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The Thermodynamic Theory of Electrocapillarity¹

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The Gibbs adsorption theorem (Gibbs' equation 508) is a relationship between the change in the interfacial tension between two phases, the change in chemical potential of the components of the phases, the change in the superficial density of entropy in the system and the amounts of the various independent components adsorbed at the interface.^{1a} When some of the components of the system are electrically charged particles, as in an electrocapillary system, the Gibbs equation cannot be applied directly in its original form for reasons which will be pointed out below. In the study of electrocapillary phenomena it is desirable to have a thermodynamic equation analogous to the Gibbs adsorption theorem. The Lippmann equation² is a special case of such an equation.

Many discussions of this problem have focussed attention on the "potential-determining" ion, as though the causal agent producing the potential difference between the phases at equilibrium were the ions of the metal in the non-metallic phase (often present in amounts so small as to be meaningless except in a statistical sense) instead of the external apparatus by means of which the potential difference is fixed. The difficulties of this line of approach led Koenig³ to give up the hope of extending the Gibbs equilibrium treatment and to regard the polarized electrode as a system in which equilibrium does not subsist between the phases. He assumed, instead, that at the interface there exists a barrier impermeable to charged particles. On this basis Koenig has derived a general equation of electrocapillarity for the ideal polarized electrode and has applied it to the deduction of equations referring to special experimental conditions which may be realized in the laboratory. It is the purpose of this paper to show that the equations developed by Koenig are not peculiar to the type of system which he postulates but may be derived for a polarized electrode *at equilibrium* with respect to the distribution of its charged components and *not* possessed of a barrier impermeable to charged particles. It appears to the

present authors that real systems are best characterized in this manner and may be made to approach the postulated ideal condition of equilibrium as closely as the physical perfection of the experimental apparatus will permit. In addition, we shall show that the equations here developed have a wider scope and a slightly different significance from those of identical form given by Koenig.

Qualitative Considerations.—Consider a system composed of a metal in contact with an electrolytic solution and provided with some external means whereby the potential difference between the phases may be altered at will. It need not concern us that the absolute magnitude of the potential difference must remain unknown. We exclude from consideration all cases in which the system just postulated is not at equilibrium as regards ordinary chemical action or as regards the distribution of charged particles between the phases. In a system at equilibrium there will be no net transfer of charge from one phase to the other, and therefore there will be no current flowing through the external circuit by which the superimposed potential is applied. From a practical standpoint the systems we are considering form three classes of electrodes, ideal polarized electrodes, ideal non-polarizable electrodes and partially polarizable electrodes. We distinguish these three classes by the magnitude of the continuous current which flows through the external circuit when the potential difference between the phases is *altered* slightly from its value in the original (equilibrium) state. In an ideal polarized electrode no continuous current flows; in an ideal non-polarizable electrode a continuous current flows, limited only by the ohmic resistance of the system, whereas in a partially polarizable electrode a continuous current flows, but of magnitude less than that predicted by Ohm's law (if polarization e. m. f.'s are ignored). These distinctions are practical rather than thermodynamic criteria of polarizability, since Ohm's law and the concepts associated with that law are not a part of thermodynamics. Indeed, the distinction between ideal non-polarizable electrodes and partially polarizable electrodes appears to have no meaning

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(1a) J. W. Gibbs, "Collected Works," Vol. I, Longmans, Green and Co., New York, N. Y., 1928, pp. 219 *et seq.*

(2) G. Lippmann, *Pogg. Ann.*, **149**, 547 (1873); *Ann. chim. phys.*, [5] **5**, 494 (1875); **12**, 265 (1877); see also Gibbs' equation 690.

(3) F. O. Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934).

for thermodynamics, and the concept will not be used in the thermodynamic treatment which follows. The distinction between ideal polarized electrodes and the two types of electrodes just mentioned (regarded as a single class) may be made on the basis of the amounts of the charged components present in the two phases at equilibrium, as will presently appear.

When the potential difference across the phases of an electrode at equilibrium is altered slightly, there is a momentary surge of current through the external system as a result of a readjustment of the composition of the electrical double layer at the interface, but this readjustment takes place very quickly and in no way obscures the slow readjustment which may be observed as a continuous flow of current in a partially polarizable or non-polarizable electrode.

