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On the Theory of Overvoltage for Electrode Processes Possessing Electron Transfer Mechanisms. I.

by
R. A. Marcus

Foreword (March 1, 1977)

The following article was first prepared as the above Office of Naval Research Technical Report, and is being reproduced here in its entirety. The results were applied in subsequent papers on electrode kinetics [1], and the Report itself has been widely cited in the literature.

Originally intended for journal publication, the article was never submitted because of the efforts of the author towards generalization. The generalization was published some years later [2], but in some respects the approach of the 1957 Technical Report is more readable. The principal generalizations are the inclusion of inner coordination shell contributions and the use of statistical mechanics for inner and outer contributions [2,3].

The 1957 Report and a predecessor [4] had as their aims the treatment of the outer shell contribution; their equation for the dielectric continuum calculation of that contribution is the same as that in the later publication [2]. The Report draws upon some derivations in ONR Technical Report No. 11, and this latter Report is included also. The generalization of those results may be found in Ref. [5].

Elsewhere in this book we comment on more recent developments.

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ON THE THEORY OF OVERVOLTAGE FOR ELECTRODE PROCESSES POSSESSING ELECTRON TRANSFER MECHANISM. I.*

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ABSTRACT

A quantitative theory of overvoltage is developed for electrode processes possessing electron transfer mechanisms. The assumptions and general approach of the theory are related to those used in the writer's recent work on homogeneous oxidation reactions involving electron transfers.

A simple expression is derived for the electron transfer rate constant as a function of the activation overvoltage and other quantities. The latter include the ionic radii and charges, and the work required to transport the ion to the electrode surface. From this expression for the rate constant, deductions can be made concerning salt effects, temperature coefficients, transfer coefficients, and the relation between exchange currents and the rates of isotopic exchange reactions in solution. Some recent data are briefly discussed from this point of view and some suggestions made for further studies.

The theory and the final equation are free from arbitrary assumptions and adjustable parameters. Several possible refinements are noted.

INTRODUCTION

The detailed mechanisms of many electrode processes have been studied in recent years using A.C. and D.C. methods [1]. Some of these mechanisms consist only of a simple electron transfer, while in others this step is preceded or followed by chemical equilibria and by other chemical reactions.

From such studies, similarities have been noted between the rate with which certain species are oxidized or reduced by electrochemical and by chemical means. Various authors [2] have interpreted the rates

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of electrochemical electron transfers in terms of concepts related to those used for electron transfers in chemical reactions. A brief qualitative comparison of the relative rates of several isotopic exchange redox reactions and of the corresponding electrochemical systems has been given by the writer [3].

Recently, a quantitative theory has been developed for calculating the rate constant of redox reactions involving an electron transfer in solution [4,5]. It proceeded from first principles plus assumptions which appear reasonable on a priori grounds. The general approach of the theory and the final theoretical equations were free from arbitrary assumptions and adjustable parameters. An analogous theory will be formulated here for electron transfer electrode processes. As before, the theory is not applicable to atom transfer mechanisms (hydrogen overvoltage, for example).

The Electron Transfer Rate Constant

Equations describing any overall electrochemical process may include terms for the transport of ions to the electrical double layer region at the electrode, for any chemical reactions of the electrochemically active species, for the work required to penetrate the double layer (if necessary), and for the actual electron transfer. Only under certain conditions can these factors be disentangled in a relatively simple way and simple electron transfer rate constants defined: The double layer region should be sufficiently thin that (1) no chemical reaction occurs in it and (2) diffusion across it is sufficiently rapid so that the concentration of an ion at any point in the double layer is related to its concentration just outside it by the work required to transport it to that point. At appreciable salt concentrations the double layer thickness appears to be only of the order of several Angstroms [6].

Under the above conditions, one can describe the entire electrochemical process by force-free differential equations [1] (containing any chemical reaction terms [7], if necessary) outside of the double layer region, while the boundary condition, at a boundary surface S drawn just outside the double layer, contains rate constants which depend only on the electron transfer process itself. This boundary condition is that the flux of any ion through this surface S equals its net rate of disappearance by electron transfer.

If A and B represent the electrochemically active ion before and

after its electron transfer with the electrode, the electron transfer step may be written as

$$A + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B. \qquad [1]$$

where n is the number of electrons lost by the electrode. If c_A^S and c_B^S denote the concentrations of A and B just outside the double layer, then the electron transfer constants, k_f and k_b, will be defined by the relation

$$\text{Net electron transfer rate per unit area} = k_f c_A^S - k_b c_B^S. \qquad [2]$$

[Note: To avoid confusion with references, equations are referred to by ( ) in the body of the text.]

THEORY

Basic Assumptions

The basic assumptions employed here will be analogous to those made in the oxidation-reduction reaction theory [4].

(a) In the activated state of reaction (1) the spatial overlap between the electronic orbitals of the two reactants is assumed to be small. In the present instance the "reactants" are the electrode and the discharging ion or molecule (to be referred to as the "central ion"). This assumption has been discussed previously [4] and some preliminary evidence in favor of it was cited.

(b) The central ion is treated as a sphere within which no changes in interatomic distances occur during reaction (1) and outside of which the solvent is treated as a dielectrically unsaturated continuum. Some discussion of this assumption has been given [4]. For complex ions or hydrated monatomic cations the sphere includes the first coordination shell of the central atom [4,5a]. A preliminary suggestion has been made for the effective size of unsymmetrical organic molecules and has been discussed [5b]. A refinement of the theory which takes changes, if any, in interatomic distances into consideration will be presented later.

Nature of the Activated Complex

It follows [4] quantum mechanically from the first assumption that a successful electron transfer between the central ion and the electrode proceeds via two successive intermediate states, X^* and X, say. These states have the same atomic configuration and the same total energy, but in X^* the electronic configuration of the central ion is that of A and in X, it is that of B. The electronic configuration of the electrode

undergoes a corresponding change, deduced later [8].

By arguments similar to those employed in the redox theory [4], it then follows that the actual electron transfer (the formation of X from X^*) must be preceded by a reorientation of the solvent molecules in the vicinity of the discharging ion and nearby area of the electrode. For similar reasons, a change in ionic atmosphere in this region also precedes the electron transfer. The new configuration of the solvent and ionic atmosphere, which is the same in X^* and in X, will prove to be intermediate between that in the initial state and that in the final state. As such, it is not that which is predicted by the charge distribution in X^* or by that in X. That is, it is not in electrostatic equilibrium with either charge distribution, and its properties cannot be described by the usual electrostatic expressions. Instead, expressions which take this nonequilibrium behavior into account must be used. Recently, such equations have been derived for electrode systems [9].

Once again [4], there are an infinite number of pairs of states, X^* and X, satisfying the constant energy-atomic configuration restriction, and we shall be interested in determining the properties of the most probable pair, i.e. the one with the minimum free energy of formation from the initial state. This is done by minimizing the expression for this free energy of formation subject to the restriction that X^* and X have the same atomic configuration and the same energy.

Reaction Scheme

From the preceding discussion we may write for the mechanism of reaction [1] the following scheme, analogous to that in Reference 4.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^* \qquad [3]$$

$$X^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \qquad [4]$$

$$X \xrightarrow{k_3} B. \qquad [5]$$

Here, a central ion just outside the double layer is denoted in its initial electronic state by A and in its final state by B. As noted earlier, step (3) involves a suitable reorganization of configuration of the solvent and ionic atmosphere, and (if necessary) a suitable

penetration of the electrical double layer. Step (4) is the actual electron transfer itself, and step (5) involves a reversion of configuration (of solvent and atmosphere) to one in equilibrium with the new charge on the central ion. It also involves a motion away from the electrode. As in the redox theory, the reverse of (5) occurs but it need not be considered in the computation of k_f.

Steady-state considerations for c_X^* and c_X lead to the relation [4]

$$k_f = k_1 /[1 + (1 + k_{-2}/k_3)\ k_{-1}/k_2]. \qquad [6]$$

As discussed later, when the probability of electron transfer in the lifetime of the intermediate state X^* (10^{-13} sec) is large, k_f is about half of k_1. k_1 depends on the free energy of formation of X^* from the initial state in reaction (1). We proceed first to the calculation of this free energy change and later to a discussion of the evaluation of the rate constants. With this aim in view, we consider in the next section the electrochemical system, the question of equilibrium (electrostatic and electrochemical), and fluctuations therefrom.

Electrostatic vs Electrochemical Equilibrium

The electrochemical cell in which the reaction under investigation occurs may be considered to consist of two half-cells, joined with or without a salt bridge. One of the half-cells will be taken to be reversible, and only at this electrode will there be electrochemical equilibrium. At the other electrode, M say, where reaction (1) occurs, there will nevertheless be electrostatic equilibrium because of the small relaxation time of the ionic double layer [10]. The formation of X^* represents a fluctuation from this equilibrium. In the following pages, we shall, for brevity, denote "electrostatic equilibrium" by "equilibrium." When "electrochemical equilibrium" is intended, it will be explicitly stated.

