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ELECTROSTATIC FREE ENERGY AND OTHER PROPERTIES OF STATES HAVING NONEQUILIBRIUM POLARIZATION. II. ELECTRODE SYSTEMS*

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ABSTRACT

In certain electrode processes involving electron transfer mechanisms, a portion of the dielectric polarization is not in electrostatic equilibrium with the charge distribution. In the present paper expressions are deduced for the properties of such systems. These properties include the electrostatic free energy, entropy and energy, and the spatial dependence of the inner potential. The method of images provides a convenient means for determining the electrode charge distribution, due account being taken of its quantum limitations.

These expressions have been used to formulate a quantitative theory of overvoltage for electron transfer electrode processes.

INTRODUCTION

In some processes such as light absorption a transfer of charge between species may occur so rapidly that the solvent molecules do not have time to instantaneously readjust themselves to the new charge distribution. Again, in the intermediate states of such reactions the electrical polarization of the solvent medium will not be in electrostatic equilibrium with the charge distribution. Recently, expressions were obtained for the free energy and other properties of states having nonequilibrium dielectric polarization [1]. These expressions were used to develop a quantitative theory of the rates of electron transfer reactions in solution [2,3]. Electrode systems were explicitly excluded from consideration there because of the special conditions prevailing at electrode-solution interfaces. In the present paper these conditions are discussed and the expressions deduced [1] in Part I are adapted to electrode systems. The expressions obtained have been used to devise a quantitative theory of overvoltage [4].

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THEORETICAL

The properties of nonequilibrium systems to be considered include their electrical polarization, the spatial dependence of the potential, the free energy, the entropy and energy. Throughout, the definitions and, with minor modifications, the symbols will be similar to those employed in Part I. For brevity, some familiarity with them will be assumed.

U- and E-type Polarization

As in Part I, the total dielectric polarization $\mathbf{P}(\mathbf{r})$ at any point r is written as the sum of two terms:

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_e(\mathbf{r}) + \mathbf{P}_u(\mathbf{r}) \qquad [1]$$

where $\mathbf{P}_e(\mathbf{r})$, the E-type polarization (usually electronic), is in electrostatic equilibrium with the electric field strength, $\mathbf{E}(\mathbf{r})$, and has the value given in Eq. (2)* below [4a]. The function $\mathbf{P}_u$ is not in electrostatic equilibrium, but in any physical problem it will either be known or will appear as the solution of some variational equation [2]. The value of the function $\mathbf{P}_e(\mathbf{r})$ depends, through $\mathbf{E}(\mathbf{r})$, on the charge distribution and on the function $\mathbf{P}_u(\mathbf{r})$.

$$\mathbf{P}_e(\mathbf{r}) = \alpha_e \mathbf{E}(\mathbf{r}) \quad , \qquad [2]$$

where α_e, the E-type polarizability is related to D_{op}, the square of the refractive index [1].

$$4\pi\alpha_e = D_{op} - 1 \quad . \qquad [3]$$

The U-type polarizability α_u depends on D_{op} and on D_s, the static dielectric constant [1].

$$4\pi\alpha_u = D_s - D_{op} \quad . \qquad [4]$$

Oriented Solvent Layer at Electrode-Solution Interface

It is usually supposed that an oriented solvent layer exists at the electrode-solution interface and, for simplicity, that it is thin and non-polarizable [5]. In this case it simply produces across the interface a fixed potential difference, χ, whose magnitude depends on the solvent, on the electrode, and on the temperature. In the text, χ is treated

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

as being independent of the average electrode charge density, but in Appendix V we consider the modifications to be made when χ varies with this quantity.

The Electrostatic Potential

In any system each central ion under consideration is usually treated as a sphere having a surface charge density $\sigma(\underset{\sim}{r})$ equal to the ionic charge divided by its area. The remaining ions are described in terms of some continuous volume charge density $\rho(\underset{\sim}{r})$. There will also be a surface charge distribution on the electrode surface.

