

## Entropy, Enthalpy, and Free Energy of the Electrical Double Layer at an Ideal Polarized Electrode. Part I. Thermodynamic Theory

David C. Grahame

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# Entropy, Enthalpy, and Free Energy of the Electrical Double Layer at an Ideal Polarized Electrode. Part I. Thermodynamic Theory

DAVID C. GRAHAME

*Moore Laboratory of Chemistry, Amherst College, Amherst, Massachusetts*

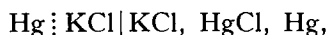
(Received June 7, 1948)

There are several kinds of entropy, enthalpy, and free energy changes associated with the electrical double layer. Definitions of the thermodynamically significant quantities are given, together with equations for their evaluation. It is shown that the ideal polarized electrode may be regarded as one electrode in a galvanic cell and that the usual thermodynamic treatment of cells may be applied. The electrochemical process occurring in such a cell is identified, and a method of evaluating a new property, the transference number of the ions of the double layer, is given. The relationship between electrocapillary properties of metals and the thermodynamic properties of colloids is indicated. The thermodynamics of gas adsorption on solids is presented as an aid to the interpretation of the above.

THE thermodynamic properties of the electrical double layer most often considered are those of interfacial tension and its related properties, surface charge density, differential capacity, and electrical potential. There are, in addition, a number of properties ascribable to the ionic species separately and derivable by methods previously described.<sup>1</sup> Beyond these, it is possible to define and to outline methods of measurement for thermodynamic quantities such as the entropy, enthalpy, free energy, heat capacity, and the like of the double layer. Except in the work of Gibbs, who defines the entropy of an interface, the very existence of these quantities as properties of the double layer has gone almost unremarked and presumably unrecognized. It is the purpose of this paper to define the more important of these properties and to outline the steps by which they may be evaluated. In a later paper some of them will be evaluated in an actual case.

## I. THE ELECTROCHEMICAL PROCESS AT AN IDEAL POLARIZED ELECTRODE

From an experimental point of view the easiest thermodynamic quantities to evaluate, apart from the familiar electrocapillary properties, are those related to the electrochemical process which accompanies the transfer of charge into or out of the electrical double layer in a reversible manner. Consider the cell



<sup>1</sup> D. C. Grahame, *Chem. Rev.* 41, 441 (1947).

where the dotted vertical line represents the interface of an ideal polarized electrode, an interface which charges may approach in the manner of charges on a condenser, but which they do not cross. Such a cell has a definite electromotive force, dependent upon the total electronic charge  $q$  on the plates of the "condenser," i.e., on the charge per square centimeter of interface. It is in every sense a galvanic cell except that the electrochemical process is not what is ordinarily called a chemical reaction but resembles more closely a process of adsorption or desorption. The ordinary thermodynamic treatment of galvanic cells is not thereby invalidated, however, so that one may use the familiar equations of the galvanic cell:

$$\Delta G' = -n\mathcal{F}E, \quad (1)$$

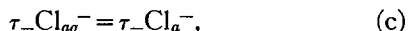
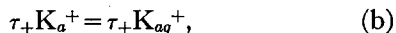
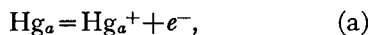
$$n\mathcal{F}(dE/dT)_q = \Delta S', \quad (2)$$

$$\Delta H' = \Delta G' + T\Delta S', \quad (3)$$

where the symbols have their usual meanings and the primes designate that the process involved is the special electrochemical process to which we have been referring and which we shall presently identify. In practice one actually imposes the desired value of the electromotive force,  $E$ , from an external source and then measures  $q$ , the electronic surface charge density, but this is of no consequence to the thermodynamic treatment.

