CONCEPT OF ELECTRODE CHARGE AND THE LIPPMANN EQUATION

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The concept of charge is examined for the case of the ideally polarizable electrode. It is shown that one must distinguish between the quantities total charge, which enters the thermodynamic relations, and free charge, which can only be defined within the framework of some electric-double-layer model. With the platinum – hydrogen and the thallium – amalgam electrode as examples it is shown that in the simplest reversible redox systems two characteristic electrocapillary curves can be realized. Which one is realized depends on the component – oxidant or reductant – whose chemical potential is kept constant while varying the electrode potential. Expressions are given for the total charge of the system in the two cases; these satisfy the Lippmann equation. In the general case the number of characteristic electrocapillary curves is determined by the number of independent variables in the Nernst equation reflecting the equilibrium condition for the system. The results obtained are used to interpret electrocapillary dependences observed under polarographic conditions.

The idea of electrode charge is one of the fundamental concepts of electrochemistry; however, the meaning which is attached to it is different in different cases. This is, in particular, one of the reasons for the disagreement between values of the potential of zero charge given by different authors, which persists in spite of the relatively large number of experimental studies devoted recently to the determination of the pzc [1-4]. In this connection we thought that it is appropriate to carry out a more detailed analysis of this concept as well as of the substance of the Lippmann equation as a fundamental thermodynamic relation into which the quantity charge enters.

In the usual definition of the quantity charge one starts from the concept that there exists at the metal/electrolyte interface an electric double layer, and the electrode charge is identified as the charge on the metal side of the double layer. In this case the definition of the quantity charge and consequently also of the pzc becomes dependent on the assumed model of the electric double layer.

The Ideally Polarizable Electrode

Let us consider at first the case of the ideally polarizable electrode on the surface of which there is no transfer of charged species from one phase to the other. The charge on the metallic side of the double layer, Q, is equal in absolute value and opposite in sign to the charge of the ionic side:

$$Q = -\Sigma\Gamma_i + \Sigma\Gamma_j, \tag{1}$$

where Γ_i are the Gibbs surface excesses of the cations, and Γ_j those of the anions of the solution. which make up the ionic side of the electric double layer; the values of Γ_i and Γ_j are expressed in coulombs per cm^2 according to the values of the charges of the ions in the bulk of the solution. The value of Q in (1) does not depend on the position of the interface. We shall assume here and in the following that, unless stated

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otherwise, the latter is defined by the condition $\Gamma_{H_2O}=0$. It is, however, necessary that the value of the charge of the adsorbing particles does not change during their adsorption if Q in (1) is actually to denote the charge on the metal side of the double layer. Nonetheless, according to Lorenz [5, 6], a considerable part of the charge on the ions of the double layer on mercury and liquid gallium is transferred to the electrode, in particular also in the case of alkali metal cations. There is no doubt about the principal possibility of such a transfer although the method of determining the fraction of charge transferred as proposed by Lorenz draws objections [7]. Negating this possibility is equivalent to asserting complete absence of covalent bonding between the electrode and the ions present in the double layer. Such an assertion was pronounced by some authors [8] but can by no means be taken as proven.

The notion of an "ideally polarizable" electrode was widely used in the modern electrochemical literature [9-13] and served as a basis for creating a quantitative theory of the double layer. Many of the conclusions of this theory were confirmed experimentally, while the experimental material was mainly obtained on the mercury electrode. In this case the concept of electrode charge as based on a portrayal of the metal/electrolyte interface with the aid of electric double-layer theory could be accpeted as satisfactory if it is assumed that Lorenz' data can be explained otherwise. However, important experimental material has not been accumulated concerning the structure of the metal/electrolyte interface for metals of the platinum group, and here this is a different matter because charge transfer undoubtedly takes place during the adsorption of most ions on platinum [14-18]. In the presence of such a transfer the definition of the quantity surface charge would require detailed information on the nature of the interaction between the adsorbed ions and the surface, which is not at our disposal; in this connection the value of the pzc also becomes vague.