As in Part I, the potential can be expressed in terms of contributions from the charges and from the polarized volume elements. The potential arising from these contributions - the charge distribution, the oriented dipolar layer at the interface, the polarized medium - is the same as the "inner potential" $\varphi(\underset{\sim}{r})$ discussed by Parsons [5] and Lange [6]. With the exception of the β term, we have from Part. I,

$$\varphi(\underset{\sim}{r}') = \int \frac{\rho(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \int \frac{\sigma(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS + \int \underset{\sim}{P}(\underset{\sim}{r})\cdot\nabla_r \frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dV + \beta \qquad [5]$$

where ∇_r is the gradient operator and where

$$\beta = \chi\,, \quad \text{(electrode phase)}$$

and

$$\beta = 0\,, \quad \text{(solution phase)} \quad . \qquad [6]$$

The volume integrals are over the entire volume of the dielectric. The surface integral is over the surface of each central ion and over the surface of the electrode M:

$$\int \frac{\sigma(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS = \int_{\text{ions}} \frac{\sigma(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS + \int_{M} \frac{\sigma(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, dS \quad . \qquad [7]$$

To make maximum use of Part I, it is convenient to define a function $\psi(r)$, which is identical with the potential employed in Part I.

$$\psi(\underset{\sim}{r}) = \varphi(\underset{\sim}{r}) - \beta \quad . \qquad [8]$$

For the electric field strength $E(r)$, we have

$$\underset{\sim}{E}(\underset{\sim}{r}) = -\nabla\varphi = -\nabla\psi \quad . \qquad [9]$$

Electrostatic Free Energy

The electrostatic free energy F_e of an electrode system is the reversible work required to charge up the system to its final configuration, in the presence of the fixed oriented solvent layer at the electrode-solution interface. The method used in Part I for calculating F_e was based upon finding a reversible path for charging up the system to the final nonequilibrium state and then computing the work done during this charging process. As discussed in Part I, F_e is given by

$$F_e = F + kT \sum_i \int c_i \ln(c_i/c_i^0)\,dV \qquad [10]$$

where $c_i(r)$ and c_i^0 denote the local and average concentration of the i^{th} ionic species. F is the reversible work required to charge up the system when all the ions are held fixed in their final configuration.

F is computed by a two-stage charging process employed in Part I, the work done during each stage being calculated from the equation

$$W = \iint \varphi^\lambda \frac{d\rho}{d\lambda}\,d\lambda\,dV + \iint \varphi^\lambda \frac{d\sigma}{d\lambda}\,d\lambda\,dS \quad , \qquad [11]$$

where λ is increased from 0 to 1 during each stage and where φ^λ denotes the value of φ at any λ.

Introducing Eqs. (6) and (8) into this expression for W, Eq. (11) becomes

$$W = \iint \psi^\lambda \frac{d\rho}{d\lambda}\,d\lambda\,dV + \iint \psi^\lambda \frac{d\sigma}{d\lambda}\,d\lambda\,dS + \chi \iint_M \frac{d\sigma}{d\lambda}\,d\lambda\,dS \qquad [12]$$

where M indicates integration over the electrode surface only. Eq. (12) differs from the corresponding expression used in Part I only in the last term. For this reason the formula deduced in Part I for F by this two-stage process will also differ from the one for electrode systems in this term alone, and we find [7]:

$$F = \frac{1}{2}\int [-\mathbf{P}\cdot\mathbf{E}_c - \mathbf{P}_u\cdot(\mathbf{E}-\mathbf{P}_u/\alpha_u) + \mathbf{E}_c\cdot\mathbf{E}_c/4\pi]\,dV + \chi \int_M \sigma\,dS \qquad [13]$$

where $\mathbf{E}_c(\mathbf{r})$ is the electric field which this given ionic and electrode charge distribution would exert in a vacuum,

$$\mathbf{E}_c(\mathbf{r}') = -\nabla_{r'}[\int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,dV + \int \frac{\sigma(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,dS] \quad . \qquad [14]$$

On the electrode, this $\sigma(\mathbf{r})$ arises from all the induced charges, including those induced by the polarized dipoles. For later applications it will be convenient to define a function $\mathbf{E}_v(\mathbf{r})$ which depends only on the ionic charges in the solution and on the surface charge density $\sigma_v(\mathbf{r})$ which they would induce in a vacuum. The potential $\psi_v(\mathbf{r}')$ in that system must be a constant on the electrode. $\mathbf{E}_v(\mathbf{r}')$ and $\psi_v(\mathbf{r}')$ are given by

$$\underset{\sim}{E}_v(\underset{\sim}{r}') = -\nabla_{r'}\psi_v(\underset{\sim}{r}') \qquad [15]$$

$$\psi_v(\underset{\sim}{r}') = \int \frac{\rho_v(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dV + \int \frac{\sigma_v(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dS \quad , \qquad [16]$$

where $\rho_v(\underset{\sim}{r}) = \rho(\underset{\sim}{r})$, and where $\sigma_v(\underset{\sim}{r})$ and $\sigma(\underset{\sim}{r})$ are equal on the surface of each central ion but differ on the electrode. They differ there by an amount equal to surface charge density induced in the electrode by the polarized dielectric, i.e., by $\underset{\sim}{P}(\underset{\sim}{r})$.