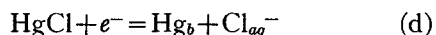
We now proceed to identify the electrochemical process to which these equations refer. Following the usual convention, we write all cell reactions in the direction corresponding to the flow of positive

charge from left to right within the cell. Then at the left-hand electrode, designated by the subscript  $a$  (which may also be thought of as designating "adsorbed" since ions at that electrode are adsorbed on the surface of the mercury),

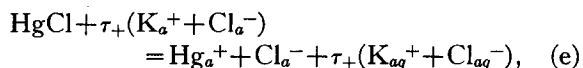


where the subscript  $aq$  designates the solution phase (unadsorbed ions), and  $\text{Hg}_a^+$  is not an ion in the ordinary sense but an atom of mercury in the metallic phase which has lost an electron.  $\tau_+$  is the number of equivalents of cation transferred from the interface to the solution per faraday of charge transferred from the left to the right-hand electrode.  $\tau_+$  will be called the transference number of the cation within the double layer. As usual,  $\tau_+ + \tau_- = 1$ , but values of  $\tau$  are not restricted to positive values, and negative values of  $\tau_+$  prove to be very common.

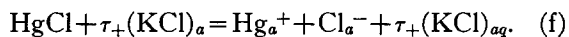
At the right-hand electrode (subscript  $b$ ) the half-cell reaction is the familiar calomel cell reaction



The sum of these four reactions is



or



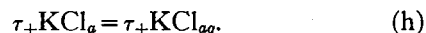
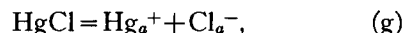
In arriving at Eq. (e) we have made use of the fact that the transfer of a mercury atom from one electrode to the other involves no change of entropy, enthalpy, or free energy, so that it is proper to cancel  $\text{Hg}_a$  against  $\text{Hg}_b$ . Although the transfer of potassium and chloride ions from the interface to the interior of the solution involves no change of free energy (since they are in equilibrium), the same cannot be said of their entropy and enthalpy.<sup>2</sup> Hence it is not permissible to cancel  $\text{K}_a^+$  against  $\text{K}_{aq}^+$  or  $\text{Cl}_a^-$  against  $\text{Cl}_{aq}^-$ . Equation (f) is written as a shorthand notation for Eq. (e).

In the preceding equations it would have been

<sup>2</sup> In ordinary galvanic cells this point does not arise because the substances involved are always transferred or transformed with a change of free energy.

possible to write for  $\text{Hg}^+$  and  $\text{Cl}^-$  any other metallic cation and anion whose salt is relatively insoluble. For combinations of ions whose salts are soluble, the counterpart of Eq. (e) does not lead to results of any apparent interest.

It is sometimes convenient to break Eq. (f) into two equations whose sum represents the over-all cell reaction, thus:



It is seen that the first of these reactions involves the transfer of one mole of mercurous chloride to the polarized interface, the mercurous ion being within the metallic phase and the chloride ion being within the solution phase of the electrical double layer. The second reaction, (h), involves the transfer of  $\tau_+$  equivalents of potassium and chloride ions from the solution phase of the double layer to the interior of the solution itself.

One important result may be deduced immediately. Since there is no free energy change associated with reaction (h), the whole free energy change associated with the potential  $E$  is ascribable to reaction (g). Therefore

$$\Delta G_g = -\mathcal{F}E. \quad (\text{4})$$

This result has immediate application in correlating the properties of the electrical double layer with the properties of colloids, as will be shown in Section II.

In order to interpret experimental values of  $\Delta H'$  and  $\Delta S'$  it is necessary to understand the significance of Eqs. (g) and (h). This understanding is facilitated by considering various particular values of  $\tau_+$ . There is a potential (called the  $\Gamma_{\text{min}}^+$ -potential in reference 1) where  $\tau_+ = 0$ . At that potential Eq. (h) drops out and a transfer of charge through the external circuit has the effect of converting solid mercurous chloride into mercurous ions within the mercury surface and chloride ions in the immediate vicinity of the surface. Values of  $\Delta H'$  and  $\Delta S'$  measured at this potential thus correspond to a single definite chemical reaction. Since these values of  $\Delta H'$  and  $\Delta S'$  correspond to the particular value of  $q$  prevailing at the  $\Gamma_{\text{min}}^+$ -potential, a series of values corresponding to different values of  $q$  may be obtained by working at various concentrations of electrolyte.