When an electron transfer occurs at M, completion of the electrochemical process requires the transfer of an equivalent number of electrons at the reversible electrode and of an equivalent number of ions from one half-cell to the other. This other transfer actually represents a fluctuation from electrochemical equilibrium and accordingly involves no free energy change. The fluctuation may occur before, after or during reaction (1), but k_f is the same in each case. For convenience of computation, we can let it occur before or after, so that the initial,

intermediate, and final states of the system in the reaction sequence (3) to (5), designated by A, X^*, X and B, have the same number of each type of ionic species, except for the particular central ion undergoing electron transfer.

Free Energy of Formation of State X^*

The electrostatic contribution, ΔF^*, to the free energy of formation of state X^* from state A will be different from zero because of (1) the work which may be required to transport the central ion from a point just outside the double layer to some particular point in it (if necessary), and (2) the work required to reorient the solvent molecules and the ionic atmosphere to a nonequilibrium configuration, for this position of the central ion.

Let F_e^A, F_e^*, F_e, and F_e^B denote the electrostatic free energy of the electrode M and of its solution when the system is in the state A, X^*, X and B, respectively. (Throughout, asterisks will be used to designate the properties of X^* and will be omitted in designating the properties of X.) We have therefore for ΔF^*,

$$\Delta F^* = F_e^* - F_e^A \qquad [7]$$

F_e^* is given by the general expression (8) and F_e is given by a similar equation, minus the asterisks [9a].

$$F_e^* = \frac{1}{2}\int[\underset{\sim}{E}_v^* \cdot \underset{\sim}{E}_v^* - \alpha_e \underset{\sim}{E}^* \cdot \underset{\sim}{E}_v^* - \underset{\sim}{P}_u \cdot (\underset{\sim}{E}^* + \underset{\sim}{E}_v^* - \underset{\sim}{P}_u/\alpha_u)]\, dV + kT \sum_i \int c_i \ln c_i/c_i^0\, dV + \chi \int_M \sigma^*\, dS \qquad [8]$$

where $\underset{\sim}{E}_v^*(\underset{\sim}{r})$ = electric field at point r exerted in a vacuum by all the ionic charges in the state X^* and by those electrode charges which they would induce in a vacuum.

$\underset{\sim}{E}^*(\underset{\sim}{r})$ = electric field in state X^*. It equals $-\nabla\varphi^*$.

$\varphi^*(\underset{\sim}{r})$ = inner potential in state X^*. (cf Eq. (5) of Reference 9a).

α_e = E-type[9] polarizability = $(D_{op}-1)/4\pi$. [9]

α_u = U-type[9] polarizability = $(D_s - D_{op})/4\pi$. [10]

$c_i(\underset{\sim}{r})$ = concentration of ions of type i in states X^* and X.

c_i^0 = average concentration of ions of type i. It equals their number n_i in the solution divided by the latter's volume V.

$\underset{\sim}{P}_u(\underset{\sim}{r})$ = U-type polarization in states X^* and X.

χ = potential drop at electrode-solution interface due to an oriented solvent dipolar layer.

The volume integrals in this equation are over the volume V, and the surface integral is over the surface of electrode M. In Eqs. (9) and (10) D_S and D_{op} are the static dielectric constant and the square of the refractive index, respectively. The functions $c_i(\underset{\sim}{r})$ and $\underset{\sim}{P}_u(\underset{\sim}{r})$ in state X* are the same as those in state X because of the constant atomic configuration restriction.

F_e^A is given by the same type of equation as (8), but with the equilibrium relations for $\underset{\sim}{P}_u(\underset{\sim}{r})$ and $c_i(\underset{\sim}{r})$ introduced. (cf Eqs. (21) and (22) of Reference 9a). F_e^B is given by a similar equation, but the functions in the integrand now refer to state B. Eq. (8) and subsequent equations treat X as being independent of the average electrode charge density. However, in Appendix X it is shown that the final equations, Eqs. (25) to (27), are unchanged even if X were a function of this quantity.

Restraint Imposed by the Constant Energy - Atomic Configuration Restriction

The free energy of formation of X^* from state A consists of the electrostatic contribution ΔF^* and of a term, described later, associated with the localization of the center of gravity of the central ion in a narrow region near the electrode [11]. The free energy of formation of X from B contains an electrostatic term $F_e - F_e^B$, ΔF say, and a center of gravity term equal to that noted previously.

As in the redox theory, it follows from assumption (a) given earlier that no energy change and no configurational entropy change accompany the formation of state X from X^*. The electronic entropy change arising from any possible change in the electronic degeneracy of the central ion and of the electrode is zero or negligible. Accordingly, X* and X have the same free energy.

The net free energy change in forming B from A is therefore

$$F_e^* - F_e^A + (F_e^B - F_e) = \Delta F^* - \Delta F \qquad [11]$$

Independently, this free energy of reaction (1) can be written as the sum of the following terms:

(a) The change in chemical potentials of ions A and B and of the electron in electrode M. This is $\mu_B - \mu_A - n\,\mu_e^M$, where n is the number of electrons transferred in reaction (4).

(b) the change in free energy due to the transfer of a charge $(e^* - e)$ from a solution of inner potential φ_s to a metal of of inner potential φ_M, e^* and e denoting the charges of ions A

and B, respectively. This term is $(e^* - e)(\varphi_M - \varphi_S)$, which we shall denote by $(e^*-e)\,\Delta\varphi$.

If electrode M were in electrochemical equilibrium with the actual concentrations of A and B just outside the double layer, then the sum of these two terms would be zero. The corresponding value of $\Delta\varphi$, denoted by $\Delta\varphi'$, equals the chemical potential term in (a) divided by $-(e^* - e)$.

Using this relation, the net free energy change, (a) plus (b), then becomes:

$$(e^*-e)\,(\Delta\varphi - \Delta\varphi') = (e^* - e)\,\eta_a, \qquad [12]$$

where η_a is the activation overvoltage defined by Eq. (12).

Equating this to expression (11), we obtain the equation of restraint imposed by the constant energy - constant atomic configuration restriction.

$$\Delta F^* - \Delta F = (e^* - e)\,\eta_a \qquad [13]$$

This equation is the equivalent of Eq. (19) of the redox theory [4].

It may be remarked that $(\mu_B - \mu_A)$ is related to its standard value, $(\mu_B^o - \mu_A^o)$, and $\Delta\varphi$ to its standard value, $\Delta\varphi^o$, by Eqs. (14) and (15), where the f's denote activity coefficients and the c^S's denote concentrations just outside the double layer.

$$\mu_B - \mu_A = \mu_B^o - \mu_A^o + kT \ln (f_B/f_A)(c_B^S/c_A^S) \qquad [14]$$

$$(e-e^*)(\Delta\varphi - \Delta\varphi^o) = kT \ln (f_B/f_A)(c_B^S/c_A^S) \qquad [15]$$

Minimization of ΔF^* Subject to Restraint Imposed by Eq. (12)

We minimize ΔF^* with respect to arbitrary variations $\delta P_u(r)$ and $\delta c_I(r)$.

$$\delta\Delta F^* = 0 \qquad [16]$$

This variation is performed subject to the condition of fixed number of ions n_I and subject to Eq. (12) at fixed η_a.

$$\delta n_I = \int \delta c_I \, dV = 0 \qquad [17]$$

$$\delta\Delta F^* - \delta\Delta F = 0 \qquad [18]$$

Introducing Eqs. (7) and (11) for ΔF^* and ΔF into Eqs. (16) and (18), we note that δF_e^A and δF_e^B equal zero since they are independent of δP_u and δc_I, while δF_e^* and δF_e are given by Eq. (20) of Reference 9a. Introducing these results into Eqs. (16) to (18), we obtain

$$-\int (\underset{\sim}{E}^* - \underset{\sim}{P}_u/\alpha_u)\cdot \delta\underset{\sim}{P}_u \, dV + \sum_i \int (kT \ln c_i/c_i^o + e_i \varphi^*) \, \delta c_i \, dV = 0 \quad [19]$$

$$\int (\underset{\sim}{E} - \underset{\sim}{E}^*)\cdot \delta\underset{\sim}{P}_u \, dV + \sum_i e_i (\varphi^* - \varphi) \, \delta c_i \, dV = 0 \quad [20]$$

Multiplying Eq. (20) by a constant m, the Lagrangian multiplier, multiplying Eq. (17) by another multiplier, $-\ln l_i$ say, and adding to Eq. (19), we obtain

$$\int(-\underset{\sim}{E}^* - m\,\underset{\sim}{E}^* + m\,\underset{\sim}{E} + \underset{\sim}{P}_u/\alpha_u)\cdot \delta\underset{\sim}{P}_u \, dV + \sum_i \int [kT \ln c_i/c_i^o + e_i(\varphi^* + m\varphi^* - m\varphi) - \ln l_i]\delta c_i \, dV = 0 \quad [21]$$

This equation is an identity for all arbitrary variations $\delta\underset{\sim}{P}_u(\underset{\sim}{r})$ and $\delta c_i(\underset{\sim}{r})$, so that the coefficients of these quantities equal zero at each point $\underset{\sim}{r}$.

$$\underset{\sim}{P}_u = \alpha_u (\underset{\sim}{E}^* + m\,\underset{\sim}{E}^* - m\,\underset{\sim}{E}) \quad [22]$$

$$c_i = c_i^o \, l_i \exp [-e_i(\varphi^* - m\varphi^* - m\varphi)/kT] \quad [23]$$

By integrating both sides ofEq. (23) over the volume V and setting the LHS equal to n_i, l_i can be determined.

$$l_i = V/\int \exp [-e_i(\varphi^* + m\varphi^* - m\varphi)/kT] \, dV \quad [24]$$

Eqs. (22) to (24) describe the solvent and ionic configuration in the pair of intermediate states X* and X.