Beginning with the first papers concerning the platinum/electrolyte interface the assumption was accepted that besides the adsorbed ions there are on the metal/electrolyte interface adsorbed hydrogen and oxygen atoms [19, 20] (or even only these [21]). Consider from this viewpoint the behavior of a platinum electrode in a solution which is 1 N with respect to K^+ and Cl^- ions and 0.01 N with respect to H^+ ions, with the potential range limited from 0.15 to 0.6 V vs the reversible hydrogen electrode in the same solution (this range can also be extended in practice). With the condition $[H^+] \ll [K^+]$ it is reasonable to assume that the quantity of H^+ ions contained in the ionic part of the double layer can be neglected [15, 22, 23] and that the observed adsorption of H^+ ions depends on their transition to adsorbed H atoms or vice versa. With this assumption the pzc in the system considered, which is defined by the condition $\Gamma_{K^+}=\Gamma_{Cl^-}$, is 0.4 V [23, 24].*

Consistent with the assumption that the transition ion $\rightleftharpoons$ atom is possible on the electrode surface, the electrode considered cannot be taken as ideally polarizable if the adsorbed atoms are attributed to the metal phase. However, formally another explanation is also possible. In the potential range indicated the concentration of dissolved molecular hydrogen, H_2, is rather small (on the order of 10^{-9} mole/liter or less) so that it could be excluded from the components of the solution. With the use of platinized electrodes the total quantity of hydrogen dissolved in the bulk of the solution can easily be made small as compared to the quantity adsorbed on the electrode surface. Thus, if a platinized electrode with an apparent surface area of 4 cm^2 and a true surface area of 4000 cm^2 is in equilibrium with 1 cm^3 of solution, which corresponds to the actual conditions of our experiments, then the amount of dissolved hydrogen is on the order of 10^{-12} moles when the potential is 0.15 V removed from that of the reversible hydrogen electrode in the same solution, while the amount of adsorbed hydrogen is on the order of 10^{-6} moles. Under these conditions it becomes possible to vary the electrode potential practically without changing the composition of the bulk phases of the system, in other words, the electrode possesses the additional degree of freedom characterizing the ideally polarized electrodes [12]. The maximum stationary current density which can flow under these conditions from the surface of this electrode into the bulk of the solution previously purged of H_2 does not exceed 10^{-8} A/cm^2 of geometric surface area of the electrode unless there is forced convection. Thus, the requirement that practically no stationary current can flow when the electrode is ideally polarizable [10] is also practically fulfilled. Developing such an explanation further one could finally suggest that the H^+ ions retain their ionic nature although they are tightly adsorbed. In this case the pzc is defined by the condition $\Gamma_{H^+}{}^s+\Gamma_{K^+}=\Gamma_{Cl^-}$, which leads to a value of pzc of 0.14 V [22, 24].† Such a treatment of the Pt – H

*Unless otherwise stated, the potentials are given here and in the following vs nhe.

†The index s in $\Gamma_{H^+}{}^s$ is added in order to distinguish this connotation of Γ_{H^+} from the one ascribed to the quantity Γ_{H^+} in our earlier papers. In [29] the quantity $\Gamma_{H^+}{}^s$ was denoted by $(\Gamma_{H^+})_\varphi$.

electrode is unusual,* and one could raise certain objections against it. Thus, if we assumed, for example, that all the adsorbed hydrogen ions retain their charge, then we would arrive at large values of surface charge which are not accepted in the usual picture of the electric double layer. The charge of platinum at φ = 0.04 V in a solution of the composition quoted would be $-32\ \mu C/cm^2$ not zero, and at the reversible hydrogen potential it would be in excess of 200 $\mu C/cm^2$ in absolute value. However, this type of argument can obviously not be taken into account in a thermodynamic treatment of the problem where the adsorbed atom H and the pair: electron on the metal and ion H^+ attracted from the bulk of the solution, are entirely equivalent.

Further difficulties, which have already been examined sufficiently in earlier papers, arise when considering the adsorption of ions on Pt from solutions containing strongly adsorbable cations such as Cd^{2+} and Tl^+ [14, 15, 18, 26]. The entire behavior of adsorbed Cd^{2+} and even more so of Tl^+ indicates that their bonding to platinum is basically covalent; it is possible that they form a surface alloy with Pt [15, 27]. In this case the charge of the adsorbing ions would have to be attributed not to the ionic but to the metal side of the double layer. Thus, in the presence of strongly pronounced chemisorption, the definition of charge and pzc on the Pt electrode becomes unrealistic in the usual understanding of these terms; to a certain approximation this definition becomes feasible for ions such as the anion SO_4^{2-} and the cations Li^+, Na^+, and K^+ which are relatively weakly adsorbed on Pt. Similar difficulties arise also in the adsorption of halide ions on iron-group metals [28].