When an ideal polarized electrode is made negative by imposing a negative electronic charge on the metallic surface,  $\tau_+$  is found to approach unity rapidly and asymptotically. Then Eqs. (g) and (h) reduce to



$$K_a^+ = K_{aq}^+. \quad (\text{j})$$

These correspond to the transformation of one mole of mercurous chloride to a gram atom of mercurous ion within the metallic phase (where it reduces the negative charge by one faraday) and one equivalent of chloride ion within the solution. At the same time one gram atom of potassium ion leaves the interface (because of the disappearance of negative charge on the metal) and enters the solution. It is equally easy to visualize Eqs. (g) and (h) in this case by imagining chloride ions to be adsorbed in reaction (g) and desorbed in reaction (h). The process then consists in the transfer of one mole of mercurous chloride to the double layer and the removal of one mole of potassium chloride.

At sufficiently large positive polarization  $\tau_+$  becomes negative. Under these circumstances no simplification of Eqs. (g) and (h) is possible, but the process is conceptually easy to grasp. It involves the conversion of one mole of  $\text{HgCl}$  to the adsorbed state, with the mercurous ions in the metallic phase, and the transfer of  $-\tau_+$  equivalents of potassium chloride from the interior of the solution to the interface. From kinetic considerations it is quite certain that the anions are held to the interface by forces analogous to those prevailing in solid mercurous chloride, that is to say, by a combination of Coulombic and covalent bond forces. The positive ions are undoubtedly held by Coulombic forces, which means that they are kinetically a part (the major part) of the diffuse double layer. The whole electrochemical process is conveniently viewed as a chemisorption of mercurous chloride and potassium chloride.

It will be noted that when  $\tau_+$  is positive, Eq. (h) represents a desorption. Equation (g) always represents an adsorption. It is therefore misleading to call  $\Delta G'$  for the process (f) (which is the sum of Eqs. (g) and (h)) either the free energy of adsorption or of desorption. Since it is both conventional and convenient to identify a process by a name which suggests its direction as well as its

nature, we shall call  $\Delta G'$  of reaction (f) the differential free energy of adsorption-desorption.<sup>3</sup> Thus the first-named process refers to the calomel adsorption, which never changes sign (reaction (g)), while the last-named process refers to the salt adsorption and is named for the process which occurs when  $\tau_+$  is positive.

From reaction (b) it will be seen that  $\tau_+$  is equal to  $-d\Gamma_+/dq$ ,<sup>3a</sup> since this gives the rate at which positive ions accumulate in the electrical double layer per faraday of charge transferred. Methods of evaluating  $\Gamma_+$  and  $q$  as a function of  $E$  have already been presented,<sup>1</sup> so that the evaluation of  $\tau_+$  offers no new difficulty.  $\Delta G'$  is readily evaluated from Eq. (1) and is rendered significant by the evaluation of  $\tau_+$ , since this is the only unknown in the electrochemical reaction.  $\Delta S'$  is given by Eq. (2), where the coefficient  $(dE/dT)_q$  is to be evaluated not only at constant surface charge density but also under conditions such that the reference electrode changes temperature at the same time. Thus there are no liquid junction potentials involved in this or any other measurement here discussed.  $\Delta H'$  is given by Eq. (3).

## II. APPLICATION TO COLLOIDAL ELECTROLYTES

The foregoing treatment includes as a special case such systems as  $\text{AgCl} \vdash \text{Cl}^-$  or  $\text{BaSO}_4 \vdash \text{SO}_4^{2-}$ , and suggests an interesting and possibly important new approach to the study of colloids. Consider again the system



When  $E=0$  the mercury in the left-hand electrode is covered with chloride ions to such an extent that the transfer of mercurous chloride from the adsorbed state to the solid state can occur without change of free energy Eq. (4). Thus the surface is thermodynamically equivalent to the surface of solid mercurous chloride. By extending measurements of ideal polarized electrodes into the non-polarized range of potentials (which is easily done), information can be obtained about the composition of the electrical double layer in systems of colloidal electrolytes. For example, it may be observed from data

<sup>3</sup> The reverse process would be called desorption-adsorption.

