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Free Energy of Nonequilibrium Polarization Systems. II. Homogeneous and Electrode Systems*

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The polar contribution to the free energy is calculated for a system containing "particles" imbedded in a continuum having nonequilibrium dielectric polarization. Each particle may either be a single molecule or a whole collection of molecules (such as an electrode) at specified nuclear configuration and may possess a general permanent and induced charge distribution. Thereby, the results of Part I of this series are extended to a variety of systems. It is also shown that the polar contribution to the free energy can be written as the sum of free energies of equilibrium polarization systems, thereby permitting the immediate application of literature expressions for the latter to calculating the former. This expression is also derived for systems possessing partial dielectric unsaturation under a certain typical condition. Applications are made to the theory of electron-transfer reactions in solution and at electrodes and to the theory of the shift of electronic spectra of polar solutes by polar solvents.

INTRODUCTION

IN Part I of this series, the free energy and other properties of systems having nonequilibrium dielectric polarization were discussed, the system being treated for quantitative purposes as a dielectric continuum.[1] This treatment was employed to formulate a theory of electron-transfer rates in solution[2,3] and at electrodes,[4,5] and to develop a theory of shifts of electronic spectra of polar solutes due to interactions with polar solvents.[6] Certain molecules under special consideration, which will be termed central species, were regarded as being electronically polarizable regions (continua) imbedded in the remainder of the system treated as an orientationally and electronically polarizable dielectric continuum. Examples of the central species are two reacting ions, a reacting ion and the electrode, and a fluorescing solute molecule.

The treatment in Part I can be extended considerably by using a recent and more general description of the central species[7]: One may regard them as being particles, each of which represents a single molecule or any collection of molecules at any specified configuration of the particles' nuclei. These particles are assigned general, permanent, and induced charge distributions and can be embedded as before in the remainder of the system and treated as a dielectric continuum. (A statistical-mechanical description of nonequilibrium polarization systems, based on this model of a particle, is given in Part III of this series.)

Two special cases of this model of a particle are, it has been shown,[8] the usual models employed in the literature of dielectric behavior and polar phenomena. These are the induced dipole and the electronically polarizable continuum models of the induced charge distribution on a particle. In this literature the particle is a single molecule or, in electrode systems, an entire electrode treated as a continuum. We need not restrict ourselves to such special cases, however.

In the present paper we describe this extension of Part I. Because of the general nature of these particles, electrode systems are automatically included, and thereby Part I is further generalized since it was concerned with homogeneous systems only. Electrode systems had to be described separately.[9]

An expression is obtained for the polar contribution to the free energy of systems in which the medium surrounding the particles is treated as an orientationally and electronically polarizable dielectric continuum having nonequilibrium dielectric polarization. It will then be shown that this free energy can be expressed as a sum of free energies of hypothetical systems having equilibrium dielectric polarization. An advantage of this relation is that literature expressions for equilibrium polarization systems can then be immediately used to compute the free energy of nonequilibrium ones. Several examples of this application are given later.

It will be useful to regard each ion and its inner coordination shell as forming a single particle. In electrochemical systems it will also be useful to treat the electrode and any strongly bound adjacent layer of molecules or ions as another particle. The interactions

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[1] R. A. Marcus, J. Chem Phys. 24, 979 (1956) (homogeneous systems), hereinafter referred to as Part I.
[2] R. A. Marcus, J. Chem. Phys. 24, 966 (1956).
[3] Compare R. A. Marcus, Discussions Faraday Soc. 29, 21 (1960).
[4] R. A. Marcus, Can. J. Chem. 37, 155 (1959); Trans. Symp. Electrode Processes, Philadelphia, Pa., 1959, 239 (1961); O. N. R. Technical Report No. 12, Project NR-050-331 (1957).
[5] Compare R. A. Marcus, "On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer," J. Phys. Chem. (to be published).
[6] R. A. Marcus, paper presented at 133rd National American Chemical Society Meeting, 1958; NSF Rept. No. 4, Grant 3690 (1958).
[7] R. A. Marcus, J. Chem. Phys. 38, 1335 (1963).
[8] R. A. Marcus, "Interactions in Polar Media. II. Continua," J. Chem. Phys. (to be published).
[9] R. A. Marcus, ONR Tech. Rept. No. 11, Project NR-050-331 (1957). The basic contents of this report are now automatically included in the present paper, since the electronically polarizable continuum model used there for the electrode and for the reacting ions has been shown[8] to be a special case of the general particle equations (1) to (4) of the present paper.