It is shown in Appendix I that Eq. (13) can be rewritten in terms of $\underset{\sim}{E}_v$.

$$F = \frac{1}{2}\int [-\underset{\sim}{P}\cdot\underset{\sim}{E}_v - \underset{\sim}{P}_u\cdot(\underset{\sim}{E}-\underset{\sim}{P}_u/\alpha_u) + \underset{\sim}{E}_v\cdot\underset{\sim}{E}_v/4\pi]\,dV + \chi\int_M \sigma\, dS \quad . \qquad [17]$$

Entropy and Energy of Nonequilibrium Systems

When the E-type polarization is electronic and the U-type is atomic plus orientation, there will be an entropy change when the ions and (outside of the oriented solvent layer) solvent molecules form the final specified configuration from the initial random one. This change is given by Eq. (18) (cf Eqs. (33) and (25a) of Part I). There will also be other entropy and free energy terms arising from interactions of the molecules in the oriented layer, with each other and with the electrode.

$$S_e = -\left(\frac{\partial W_I}{\partial T}\right)_{E^0_{v,\chi}} - k\sum_i \int c_i \,\ell n(c_i/c_i{}^0)\,dV \quad , \qquad [18]$$

where W_I is the work done during the first stage [1] of the two-stage charging process. $\underset{\sim}{E}_v{}^0$, the value of $\underset{\sim}{E}_v$ at the end of this first stage, is related to the charge distribution at the end of this stage, $\rho^0(\underset{\sim}{r})$ and $\sigma^0(\underset{\sim}{r})$, by equations similar to (15) and (16). Methods are discussed in Part I for computing this charge distribution and for computing W_I.

The corresponding contribution U to the energy of the system is

$$U = F_e + TS_e \quad . \qquad [19]$$

The Equilibrium State

It can be shown from Eq. (13) for F that the function $\underset{\sim}{P}_u(\underset{\sim}{r})$ assumes its equilibrium value $\alpha_u\underset{\sim}{E}(\underset{\sim}{r})$ when this free energy expression is minimized with respect to the vector point function $\underset{\sim}{P}_u(\underset{\sim}{r})$. A procedure closely related to the following will also be adopted in a later paper for finding the most probable intermediate state in some electrode processes.

In Appendix II it is shown that at fixed charge density on each ionic surface,

$$\delta F_e = \int(-\mathbf{E}+\mathbf{P}_u/\alpha_u)\cdot\delta\mathbf{P}_u dV + \sum_i\int[kT\, \ell n(c_i/c_i{}^0) + e_i(\varphi-\varphi_M)]\,\delta c_i\ dV \qquad [20]$$

where φ_M is the inner potential of the electrode.

F_e is a minimum, and therefore δF_e is zero, for fluctuations $\delta\mathbf{P}_u$ and $\delta c_i(\mathbf{r})$ from the equilibrium state. The fluctuations $\delta c_i(\mathbf{r})$ are subject only to the restraint of constant number of particles of each ionic species, $\int\delta c_i(\mathbf{r})dV = 0$ for each i. Multiplying the latter set of equations by individual constants and adding to the equation $\delta F_e = 0$, we obtain an identity which can be satisfied for all arbitrary variations $\delta\mathbf{P}_u(\mathbf{r})$ and $\delta c_i(\mathbf{r})$ only if the coefficients of these quantities are everywhere zero. We deduce in this way, that at equilibrium,

$$\begin{aligned} \mathbf{P}_u &= \alpha_u\mathbf{E}\ , \\ kT\,\ell n\ c_i + e_i\varphi + \text{constant} &= 0\ . \end{aligned} \qquad [21]$$

Integrating c_i over the volume, the constant can be evaluated, and we obtain

$$c_i = n_i\, e^{-e_i\varphi/kT}/V_i \qquad [22]$$

$$V_i = \int e^{-e_i\varphi/kT}\, dV\ , \qquad [23]$$

where n_i is the number of ions of type i.