It follows from the above that one must distinguish between two definitions of the term "charge" [15, 22, 29, 30], one referring to the quantity entering thermodynamic relations, and the other referring to the charge on the metal side of the double layer which portrays with a certain approximation the charge distribution at this interface. The investigation of the thermodynamics of reversible electrodes led long ago to the necessity of accounting for this difference [31, 32]; in the framework of the theory of the ideally polarizable electrode this was formulated by Lorenz [5]. We should think that it is expedient to call the first quantity total or thermodynamic, and the second quantity the free charge of the electrode surface; Lorenz calls the first quantity "conventional" charge [5]. The motivation for the term "total" charge will become clear from the following. In the following we shall denote the first quantity by Q, and the second by ε.

In the case of an ideally polarizable electrode, the quantity Q equals the right-hand side of Eq. (1) if all Γ_i and Γ_j are taken into account regardless of the form in which the charged components of the solution transfer into the surface layer.† If all the other components of the metal phase are taken as uncharged, which is always admissible, then the quantity Q on the left-hand side of Eq. (1) can be equated to the Gibbs surface excess of electrons with a minus sign: $Q = -\Gamma_e$.

The total charge of an ideally polarizable electrode can also be defined in another way, while the analogy with the usual capacitor is fully retained, viz., as the amount of electricity which must be imparted on the electrode when increasing its surface area by 1 cm^2 in order to keep the electrode/solution potential difference constant while keeping the chemical potentials of all solution components (charged as well as uncharged) and components of the metal phase also constant. Such a definition of charge was already given by Lippmann [33, 34] who called this quantity the "electrode capacity at constant potential." Lippmann, however, did not mention the necessity of keeping the chemical potentials of all components of the system constant as well, rather than only the potential of the electrode. It is obvious that in the case of an ideally polarizable electrode the quantity Q thus defined is identical with the left-hand side of Eq. (1).

*It is here asserted that such a treatment is possible in order to prove that the concept of electrode charge requires a definition independent of the concepts about double layer structure. As a matter of fact, in their entirety the data on the platinum-hydrogen electrode demonstrate that it is appropriate to distinguish between adsorbed ions and adsorbed atoms of hydrogen in the surface layer [15, 22, 23]. Accordingly we have pointed out in our previous papers concerning this problem that the platinum-hydrogen electrode is not "ideally polarizable" but "perfectly polarizable" in the sense of Planck [25], i.e., that it is an electrode whose state is fully determined by the amount of electricity passed through it beginning at a certain point in time. However, it can also be called "ideally polarizable" within the framework of a purely thermodynamic treatment, as shown above.

†The adsorption of uncharged components at the ideally polarizable electrode does not contribute to the value of Q.

The derivation of the Lippmann equation for the ideally polarizable electrode has often been discussed in the literature [9-12], and there is no necessity for returning to it here; however, there has usually been no attention given to the difference between the quantities Q and ε. It follows already from the derivation given by Lippmann that this equation must be written in the form

$$\frac{\partial \sigma}{\partial \varphi} = -Q, \tag{2}$$

where σ is the surface free energy (in the case of a liquid metal, the interfacial tension), and φ is the electrode potential measured against a constant reference electrode. Lorenz stressed [5] that the quantity Q, not ε, enters the right-hand side of Eq. (2) in the case of the ideally polarizable electrode.

The Platinum-Hydrogen Electrode Considered as a Reversible Electrode

The definition of the value of total charge on the basis of Eq. (1) is evidently inapplicable to the reversible electrode because of the possibility of charge transfer across the interface. We shall show that the second definition, which should be called Lippmann's, can be extended to reversible electrodes even though in this case certain difficulties arise. In such a treatment the difference between the cases of the ideally polarizable and the reversible electrode is connected with the following. It has already been pointed out that in the case of an ideally polarizable electrode one must, besides introducing a quantity of electricity Q, also introduce quantities Γ of all independent components of the solution and similar quantities for the metallic phase (the Gibbs surface excesses) in order to keep the state of the system unchanged when increasing the surface area by 1 cm^2. In the case of a reversible electrode there are components whose concentrations remain automatically constant at given values of the electrode potential and of the concentrations of other components; for example, the concentration of H_2 remains constant in the case of a platinum-hydrogen electrode in a solution containing H^+ ions of a given concentration. Moreover, the surface layer of a reversible electrode can be constructed entirely from uncharged components because the free charges of the double layer can be obtained through the electrode process.