within these particles may then be described by molecular methods[10] while dielectric continuum theory is used in this paper to calculate the polar contribution to the free energy arising from the mutual interactions of the particles and from their interactions with the medium. The calculation is made at any specified nuclear configuration of the particles. One may then integrate over these nuclear configurations, suitably weighted as in statistical mechanics. We consider first dielectrically unsaturated systems and then deduce Eq. (23) for partially saturated systems as well.

DIELECTRICALLY UNSATURATED NONEQUILIBRIUM POLARIZATION SYSTEMS

We let each particle i have a total density $\rho_i(\mathbf{r})$, the sum of a permanent charge density $\rho_i^0(\mathbf{r})$ (the charge density when i is isolated) and an induced charge density $\rho_i^{in}(\mathbf{r})$. The latter is related to $\phi_i(\mathbf{r}')$, the potential due to all sources but i, via a linear Hermitian operator A_i.[7]

$$\rho_i(\mathbf{r})=\rho_i^0(\mathbf{r})+\rho_i^{in}(\mathbf{r}), \tag{1}$$

$$\phi_i(\mathbf{r}')=\sum_{j\neq i}\int\frac{\rho_j(\mathbf{r})}{r}d\tau+\int\mathbf{P}(\mathbf{r})\cdot\nabla\frac{1}{r}d\mathbf{r}, \tag{2}$$

$$\rho_i^{in}(\mathbf{r})=A_i(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}'), \tag{3}$$

where $\mathbf{P}(\mathbf{r})$ is the polarization of the medium (it vanishes inside the volume V_i occupied by any particle i) and $1/r$ is $1/|\mathbf{r}-\mathbf{r}'|$. Integration in (2) is over the entire volume of the system, and ρ_i vanishes outside V_i.

In the nonequilibrium polarization systems which we have investigated thus far,[2-4,6] the orientational contribution to $\mathbf{P}(\mathbf{r})$ has proved to be one which is in equilibrium with ρ_i's different from the existing ones. We shall denote by a subscript 0 the properties of this equilibrium system (the "equivalent equilibrium system"[3]). We also introduce three other equilibrium polarization systems: (i) one denoted by a subscript 1, having the same ρ_i^0's as the nonequilibrium system ρ_{i1}^0 but having a $\mathbf{P}(\mathbf{r})$ in equilibrium with them; (ii) one denoted by a subscript $1-0$, having $\rho_{i_{1-0}}^0=\rho_{i_1}^0-\rho_{i_0}^0$ and having a $\mathbf{P}(\mathbf{r})$ in equilibrium with the $\rho_{i_{1-0}}^0$'s; (iii) one having $\rho_i^0=\rho_{i_{1-0}}^0$ and responding to these ρ_i^0's only via an electronic polarization. We denote this system by a superscript op and subscript $1-0$. The four equilibrium systems will be referred to as the [0], [1], [1−0], and [1−0, op] systems, respectively.[11]

Let $\chi(\mathbf{r})$ and $\chi_e(\mathbf{r})$ denote the static and electronic dielectric susceptibilities of the medium, respectively, at any point $\mathbf{r}$ in the medium.

$$\chi(\mathbf{r})=(D_s-1)/4\pi, \qquad \chi_e(\mathbf{r})=(D_{op}-1)/4\pi,$$

where $D_s(\mathbf{r})$ and $D_{op}(\mathbf{r})$ denote the static dielectric constant and the square of the refractive index of the medium, respectively. (Usually the χ's and the D's are constant scalars, but we include the possibility that they are variable tensors.) Let $\psi(\mathbf{r})$ denote the potential at any point $\mathbf{r}$ due to all parts of the system[7]:

$$\psi(\mathbf{r})=\sum_i\int\frac{\rho_i}{r}d\mathbf{r}+\int\mathbf{P}\cdot\nabla\frac{1}{r}d\mathbf{r}, \tag{4}$$