Eq. (24) for the F_e-value of equilibrium systems, $F_e{}^{eq}$, can be deduced directly from Eqs. (10) and (12), or indirectly from Eqs. (13), (21) and (22) when Eq. (33) is used to transform the integrals in Eq. (13).

$$F_e{}^{eq} = -\frac{1}{2}\int\rho\varphi dV + \frac{1}{2}\int\sigma\varphi dS + \chi\int_M\sigma dS + kT\sum_i n_i\ \ell n\ V/V_i \qquad [24]$$

In some applications of these results we shall have occasion to apply Eq. (24) in a different but entirely equivalent form, deduced in Appendix IV.

Field Equation and Boundary Conditions

By operating with $\nabla_{r'}{}^2$ on Eq. (5), a differential equation can be obtained for φ identical with Eq. (43) of Part I, except that ψ there is replaced by φ. As in Part I this equation reduces to Poisson's equation when $\underset{\sim}{P}_u$ assumes its equilibrium value.

The boundary condition for this equation which prevails at any interface can be obtained from Eq. (5) by the method employed in Part I. It is identical with Eq. (46) there, except that again ψ there is replaced by φ. At the interface of any conductor the boundary condition is a special case of this relation and is given by Eqs. (55) and (48) of Part I (where ψ is replaced by φ). These boundary conditions reduce to the usual ones when $\underset{\sim}{P}_u$ assumes its equilibrium value (cf Part I).

The boundary condition for ions was also discussed in Part I. As noted there, a "pseudo-point charge approximation" is commonly employed for computing the electrostatic potential in ionic solutions. Specifically, for any specified ionic configuration, it is commonly assumed in systems having equilibrium polarization that the potential due to these charges, in a solution of dielectric constant D, is (1/D)th of that in a vacuum. If α is the polarizability, we have for such systems,

$$\psi(\underset{\sim}{r}) = \psi_V(\underset{\sim}{r})/D = \psi_V(\underset{\sim}{r})/(1+4\pi\alpha) \qquad [25]$$

and therefore for φ we have

$$\varphi(\underset{\sim}{r}') = \frac{1}{D}\int \frac{\rho(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dV + \frac{1}{D}\int \frac{\sigma(\underset{\sim}{r})}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\,dS + \beta \ . \qquad [26]$$

For systems having nonequilibrium polarization, a method of employing an analogous approximation was devised in Part I. An equivalent but simpler procedure for applying it was used in the Appendix of Reference 2 and in Reference 4: The problem is expressed in terms of an equivalent equilibrium one, and Eq. (25) is then used.

Electrode Charge Distribution and the Method of Images

The surface charge distribution on the electrode will be such as to satisfy the condition of zero electric field strength on the electrode and the boundary condition at large distances from it. The electric field strength at large distances from either electrode frequently has some known, constant value. This is zero in the presence of sufficient salt, since the effects of the electrode charges are then neutralized within a short distance from each electrode. In this case, each electrode and its nearby dielectric can be regarded as a separate, electrically neutral subsystem. Indeed, it is usually treated in this way in discussions of properties of the electrode double layer. The following expressions for the electrode charge distribution, derived for this condition of zero field strength in the body of the solution, can readily be adapted to the condition of constant but nonzero field strength. A constant charge density is merely added to one electrode and subtracted from the other.

In systems having equilibrium polarization the method of images [8] can be used to determine the charge distribution [9]. The same method is also suitable for systems having nonequilibrium polarization.

For simplicity, we consider a planar electrode, i.e., any electrode whose radius of curvature is appreciably greater than the thickness of the double layer. Let the electrode-dielectric interface be situated in the plane $x = 0$, and let the dielectric occupy the semi-infinite region, $x > 0$. As before, the coordinates of any point in the dielectric will be specified by the vector $\mathbf{r}$ drawn from any arbitrary origin to the point. The coordinates of the "image" point having the same y and z and differing only in the sign of x will be specified by a vector $\mathbf{r}_{im}$. Mirror image functions $\bar{\rho}(\mathbf{r}_{im})$, $\bar{\sigma}(\mathbf{r}_{im})$ and $\bar{\mathbf{P}}(\mathbf{r}_{im})$ will then be defined in the region of negative x, according to Eq. (27). They are undefined in the region of positive x, i.e., in the dielectric.

$$\bar{\rho}(\mathbf{r}_{im}) = \rho(\mathbf{r}),\quad \bar{\sigma}(\mathbf{r}_{im}) = \sigma(\mathbf{r})$$
$$\bar{P}_x(\mathbf{r}_{im}) = -P_x(\mathbf{r}),\quad \bar{P}_y(\mathbf{r}_{im}) = P_y(\mathbf{r}),\quad \bar{P}_z(\mathbf{r}_{im}) = P_z(\mathbf{r}) . \qquad [27]$$

The last three expressions relate the three components of the vector $\bar{\mathbf{P}}$ to those of $\mathbf{P}$. In Eq. (27) σ refers only to the surface charge density on the central ions and not to that on the electrode.