Equation for ΔF^*

In order to compute ΔF^* in the most direct manner, Eqs. (22) and (23) for $\underset{\sim}{P}_u$ and c_i are first introduced into expressions for $\varphi(\underset{\sim}{r})$ and $\varphi^*(\underset{\sim}{r})$, (cf Eq. (5) of Reference 9a). The resulting integral equations for these potentials are then solved and $\underset{\sim}{E}$ and $\underset{\sim}{E}^*$ computed from them. F_e^* is then calculated from Eq. (8), F_e is obtained from an analogous equation, and an expression for ΔF^* is then derived.

However, we shall find it convenient to proceed more indirectly in the following manner which leaves the problem of solving the actual integral equations for the last step.

We first show (Appendix I) that there is a hypothetical equilibrium system (i.e. equilibrium configuration of solvent and ionic atmosphere) having the same $\underset{\sim}{P}_u(\underset{\sim}{r})$ and $c_i(\underset{\sim}{r})$ as states X* and X, but having different

charges on the central ion and on the electrode. The various properties of this hypothetical system are determined in Appendix I. F_e^* is next expressed in terms of the electrostatic free energy of the hypothetical system, $F_e^\dagger$, in Appendix III. In Appendix IV, $F_e^\dagger$ is then related to F_e^A and F_e^* - F_e. After obtaining expressions in Appendix V for $\underset{\sim}{E}^*$ and $\underset{\sim}{E}$, F_e^* - F_e is evaluated in Appendix VI. The final theoretical equations for ΔF^*, Eqs. (25) to (27) below, are then deduced from this value of F_e^* - F_e in Appendices VI and VII, after utilizing some relations obtained in Appendix VIII.

In this way it is shown that

$$\Delta F^* = w^* + \frac{m^2}{2}\lambda \qquad [25]$$

where m satisfies the equation

$$-(m + \tfrac{1}{2})\lambda = (e^* - e)\eta_a + w - w^* \qquad [26]$$

and where

$$\lambda = (\Delta e)^2 \left(\frac{1}{a} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad [27]$$

In these equations, Δe denotes $(e^* - e)$, the charge transferred to the electrode in reaction (1); a denotes the effective radius of the central ion, discussed earlier; R/2 is the distance of the ion to the electrode surface in the state X^*; w^* and w denote the work required to transport the central ion from the body of the solution to a distance R/2 from the electrode surface when the ion is in its initial state, respectively; the remaining quantities have been defined previously.

We shall return later to a discussion of the work terms w^* and w in Eqs. (25) and (26).

Rate Constants of Elementary Steps

(a) Estimation of k_{-1} and k_3

The rate constants k_{-1} and k_3 in reactions (3) and (5) are associated with the disappearance of X^* and of X, as a result of disorganization of the solvent polarization or of a suitable motion of the central ion [4]. As shown previously [4], these constants are equal to each other and have a value of about 10^{13} sec^{-1}.

(b) Estimation of k_2 and k_{-2}

The ratio k_2/k_{-2} is the equilibrium constant of reaction (4), exp

$(\Delta S_e/R)$, ΔS_e being the electronic entropy change accompanying this reaction. As noted earlier, this change is either zero or negligible, and we have $k_2 \sim k_{-1}$. Eq. (6) thus reduces to

$$k_f = p\, k_1 \qquad [28]$$

where p, a function of R defined by Eq. (29), is the probability that a successful electron transfer occurs during the lifetime of the intermediate state, 10^{-13} sec.

$$p(R) = 1/(2 + k_3/k_2) \qquad [29]$$

When the overlap between the electronic orbitals of the ion and electrode in the intermediate state is not too small, then k_2 will be of the same order or larger than k_3 and we will have

$$p \cong \frac{1}{2}\,, \quad k_f \cong k_1/2 \qquad [30]$$

The evaluation of k_2 and $p(R)$ for electron transfers between ions in solution was discussed previously, several methods being available [4]. A preliminary calculation for one system indicated that p was of the order of magnitude of unity [12], but a more detailed estimate would be desirable. In preliminary applications, we shall take $p \sim 1/2$. Its value in various systems can be inferred from the temperature-independent factor in the experimental value of k_f, when the work terms w^* and w are small. If, because of any large repulsion between ion and electrode, R is especially large, then p will be correspondingly small.

(c) Evaluation of k_f

We first observe that k_f in Eq. (28) can be expressed in terms of the equilibrium constant for the formation of X^* in reaction (3).

$$k_f = p\, (k_1/k_{-1})\, k_{-1} \qquad [31]$$

If the reaction were confined to a plane, the value of k_f could be shown to be Z_w, the collison frequency of an uncharged molecule with unit area of the electrode, multiplied by the value of $p \exp(-\Delta F^*/kT)$ in that plane [12a]. Z_w equals $\sqrt{kT/2\pi m}$, which is about 10^4 cm sec^{-1} at 25°C, for an ion of mass 100 gm $mole^{-1}$.

Unlike atom transfer processes, however, electron transfers at electrodes can occur at various R's, rather than just at the plane of the

electrode-solution interface. Taking this fact into consideration, Eq. (32) can be deduced [13].

$$k_f \cong 5 \times 10^4 \; p \; e^{-\Delta F^*/kT} \text{ cm sec}^{-1} \qquad [32]$$

Of the various terms appearing in Eq. (25), the values of the radii a have been discussed elsewhere [4,5]. The value of R is that which maximizes p exp(-ΔF^*/kT). When w* and w are zero (sufficiently high salt concentrations) or when they do not tend to increase ΔF^*, R equals its minimum value. This is 2a, if an oriented solvent layer at electrode-solution interface does not hinder the approach of the ion. (cf Appendix X.)

The term w* can be evaluated by solving the usual Poisson-Boltzmann equation when the central ion A is at a distance R/2 from the electrode, solving it when the ion is in the body of the solution, and then introducing these solutions for the electrostatic potential into the appropriate equations for the electrostatic free energy of the system (Eqs. (39) and (41) of Appendix II). The difference in electrostatic free energy is w*. Similarly, w can be computed from analogous equations for the central ion B.

However, a considerably simpler though less rigorous procedure has generally been assumed for calculating the work required to transport an ion to some distance (R/2) from the electrode. The assumption is generally made that this work equals the charge on the central ion multiplied by the difference in the value of the electrostatic potential at R/2 and in the body of the solution (i.e., outside the double layer), this potential being computed in the absence of the central ion. This particular potential can also be inferred from measurements on the electrical double layer by various methods [6,14]. In this way Franklin [14] has obtained a correlation between salt effects on hydrogen overvoltage, double layer computations, and measurements on the electrical double layer.

APPLICATIONS OF THE THEORETICAL EQUATION

A detailed quantitative application of Eq. (32) for k_f, using Refinement (1) noted in the following section when necessary, will be presented in a later paper. However, several preliminary remarks will be made here:

(1) Little information is available on salt effects for simple electron transfer systems. It would be particularly desirable to see

what correlations exist between k_f values (at $\eta_a = 0$) and double layer measurements in the presence of various salts. Judging from data on isotopic exchange reactions, the use of electrochemically active ions which do not readily form specific complexes with the salt, such as the cobalt ethylenediamines, the cobalt amines, the manganate-permanganate ions and other complex ions, e.g. the iron cyanides perhaps, rather than hydrated metal cations, would be of especial interest.

(2) When the temperature-dependent work terms w* and w are zero (sufficient concentration of added salt), the temperature-independent factor equals 5×10^4 p cm sec^{-1}. Randles and Somerton [15] found values for this factor usually in the range $10^3 - 10^5$ cm sec^{-1}, suggesting perhaps that p has its maximum value, 1/2. However, further studies on temperature-independent factors using complex ions, such as those indicated earlier, and on the effects of added salt would be of particular interest.