with ρ_i given by (1). When appropriate subscripts are added, these equations refer to any of the five systems described above. $\mathbf{P}(\mathbf{r})$ for the nonequilibrium polarization system differs from $\mathbf{P}$ of the [0] system, $\mathbf{P}_0(\mathbf{r})$, only in electronic polarization. Assuming the electronic polarization to be dielectrically unsaturated, we have[7,12]:

$$\mathbf{P}-\mathbf{P}_0=-\chi_e\nabla(\psi-\psi_0). \tag{5}$$

When from the coupled Eqs. (1) to (4) one subtracts their counterparts for the [0] system, we obtain coupled equations for the $(\phi_i-\phi_{i_0})$'s and $\psi-\psi_0$ as a function of the $(\rho_i^0-\rho_{i_0}^0)$'s. Denoting the totality of the latter $\delta\rho_i^0$'s by $\rho^0(\mathbf{r})-\rho_0^0(\mathbf{r})$,

$$\rho^0-\rho_0^0=(\rho_1^0-\rho_{1_0}^0,\ \rho_2^0-\rho_{2_0}^0\cdots,\ \rho_i^0-\rho_{i_0}^0,\ \cdots),$$

we then see that when the ρ_i^0 are permitted to vary, the $\phi_i-\phi_{i_0}$ are linearly dependent on $\rho^0-\rho_0^0$ via a linear operator C_i[13]:

$$\phi_i(\mathbf{r})-\phi_{i_0}(\mathbf{r})=C_i(\mathbf{r},\mathbf{r}')\{\rho^0(\mathbf{r}')-\rho_0^0(\mathbf{r}')\}. \tag{6}$$

The polar contribution to the free energy of a system

[10] These molecular methods for the internal nuclear coordinates of the particles were used in references 3 and 5.

[11] We assume in the present paper that the A_i for any i is the same in the nonequilibrium and equivalent equilibrium polarization systems. There is no obvious reversible path for changing these A_i's, and the extension of the present work to include such changes lies more properly within the scope of a statistical mechanical treatment. This extension is given in Part III. The additional contribution to ΔF in Eq. (7) is shown there to involve certain fluctuation terms. This extension is of interest when there is a sufficient change in the generalized polarizability operator A_i. One possible example is in fluorescence or light absorption, where the excited and ground states of the radiating or absorbing molecule have a different polarizability.

[12] Cf. Part I, where we wrote (in terms of the present notation):

$$\mathbf{P}(\mathbf{r})=\mathbf{P}_u(\mathbf{r})-\chi_e\nabla\psi.$$

$\mathbf{P}_u$, a convenient function for the minimizations performed there and elsewhere, equals $\mathbf{P}_0+\chi_e\nabla\psi_0$. It was termed the orientation component of P in Part I, although it also contains an electronic component of the [0] system. This terminology was misleading but did not affect either the formulas of Part I or their application.

[13] Let u_i denote $\phi_i-\phi_{i_0}$. To show that C_i is a linear operator we must show that

$$u_i(\alpha a+\beta b)=\alpha u_i(a)+\beta u_i(b),$$

where α and β are scalars, and a denotes a charge distribution described by $\rho_a^0-\rho_0^0$, so that $\alpha a+\beta b$ denotes a charge distribution described by $\alpha(\rho_a^0-\rho_0^0)+\beta(\rho_b^0-\rho_0^0)$, and $u_i(a)$ denotes $\phi_{i_a}(\mathbf{r})-\phi_{i_0}(\mathbf{r})$. By subtracting Eqs. (1) to (5) for System [a] from those for System [a] then multiplying by α, and by subtracting (1) to (5) for [0] from those for [b] and multiplying these by β, and finally adding these two sets of equations one obtains equations satisfied by $\alpha u_i(a)+\beta u_i(b)$. Because of the linearity of A_i and of $-\chi_e\nabla$ in (3) and (5), the same equations for u_i are also satisfied when the permanent charge density is $\alpha(\rho_a^0-\rho_0^0)+\beta(\rho_b^0-\rho_0^0)$, i.e., they are also satisfied by $u_i(\alpha a+\beta b)$. Because of the uniqueness theorem for the potentials, we may conclude that $u_i(\alpha a+\beta b)$ and $\alpha u_i(a)+\beta u_i(b)$ are equal, i.e., that C_i is linear.

equals the reversible work done to charge the system.[14] The free-energy change ΔF, when that system is changed from one set of charges on the particles to another, equals the reversible work done to form one system from the other[14,15]:

$$\Delta F=\iint_{\lambda=0}^{1}\phi_i^{\lambda}d\rho_i^{0\lambda}d\mathbf{r}, \tag{7}$$

where λ is a charging parameter.