Applying the method of images, the electrode charge distribution which satisfies the condition of constant potential on the electrode M and in the body of the solution obeys the following equation.

$$\int_M \frac{\sigma(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,dS = -\int_{\text{ions}} \frac{\bar{\sigma}(\mathbf{r}_{im})}{|\mathbf{r}_{im}-\mathbf{r}'|}\,dS_{im} - \int \frac{\bar{\rho}(\mathbf{r}_{im})}{|\mathbf{r}_{im}-\mathbf{r}'|}\,dV_{im} - \int \bar{\mathbf{P}}(\mathbf{r}_{im}) \cdot \nabla \frac{1}{|\mathbf{r}_{im}-\mathbf{r}'|}\,dV_{im} . \qquad [28]$$

In Eq. (28) $\mathbf{r}$ and $\mathbf{r}'$ denote any points on the electrode surface M and in the dielectric medium, respectively. The first surface integral is over M and the second is over the surface of the mirror image of each central ion. The volume integrals are over the entire mirror image of the volume of the dielectric.

Using Eqs. (5) and (27) it is seen that the electrode charge distribution specified by (28) satisfies the condition of constant potential on the electrode. (When the field point $\mathbf{r}'$ is at the electrode-solution interface, its distance to any point in the dielectric equals that to the latter's mirror image.) Because of Eq. (27) the total charge in the dielectric is equal and opposite to the total image charge, which in turn equals the total electrode charge. Thus, the condition of electroneutrality in the region containing the electrode and the nearby dielectric is also satisfied, thereby fulfilling the condition of constant potential in the body of the dielectric.

Evaluation of Some Integrals

In some applications of the equations of this paper we shall have occasion to make use of the following surface integrals (29) and (30).

Treating the surface of an ion as a sphere of uniform charge density it can be readily shown that

$$\int_{\text{ion}} \frac{\sigma\, dS}{|\mathbf{r}-\mathbf{r}'|} = \frac{\int_{\text{ion}} \sigma\, dS}{r} = \frac{q}{r} \qquad [29]$$

where $\mathbf{r}$ is the distance from the center of the ion to the field point, and where q is the ionic charge.

Similarly, it can be shown that

$$\int_{\text{ion}} \frac{\bar{\sigma}(\mathbf{r}_{\text{im}})\, dS_{\text{im}}}{|\mathbf{r}_{\text{im}}-\mathbf{r}'|} = \frac{q}{r_i} \qquad [30]$$

where r_i is the distance from the field point to the center of the electrical image of this ion.

APPENDIX I. PROOF OF EQUIVALENCE OF THE FREE ENERGY EXPRESSIONS, EQS. (13) AND (17)

Eqs. (13) and (17) for F differ only in their first two terms, the difference being equal to

$$\frac{1}{2}\int \left[\frac{\mathbf{E}_v^{\,2}-\mathbf{E}_c^{\,2}}{4\pi} - \mathbf{P}\cdot\mathbf{E}_v + \mathbf{P}\cdot\mathbf{E}_c\right]dV \ . \qquad [31]$$

Writing $\mathbf{E}_v^{\,2}-\mathbf{E}_c^{\,2}$ as $(\mathbf{E}_v-\mathbf{E}_c)\cdot(\mathbf{E}_v+\mathbf{E}_c)$ and collecting terms, this becomes

$$\frac{1}{2}\int (\mathbf{E}_v-\mathbf{E}_c)\cdot(-\mathbf{P}+\mathbf{E}_c/4\pi)\,dV + \frac{1}{2}\int(\mathbf{E}_v-\mathbf{E}_c)\cdot\mathbf{E}_v/4\pi\ dV \ . \qquad [32]$$

Now, the following general equation, applicable to any system, was established in Appendix I of Part I.

$$-\int(\underset{\sim}{P}^{i}-\underset{\sim}{E}_{c}{}^{i}/4\pi)\cdot\underset{\sim}{E}_{c}{}^{j}dV=\int\psi^{i}\rho^{j}dV+\int\psi^{i}\sigma^{j}\,dS\quad, \qquad [33]$$

where the superscripts _i_ and _j_ designate functions of the same or of different systems, and where any potentials involved in (33), directly (ψ^i) or indirectly ($\psi_c{}^i$, $\psi_c{}^j$), are continuous functions.