We shall elucidate these relations at the realistic example of a platinum-hydrogen electrode in acidified solution of the neutral salt CA. We quote the basic equation of electrocapillarity for this electrode while considering it at first, however, as ideally polarizable. Following presently accepted methods of description [11-13], this has the form

$$d\sigma = -Q\, d\varphi_A - \Gamma_{C^+}\, d\mu_{CA} - \Gamma_{H^+}^{s}\, d\mu_{HA}, \tag{3}$$

where Q is the total charge of the electrode surface, φ_A is the electrode potential measured relative to a reference electrode which is reversible with respect to the anion A^-, Γ_{C^+}, and $\Gamma_{H^+}^{S}$ are the Gibbs surface excesses of the cations C^+ and H^+. The chemical potentials μ as well as the surface excesses Γ are expressed in electrical units (μ in V and Γ in C/cm^2). In this case the electrons and the ions H^+, C^+, and A^- are the components of which the system is constructed. We do not account for water because $\Gamma_{H_2O} = 0$. Let us consider in more detail the physical meaning of the quantities Q and $\Gamma_{H^+}^{S}$ in (3). The quantity Q is the amount of electricity which must be imparted on the electrode from the outside when increasing its surface area by unity in order to keep the potential φ_A constant and while assuming that the constancy of the quantities μ_{CA} and μ_{HA} is secured by introducing into the solution the ions A^-, C^+, and H^+ in quantities of Γ_{A^-}, Γ_{C^+}, and $\Gamma_{H^+}^{S}$. According to (1) the relation

$$Q = \Gamma_{A^-} - \Gamma_{C^+} - \Gamma_{H^+}^{s} \tag{4}$$

is here fulfilled. We shall now account for the fact that part of the adsorbed H^+ ions goes over to the atomic state. The free surface charge ε arises both on account of the charge Q imparted on the system from the outside and on account of the charge of adsorbed H^+ ions going over to the atomic state. If the surface density of adsorbed H atoms (in electrical units) is designated A_H and if it is assumed that the ions C^+ and A^- present on the ionic side of the double layer do not transfer part of their charge to the Pt surface, then

$$\varepsilon = Q + A_H. \tag{5}$$

Adsorbed H^+ ions either remain in the outer part of the double layer, i.e., do not transfer their charge to Pt, or they go over to the atomic state. Denoting the surface density of the former by A_{H^+},* we obtain

$$\Gamma_{H^+}^{s} = A_{H^+} + A_H. \tag{6}$$

Since the free surface charge must correspond to the sum of charges in the ionic part of the double layer,

$$\varepsilon = \Gamma_{A^-} - A_{H^+} - \Gamma_{C^+}. \tag{7}$$

The quantity Q defined by (5) is identical to the quantity Q defined by (4). In fact, according to (4), (6), and (7)

$$Q = -\Gamma_{H^+}^{s} - \Gamma_{C^+} + \Gamma_{A^-} = -A_{H^+} - \Gamma_{C^+} + \Gamma_{A^-} - A_H = \varepsilon - A_H.$$

From (3), (5), and (6), we obtain

$$d\sigma = (A_H - \varepsilon)\, d\varphi_A - \Gamma_{C^+} d\mu_{CA} - (A_{H^+} + A_H)\, d\mu_{HA}. \tag{8}$$