<sup>3a</sup>  $\Gamma_+$  is defined in Section V or more fully in reference 1.

already in the literature that mercurous chloride in contact with unimolar alkali metal chloride solutions has a diffuse double layer containing about  $14 \mu\text{coulomb}/\text{cm}^2$  of the alkali metal ion. About  $4 \mu\text{coulomb}/\text{cm}^2$  of chloride ions are repelled from the interface by the Coulombic repulsion of the adsorbed chloride ions, which must therefore be present at a concentration of about  $18 \mu\text{coulomb}/\text{cm}^2$ .<sup>4</sup> In the same way one could calculate the approximate potentials of the inner and outer Helmholtz planes.<sup>5</sup> The latter is presumably identical with the zeta-potential.

In addition to the thermodynamic properties discussed above there are a considerable number of properties which it is theoretically possible to evaluate but for which there are at present no adequate experimental methods of investigation. For the sake of completeness, we shall indicate what these are and how they are to be evaluated in principle. Since the problem is closely related to the corresponding problem in the thermodynamics of gas adsorption on solids, we shall clarify the ideas involved by first summarizing the thermodynamic treatment of that type of system. Parts of what we shall have to say on this latter subject have been said before, but not in a form to which we can conveniently refer in the discussion which follows.

### III. GAS ADSORPTION AT AN INTERFACE

Consider a system composed of a solid in equilibrium with a gas at fugacity  $f$ . The free energy change  $dG$  involved in transferring  $dn$  moles of gas from a standard state of fugacity  $f^0$  to the surface is equal to the free energy change accompanying its decompression to the equilibrium pressure.

$$dG/dn = RT \ln f/f^0. \quad (5)$$

The quantity  $dG/dn$  is the differential free energy of adsorption, and its numerical value depends upon one's choice of the standard state. We take for this the liquid state at the temperature  $T$  and at a constant pressure of one atmosphere. Then  $f/f^0$  is the activity  $a$  of the adsorbed vapor, and

Eq. (5) becomes

$$dG/dn = RT \ln a. \quad (6)$$

The integral free energy of adsorption,  $\Delta G$ , is given by

$$\Delta G = RT \int_0^n \ln a \, dn, \quad (7)$$

which gives the free energy change associated with the process of taking  $n$  moles of liquid and putting them on a surface initially bare.

From the definition of free energy we are entitled to write for an isothermal process

$$dG/dn = dH/dn - TdS/dn. \quad (8)$$

The quantity  $dH/dn$  is the differential heat of adsorption, and the quantity  $dS/dn$  the differential entropy of adsorption.

Consider the adsorption process

Liquid (st'd state)  $\rightarrow$  Gas (adsorbed)

and apply to this the familiar equation  $(d\Delta G/dT)_p = -\Delta S$ . In accord with our previous nomenclature we shall, however, write  $dG/dn$  for  $\Delta G$ , and so on, giving

$$[d(dG/dn)/dT]_{p,N} = -(dS/dn). \quad (9)$$

The condition of constancy of pressure, it will be recalled, applies to each phase separately and does not mean that the phases need be at the same pressure. The standard state is maintained at constant pressure by definition. The adsorbed gas plus adsorbent (the solid phase) is not ordinarily maintained at constant pressure during a change of temperature, although this could be done by the introduction of an inert, non-adsorbable gas whose pressure is maintained constant, or by other means. The neglect of this thermodynamic requirement introduces an exceedingly small error for which a correction could in principle be made through the relationship  $d \ln a/dP = (\bar{V}_1 - V_l)/RT$  where  $\bar{V}_1$  is the partial molal volume of the adsorbed gas and  $V_l$  the molal volume of the pure liquid. Although  $\bar{V}_1$  is not ordinarily known, it is doubtless substantially equal to  $V_l$ . In any case the correction is very small because  $V_l/RT$  is of the order of 0.3 percent per atmosphere for typical adsorbates.