Starting with system [0] and holding the orientation polarization of the medium fixed, we can form the nonequilibrium polarization system by changing the $\rho_i^{0\lambda}$ according to (8)

$$\rho_i^{0\lambda}=\rho_{i_0}^{0}+\lambda(\rho_{i_1}^{0}-\rho_{i_0}^{0}). \tag{8}$$

Since $\mathbf{P}_0$ is being held fixed we may apply the linearity relation (6) and conclude:

$$\phi_i^{\lambda}=\phi_{i_0}^{0}+\lambda(\phi_{i_1}-\phi_{i_0}). \tag{9}$$

Moreover, the collection $(\psi-\psi_0, \cdots, \varphi_i-\varphi_{i_0}, \cdots)$ satisfies the same set of equations as does $(\psi_{1-0}{}^{\mathrm{op}}\cdots, \phi_{i_{1-0}}{}^{\mathrm{op}}, \cdots)$ so that by the uniqueness theorem for potentials[16] we have

$$\phi_i-\phi_{i_0}=\phi_{i_{1-0}}{}^{\mathrm{op}}. \tag{10}$$

From (7) to (10) Eq. (11) then follows; i.e., for nonequilibrium polarization,

$$F=F_0+\sum_i\int(\phi_{i_0}+\tfrac{1}{2}\phi_{i_{1-0}}{}^{\mathrm{op}})(\rho_{i_1}^{0}-\rho_{i_0}^{0})d\mathbf{r}. \tag{11}$$

where F_0 is the polar contribution to the free energy of the equilibrium polarization system [0].

We need, too, the value of F for equilibrium polarization systems. Starting from an uncharged system, this F is obtained from (7) by setting:

$$\rho_i^{0}=\lambda\rho_i^{0}, \tag{12}$$

$$\mathbf{P}^{\lambda}(\mathbf{r})=-\chi(\mathbf{r})\nabla\psi^{\lambda}. \tag{13}$$

Relation (13) assumes dielectric unsaturation. Once again, because of (1) to (4) and (13) one can prove a linear dependence of φ_i on ρ^0.

$$\phi_i(\mathbf{r})=D_i(\mathbf{r},\mathbf{r}')\rho^0(\mathbf{r}'), \tag{14}$$

where D_i is a linear operator. Using (12) we conclude from (14) that

$$\phi_i^{\lambda}=\lambda\phi_i. \tag{15}$$

From (7), (12), and (15) we obtain (16) for the polar contribution to the free energy of an equilibrium polarization system.

For equilibrium polarization

$$F=\tfrac{1}{2}\sum_i\int\phi_i\rho_i^{0}d\mathbf{r}. \tag{16}$$

Equations for F for the four equilibrium polarization systems described earlier are obtained from (16) by adding appropriate subscripts and superscripts. For the [1−0] and [1−0, op] systems, we thus have

$$F_{1-0}=\tfrac{1}{2}\sum_i\int\phi_{i_{1-0}}(\rho_{i_1}^{0}-\rho_{i_0}^{0})d\mathbf{r}, \tag{17}$$

$$F_{1-0}{}^{\mathrm{op}}=\tfrac{1}{2}\sum_i\int\phi_{i_{1-0}}{}^{\mathrm{op}}(\rho_{i_1}^{0}-\rho_{i_1}^{0})d\mathbf{r}. \tag{18}$$

Another consequence of (14) is (19), since both sides of (19) depend on $(\rho_{1_{1-0}}{}^{0}, \rho_{2_{1-0}}{}^{0}, \cdots, \rho_{i_{1-0}}{}^{0}, \cdots)$, i.e., on $\rho_{1-0}{}^{0}$, via the linear operator D_i.

$$\varphi_{i_1}-\varphi_{i_0}=\varphi_{i_{1-0}}. \tag{19}$$

We shall need an expression for F_1-F_0, which for subsequent discussion of the effect of dielectric saturation is best obtained from (7) using (8).