(3) When the work terms w* and w are zero, the transfer coefficient (defined as $-[\partial \ln i/\partial(\eta_a \Delta e/kT)]_T$, where i is the electrical current density in the forward direction) is 0.50. Using platinum electrodes, Rubin and Collins [16] found a value of about 0.42 for the $Fe(CN)_6^{-4}$ system and 0.46 for the $Mo(CN)_8^{-4} - Mo(CN)_8^{-3}$ couple when the concentration of added potassium chloride was 0.1 M.

(4) The theoretical equation bears a very close relationship to that obtained for isotopic exchange reactions [4], in qualitative agreement with the data [3]. This close relationship is preserved in the Refinement (1) discussed in the following section. In a subsequent paper it is planned to discuss this correlation in a quantitative way. However, more detailed experimental studies on the rates of simple electron transfer electrode processes whose isotopic exchange counterparts have been investigated would be especially interesting.

The general sparsity of data on electrode kinetics of simple electron transfers can be ascribed to experimental difficulties in measuring the very fast rates of these systems. Recent innovations in technique and interpretation, such as those introduced in Reference 15 and those summarized in Reference 1, have begun to remedy this situation.

REFINEMENTS

Some refinements of the theory described in this paper are noted below.

(1) Changes in Interatomic Distances within the Central Ion

When a particular interatomic distance within the central ion is different in the two valence states, A and B, a change in this distance will occur during reaction (1) and this will contribute to ΔF^*. The effect appears [5a] to be appreciable for hydrated metal cations such as Fe^{+2} - Fe^{+3} and small for others, such as MnO_4^- - MnO_4^{-2}, $Fe(CN)_6^{-3}$ - $Fe(CN)_6^{-4}$. In unpublished work (cf [3]) we have computed it for the electron transfers between ions in solution in terms of certain force constants and of differences in interatomic distances. A similar calculation will be described for electrode processes in a later paper.

(2) Quantum Limitation of the Image Force Theory

The electrical image force theory was employed in the derivation of Eq. (25) for ΔF^*. Recently the quantum limitation on the image theory was estimated by Sachs and Dexter [17] and their results can be applied here. We first note that ΔF^* equals its value at $R = \infty$ minus an amount whose maximum value, which occurs at $R = 2a$, is half of this R_∞ value when the work terms are zero. The quantum limitation causes no error in the R_∞ value [17], while the error in the second term is perhaps about 8% when the distance from the ion to the electrode is 5 Å [18], so that the overall error is about 8% or less.

(3) Electrode Double Layer Containing Specifically Adsorbed Ions

Until now, we have omitted from consideration electrical double layers in which some of the ions are specifically adsorbed on the electrode. In the case of specifically adsorbed ions which do not form specific complexes with the central ion itself, a rigorous analysis would take into account the detailed manner in which the adsorbed ionic layer was perturbed by the approach of the central ion. In the interest of simplicity, a less accurate analysis will be undertaken here.

Let us consider the simplest case - one in which the adsorbed ions are essentially not perturbed by the approach of the central ion. (This assumption is indeed implied in current interpretations of measurements of salt effects on hydrogen overvoltage [14].) We then may treat the adsorbed ions as fixed in position. Let us regard each of these ions as being a sphere having a surface density equal to its charge divided by its area [19].

Under this condition, Eq. (8) still applies for the value of F_e^*. Since the positions of these ions are fixed, they cannot vary during the

minimization process in Eqs. (16) to (18). The c_i there refer to the ions in the diffuse portion of the electrical double layer. As a result, it is found that the subsequent equations, Eqs. (22) and (23) are still applicable. It is shown in Appendix IX that the final equations for ΔF^* also remain intact. The terms w and w* now represent the work required to transport an ion of charge e and e*, respectively, in the presence of the adsorbed layer.

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APPENDIX I. PROPERTIES OF AN EQUILIBRIUM SYSTEM HAVING THE SAME $c_i(\underset{\sim}{r})$ AND $\underset{\sim}{P}_u(\underset{\sim}{r})$ AS X*

The properties of an equilibrium system will be denoted in this Appendix by the superscript †.

At any point in a system having an equilibrium configuration, $c_i^\dagger(\underset{\sim}{r})$ and $P_u^\dagger(\underset{\sim}{r})$, the inner potential $\varphi^\dagger(\underset{\sim}{r})$ depends on the charge density $\sigma^\dagger(\underset{\sim}{r})$ on every surface [20], on the ionic concentration $c_i^\dagger(r)$ and on the polarizability $\alpha^\dagger$ according to Eqs. (5), (21) and (22) of Reference 9a:

$$\varphi^\dagger(\underset{\sim}{r}') = \int \frac{\Sigma_i e_i c_i^\dagger}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \int \frac{\sigma^\dagger}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS - \int \alpha^\dagger \nabla\varphi^\dagger \cdot \nabla \frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \beta \qquad [33]$$

where β equals χ on the electrode and equals zero in solution and where $c_i^\dagger$ satisfies the Boltzmann relation:

$$c_i^\dagger = n_i^\dagger\, e^{-e_i\varphi_i^\dagger/kT} \Big/ \int e^{-e_i\varphi_i^\dagger/kT}\, dV \ . \qquad [34]$$

Introducing Eq. (22) of the present paper for $\underset{\sim}{P}_u$ into Eq. (5) of Reference 9a for φ and into an analogous equation for φ^* we also find

$$\varphi^* + m(\varphi^*-\varphi) = \int \frac{\Sigma_i e_i c_i}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \int \frac{\sigma^*+m(\sigma^*-\sigma)}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS - \int \alpha\nabla(\varphi^*-m\varphi^*-m\varphi)\cdot\nabla \frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \beta \ , \qquad [35]$$

where c_i is given by Eq. (23), $\alpha = \alpha_u + \alpha_e$, and the electrode charge density is uniquely determined by the charges in solution and by the solvent polarization.

We note from Eqs. (23) and (34) that $c_i^\dagger$ depends on $\varphi^\dagger$ in the same way that c_i depends on $\varphi^* + m(\varphi^*-\varphi)$ if we set $n_i^\dagger = n_i$. It then follows from Eqs. (33) and (35) that $\varphi^\dagger$ and $\varphi^* + m(\varphi^*-\varphi)$ satisfy the same integral equation if we set $\alpha^\dagger$ equal to α, (i.e., $D_s^\dagger$ equal to D_s), and if on each ionic surface we set $\sigma^\dagger$ equal to $\sigma^* + m(\sigma^*-\sigma)$. (There is no freedom of choice with the value of $\sigma^\dagger$ on the electrode surface, since it is uniquely determined by the magnitude and configuration of all the charges and dipoles in solution [9a].)

Since the potential function is unique, it follows that $\varphi^\dagger = \varphi^* + m(\varphi^*-\varphi)$, and accordingly, that $\underset{\sim}{E}^\dagger = \underset{\sim}{E}^* + m(\underset{\sim}{E}^*-\underset{\sim}{E})$, that $c_i^\dagger = c_i$ and $\underset{\sim}{P}_u^\dagger$ $(= \alpha_u \underset{\sim}{E}^\dagger)$ equals α_u $(\underset{\sim}{E}^* + m\underset{\sim}{E}^* - m\underset{\sim}{E})$, and therefore (by Eq. (22)) equals $\underset{\sim}{P}_u$.

A corollary of the relation between the σ's is:

$$e^\dagger = e^* + m(e^*-e) \quad , \qquad [35a]$$

where $e^\dagger$ is the charge on the central ion in the hypothetical system.

APPENDIX II. EVALUATION OF THE F_e OF AN EQUILIBRIUM SYSTEM

We shall have occasion to use an expression for the electrostatic free energy of an equilibrium system, F_e^{eq}. According to Eq. (43) of Reference 9a, it is given by

$$F_e^{eq} = \int_S \int_{\sigma=0}^{\sigma=\sigma} \varphi^{eq} d\sigma dS \quad , \qquad [36]$$

the integration being over all surfaces.

The value of φ^{eq} in an equilibrium system, consisting of a central ion of charge q, of an electrode M, of mobile ions, and of a medium of dielectric constant D_s, is [21]

$$\varphi^{eq} = \varphi_\rho^q + \frac{q}{D_s}\left(\frac{1}{r} - \frac{1}{r_i}\right) + \beta \quad , \qquad [37]$$

where r and r_i denote the distances from the field point to the center of the ion and to the latter's electrical image, respectively, and where φ_ρ^q is the contribution from the mobile ions, together with that form the electrode charges which they induce.