It will be recalled that in the derivation of the equation  $(d\Delta G/dT)_p = -\Delta S$  no change in the

<sup>4</sup> These figures are obtained by a slight extrapolation of data in Fig. 10, reference 1. The point of view here adopted is different from that suggested there on p. 497.

<sup>5</sup> The calculation will be identical with that described in reference 1, p. 487. See also Fig. 16.

amounts of the reactants is envisaged, i.e., the reaction to which  $\Delta G$  and  $\Delta S$  refer is not allowed to take place as a result of the change of temperature to which the equation refers. Applied to our system this means that the amount of adsorbed gas must not change, or what are called isosteric conditions must prevail. This result, indicated by the subscript  $N$ , has long been familiar, although its logical basis has sometimes been thought obscure.

Combination of Eqs. (6), (8), and (9) gives

$$(d \ln a / dT)_{p,N} = -(dH/dn)/RT^2, \quad (10)$$

which is the counterpart of the Clausius-Clapeyron equation applied to the system here considered.

It is probably helpful to show how these equations are related to the Gibbs adsorption theorem. Recalling the identity

$$uv = \int u dv + \int v du,$$

one has from Eq. (7)

$$\Delta G = nRT \ln a - RT \int_0^n nd \ln a. \quad (11)$$

It will be recalled that this is the free energy change accompanying the transfer of  $n$  moles of gas from the standard state to a surface initially bare, but not remaining so, since the surface is not assumed infinite. We wish to find the free energy change  $\Delta G_1$  accompanying the formation of one square centimeter of covered surface, starting not with a bare surface, but with no surface at all. Calling  $\sigma^0$  the surface tension of the bare surface, the total free energy change will be

$$\Delta G_1 = \sigma^0 + \Delta G = \sigma^0 + nRT \ln a - RT \int_0^n nd \ln a. \quad (12)$$

This is the free energy change when the gas is initially in its standard state. The free energy change  $\Delta G_2$  involved in reducing the gas from the initial (standard) state to the final equilibrium pressure is the same as that given in Eq. (6), except that we now deal with  $n$  moles of gas. Therefore

$$\Delta G_2 = nRT \ln a. \quad (13)$$

The free energy change  $\Delta G_3$  accompanying the formation of one square centimeter of new surface and the covering of it with  $n$  moles of gas which is initially (and continuously) at the equilibrium pressure is therefore given by

$$\Delta G_3 = \Delta G_1 - \Delta G_2 = \sigma^0 - RT \int_0^n nd \ln a. \quad (14)$$

We note that  $\Delta G_3$  is the surface tension  $\sigma$  of the covered surface, since it represents the free energy change accompanying the formation of one square centimeter of new surface from a system in equilibrium with the surface. Also,  $n$  is now the number of moles adsorbed per square centimeter, which is usually called  $\Gamma$  in discussions of the Gibbs adsorption theorem. Making these substitutions and differentiating Eq. (14) gives

$$d\sigma = -\Gamma d\mu, \quad (15)$$

where  $\mu$  is the chemical potential defined by the relation

$$d\mu = RT d \ln a.$$

This is the Gibbs adsorption theorem applied to a single component and held at constant temperature. Its extension to any number of components involves nothing more than a repetition of the above steps for each component. Although this is probably not the simplest possible derivation of the theorem, it has the advantage of displaying the relationship of the theorem to the thermodynamic theory of surfaces presented above.