Although the two ideal types of electrode cannot be attained in practice, it is possible to prepare electrodes which approach ideal conditions almost as closely as desired. Thus a large reversible electrode is practically non-polarizable under favorable conditions, and a system composed of mercury in contact with aqueous potassium chloride is, to all intents and purposes, ideally polarized over a considerable range of superimposed potentials. The same system becomes partially polarizable when the potential difference between the phases is such that the concentration of mercurous ions in the aqueous phase is not negligible at equilibrium.

It will be recognized that *at equilibrium* the concentration of the so-called potential-determining ion in the non-metallic phase varies with the applied potential difference between the phases. In an ideal polarized electrode this concentration is necessarily extremely small in one of the two phases, for if it were not so, a change in the potential difference between the phases would result in a finite current flow during the relatively long period of time required for the system to attain a new state of equilibrium. Since any ion in the system might be regarded as a potential-determining ion, it follows that in an ideal polarized electrode the concentration of every charged species must be negligibly small in one of the two bulk phases. It is this circumstance which makes it unnecessary to postulate a barrier impermeable to charged particles in an ideal polarized electrode.

From the standpoint of thermodynamics it is desirable to *define* the ideal polarized electrode as

one in which each charged species is present in appreciable amounts in only one of the two bulk phases. This definition is equivalent to the practical definition first given. An electrode at equilibrium and containing one or more charged components at finite concentrations in both phases would be classed as a non-polarized electrode. It should not be inferred from this nomenclature that the electrode is necessarily non-polarizable, however.

On the Application of the Gibbs' Adsorption Theorem to Systems in which Charged Substances Are Regarded as Independent Components.—The Gibbs' adsorption theorem, in its original form, applies to systems in which all components are regarded as neutral substances. (Any actual system may be so regarded, of course, provided the system as a whole remains electrically neutral.) It would appear reasonable to rewrite the equation, substituting electrochemical potentials for chemical potentials,⁴ and to assume that the rewritten equation would apply to systems in which charged components are regarded as independent components. Such an assumption would not be strictly correct, however, as we now proceed to show.

The physical system treated by Gibbs is chosen as an internal part of a larger system of the same kind in order to eliminate from the discussion phase boundaries other than the one specifically under consideration. This is an important characteristic of the derivation not easily dispensed with if thermodynamic rigor is to be maintained. Such a system must remain electrically neutral as a result of the fact that any excess charge will accumulate on the external surfaces of the conducting system.⁵ In a system constrained to remain electroneutral, the principal charged components⁶ cannot be added or removed independently of one another. One of these components is not an independent component, yet the system cannot be regarded as formed from its independent

(4) For an uncharged component, the electrochemical potential may be regarded as identical with the chemical potential.

(5) It is debatable whether or not one may consider infinitesimal deviations from electrical neutrality in the interior of a conducting system. We avoid this question, and at the same time simplify our treatment, by restricting the allowable variations to those which can be carried out without destroying the electrical neutrality of the system as a whole. Since actual systems do remain electroneutral, the applicability of our final equations is not thereby impaired.

(6) By principal charged components we mean those substances which must be added to make up the system under consideration. Electrolytes which dissociate into two or more ionic species we regard as mixtures of these substances. Water is regarded as a single substance. Metals are regarded as mixtures of ions and electrons, each of which is a principal component.

components only. One of the principal charged components may be singled out and called a dependent component, yet its presence must be taken into account, either explicitly or implicitly, in any equation relating to the energy content of the system.

In the derivation of the adsorption theorem in its original form the chemical potentials enter as a substitution for the quantity $\partial E/\partial n_i$ where E is the energy of the system (regarded as a function of the entropy and the number of moles of the *independent* components) and n_i is the number of moles of the component X_i . In the particular kind of system we are now considering, it is not valid to write $\partial E/\partial n_i = \bar{\mu}_i$,⁷ where $\bar{\mu}_i$ is the electrochemical potential, because the addition of a charged component necessitates the addition or removal of another charged component, regarded as a dependent component. It is this fact which makes it incorrect simply to write $\bar{\mu}_i$ for μ_i in the Gibbs' adsorption theorem.