Let us now use H atoms rather than electrons in creating the surface layer. The adsorption of hydrogen we shall denote by Γ_H.† During formation of the surface layer hydrogen partly goes over into the ionic state leaving negative charges on the surface and thus generating electrons, and partly it is adsorbed in the form of neutral atoms; thus, according to (5),

$$\Gamma_H = A_H - \varepsilon = -Q. \tag{9}$$

We also introduce the quantity Γ_{H^+} which is defined by the equation

$$\Gamma_{H^+} = A_{H^+} + \varepsilon. \tag{10}$$

It follows from (8), (9), and (10) that

$$d\sigma = \Gamma_H d\varphi_A - \Gamma_{C^+} d\mu_{CA} - (\Gamma_{H^+} + \Gamma_H)\, d\mu_{HA} = \Gamma_H (d\varphi_A - d\mu_{HA}) - \Gamma_{C^+} d\mu_{CA} - \Gamma_{H^+} d\mu_{HA}. \tag{11}$$

When replacing the electrons by H atoms as the component used for the formation of the surface layer we change the adsorption balance of H^+ ions because atom formation from H^+ ions, which causes them to disappear from the solution, is now the only source of free surface charges, while the formation of the layer of adsorbed H atoms can under these conditions also occur at the expense of Γ_H, in agreement with (9). The quantity Γ_{H^+} defined in (10) thus expresses the adsorption of H^+ ions under these conditions. From (11) we obtain, using the obvious relations $\mu_{HA} = \mu_{H^+} + \mu_{A^-}$, $\Gamma_{C^+} = \Gamma_{CA}$, and $\Gamma_{H^+} = \Gamma_{HA}$, and also $d\varphi_A = d\mu_{A^-} + d\mu_{H^+} - d\mu_H$, where μ_H is the chemical potential of hydrogen:

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{CA} d\mu_{CA} - \Gamma_{HA} d\mu_{HA}. \tag{12}$$

Thus, starting from the equation of electrocapillarity of the ideally polarized electrode (3) we have arrived at the Gibbs adsorption equation which can be used for a reversible system constructed from the uncharged components H, HA, and CA. Equation (12) is strictly thermodynamic and could have been given without the above derivation, as we have done in earlier papers where it was adduced for treating the thermodynamics of the Pt – H system [16, 17, 35]. We have preferred, however, to adduce a derivation in which the non-

*In [16, 17, 23] this quantity was denoted by $\Gamma_{H^+}^{i}$.

†In experimental determinations of the thermodynamic quantity Γ_H reported so far, assumptions about the double layer structures at the platinum/solution interface were used which go beyond the framework of thermodynamics [22, 24]. A determination of Γ_H which is independent of such assumptions is possible via measurements of adsorption on a platinum electrode degassed in advance in vacuum. Such measurements can in principle be realized regardless of certain experimental difficulties.

thermodynamic quantities ε and A_{H^+} play a role in order to show the internal connection between the two methods of treating the same system. Equation (11) can be written in the form

$$d\sigma = \Gamma_H(d\varphi_A - d\mu_{HA}) - \Gamma_{CA}d\mu_{CA} - \Gamma_{HA}d\mu_{HA}, \tag{13}$$

whence

$$\left(\frac{\partial\sigma}{\partial\varphi_A}\right)_{\mu_{CA},\mu_{HA}} = \Gamma_H = A_H - \varepsilon. \tag{14}$$

We shall now show that the quantity $-\Gamma_H$ corresponds to the above definition of total charge as the quantity of electricity which must be supplied to the system so that the electrode potential will remain unchanged when increasing the surface area while keeping the chemical potentials of all components constant. In order to satisfy the last condition when introducing electricity from the outside it suffices to compensate for the overall change in hydrogen content upon adsorption (it would not be necessary to introduce electricity if we compensated the changes in H^+ and H content separately). This quantity is given as $\Gamma_H + \Gamma_{H^+} = A_H + A_{H^+}$. Said quantity of hydrogen can be introduced in the form of ions or in the form of atoms. We here select the first way (see below) and besides $\Gamma_H + \Gamma_{H^+} = A_H + A_{H^+}$ we introduce into the system a quantity of electricity $Q = -\Gamma_{H^+} = \varepsilon - A_H$. Performing these two operations is equivalent to introducing into the system $\Gamma_H = A_H - \varepsilon$ atoms and $\Gamma_{H^+} = A_{H^+} + \varepsilon$ ions of hydrogen, i.e., it fully reestablishes the initial state of the system and secures thus the constancy of potential at the interface. The quantity $Q = -\Gamma_H = \varepsilon - A_H$ thus really expresses the total charge of the electrode according to the definition given above, while (14) is the Lippmann equation for the reversible system considered [15, 22]. One cannot agree, therefore, with the assertion made in [36] that for a reversible system the Lippmann equation does not exist, if only one understands under charge the total electrode charge. This charge equals the Gibbs adsorption of the reductant H in the redox system H/H^+ with a minus sign when the term Gibbs adsorption is understood as used in the present paper, i.e., when including into it not only the amount of material corresponding to its surface excess (A_H) but also the amount of material consumed as a result of potential-determining adsorption and which during the formation of fresh surface goes over into the ox-form ($-\varepsilon$). However, it is readily shown that in the case of a reversible system the choice of the quantity which we identify as total electrode charge is not unambiguous.