$$\rho_i^{0\lambda}=\rho_{i_0}+\lambda(\rho_{i_1}^{0}-\rho_{i_0}^{0}). \tag{8}$$

As this $\rho_i^{0\lambda}$ is varied, incidentally, $\mathbf{P}^{\lambda}$ changes from $\mathbf{P}_0$ according to (20), $\mathbf{P}^{\lambda}$ being linearly dependent on ρ^0.

$$\mathbf{P}^{\lambda}-\mathbf{P}_0=-\chi\nabla(\psi^{\lambda}-\psi_0). \tag{20}$$

Because of (14) we have from (8)

$$\phi_i^{\lambda}=\phi_{i_0}+\lambda(\phi_{i_1}-\phi_{i_0}), \tag{21}$$

and from (7), (8), and (21) we obtain

$$F_1-F_0=\tfrac{1}{2}\sum_i\int(\phi_{i_1}+\phi_{i_0})(\rho_{i_1}^{0}-\rho_{i_0}^{0})d\mathbf{r}. \tag{22}$$

Finally, from (11), (17), (18), (19), and (22) the desired relation is obtained:

$$F=F_1+F_{1-0}{}^{\mathrm{op}}-F_{1-0}. \tag{23}$$

PARTIALLY DIELECTRICALLY SATURATED NONEQUILIBRIUM POLARIZATION SYSTEMS

Any solvent present in the inner coordination shell of an ion will be at least partially dielectrically saturated. Partly for this reason the inner coordination shells are treated separately and by a noncontinuum method.[10] However, partial saturation can also occur in the solvent just outside this shell if the ion is highly charged, and in this section this latter saturation will be considered.

Equation (23) can be derived for systems having this partial dielectric saturation, provided the change

[14] Compare reference 7 for a discussion of the *potential energy* of any configuration of particles, based on a Hartree approximation for the Schrödinger equation describing the interparticle interactions and based alternatively on the electrostatic reversible work to charge up the system. (The two expressions agree.) The same argument can then be extended to the problem of calculating the free energy when an orientationally polarizable medium is present.[7]

[15] Initially, in using (7) to derive (23), the electrostriction which may result when this work is performed at constant pressure is ignored. It can be included by taking into account any dependence of $\chi(r)$ and $\chi_e(r)$ on λ. We note that this electrostriction is the one which occurs outside the inner coordination shell of each ion. In the derivation of Eq. (23′), the electrostriction on forming system [0] is not neglected. Rather one makes the normally milder assumption of neglecting the additional electrostriction on forming system [1] from [0]. Systems [1–0]′ and [1–0, op]′ have the $\chi(r)$ and $\chi_e(r)$ of system [0].

[16] For example, O. D. Kellogg, *Foundations of Potential Theory* (Dover Publications, Inc., New York, 1953).

in permanent charges of the particles on going from the equivalent equilibrium system [0] to the nonequilibrium one is not too large. These changes are, in fact, normally small. In electron-transfer reactions, for example, they usually involve a change of $\frac{1}{2}$ a charge unit on each reacting particle.[17]

There are two types of dielectric saturation to be included, electronic and orientational. We can consider both at once. It will be assumed that the change in charge on any species on going from the equivalent equilibrium system [0] to the nonequilibrium one and, therefore, to the equilibrium system [1] is sufficiently small that although the linear equations (3), (5), and (20) may not be applicable, each may be replaced by a linear relation between increments:

$$\delta\rho_i^{in} = A_i'\delta\phi_i. \tag{24}$$

(For nonequilibrium polarization systems)

$$\delta\mathbf{P} = -\chi_e'\delta\nabla\psi. \tag{25}$$

(For equilibrium polarization systems)

$$\delta\mathbf{P} = -\chi'\delta\nabla\psi. \tag{26}$$

For example, it is assumed that when the plot of $\mathbf{P}$ vs $\nabla\psi$ becomes curved due to dielectric saturation we may compute the change $\delta\mathbf{P}$ from the tangent, $-\chi'$, and from $\delta\nabla\psi$.

Because of (24) and (25), Eq. (6) is once again obtained, but now the C_i depend on the A_i''s and χ_e' rather than on the A_i's and χ_e. Accordingly (9) again follows.