Derivation of the General Equations of Electrocapillarity.—If we choose to regard the electrons of the metallic phase as the dependent component whose amount varies with the addition or removal of charged components in such a way that electrical neutrality is always preserved, we may write

$$\partial E/\partial n_i = \bar{\mu}_i + z_i \bar{\mu}_e \quad (1)$$

where z_i is the "valence" (including sign) of X_i , and $\bar{\mu}_e$ is the electrochemical potential of the electrons in the system.

The derivation of the adsorption theorem can be carried through in the usual manner without substituting any new symbol for the quantity $\partial E/\partial n_i$. Then Gibbs' equation 508 becomes

$$d\sigma + S_s dT = -\sum \Gamma_i d\left(\frac{\partial E}{\partial n_i}\right) \quad (2)$$

In this equation σ is the interfacial tension of the interface under consideration, Γ_i is the excess of the component X_i , in moles per unit area, over that which would be present in the system if the density of X_i in each phase remained constant (at its value in the internal parts of the bulk phases) right up to a mathematical surface drawn parallel to, but not necessarily coincident with, the physical interface. The physical interface is assumed to be effectively plane, by which it is meant that its radius of curvature is very large relative to the thickness of the region of discontinuity at the

interface. S_s is the superficial density of entropy (entropy per unit area) defined in a manner analogous to the Γ 's. T is the (absolute) temperature. The summation is carried out over the c *independent* components. If charged substances are regarded as independent components, c will be less by one than the number of principal components.

Equation 2 is valid for any two-phase system at equilibrium, subject only to the usual limitations with regard to gravitational and electric fields, strains in solids, etc.^{1a} If we agree to adopt the conventions appropriate to Eq. 1, we may write

$$d\sigma + S_s dT = -\sum \Gamma_i d\bar{\mu}_i - \sum \Gamma_i z_i d\bar{\mu}_e \quad (3)$$

It may be noted in passing that this equation may be obtained somewhat more readily, if not so rigorously, by overlooking the requirement of electrical neutrality imposed upon the system by its physical arrangement. In that case the adsorption equation would be written

$$d\sigma + S_s dT = -\sum \Gamma_i d\mu_i$$

where the $c + 1$ components include the electrons. Expanding this equation, and noting that *when* the system is electrically neutral $\sum \Gamma_i z_i = \Gamma_e$, we obtain

$$\begin{aligned} d\sigma + S_s dT &= -\sum \Gamma_i d\bar{\mu}_i - \Gamma_e d\bar{\mu}_e \\ &= -\sum \Gamma_i d\bar{\mu}_i - \sum \Gamma_i z_i d\bar{\mu}_e \end{aligned}$$

In these equations, as elsewhere, the subscript e refers to the electrons.

We may express electrochemical potentials in terms of chemical potentials and electrical potentials by the substitution⁷

$$d\bar{\mu}_i = d\mu_i + z_i F d\varphi_i \quad (4)$$

where F is the faraday and $d\varphi_i$ is the change in the electrical potential of the phase in which the chemical potential, μ_i , is reckoned. Equation 4 is valid for electrons, as for ions. It is also valid for uncharged substances, since for these latter, $z_i = 0$. Substitution of Eq. 4 into Eq. 3 gives

$$d\sigma + S_s dT = -\sum \Gamma_i d\mu_i - \sum \Gamma_i z_i d\mu_e - F \sum \Gamma_i z_i d\varphi^\alpha - F \sum \Gamma_i z_i d\varphi^\beta + F \sum \Gamma_i z_i d\varphi^\alpha + F \sum \Gamma_i z_i d\varphi^\alpha \quad (5)$$

$$= -\sum \Gamma_i d\mu_i - F \sum \Gamma_i z_i d(\varphi^\beta - \varphi^\alpha) - \sum \Gamma_i z_i d\mu_e \quad (6)$$

In these equations we have divided the summations containing φ 's into two parts according to the phase in which the chemical potential of each

(7) E. A. Guggenheim, "Modern Thermodynamics," Methuen and Co., London, 1933, p. 133.

particular component has been reckoned. The symbols α and β over the signs of summation signify that the summation is to include those independent components whose chemical potentials have been reckoned in the metallic and non-metallic phases, respectively. φ^α and φ^β are the electrical potentials of these phases. It will be noted that in a system at equilibrium the electrochemical potential of every component is the same in the two phases, and it will therefore make no difference in which phase a component is reckoned. But it will usually be more convenient to measure the *chemical* potential in one phase rather than in the other, and this consideration will generally indicate the phase in which a given component may most conveniently be reckoned. Equations 5 and 6 have been written on the assumption that the electrons will be regarded as a component of the metallic phase. This is a matter of convenience rather than of thermodynamic necessity.