We apply this equation to the first integral of (32). As a special case of Eq. (33) we can set $\underset{\sim}{E}_c{}^j = \underset{\sim}{E}_v-\underset{\sim}{E}_c$. We will then have $\rho^j = \rho_v-\rho = 0$, and $\sigma^j = \sigma_v-\sigma$, all of these terms having been defined earlier (_cf_ Eq. (16)_ff_). Again, we can set $\underset{\sim}{P}^i = \underset{\sim}{P}$, $\underset{\sim}{E}_c{}^i = \underset{\sim}{E}_c$ and, therefore, $\psi^i = \psi$. Thus, with the aid of Eq. (33) and these substitutions the first integral in Eq. (32) becomes

$$\frac{1}{2}\int\psi(\sigma_v-\sigma)\,dS\quad. \qquad [34]$$

On the electrode surface ψ equals a constant ψ_M, and $\int(\sigma_v-\sigma)dS$ equals the charge induced by the dipoles of the polarized medium. In magnitude this charge equals that of the dipoles, zero, so that (34) vanishes.

Making the following substitutions in Eq. (33) in order to evaluate the second integral of (32), $\underset{\sim}{E}_c{}^j = \underset{\sim}{E}_v-\underset{\sim}{E}_c$ (i.e., $\rho^j = \rho_v-\rho = 0$ and $\sigma^j = \sigma_v-\sigma$), $\underset{\sim}{P}^i = 0$, $\underset{\sim}{E}_c{}^i = \underset{\sim}{E}_v$ (and, therefore, $\psi^i = \psi_v$), and using arguments analogous to those above, it may be verified that this integral also vanishes.

Thus, Eqs. (13) and (17) for F are equivalent.

APPENDIX II. PROOF OF EQ. (20)

We find from Eqs. (10) and (13) that

$$\delta F_e = \delta F + kT\sum_i\int \ln(c_i/c_i{}^0)\,\delta c_i\;dV \qquad [35]$$

where

$$\delta F=\frac{1}{2}\int\Big[\frac{2\underset{\sim}{E}_c\cdot\delta\underset{\sim}{E}_c}{4\pi}-\underset{\sim}{P}\cdot\delta\underset{\sim}{E}_c-\underset{\sim}{E}_c\cdot\delta\underset{\sim}{P}+\frac{2\underset{\sim}{P}_u}{\alpha_u}\cdot\delta\underset{\sim}{P}_u-\underset{\sim}{E}\cdot\delta\underset{\sim}{P}_u-\underset{\sim}{P}_u\cdot\delta\underset{\sim}{E}\Big]dV+\chi\int_M\delta\sigma\,dS\quad. \qquad [36]$$

Introducing the value of $\delta\underset{\sim}{P}$ computed from Eqs. (1) and (2), we obtain

$$\delta F=\frac{1}{2}\int\Big[(-\underset{\sim}{P}+\underset{\sim}{E}_c/2\pi)\cdot\delta\underset{\sim}{E}_c-(\underset{\sim}{E}_c+\underset{\sim}{E}-2\underset{\sim}{P}_u/\alpha_u)\cdot\delta\underset{\sim}{P}_u-(\alpha_e\underset{\sim}{E}_c+\underset{\sim}{P}_u)\cdot\delta\underset{\sim}{E}\Big]dV+\chi\int_M\delta\sigma\,dS\quad. \qquad [37]$$

In Part I it was shown that $\delta\underset{\sim}{P}_u$ and $\delta\underset{\sim}{E}$ are not independent. From Eqs. (1), (36) and (38) there, we find

$$\int(\alpha_e\mathbf{E}_c+\mathbf{P}_u)\cdot\delta\mathbf{E}\,dV=\int[\mathbf{P}\cdot\delta\mathbf{E}_c+(\mathbf{E}-\mathbf{E}_c)\cdot\delta\mathbf{P}_u]\,dV \quad . \qquad [38]$$

Eliminating the $\delta\mathbf{E}$ term between the last two equations, we obtain

$$\delta F=\int(-\mathbf{P}+\mathbf{E}_c/4\pi)\cdot\delta\mathbf{E}_c\,dV+\int(-\mathbf{E}+\mathbf{P}_u/\alpha_u)\cdot\delta\mathbf{P}_u\,dV+\chi\int_M\delta\sigma\,dS \quad . \qquad [39]$$

The system is electrically neutral, so that at fixed surface charge density on the central ions,

$$\int_M\delta\sigma\,dS=-\sum_i\int e_i\,\delta c_i\,dV \quad . \qquad [40]$$

Introducing Eqs. (40) and (42) (below) into Eq. (39), we obtain Eq. (20) for δF_e.