We next introduce dielectrically unsaturated equilibrium polarization systems whose A_i's, χ_e and χ are equal to the A_i''s, χ_e' and χ', namely the [1−0] and [1−0, op] systems, designated now by primes. Equation (10) then follows and, hence, so does (11). We may again use (14) for these two systems but because of (24) and (26) the D_i's now depend on A_i''s and χ' rather than on A_i's and χ. Accordingly (17) and (18) obtain, but with $F_{1-0}{}^{op'}$ and F_{1-0}' replacing $F_{1-0}{}^{op}$ and F_{1-0}.

Because of (26), Eq. (21) and thereby (22) again follow. Accordingly, so does the derived relation (23), with [1−0, op] and [1−0] systems being dielectrically unsaturated but having properties A_i', χ_e' and χ':

$$F = F_1 + F_{1-0}{}^{op'} - F_{1-0}'. \tag{23'}$$

SOME APPLICATIONS OF EQ. (23)

Although detailed applications of (23) will be made in a subsequent series of papers, several examples may be cited, drawn from the theory of electron-transfer reactions and of solvent shifts on solute absorption or fluorescence.

I. Electron Transfers in Solution

If $(e_a, e_b, \cdots, e_j, \cdots)$ denotes the charges of the reactants A and B and of any other ions j present before electron transfer, and if $(e_a{}^p, e_b{}^p, \cdots, e_j{}^p, \cdots)$ denotes the charges after, then $e_j{}^p = e_j$. It has been shown[2,3] that in the activated complex, the medium has an orientation-atomic polarization which would be in dielectric equilibrium only with the hypothetical charges $e_i + m(e_i - e_i{}^p)$ ($i = a$, b or j) where m satisfies a given equation. State [0] has, therefore, the charge distribution described by:

$$\text{State } [0] \equiv (e_a + m\Delta e, e_b - m\Delta e, \cdots, e_j \cdots), \tag{27}$$

where $\Delta e = e_a - e_a{}^p = e_b{}^p - e_b$.

State [1], which consists of the equilibrium polarization system having the same nuclear configuration of i's and having the e_i's existing before electron transfer, is represented by (28). Hence the state [1−0] is given by (29).

$$\text{State } [1] \equiv (e_a, e_b, \cdots, e_j, \cdots), \tag{28}$$

$$\text{State } [1-0] \equiv (-m\Delta e, m\Delta e, \cdots, 0, \cdots), \tag{29}$$

i.e., F_{1-0} is the free energy of an equilibrium polarization having *no charged particles* other than those undergoing electron transfer.

If A and B are treated as spherical, and if electrostatic image effects are ignored (they contribute about 10% to the free-energy change[3]), then the polar contribution to the free energy of the activated complex minus that of an equilibrium polarization system with charges e_a, e_b and $\cdots$, e_j, $\cdots$ in the same specified positions is given by $F - F_1$, i.e., by $F_{1-0}{}^{op} - F_{1-0}$. However, using a well-known formula, F_{1-0} equals the sum of the Born charging terms at infinity plus the work required to bring the ions from ∞ to some mean distance r apart. (It will be recalled that these F's do not include interactions within the inner coordination shells.) Since the 1−0 system has no ions other than A and B, we then find:

$$F_{1-0} = -\frac{1}{2a_1}\left(1-\frac{1}{D_s}\right)(m\Delta e)^2 - \frac{1}{2a_2}\left(1-\frac{1}{D_s}\right)(m\Delta e)^2 + \frac{(m\Delta e)(-m\Delta e)}{D_s r},$$

and

$$F_{1-0}{}^{op} = -\frac{1}{2a_1}\left(1-\frac{1}{D_{op}}\right)(m\Delta e)^2 - \frac{1}{2a_2}\left(1-\frac{1}{D_{op}}\right)(m\Delta e)^2 + \frac{(m\Delta e)(-m\Delta e)}{D_{op} r},$$

where a_1 and a_2 denote the radii of the reactants, each including any inner coordination shell. Accordingly, this contribution to the free-energy change is:

$$F - F_1 = (m\Delta e)^2\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right), \tag{30}$$

[17] The change is given by $m\Delta e$ in the section on applications and m is usually about −0.5. (cf. references 3 and 5).

a simple derivation of a result derived[2] and used[2-5] elsewhere.