Equation 6 may be regarded as a general equation of electrocapillarity. It is applicable to polarized and non-polarized electrodes alike. In order to apply it more conveniently to ideal polarized electrodes we may define a quantity ϵ^β by the equation

$$\epsilon^\beta = F \sum \Gamma_i z_i \quad (7)$$

Because of the electrical neutrality of the system as a whole we may write

$$\sum \Gamma_i z_i = \Gamma_e \quad (8)$$

Substitution of Eqs. 7 and 8 into Eq. 6 yields the simplest form of the general equation, when this is to be used in connection with ideal polarized electrodes, as follows

$$d\sigma + S_s dT = -e^\beta d(\varphi^\beta - \varphi^\alpha) - \sum_{i=1}^{c+1} \Gamma_i d\mu_i \quad (9)$$

Like Eq. 6, this equation applies to any electrode at equilibrium. It is restricted only by the requirement that the physical interface be essentially plane, as defined above. This restriction limits the possible variation of $\varphi^\beta - \varphi^\alpha$ and of the μ 's to values such that the pressures within the two phases are (nearly) equal. Since this is also the requirement that the interfacial tension be measurable by the usual methods, the equations may be applied to any system for which the interfacial tension is measurable.⁸

(8) Our equations are valid for a system in which the interface is not essentially plane if the position of the dividing surface, with reference to which the Γ 's are reckoned, is sensibly coincident with the physical interface. This point is discussed in detail by Gibbs, ref. 1a.

It is particularly to be noted that the position of the surface of reference, with respect to which S_s and the Γ 's are reckoned, is not specified in the foregoing treatment but may be taken as any surface parallel to the (essentially plane) interface. This makes it possible to set any one of the Γ 's equal to zero, whereby the position of the surface of reference is fixed. The component for which Γ is set equal to zero may be called the reference component. If it is desired to place the surface of reference as nearly coincident with the physical interface as possible, the reference component must be chosen as that component which may most reasonably be assumed not to undergo concentration or dilution at the physical interface. From the standpoint of thermodynamics alone, it is a matter of indifference which component is selected as a reference component except in certain very unusual cases discussed by Gibbs, ref. 1a, p. 234.

In an *ideal polarized electrode* the value of ϵ^β will be independent of the position of the surface of reference. This results from the fact that every charged component is to be found in only one of the bulk phases, and since the interior of each phase is electrically neutral, the *excess* of charge is uninfluenced by changes in the assumed volume of each such neutral phase.

For an ideal polarized electrode the quantity ϵ^β is nearly identical with what is commonly called the surface charge density, but it happens that the thermodynamically significant quantity is ϵ^β and not the surface charge density, as that term is commonly understood. For example, it is ϵ^β which is actually measured in experiments which purport to measure the surface charge density.^{9,10} If physical interfaces are as sharply defined as is generally believed, the practical difference between these quantities is wholly negligible, but it is important from the standpoint of thermodynamics to realize that the quantities are not identical. The differential capacity of an ideal polarized electrode is identical with the quantity $\partial \epsilon^\beta / \partial (\varphi^\beta - \varphi^\alpha)$.¹⁰ Thus it appears that the experimentally observable properties of an ideal polarized electrode form a self-consistent system independent of any concepts relating to the "true" surface charge density. It will be noted that the concept of a "true" surface charge density is analogous to the concept of a

(9) A. Frumkin, *Z. physik. Chem.*, **103**, 55 (1923); L. St. J. Philpot, *Phil. Mag.*, **13**, 775 (1932); I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, **36**, 128 (1940).

(10) D. C. Grahame, *THIS JOURNAL*, **63**, 1207 (1941).