On the electrode surface, φ^{eq} is a constant, X. Furthermore, on the surface of the central ion, $d\sigma$ equals $dq/(4\pi a^2)$ and also (it can be shown)

$$\int_{ion} \frac{dS}{r_i} = \frac{4\pi a^2}{R} \quad , \qquad [38]$$

where R is the distance from the center of the ion to its electrical im-

age. Remembering that r = a on the surface of the ion, we obtain from these results and from Eqs. (36) and (37),

$$F_e^{eq} = \frac{1}{4\pi a^2} \int_{ion} \int_{q=0}^{q=q} \varphi_\rho^q \, dq \, dS + \frac{q^2}{2D_s}\left(\frac{1}{a} - \frac{1}{R}\right) + \chi \int_M \sigma dS \ . \qquad [39]$$

When the ion is outside the double layer region, φ_ρ^q is the sum of three independent contributions.

(1) φ_{atm}^q, arising from a spherically symmetric ionic atmosphere about the central ion,

(2) a contribution due to the electrode charge density induced by this atmosphere. Since the atmosphere is concentric with the central ion, spherically symmetric, and has a total charge of -q, it can be shown that the same electrode charge density would be induced by a point charge -q situated at the center of the central ion. This contribution to the potential is therefore $q/D_s R$. (cf Eq. (38) and Reference 9a.)

(3) φ_S, arising from the ions of the electrical double layer together with the electrode charges they induce.

Remembering that both φ_{atm}^q and φ_S are constant over the surface of this ion, we obtain for a system in which the central ion is outside the double layer,

$$F_e^{eq} = \int_{q=0}^{q=q} \varphi_{atm}^q dq + q\varphi_S + \chi \int_M \sigma dS + q^2/2D_s a \ . \qquad [40]$$

Since $\int_{q=0}^{q=q} \varphi_{atm}^q dq = kT \ln \gamma_q$, where γ_q is the electrostatic contribution to the activity coefficient of the ion of charge q in the body of the solution, Eq. (40) becomes

$$F_e^{eq} = kT \ln \gamma_q + q\varphi_S + \chi \int_M \sigma dS + q^2/2D_s a \ . \qquad [41]$$

APPENDIX III. RELATION BETWEEN F_e^* and $F_e^\dagger$

Eq. (8) can be used for evaluating $F_e^\dagger$ if the equilibrium relation $\underset{\sim}{P}_u^\dagger = \underset{\sim}{\alpha}_u^\dagger \underset{\sim}{E}^\dagger$ and the † superscripts are added. Using the following relations established in Appendix I,

$$\underset{\sim}{E}^\dagger = \underset{\sim}{E}^* + m(\underset{\sim}{E}^* - \underset{\sim}{E}) \quad \text{and} \quad \underset{\sim}{E}_v^\dagger = \underset{\sim}{E}_v^* + m(\underset{\sim}{E}_v^* - \underset{\sim}{E}_v) \ ,$$

and using Eq. (8) for F_e^*, an analogous one for F_e, Eq. (22) for $\underset{\sim}{P}_u$, it follows that without any approximation

$$F_e^* = F_e^\dagger - m(F_e^*-F_e) + \frac{m(m+1)}{2}\int [\alpha_e(\underset{\sim}{E}^*-\underset{\sim}{E})\cdot(\underset{\sim}{E}_v^*-\underset{\sim}{E}_v) - (\underset{\sim}{E}_v^*-\underset{\sim}{E}_v)^2/4\pi]\,dV \ . \qquad [42]$$

APPENDIX IV. RELATION BETWEEN $F_e^\dagger$, F_e^A AND $F_e^* - F_e$

$F_e^\dagger$ can be written as the sum of two terms:

(1) $F_e^{\dagger s}$, the electrostatic free energy when the central ion of charge $e^\dagger$ is just outside the double layer.

(2) $w^\dagger$, the electrostatic work required to transport this ion from that position to one it occupies in the hypothetical state (which is the same one it occupies in X* and in X).

It can be deduced from Eq. (41) of Appendix II that $F_e^{\dagger s}$ and F_e^A obey the equation [22]

$$F_e^{\dagger s} - F_e^A = (kT\,\ell n\,\gamma_\dagger + e^\dagger\varphi_S - e^\dagger\chi + e^{\dagger 2}/2a\,D_s) - (kT\,\ell n\,\gamma_A + e^*\varphi_S - e^*\chi + e^{*2}/2a\,D_s) \qquad [43]$$

where $\gamma_\dagger$ and γ_A denote the electrostatic contribution to the activity coefficient of the central ion in the body of the solution, when it has a charge $e^\dagger$ and e^*, respectively.

From Eqs. (42) and (43) we obtain for ΔF^*,

$$\Delta F^* = w^\dagger - m(F_e^*-F_e) + \frac{m(m+1)}{2}\int [\alpha_e(\underset{\sim}{E}^*-\underset{\sim}{E})\cdot(\underset{\sim}{E}_v^*-\underset{\sim}{E}_v) - (\underset{\sim}{E}_v^*-\underset{\sim}{E}_v)^2/4\pi]\,dV + kT\,\ell n\,\gamma_\dagger/\gamma_A + (e^\dagger-e^*)(\varphi_S-\chi) + (e^{\dagger 2}-e^{*2})/2a\,D_s \ . \qquad [44]$$

In Appendix VI, $(F_e^*-F_e)$ will be evaluated after determining $E^*(r)$ and $E(r)$ in Appendix V.

APPENDIX V. EVALUATION OF $E^*(r)$ AND $E(r)$

Using Eqs. (1), (2) and (5) of Reference 9a, and remembering that $\underset{\sim}{P}_u^* = \underset{\sim}{P}_u$ and $\rho^* = \rho$, we obtain

$$\varphi^* - \varphi = \int \frac{\sigma^*-\sigma}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dS - \int \alpha_e\nabla(\varphi^*-\varphi)\cdot\nabla_r\,\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dV \ , \qquad [45]$$

where the first integral is over all surfaces. On the surface of the central ion, $\sigma^*-\sigma$ equals $(e^*-e)/4\pi a^2$; on the electrode surface, its value is dictated by [9a] this charge difference and by the functions in the volume integral of Eq. (45).

Comparison of Eq. (45) with the equilibrium expression (33) shows

that $\varphi^* - \varphi + \beta$ is actually the potential which would be produced in an equilibrium system whose central ion had a charge (e^*-e), whose volume charge density was zero, and whose polarizability was α_e. We see that its $\underset{\sim}{E}_v$-value would be $\underset{\sim}{E}_v^* - \underset{\sim}{E}_v$. Using the relation which one obtains between $\underset{\sim}{E}_v$'s and $\underset{\sim}{E}$'s in equilibrium systems when the usual ionic approximation is made [23], we find

$$\underset{\sim}{E}^* - \underset{\sim}{E} = (\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)/(1 + 4\pi\alpha_e) \quad , \qquad [46]$$

and we note that the denominator equals D_{op}.

Combining Eqs. (22) and (46) we obtain

$$\underset{\sim}{P}_u = \alpha_u[\underset{\sim}{E}^* + m(\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)/D_{op}] \quad . \qquad [47]$$

Introducing this value of $\underset{\sim}{P}_u$ into the general equation for the inner potential (Eq. (5) of Reference 9a) it can be shown that [24]

$$\varphi^* = \int \frac{\rho^*}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \int [\frac{\sigma^* - 4\pi\alpha_u m(\sigma^*-\sigma)/D_{op}}{|\underset{\sim}{r}-\underset{\sim}{r}'|}]\, dS$$

$$- \int (\alpha_e + \alpha_u) \nabla\varphi^* \cdot \nabla \frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \beta \quad . \qquad [49]$$

[Note: Eq. (48) is in Reference 24.]

Comparison with the equilibrium expression (33) shows that φ^* is also actually equal to the potential in an equilibrium system whose polarizability is $(\alpha_e + \alpha_u)$ and whose $\underset{\sim}{E}_v$-value is $[\underset{\sim}{E}_v^* - 4\pi\alpha_u m(\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)/D_{op}]$. Using the usual relation between $\underset{\sim}{E}_v$'s and $\underset{\sim}{E}$'s in equilibrium ionic systems [23], we find

$$\underset{\sim}{E}^*(r) = \frac{\underset{\sim}{E}_v^*}{D_s} - m(\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)(\frac{1}{D_{op}} - \frac{1}{D_s}) \quad . \qquad [50]$$

Eqs. (46) and (50) are the desired expressions for $\underset{\sim}{E}^*$ and $\underset{\sim}{E}$.