#### IV. SALT ADSORPTION AT THE ELECTROCAPILLARY MAXIMUM OF AN IDEAL POLARIZED ELECTRODE

At the potential of the electrocapillary maximum of an ideal polarized electrode the results obtained above can be applied with no more than a change of terminology. The differential free energy of adsorption is related to the activity of the dissolved salt in equilibrium with the electrical double layer through Eq. (6). Equation (9) gives the differential entropy of adsorption which may be written, with the aid of Eq. (6),

$$R \ln a + RT d \ln a / dT = -dS/dn, \quad (16)$$

it being understood that here, as in Eq. (9), the amount of adsorbed material per gram of ad-

sorbate is to be held constant. The interpretation of this equation is as follows: If one measures the amount of salt adsorbed at an interface at the potential of the electrocapillary maximum, then it is possible in principle to find another temperature and concentration of electrolyte such that the amount of salt adsorbed per gram of adsorbent (whose geometric shape must not be allowed to change if the adsorbent is a liquid, such as mercury) is unchanged. This information permits one to evaluate  $\ln a$  and  $d \ln a/dT$  in Eq. (16), giving all that is needed to evaluate the differential entropy of adsorption. The differential heat of adsorption is found most easily from Eq. (10).

#### V. SALT ADSORPTION AT POTENTIALS OTHER THAN THAT OF THE ELECTROCAPILLARY MAXIMUM

At potentials other than that of the electrocapillary maximum the amounts of positive and negative ions adsorbed are unequal and one can no longer treat the problem in exactly the manner described above. The necessary modifications are very slight, however. Consider a polarized electrode having an electrical double layer of electronic charge  $q$ , a surface concentration of cations  $\Gamma_+$ , and a surface concentration of anions  $\Gamma_-$ .<sup>6</sup> Then from considerations of electrical neutrality

$$q/\mathcal{F} + \Gamma_+ z_+ + \Gamma_- z_- = 0, \quad (17)$$

where  $z_+$  and  $z_-$  are the valences of cations and anions, respectively, including sign. It is possible now to hold  $q$  constant while varying temperature and composition independently. This is so because one can always vary the imposed electrical potential in such a way as to maintain a constant value of  $q$ . At one particular value of  $d \ln a/dT$ ,  $\Gamma_+$  and  $\Gamma_-$  will also be constant. Therefore one can evaluate  $d \ln a/dT$  at constant  $q$ ,  $\Gamma_+$ , and  $\Gamma_-$ , that is to say, under isosteric conditions. Pressure is constant in the standard and in the adsorbed states. These are the conditions upon which the validity of the equations derived in Sections III and IV depend, and one can therefore apply them to the present case also.

Equation (16) gives  $dS/dn$ , the differential

<sup>6</sup> Strictly speaking, the excess per sq. cm over that which would be present if the concentration were uniform up to a plane defined by the condition that  $\Gamma_{\text{solvent}} = 0$ .

entropy of adsorption of equivalent amounts of cations and anions in the double layer. Equation (6) gives the obvious result that the differential free energy of adsorption of the salt is equal to  $RT$  times the logarithm of its activity in the solution with which it is in equilibrium. It may be necessary to recall in this connection that the adsorbed material is always regarded as having started in its standard state. The heat of adsorption,  $dH/dn$ , is given either by Eq. (8) or Eq. (10).

It will be noted that reaction (h), Section I, is identical with the reaction discussed here except for the factor  $\tau_+$  and except for the fact that it is written as a desorptive rather than as an adsorptive process. Therefore the thermodynamic property changes of Eq. (h) can be computed by the methods of this section. Since the sum of the changes in Eqs. (g) and (h) can also be evaluated by the methods of Section I, the property changes of Eq. (g) can also be found. There are as yet no data sufficiently extensive for the full realization of all the calculations here envisaged.

#### VI. ADSORPTION OF CATION-ELECTRON PAIRS

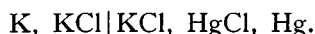
The electrical double layer at an electrode may be thought of as consisting of adsorbed salt molecules plus adsorbed cation-electron pairs, the cation being in the solution phase and the electron in the metallic phase. Positively charged surfaces would then be thought of as surfaces from which a certain number of cation-electron pairs had been desorbed, the cations having come initially from adsorbed salt molecules.