APPENDIX III. TO EVALUATE $\int(\mathbf{P}-\mathbf{E}_c/4\pi)\cdot\delta\mathbf{E}_c\,dV$

Setting as a special case of Eq. (33), $\mathbf{E}_c^j=\delta\mathbf{E}_c$, we have $\rho^j=\delta\rho$ and $\sigma^j=\delta\sigma$. Setting $\mathbf{E}_c^i=\mathbf{E}_c$, $\mathbf{P}^i=\mathbf{P}$, and $\psi^i=\psi$ there, we obtain

$$-\int(\mathbf{P}-\mathbf{E}_c/4\pi)\cdot\delta\mathbf{E}_c\,dV=\int\psi\,\delta\rho\,dV+\int\psi\,\delta\sigma\,dS \quad . \qquad [41]$$

On the electrode surface ψ is a constant, ψ_M. On the surface of any central ion, $\delta\sigma=0$. Thus, the surface integral in Eq. (41) becomes $\psi_M\int_M\delta\sigma\,dS$. As discussed in Appendix I, such an integral cannot have any contribution arising from the $\delta\mathbf{P}(\mathbf{r})$'s. It can only be different from zero if there is a net change in the ionic charge in solution. It will equal $-\psi_M\int\delta\rho\,dV$ and therefore $-\psi_M\sum_i e_i\int\delta c_i\,dV$.

Introducing these results into Eq. (41) and also expressing the ψ's in terms of the φ's, we obtain

$$-\int(\mathbf{P}-\mathbf{E}_c/4\pi)\cdot\delta\mathbf{E}_c\,dV=\sum_i\int(\varphi-\varphi_M+\chi)e_i\,\delta c_i\,dV \quad . \qquad [42]$$

APPENDIX IV. TWO EQUIVALENT EXPRESSIONS FOR F_e FOR SYSTEMS HAVING EQUILIBRIUM $\mathbf{P}_u$ AND c_i

An expression equivalent to Eq. (24) but more convenient for certain applications in equilibrium systems will be deduced. We shall also have occasion to use it indirectly in nonequilibrium systems, as in Reference 4.

Introducing the equilibrium relation (21) into Eq. (39) for δF, and at the same time computing $\delta(kT \sum_i \int c_i \ln c_i/c_i^0 \, dV)$, c_i being given by the equilibrium relation (22), we obtain at fixed n_i

$$\delta F_e^{eq} = -\int(\mathbf{P}-\mathbf{E}_c/4\pi)\cdot\delta\mathbf{E}_c + \chi \int_M \delta\sigma \, dS - \int \varphi\delta\rho \, dV \quad .$$

Using Eqs. (8), (40) and (41) this becomes

$$\delta F_e^{eq} = \int \varphi\delta\sigma \, dS \quad .$$

Thus, by charging up all the surfaces we obtain

$$F_e^{eq} = \int_{\sigma=0}^{\sigma=\sigma} \int_S \varphi d\sigma \, dS \quad , \tag{43}$$

which is the desired relation.

Since the Boltzmann relation was used in deriving Eq. (43), the mobile ions continually readjust their configuration throughout this charging process. This differs from the process used in Eqs. (10) and (12), where the configuration of these ions is fixed.

APPENDIX V. MODIFICATIONS IN TREATMENT ARISING FROM ANY DEPENDENCE OF χ ON MEAN ELECTRODE CHARGE DENSITY

In the present paper, it was assumed that χ, the potential drop at the interface due to solvent-solvent and solvent-electrode interactions, was a constant. However, recent studies [10] on the equilibrium properties of the electrode double layer suggest that the degree of orientation of the solvent molecules at this interface (and hence χ) depend on the electrode charge density.