APPENDIX VI. EVALUATION OF $F_e^* - F_e$ AND PROOF OF EQ. (26)

Introducing expressions (46), (47) and (50) of Appendix V into Eq. (8) and into an analogous one for F_e it is found that

$$F_e^* - F_e = \frac{1}{8\pi}\int [\frac{\underset{\sim}{E}_v^{*2} - \underset{\sim}{E}_v^2}{D_s} - (2m+1)(\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)^2(\frac{1}{D_{op}} - \frac{1}{D_s})]\, dV + (e-e^*)\chi \quad . \qquad [51]$$

This equation will be rewritten as:

$$F_e^* - F_e^A - F_e + F_e^B = -\frac{2m+1}{8\pi}(\frac{1}{D_{op}} - \frac{1}{D_s}) \int (\underset{\sim}{E}_v^* - \underset{\sim}{E}_v)^2 dV + T + w^* - w \qquad [52]$$

where T is defined by Eq. (53)

$$T = \frac{1}{8\pi D_s}\int (\underset{\sim}{E}_v^{*2}-\underset{\sim}{E}_v^{2})dV - (w^*+F_e^{A}-w-F_e^{B}) + (e-e^*)\chi \quad . \qquad [53]$$

Using Eq. (33) of Reference 9a, the integral in Eq. (52) can be written as [25]

$$\frac{1}{4\pi}\int (\underset{\sim}{E}_v^{*}-\underset{\sim}{E}_v)\cdot(\underset{\sim}{E}_v^{*}-\underset{\sim}{E}_v)dV = \frac{1}{4\pi}\int (\psi_v^{*}-\psi_v)(\sigma^{*}-\sigma)dS \quad . \qquad [54]$$

According to Eqs. (16), (29), and (30) of Reference 9a, and to the relation $\rho^* = \rho$, we also have

$$\psi_v^{*} - \psi_v = (e^{*}-e)(\frac{1}{r} - \frac{1}{r_i}) \quad . \qquad [55]$$

The integral in (54) is to be evaluated over the electrode surface and over that of the central ion. The electrode's contribution is zero, since $\psi_v^* = \psi_v$ on the electrode according to Eq. (55) ($r = r_i$ there). The ion's contribution is readily evaluated with the aid of Eqs. (38) and (55). We find:

$$\frac{1}{4\pi}\int (\underset{\sim}{E}_v^{*}-\underset{\sim}{E}_v)^2 dV = (\Delta e)^2(\frac{1}{a} - \frac{1}{R}) \quad . \qquad [56]$$

We thus obtain

$$F_e^{*} - F_e - F_e^{A} + F_e^{B} = -(m+\frac{1}{2})(\Delta e)^2(\frac{1}{a}-\frac{1}{R})(\frac{1}{D_{op}}-\frac{1}{D_s}) + w^* - w + T \quad . \qquad [57]$$

The LHS of Eq. (57) is simply $\Delta F^*-\Delta F$.

In Appendix VIII (a) it is inferred that to a good approximation

$$T = 0 \quad . \qquad [58]$$

Using Eq. (13), Eq. (26) of the text is thereby established.

In utilizing Eq. (57) for evaluating $F_e^*-F_e$, we shall make use of the following expression for $F_e^{B}-F_e^{A}$, deduced from Eq. (41).

$$F_e^{B}-F_e^{A} = (kT\ell n\gamma_B + e\varphi_S - e\chi + e^2/2a\,D_s) - (kT\ell n\gamma_A + e^*\varphi_S - e^*\chi + e^{*2}/2a\,D_s) \quad . \qquad [59]$$

APPENDIX VII. PROOF OF EQ. (25)

We obtain from Eqs. (44), (46), (56), (57) and (58)

$$\Delta F^* = w^{\dagger} - m(w^*-w) + \frac{m^2}{2}(\Delta e)^2(\frac{1}{a}-\frac{1}{R})(\frac{1}{D_{op}}-\frac{1}{D_s}) + \frac{m(m+1)}{2D_sR}(\Delta e)^2 + kT\ell n\,\gamma_{\dagger}\gamma_B^{m}/\gamma_A^{1+m} - mT \quad . \qquad [60]$$

In Appendix VIII (b) it is inferred that to a good approximation (the same as that made in deducing that $T = 0$),

$$w^{\dagger} - w^{*} - m(w^{*}-w) + \frac{m(m+1)}{2D_s R}(\Delta e)^2 + kT \ln Y_{\dagger} Y_B^{m} / Y_A^{1+m} - mT = 0 \ . \qquad [61]$$

Eq. (25) of the text then follows from Eqs. (60) and (61).

APPENDIX VIII. PROOF OF EQS. (58) AND (61)

(a) Proof of Eq. (58)

We evaluate separately the terms $\int(\underset{\sim}{E}_v^{*2}-\underset{\sim}{E}_v^{2})dV/8\pi D_s$, $F_e^{A+w^*}$, and F_e^{B+w} that appear in Eq. (53) for T.

Setting $(\underset{\sim}{E}_v^{2*}-\underset{\sim}{E}_v^{2}) = (\underset{\sim}{E}_v^{*}-\underset{\sim}{E}_v)\cdot(\underset{\sim}{E}_v^{*}+\underset{\sim}{E}_v)$, we obtain from Eq. (33) of Reference 9a [27],

$$\frac{1}{8\pi D_s}\int(\underset{\sim}{E}_v^{*2}-\underset{\sim}{E}_v^{2})dV = \frac{1}{2D_s}\int(\psi_v^{*}+\psi_v)(\sigma^{*}-\sigma)dS \ . \qquad [62]$$

We note that ψ_v is given [28] by Eq. (63) and that ψ_v^{*} is given by the same equation if e is replaced by e*.

$$\psi_v = e\left(\frac{1}{r} - \frac{1}{r_1}\right) + D_s\varphi_{\rho\dagger} \ . \qquad [63]$$

In this equation $\varphi_{\rho\dagger}$ represents the potential due to the mobile ions and the electrode charges they induce, in the hypothetical system of Appendix I.

Both ψ_v^{*} and ψ_v are zero on the electrode surface, since $(r-r_1)$ and $\varphi_{\rho\dagger}$ vanish there (cf Reference 9a). Evaluating the integral in Eq. (62) over the surface of the central ion, we find

$$\frac{1}{8\pi D_s}\int(\underset{\sim}{E}_v^{*2}-\underset{\sim}{E}_v^{2})dV = \frac{(e^{*2}-e^2)}{2D_s}\left(\frac{1}{a}-\frac{1}{R}\right) + \int_{ion}\varphi_{\rho\dagger}\frac{(e^{*}-e)}{4\pi a^2}dS \ . \qquad [64]$$

Remembering that F_e^{B+w} is the electrostatic free energy of an equilibrium system when the central ion B occupies the same position as in the intermediate state, we can compute this quantity using Eq. (39). $F_e^{A+w^*}$ can be computed in a similar way.

In this way we find for T

$$T = \int_{ion}\varphi_{\rho\dagger}\frac{(e^{*}-e)}{4\pi a^2}dS - \int_{ion}\int_{q=e}^{q=e^{*}}\frac{\varphi_\rho^{\,q}\,dq\,dS}{4\pi a^2} \ . \qquad [65]$$

In the absence of added salt, these φ_ρ's are zero so that T is then exactly zero. In the presence of added salt, an approximate solution

[29] of the Poisson-Boltzmann equation (solved in the presence of the central ion) leads to the relation

$$\varphi_\rho^{\,q}(\underset{\sim}{r}) = \varphi_{\rho\dagger}(\underset{\sim}{r}) + (q-e^\dagger)\varphi_1(\underset{\sim}{r}) \quad , \qquad [66]$$

where $\varphi_1(\underset{\sim}{r})$ is independent of q.

Introducing this expression into Eq. (65) we obtain Eq. (67), where we have set $\varphi_1(r)$ equal to its value at the center of the ion, φ_1, say.

$$T = (m + \tfrac{1}{2})(\Delta e)^2\varphi_1 \quad . \qquad [67]$$

As noted above, φ_ρ and hence φ_1 equal zero when there is no added salt. If, in the presence of excess salt, the ion is effectively outside the double layer, these quantities can again be simply evaluated, utilizing the discussion following Eq. (39). Estimating φ_{atm} from the Y's, φ_1 is found to be negligible. In intermediate cases, too, we judge that the RHS of Eq. (67) is a small term [29], probably of the order of $(m+1/2)kT$ or less. Numerical computation shows that the term in Eq. (57) involving $(m+1/2)(\Delta e)^2/2a\,D_{op}$ is extremely large in comparison with $(m+1/2)kT$, and therefore we may set $T = 0$ in Eq. (57).