In fact, taking into account that

$$\Gamma_{HA} = \Gamma_{H^+} \text{ and } d\mu_{HA} = d\varphi_A + d\mu_H,$$

it also follows from (12) that

$$\begin{aligned} d\sigma &= -\Gamma_H d\mu_H - \Gamma_{CA}d\mu_{CA} - \Gamma_{HA}(d\varphi_A + d\mu_H) \\ &= -(\Gamma_H + \Gamma_{H^+})d\mu_H - \Gamma_{CA}d\mu_{CA} - \Gamma_{H^+}d\varphi_A. \end{aligned} \tag{15}$$

From (15) we obtain, with (9) and (10),

$$d\sigma = -(A_H + A_{H^+})d\mu_H - \Gamma_{CA}d\mu_{CA} - \Gamma_{H^+}d\varphi_A, \tag{16}$$

and also

$$\left(\frac{\partial\sigma}{\partial\varphi_A}\right)_{\mu_H,\mu_{CA}} = -\Gamma_{H^+} = -\varepsilon - A_{H^+}. \tag{17}$$

Thus, if the change in potential is produced through a change in μ_{H^+} rather than μ_H, then the total (thermodynamic) electrode charge must be expressed through $\varepsilon + A_{H^+}$ rather than through $\varepsilon - A_H$. We arrive at the same value of charge $Q = \Gamma_{H^+}$ by repeating the reasoning given above and compensating for the overall variation in hydrogen content in the system when increasing the surface area by 1 cm^2, which equals $\Gamma_H + \Gamma_{H^+} = A_H + A_{H^+}$, by introducing hydrogen in the form of H atoms rather than in the form of H^+ ions. The amount of electricity which we must introduce into the system in order to keep the potential constant equals Γ_{H^+}, i.e., equals the Gibbs adsorption of the oxidizing component of the redox system.

Thus, Lippmann's definition of the quantity Q as being equal to $-\partial\sigma/\partial\varphi$ remains in force also in this case but the magnitude of Q turns out to depend on whether we keep the chemical potential of the reducing or the oxidizing component constant when changing the electrode potential.

In the presence of a sufficiently large excess of a foreign cation where the H^+ ions are displaced from the ionic part of the double layer and $A_{H^+} = 0$, Γ_{H^+} equals the free charge (with the limitations indicated above which refer to the behavior of the A^- and C^+ ions in the surface layer). This conclusion is a natural one because the thermodynamics of the reversible hydrogen electrode (e.g., one which is in equilibrium with hydrogen at atmospheric pressure) must by no means differ from the thermodynamics of a reversible metal electrode for which a similar relation holds.

In our earlier papers we have reported $\varphi_{Q=0}$ values for the platinum-hydrogen electrode which were obtained with both the possibilities of varying the potential, viz., the quantities $\varphi_{\Gamma_{H}=0}$ and $\varphi_{\Gamma_{H^+}=0}$ [16, 22, 24, 29, 30, 37]. Thus, e.g., for Pt in 0.1 N HCl + 1 N KCl

$$\varphi_{\Gamma_{H}=0} = 0.14\,\text{V}, \text{ but } \varphi_{\Gamma_{H^+}=0} = 0.04\,\text{V}.$$

The former quantity we have called the potential of zero total charge, and the latter the potential of zero free charge. The last term, however, is only approximately correct, viz., to the degree of accuracy with which one can assume $A_{H^+} = 0$ and neglect chemisorptive interaction of all ions in solution other than H^+ with the electrode surface. In the more general case $\varphi_{\Gamma_{H^+}=0}$ is the potential of zero total charge when the condition $\mu_H = \text{const}$ is fulfilled.