It is interesting that this degree of orientation did not appear to vary with the salt concentration over the concentration range studied [10]. The close approach of ions could affect this layer by interacting with the solvent molecules directly and by changing the local electrode charge density. (The local surface charge density induced by an ion increases as the ion approaches the electrode.) The average distance of approach, the thickness of the electrode double layer, depends, of course, on the salt concentration. Thus, under the conditions studied, the degree of orientation (and therefore χ) depended on the mean electrode charge density, $\bar{\bar{\sigma}}$ say, but not on any local fluctuations caused by the close approach of the ions.

These considerations suggest that as a first approximation we treat

χ as a function of $\bar{\bar{\sigma}}$, and not of these local fluctuations. In this case, we note that Eq. (5) for the potential will be unaffected. However, the free energy expressions (13), (17), (24), and (43) do change for several reasons:

(1) $\chi\int\sigma dS$ should now be replaced by $\iint\chi(\bar{\bar{\sigma}})d\sigma(\underset{\sim}{r})dS$.

(2) The <u>molecular</u> interactions of the solvent molecules in the interfacial layer, with each other and with electrode, give rise to an additional free energy term. This extra term depends on the average degree of orientation of the molecules in this layer, and therefore on the mean electrode charge density. We shall write this term simply as $g(\bar{\bar{\sigma}})$.

Integrating the first term over the electrode area, we note that $\int_S d\sigma(r)dS$ equals dq, where dq is the total increase in charge when an amount $d\sigma(r)$ is added to each area element. Thus, we obtain for the sum of both terms:

$$\int\chi(\bar{\bar{\sigma}})dq + g(\bar{\bar{\sigma}}) \quad ,$$

and remark that $\bar{\bar{\sigma}}$ equals q/S.

In any electrode process to which the present nonequilibrium treatment will be applied, there will usually be a transfer of a few electrons across the interface. Clearly, such transfers have but a negligible effect on the average electrode charge density. Thus, the contribution of the above sum to the free energy of the system, when the electrode charge differs from q by some small amount δq, is simply

$$\int_{q=0}^{q=q}\chi(\bar{\bar{\sigma}})dq + \chi(\bar{\bar{\sigma}})\delta q + g(\bar{\bar{\sigma}}) \quad .$$

That is, in such processes, this sum is a linear function of q, over the small δq's involved, and will be written as

$$\chi''(\bar{\bar{\sigma}}) + \chi'(\bar{\bar{\sigma}})\int\sigma dS \quad , \qquad [44]$$

since q equals $\int\sigma dS$. In summary, wherever a term $\chi\int\sigma dS$ appears in a free energy expressions, it should be replaced by (44) when χ varies with $\bar{\bar{\sigma}}$.

In any physical process, only free energy changes are important. The first term in (44) is the same in the initial and final states of any step in the process, and so contributes nothing to the free energy change of this step. The second term, in effect, replaces the term $\chi\int\sigma dS$ in the various free energy expressions which occur in the text.

The variation processes in the text are performed at fixed $\bar{\bar{\sigma}}$, so that in those equations χ should merely be replaced by χ'.

In application of the present work to the theory of overvoltage [4], we shall see that the term χ (treated as a constant) cancels out in the final equations for the free energy change of forming the activated state. So, therefore, does $\chi'(\bar{\bar{\sigma}})$.

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4a For simplicity, dielectric saturation will be assumed to be absent. A modification, which treats systems having local regions of saturated dielectric in the innermost hydration layer of some ions, is employed in a forthcoming paper on overvoltage.

5 An excellent review of the equilibrium properties of electrified interfaces is given by R. Parsons in J. O'M. Bockris (Editor), Modern Aspects of Electrochemistry, Academic Press, Inc., New York, 1954, Chap. 3.

6 cf. Reference 5 for bibliography.

7 The only additional feature present in these electrode systems is the condition that $\underset{\sim}{E}(\underset{\sim}{r})$ be zero on the electrode during the entire charging process. This condition is readily fulfilled at the end of each stage by suitable choice of electrode charge distribution using the method of images discussed later. The nature of the process is such that the condition is then automatically fulfilled during each stage.

8 M. Mason and W. Weaver, The Electromagnetic Field, University of Chicago Press, Chicago, 1929.

9 The quantum limitations on the image force theory have recently been discussed by R. G. Sachs and D. L. Dexter (J. Appl. Phys., 21(1950) 1304. From their results it can be deduced that the approximate percent error in the computed energy change (computed from the image force theory) when an ion moves from infinity to a distance r from

the electrode is inversely proportional to r. It is only about 8% or less, in a vacuum or in solution, when r is 5Å.

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