II. Electron Transfers at Electrodes

Remarks similar to the above apply, but using the appropriate equations for F_{1-0} and F_{1-0}^{op} for electrode systems:

If a reacting ion A is about to undergo electron transfer with the electrode, one finds:

$$\text{State } [1] \equiv (e_a, \cdots, e_j, \cdots), \tag{31}$$

$$\text{State } [0] \equiv (e_a + m(e_a - e_a^p), \cdots, e_j, \cdots). \tag{32}$$

Hence,

$$\text{State } [1-0] \equiv (-m(e_a - e_a^p), \cdots, 0, \cdots). \tag{33}$$

In state $[1-0]$, any charge on the electrode, other than the electrostatic image charge, $m(e_a - e_a^p)$, vanishes. For such a system $[1-0]$ having all $e_j = 0$, F_{1-0} is the sum of the Born charging term when the hypothetical ion and electrode are far apart and the image term when they are brought together:

$$F_{1-0} = -\frac{1}{2a}\left(1 - \frac{1}{D_s}\right)(m\Delta e)^2 - \frac{(m\Delta e)^2}{2rD_s},$$

where r is twice the distance of the center of the ion to the electrode surface. Accordingly, we obtain

$$F - F_1 = F_{1-0}^{op} - F_{1-0} = \left(\frac{1}{2a} - \frac{1}{2r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(m\Delta e)^2, \tag{34}$$

as in an earlier paper.[4]

III. Fluorescence or Absorption of a Polar Species

A polar molecule orients polar solvent molecules about it and, for a brief instant after fluorescence or light absorption by the solute, the solvent molecules maintain their orientation-atomic polarization, because of the Franck–Condon principle. In this case the final charge distributions are described by ρ_{i1}^0, the initial ones by ρ_{i0}^0, and the state of orientation-atomic polarization by ρ_{i0}^0. The entropy associated with the latter polarization being the same for the states of the entire system just before and after the transition, the polar contribution to their energy difference equals that to their free energy difference, $F - F_0$. Thus, this contribution to the spectral shift for light absorption, for fluorescence, and for the difference of the shifts is given by (35) to (37), where e denotes the excited state and g the ground state, and where non denotes the nonequilibrium polarization system having the charges of the subscript.

$$h(\delta\nu_a)_{pol} = F_e^{non} - F_g = F_e - F_g + F_{e-g}^{op} - F_{e-g}, \tag{35}$$

$$-h(\delta\nu_f)_{pol} = F_g^{non} - F_e = F_g - F_e + F_{g-e}^{op} - F_{g-e}, \tag{36}$$

$$h(\delta\nu_a - \delta\nu_f)_{pol} = 2(F_{e-g}^{op} - F_{e-g}), \tag{37}$$

since F_{e-g} and F_{e-g}^{op} will be assumed to be quadratic in the charge distribution, and hence the same as F_{g-e} and F_{g-e}^{op}, respectively.

If the solute is treated as a sphere of radius a having a dipole moment μ and an induced dipole at its center, the usual treatment yields[18]

$$F = -[f/(1-f\alpha)]\tfrac{1}{2}\mu^2, \tag{38}$$

$$f = (1/a^3)(2D-2)/(2D+1),$$

where D is the dielectric constant of the medium (D_{op} in case of the op system) and α is the polarizability of the solute molecule. Insertion of (38) into (35) to (37), with appropriate subscript and, in one case, superscript, yields an expression for the polar contribution to the spectral shifts. The resulting equations may be compared with earlier ones used in the literature.[19] The earlier ones correspond to the assumption $\alpha f \ll 1$, and are obtained by expanding (38) in a power series in αf and retaining only terms of zeroth or first order in αf. More elaborate models of the solute are given elsewhere, in an application of the present paper.

The advantage of using (37) is that both the dispersion and exchange forces contributions to $\delta(\nu_a - \nu_f)$ vanish if the set of equilibrium solvent configurations of nearest neighbors is the same for state e as for g. On the other hand $\delta\nu_a$ (or $\delta\nu_f$) alone will also contain these other contributions, the dispersion one giving rise to the usual red shift.

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[18] For example, C. J. F. Böttcher, *Theory of Electrical Polarization* (Elsevier Publishing Company, Inc., New York 1952), p. 139.

[19] Y. Ooshika, J. Phys. Soc. Japan **9**, 594 (1954); E. Lippert, Z. Naturforsch. **10A**, 541 (1955).