From this point of view it will be seen that the application of Eqs. (6), (8), (10), and (16) made in the preceding section need not be confined to the adsorption of salt molecules but may be applied with equal validity to the adsorption of cation-electron pairs. It remains only to identify  $a$  in the equations. To avoid cumbersome circumlocution let us suppose that the salt in question is potassium chloride and that the metallic phase is mercury. Then  $a$  is the activity of *metallic* potassium in equilibrium with the potassium ion-electron pairs in the double layer. There is a concentration of metallic potassium dissolved in the mercury with which the potassium ion-electron pairs are in equilibrium. This concentration is very low and it is immaterial whether or

not equilibrium is actually attained.<sup>7</sup> The concentration of metallic potassium in the mercury has no real bearing upon the problem, in fact, except as an aid to the imagination. Regarding the mercury as a very dilute potassium amalgam in equilibrium with the solution and with the double layer, it is a simple matter to calculate the activity of the potassium in the amalgam, and this is also the activity of the potassium ion-electron pairs with which it is in equilibrium if the same standard state (the pure metal) is adopted. The activity  $a_K$  of the potassium ion-electron pairs is then given through the equation

$$E = E^0 - (RT/\mathfrak{F}) \ln a_+ a_- / a_K, \quad (18)$$

where  $E$  is the potential imposed upon the system measured relative to (say) a calomel electrode and  $E^0$  is the standard electrode potential of the cell



Note that  $E$  is not the e.m.f. of this cell.  $a_+$  and  $a_-$  are the activities of the cation and anion, respectively, in the solution.

To show this, consider the cell



whose e.m.f. is given by Eq. (18). If the potassium amalgam were made sufficiently dilute, the e.m.f. would fall in the range of potentials where the mercury is regarded as an ideal polarized electrode. Since the system is at equilibrium, the activity of metallic potassium must be the same within the mercury and in the double layer, it being a matter of no consequence that the potassium is "hydrated" in the latter.

Since the entropy, enthalpy, and free energy of adsorption of cation-electron pairs may be expressed in units of energy per faraday, it is appropriate to designate these quantities  $dS/dq$ ,  $dH/dq$ , and  $dG/dq$ . This serves to distinguish them from the corresponding quantities for salt adsorption.

<sup>7</sup> This point is discussed in reference 1, p. 445. Results of the calculation in an actual case are there given.

## VII. ENTROPY, ENTHALPY, AND FREE ENERGY OF FORMATION OF THE DOUBLE LAYER

At the potential of the electrocapillary maximum the entropy of formation of the double layer from its constituent molecules is easily evaluated by integrating  $dS/dn$  over the number of moles of salt adsorbed. One needs to know  $dS/dn$  and  $n$  at the electrocapillary maximum for a series of concentrations from the value at which one wishes the information down to concentrations so low that  $n$  is essentially zero. The *absolute* entropy of the double layer could then be evaluated by adding on the entropy of the adsorbate in its standard state.

At potentials other than that of the electrocapillary maximum the entropy of formation of the double layer can be found by first calculating the entropy at the electrocapillary maximum and then adding on the entropy of adsorption of the additional salt present together with the entropy of the cation-electron pairs. The first of these is found by integrating  $dS/dn$  over the range of values of  $n$  occurring between the electrocapillary maximum and the potential under consideration. The entropy of the cation-electron pairs is found in an analogous manner by integrating  $dS/dq$  over  $q$ .

The enthalpy and free energy of formation of the electrical double layer are to be found in exactly the same manner using  $dH/dn$ ,  $dH/dq$ ,  $dG/dn$ , or  $dG/dq$  as the case requires.

Although it is unlikely that enough experimental data will ever be accumulated for the evaluation of all of the thermodynamic quantities described in this paper for even a single case, it is the expectation of the writer that the recognition of the existence of these properties and the evaluation of some of them will prove worth while.

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