(b) Proof of Eq. (61)

Calculating $F_e^{\,B}$ and $F_e^{\,B+w}$ by the method described in Appendix II and subtracting we find

$$w = -\frac{e^2}{2D_s R} + \int_{ion}\int_{q=0}^{q=e}(\varphi_\rho^{\,q} - \varphi_S - \varphi_{atm}^{\,q})\frac{dq}{4\pi a^2}\,dS \quad . \qquad [68]$$

Analogous expressions can be written for w^* and $w^\dagger$, and we obtain for $w^\dagger - w^* - m(w^* - w)$,

$$w^\dagger - w^* - m(w^* - w) + \frac{m(m+1)(\Delta e)^2}{2D_s R} + kT\,\ell n\, Y_\dagger Y_B^{\,m}/Y_A^{\,1+m} - mT = \int_{ion}\int_{q=e^*}^{q=e^\dagger}\frac{\varphi_\rho^{\,q}\,dq\,dS}{4\pi a^2}$$

$$- m\int_{ion}\varphi_{\rho\dagger}\frac{(e^*-e)}{4\pi a^2}\,dS \quad . \qquad [69]$$

The RHS of Eq. (69) equals zero in the absence of added salt. In the presence of added salt we find with the aid of Eq. (66),

$$\text{LHS of Eq. (69)} = \frac{m^2}{2}(\Delta e)^2\varphi_1 \quad . \qquad [70]$$

This term can be neglected in comparison with the $m^2(\Delta e)^2/2a\,D_{op}$ which appears in Eq. (60), for reasons indicated in Part (a).

APPENDIX IX. MODIFICATION IN PROOF DUE TO PRESENCE OF FIXED, ADSORBED IONS IN THE ELECTRICAL DOUBLE LAYER

We consider here the modifications in the proofs of Appendices II to VIII which arise when the double layer contains the fixed, adsorbed ions discussed in the Refinements section of the text. The results deduced in Appendix I are unaffected.

In Eq. (37) of Appendix II there will be an additional contribution to the potential arising from each fixed ion of the electrical double layer. If q_k denotes the charge of the k^{th} fixed ion and if r_k and r_k' denote the distance from the k^{th} ion and from its image to the field point, then the contribution to the potential arising from all fixed ions is, in an equilibrium polarization system,

$$\sum_k \frac{q_k}{D_s}\left(\frac{1}{r_k} - \frac{1}{r_k'}\right) , \qquad [71]$$

the summation being over all fixed ions.

This can be shown to add the following terms to F_e^{eq} in Eq. (39):

$$\sum_k \int_{\text{ion}} \int_{q_k=0}^{q_k=q_k} \frac{\varphi_\rho^{q_k} dq_k}{4\pi a_k^2} dS + \sum_k \frac{q_k^2}{2D_s}\left(\frac{1}{a_k} - \frac{1}{R_k}\right) + \sum_k \sum_{k\neq j} \frac{q_k q_j}{2D_s}\left(\frac{1}{r_{jk}} - \frac{1}{R_{jk}}\right)$$

$$+ \sum_k \frac{q\, q_k}{D_s}\left(\frac{1}{\rho_k} - \frac{1}{\rho_k'}\right) \qquad [72]$$

where a_k is the radius of the k^{th} fixed ion; R_k, r_{jk}, R_{jk}, ρ_k and ρ_k' denote the distance from this ion to its electrical image, to the j^{th} fixed ion, to the latter's electrical image, to the central ion and to the latter's electrical image, respectively. The first term in Eq. (72) describes the interaction of the mobile ions with the fixed ions.

In Eqs. (40) and (41), φ_s now represents the potential in the body of the solution due to all the ions, fixed and mobile, of the double layer and so includes Eq. (71). Accordingly, $q\varphi_s$ in Eqs. (40) and (41) now includes the last term of (72). The remaining three terms of (72) should be added to Eqs. (40) and (41).

Eq. (42) of Appendix III relating F_e^* and $F_e^\dagger$ is unaffected.

Eq. (43) of Appendix IV was deduced from Eq. (41). Because of a cancellation of the newly added terms, Eq. (43) remains unchanged (except for the new significance of φ_s noted above). Accordingly, Eq. (44) is also unchanged.

The equations in Appendix V are unaffected.

The newly added terms, given by (71), cancel in Eq. (55) of Appendix VI so that this equation and the remaining ones of this Appendix and of Appendix VII are unchanged.

In Appendix VIII, the terms (71) are added to Eq. (63), and this in turn causes the addition of certain terms to (64). The sum (72) is also added to the expressions for $F_e^{B}{}_{+w}$ and $F_e^{A}{}_{+w^*}$ (with q equal to e and to e*, respectively). Once again, there is a cancellation and the final equations of Appendix VIII (a) and (b), (67) and (70) remain unchanged.

Accordingly, Eqs. (25) to (27) for ΔF^* are unaltered.

APPENDIX X. EFFECTS OF A DEPENDENCE OF χ ON MEAN ELECTRODE CHARGE DENSITY

In the present paper, it has been assumed for simplicity that χ, the potential drop due to electrode-solvent and solvent-solvent interactions at the interface, was independent of the mean electrode charge density, $\bar{\bar{\sigma}}$ say. Recent work suggests, however, that the degree of orientation of the solvent molecules next to the electrode (and hence χ) may vary with this quantity [30]. In this Appendix we examine the effects of a dependence of χ on $\bar{\bar{\sigma}}$.

The term χ enters the various formulas in two ways: It appears in expressions for the potential in Eqs. (33), (35), (37) and (49), and in expressions for the free energy, Eqs. (39), (40), (41), (43), (44), (51), (53) and (59). In a previous paper [9a] we have considered the effects of treating χ as a function of $\bar{\bar{\sigma}}$ rather than as a constant. As discussed there, when a few electrons are transferred in some process, the average electrode charge density is affected only to a negligible extent. In such cases, χ is a constant for all states in the process. The arguments made in the present paper using the expressions for the potential thus remain entirely unchanged. It was also noted [9a] that in the free energy expressions, a term, $\chi\int\sigma dS$, should be replaced for such processes by

$$\chi''(\bar{\bar{\sigma}}) + \chi'(\bar{\bar{\sigma}})\int\sigma dS \quad , \qquad [71]$$

where χ'' and χ' are constant for a given $\bar{\bar{\sigma}}$. It may be verified that this substitution leaves the final equations, Eqs. (25) to (27), unchanged. The first term of (71) always cancels out in any equation deduced for a free energy change. Thus, in effect, χ is replaced by χ'. Since χ does not appear in the final equations, neither does χ'.

Accordingly, we infer that any effect of a change in degree of orientation in the solvent layer next to the electrode is a more indirect one. It might affect the "dielectric constant" in the vicinity of the electrode, particularly the contribution from orientation polarization. But, we observe from Eq. (26), unless D_s is close to D_{op}, changes in the former have very little effect on ΔF^*. Again, it might affect to some extent the distance of closest approach of the central ion. In some studies of the equilibrium properties of the electrode double layer, Grahame [30] has shown that a self-consistent interpretation of the data can be obtained assuming such an effect. Extremely interesting inferences were drawn about the behavior of the solvent in this region towards ions of different size. It is clear that an analogous study of the electrode kinetics of simple electron transfers at various electrode charge densities should be very interesting. At certain charge densities, it appeared from the equilibrium studies, there is no oriented solvent layer. The interpretation of kinetic data obtained under such conditions would be correspondingly simplified.

REFERENCES

1 cf reviews by (a) J. O'M. Bockris, Modern Aspects of Electrochemistry, Academic Press, Inc., New York, 1954, Chap. 4; (b) P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers, Inc., New York, 1954; (c) A. E. Remick, J. Chem. Ed., 33 (1956)564.

2 cf J. E. B. Randles, Trans. Faraday Soc., 48(1952)828; A. A. Vlcek, Coll. Czech. Chem. Comm., 20(1[illegible])894.

3 R. A. Marcus, Trans. N.Y. Acad. Sci., 19(1957)423.

4 R. A. Marcus, J. Chem. Phys., 24(1956)966).

5 R. A. Marcus, (a) J. Chem. Phys., 26(1957)867; (b) ibid., 26(1957) 872.

6 cf D. C. Grahame, Chem. Rev., 41(1947)441. It may be noted that when the double layer has such a small thickness, no penetration may be necessary for an electron transfer. The conditions cited in the text would then be fulfilled automatically.

7 cf J. Koutecky, Collection Czechoslov. Chem. Communs., 18(1953)183.

8 These conclusions can also be phrased [4] in terms of the application of the Franck-Condon principle to reaction (1). It was shown [4] that only when assumption (a) in the preceding section is valid can

this principle be applied to electron transfers in chemical (and electrochemical) reactions.

9 (a) R. A. Marcus, ONR Technical Report No. 11, Project No. NR 051-339, August 15, 1957; (b) cf J. Chem. Phys., 24(1956)979.

10 cf Reference 1a, Chap. 3, page 167.

11 Changes in electronic energy and entropy of the metal can be ignored in the path involving the minimum free energy of formation of X*. The low specific heat of metals shows that such changes correspond to large free energy increases.