"true" degree of dissociation of an electrolyte.¹¹

At constant temperature and composition, Eq. 9 reduces to the familiar Lippmann equation

$$d\sigma = -\epsilon^\beta d(\varphi^\beta - \varphi^\alpha) \quad (10)$$

When the composition of the phases remains constant, $d(\varphi^\beta - \varphi^\alpha)$ is an experimentally observable quantity. At the potential of the electrocapillary maximum, $\epsilon^\beta = 0$.

Equation 9 gives rise to a number of other useful equations related to the electrocapillary properties of an ideal polarized electrode. These have been worked out in detail by Koenig³ from an equation substantially identical with our Eq. 9. The only change in these further equations which our treatment requires is in the manner of interpreting ϵ^β and in the location of the surface of reference, which latter is arbitrary in our treatment. Since the form of the equations is not changed by these considerations, we have not thought it necessary to repeat the equations here. It should be pointed out to prospective users, however, that Koenig has defined his Γ 's and μ 's in terms of equivalents rather than in moles.

It is found experimentally that the Lippmann equation is sometimes obeyed with considerable accuracy even when the system under investigation is far removed from a state of equilibrium.¹⁰ This circumstance is doubtless to be attributed to the fact that the properties of an interface are affected chiefly by the composition of the phases in the immediate neighborhood of the interface. Since this part of the system readily reaches a steady state only slightly different from an equilibrium state, it is understandable that the observable properties should be essentially those of a system at equilibrium.

Application of the General Equation to the Non-polarized Electrode.—At constant temperature, the only variation of a non-polarized electrode consistent with the condition of equilibrium is a simultaneous variation of composition and $\varphi^\beta - \varphi^\alpha$. The most important case of a system of this kind is the system formed by a pure metal in equilibrium with a solution of one of its simple salts (a salt which dissociates into two ionic species only). If we let the subscripts o , $+$ and $-$ designate, respectively, quantities related to the sol-

vent, the cation and the anion of the salt, then from Eq. 4, by equating $d\bar{\mu}_+^\alpha$ and $d\bar{\mu}_+^\beta$

$$z_+ F d(\varphi^\beta - \varphi^\alpha) = -d\mu_+^\beta \quad (11)$$

The superscripts on the chemical and electrochemical potentials designate the phase in which the chemical potential of the component is to be reckoned. Substitution of Eq. 11 into Eq. 6 gives

$$d\sigma = -\Gamma_+ d\mu_+^\beta - \Gamma_- d\mu_-^\beta - \Gamma_o d\mu_o + \Gamma_+ d\mu_+^\beta + \frac{z_-}{z_+} \Gamma_- d\mu_+^\beta \quad (12)$$

$$= -\frac{f}{z_+} \Gamma_- d\mu - \Gamma_o d\mu_o \quad (13)$$

The symbol μ , without subscript, denotes the chemical potential of the salt, which is equal to $(z_+ \mu_- - z_- \mu_+)/f$ where f is the largest common factor of z_+ and $-z_-$. In deriving Eq. 12 the cation was arbitrarily regarded as a component of the non-metallic phase. The same final result would have been obtained if it had been regarded as a component of the metallic phase. Equation 13 can also be derived very readily from the Gibbs adsorption theorem in its usual form by regarding the metal, the salt and the solvent as the three independent components of the system.

It has not been customary in the past to measure interfacial tensions of non-polarized systems under conditions suitable for the application of Eq. 13. However, there seems to be no reason why such measurements could not be carried out with mercury as the metallic phase and aqueous mercurous nitrate, for example, as the electrolyte. Taking the solvent as the reference component, one could readily calculate Γ_- at various concentrations of electrolyte, and also, by equation 8, $z_+ \Gamma_+ - \Gamma_o$. It does not appear to be possible, however, to evaluate Γ_+ and Γ_o separately.

Summary

The thermodynamic equations of electrocapilarity have been derived with no assumptions other than that of equilibrium between the phases. It is shown that the interpretation of the equations so obtained is slightly different from what had previously been supposed. A general electrocapillary equation has been derived for a non-polarized electrode, and it is shown how this may be applied to experimentally obtainable data.

(11) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 317-325.