMMARY

A treatment of the passage of current at an electrode by assuming a detailed ordering of the solvent and ionic species as a model has been presented. This treatment considered the specific transitions of the electron from the electrode, to the solvent, and then to the ion, and the reverse transitions from the ion back to the electrode. The assumption of a detailed model, used in this work, is the major difference between this work and others which have preceded it. A detailed discussion of the differences between this theory and the adiabatic theories of Hush[10] and Marcus[11] will be presented in a subsequent paper. Formerly, the ion with its solvate sphere was treated as a single entity for which density-of-energy-states functions could be approximated and the electronic transitions considered on the basis of a tunneling model.

It has been shown that the detailed model leads directly to the classical expressions for the current passed at the electrode and to the Nernst equation when the identification of the energy difference between states in the electrode interface system is made with the free energies of activation for the anodic and cathodic currents. The expressions for the current developed in this paper indicate that *a priori* calculations of the magnitude of the current are possible.

[10] N. S. Hush, Z. Elektrochem. **61**, 734 (1957); J. Chem. Phys. **28**, 962 (1958).

[11] R. A. Marcus, Can. J. Chem. **37**, 155 (1959); in *Symposium on Electrode Processes*, edited by E. Yeager (John Wiley & Sons, Inc., New York, 1961), p. 239.