12 Since then, a little more experimental information has become available on entropies of activation of electron transfer reactions in solution. These additional results tend to support the idea that p is approximately equal to its maximum value. These data will be discussed in a subsequent communication.

12a We shall use Eq. (31) to evaluate k_f. The probability that the ion will be in state X* and in a region of unit cross-sectional area in the interval R, R+dR, as compared with being in any unit volume, is $\exp(-\Delta F^*/kT)dR$. Multiplying this by $f(v_R)dv_R$, the probability that the ion has a velocity component perpendicular to the electrode in the range v_R, v_R+dv_R, we obtain the contribution to k_1/k_{-1} from this range $dR\ dv_R$. Multiplying this term by the corresponding value of k_{-1}, v_R/dR, and integrating over negative v_R's (motion away from electrode) we find

$$k_1 = \int_{-\infty}^{0} f(v_R)\, v_R dv_R e^{-\Delta F^*/kT} \quad .$$

Since $f(v_R)$ equals $\exp(-mv_R^2/2kT)/\int_{-\infty}^{+\infty}\exp(-mv_R^2/2kT)dv_R$, we obtain the formula given in the text upon integration.

13 As before, Eq. (31) is used. We first note that if the probability of reaction is very high, the probability that the ion will be in any particular interval (R,R+dR) depends on the recent history of the ion. In particular, it is a function of the probability that the ion has not undergone electron transfer shortly before reaching this dR. While such conditional probability considerations can play a role in the fast electron transfers in the gas phase, in solution the probability of reaction before reaching any dR is so small (because of ΔF^*) that the recent history is essentially one of no reaction. In this case, the chance of finding the ion in a state X* in a region

of unit cross sectional area between R and R+dR, as compared with finding the ion in a unit volume of solution, is given by the Boltzmann formula, $\exp(-\Delta F^*/kT)\,dR$.

The state X* characterized by this dR can disappear in several ways, each contributing to k_{-1}. The decay of atomic polarization of the system to a random value contributes an amount 10^{13} sec^{-1} [4]. Again, X* will disappear if the ion moves sufficiently far from this R, since F_e^* thereby changes appreciably. Presumably, this requires the escape of the ion from its solvent cage. The corresponding contribution will be [4] less than the preceding one, so that k_{-1}, the sum of these, is about 10^{13} sec^{-1}. Upon integrating over R from $-\infty$ to R_{min}, the distance of closest approach, we obtain

$$k_f = 10^{13} \int_{-\infty}^{R_{min}} p(R) e^{-\Delta F^*(R)/kT} dR \quad .$$

In a typical case, $\Delta F^*(R)$ decreases from its maximum value at R_m, say (usually at R_{min}) by a factor of e when R increases by 0.5 Å, while p(R) probably changes by a smaller factor over this distance. Thus, we can expand the exponent, $(\Delta F^*/kT)$, about R_m, retaining terms up to $(R-R_m)^2$ and integrate over R from $-\infty$ to R_m. From the cited numerical behavior it can then be deduced that the integral is essentially equal to the value of $p \exp(-\Delta F^*/kT)$ at R_m multiplied by 0.5 Å. Accordingly, we obtain Eq. (32) for k_f.

The related problem of collision frequencies in gas phase and solution, for atom and electron transfer processes, will be discussed elsewhere.

14 A. Frumkin, Trans. Faraday Soc., 36(1940)117.

15 J. E. B. Randles and K. W. Somerton, Trans. Faraday Soc., 48(1952) 937,951, though the validity of applying the present theory to the systems discussed in the second paper of these authors is open to question.

16 H. Rubin and F. C. Collins, J. Phys. Chem., 58(1954)958. The electrode may have been contaiminated by the de Khotinsky cement present, since the exchange current deduced from these measurements is much less than that in Reference 15. However, such contamination perhaps has only a minor effect on the transfer coefficient.

17 R. G. Sachs and D. L. Dexter, J. Appl. Phys., 21(1950)1304.

18 The approximate percent error in a computed energy change (computed on the basis of the image force theory) when an ion moves from in-

finity to a distance r from the electrode is inversely proportional to r [17]. It is 8% or less when r is 5 Å, in a vacuum or in solution. The calculated reduction in the value of ΔF^* caused by this approach of the ion to the electrode probably has a percent error of this magnitude, but a more detailed estimate can be made.

19 Accordingly, the $\sigma(\underset{\sim}{r})$ which appears in the various equations now includes the contribution from the adsorbed ions. This contribution is, of course, the same in states X* and X since the ions are fixed.

20 i.e., on the surface of the electrode M, of the central ion, and of the fixed ions in the "Refinement" section of the text.

21 cf Eq. (26) of Reference 9a. In that equation the integral over the surface of the central ion contributes an amount given by Eq. (29) there, while the integral over the electrode surface M contains charges induced by the central ion as well as charges induced by the mobile ions. The contribution to the potential from the electrode charges induced by the central ion is given by Eq. (30) of Reference 9a, and from those induced by the mobile ions is included in φ_ρ^q of Eq. (37).

22 In applying Eq. (41) it is noted that the electrode charge in the hypothetical state whose F_e is $F_e^{\dagger s}$ exceeds that in state A by an amount $-(e^{\dagger}-e^*)$.

23 cf Eqs. (15) and (25) of Reference 9a. This approximation is analogous to that made in using Coulomb's Law, q_1q_2/Dr, for the free energy of interaction of two charged spheres in a medium of dielectric constant, D [9a].

24 We have made use of the following relation where σ_v^* and σ_v are the surface charge densities involved in $\underset{\sim}{E}_v^*$ and $\underset{\sim}{E}_v$, respectively. On the surface of the central ion, they equal σ^* and σ, respectively.

$$-\frac{1}{4\pi}\int(\underset{\sim}{E}_v^*-\underset{\sim}{E}_v)\cdot V_r\,\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dV=\int\frac{\sigma_v^*-\sigma_v}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dS\ . \qquad [48]$$

Eq. (48) follows from Eq. (56) of Reference 9b when one introduces the following values for the $\underset{\sim}{E}_c'$ and therefore for the ρ' and σ' which appear there:

$$\underset{\sim}{E}_c' = \underset{\sim}{E}_v^* - \underset{\sim}{E}_v,\quad \rho' = \rho_v^* - \rho_v\ (=0) \text{ and } \sigma' = \sigma_v^* - \sigma_v.$$

(We have introduced primes into Eq. (56), to avoid confusion with other symbols in the present paper.)

25 In that equation we set $\underset{\sim}{P}^i = 0$ and therefore (by definition) $\underset{\sim}{E}_c^{\,i} =$

$\underset{\sim}{E}_v^{\,i}$. We also set $\underset{\sim}{E}_v^{\,i} = \underset{\sim}{E}_v^{\,j} = \underset{\sim}{E}_v^{\,*} - \underset{\sim}{E}_v$, and make use of the relation $\rho^* = \rho$.

26 In applying Eq. (41), it is noted that the electrode charge in state B exceeds that in state A by an amount $-(e-e^*)$.

27 In that equation we set $P^j = 0$ and therefore (by definition $\underset{\sim}{E}_c^{\,i} = \underset{\sim}{E}_v^{\,i}$. We also set $\underset{\sim}{E}_v^{\,i} = \underset{\sim}{E}_v^{\,*} + \underset{\sim}{E}_v$ and $\underset{\sim}{E}_c^{\,j} = \underset{\sim}{E}_v^{\,*} - \underset{\sim}{E}_v$, and make use of the relation $\rho^* = \rho$.

28 cf Eqs. (16), (29) and (30) of Reference 9a, according to which one finds

$$\psi_v = \frac{e}{r} - \frac{e}{r_i} + \varphi'' \quad .$$

Here, φ'' is the potential which the mobile ions, whose distribution is that of states X and X*, and the electrode charges they induce, exert in a vacuum.

According to the usual ionic approximation this specified mobile charge distribution would create a potential φ''/D_s in a medium of dielectric constant D_s. (cf Eq. (25) of Reference 9a.) Since this is also the actual mobile ion distribution in the hypothetical equilibrium state of Appendix I, in which it exerts a potential $\varphi_{\rho\dagger}$, we have $\varphi'' = D_s\varphi_{\rho\dagger}$.

29 R. A. Marcus, unpublished work. It is assumed that the change in equilibrium configuration of the mobile ions in the system, when the central ion undergoes a change in charge $\Delta e/2$, can be treated by Debye-Huckel approximations. This would seem to be a reasonable assumption since Δe is usually only equal to a unit charge.

In Eq. (65) this is equivalent to the assumption that $e_i(\Delta e/2)\varphi_i/kT < 1$, when e_i is the charge of a mobile ion of type i.

30 D. C. Grahame, J. Chem. Phys., 25(1956)364; J. Am. Chem. Soc., 79 (1957)2093.