The Metal Electrode in a Solution Containing the Ions of that Metal

In many cases the choice between the two above-mentioned ways of varying the electrode potential of a reversible redox system is determined by considering which of the chemical potentials of its components can more conveniently be held constant. Consider from this point of view the system Hg, Tl, K^+, A^-, H_2O where Tl can be present both as Tl^+ ions and as atoms dissolved in the mercury. We limit ourselves here to the potential range where one can neglect the appearance of mercury ions in the solution, and to sufficiently low Tl^+ and K^+ concentrations so that one can assume $\mu_{H_2O} = \text{const}$. In this case the interface is most conveniently defined by the condition $\Gamma_{Hg} = 0$. Under these assumptions the present system can be considered as a system constructed from the components Tl, TlA, and KA, and treated in the same way as that constructed from H, HA, and CA. In agreement with (12) one has the relation

$$d\sigma = -\Gamma_{Tl} d\mu_{Tl} - \Gamma_{KA} d\mu_{KA} - \Gamma_{TlA} d\mu_{TlA}\,, \tag{18}$$

In the same way as with Eqs. (14), (16), and (17) one can from Eq. (18) readily obtain the equations

$$d\sigma = -(A_{Tl} + A_{Tl^+})\, d\mu_{Tl} - \Gamma_{KA} d\mu_{KA} - \Gamma_{Tl^+} d\varphi_A = -(A_{Tl} + A_{Tl^+})\, d\mu_{Tl} - \Gamma_{KA} d\mu_{KA} - (\varepsilon + A_{Tl^+})\, d\varphi_A, \tag{19}$$

$$\left(\frac{\partial \sigma}{\partial \varphi_A}\right)_{\mu_{TlA}, \mu_{KA}} = -Q' = \Gamma_{Tl} = A_{Tl} - \varepsilon \tag{20}$$

$$\left(\frac{\partial \sigma}{\partial \varphi_A}\right)_{\mu_{Tl}, \mu_{KA}} = -Q'' = -\Gamma_{Tl^+} = -\varepsilon - A_{Tl^+}, \tag{21}$$

where A_{Tl} is the amount of Tl present as atoms in the surface layer, while A_{Tl^+} is the quantity of Tl^+ ions remaining adsorbed in the ionic part of the double layer, i.e., which do not give off their charge to the electrode surface.

Consider from the view point presented above what happens during cathodic polarization of Hg in a solution containing Tl^+ ions. The condition $\mu_{TlA} = \text{const}$ can be taken as fulfilled so long as the variation in $[Tl^+]$ due to Tl amalgam formation during cathodic polarization of the electrode is small. In this case the φ_A dependence of σ of the mercury electrode in the TlA + KA solution is defined by Eq. (20), which can be considered as the Lippmann equation of the electrocapillary curve of mercury in the given solution.*

* It has already been shown in [31] that besides the term accounting for the charge one must introduce into the right-hand side of the Lippmann equation a term accounting for the adsorption of atoms of the metal going into the mercury when an amalgam is formed upon discharge of cations of the solution.

Such curves have been obtained repeatedly [38-41] while in their analysis it was assumed that A_{Tl} can be neglected, i.e., the electrode was considered as ideally polarizable in the presence of specific adsorption of Tl^+ ions.* However, according to Lorenz [6] part of the charge of the Tl^+ ions goes over to mercury, which is equivalent to assuming a finite value of A_{Tl} in (20). At sufficiently negative potentials thallium practically completely passes into the amalgam, the concentration of Tl^+ in the solution becomes negligibly small, and μ_{Tl} becomes a constant quantity. In this potential range the electrocapillary curve of the electrode obeys (21), and the total charge of the electrode has another connotation, which in (21) is denoted by changing Q' into Q''. In the presence of an excess of K^+ ions one can probably neglect A_{Tl^+} in this potential range, and consider the behavior of the electrode as that of an ideally polarizable Tl amalgam electrode [26] if, of course, the assumption of partial charge transfer from K^+ ions to the electrode [6] is discarded. Thus it follows from the analysis of the electrocapillary behavior of a reversible system given here that two types of electrocapillary curves can be obtained in the system considered.

During cathodic polarization of a mercury electrode in acidified solution of 0.2 N $TlNO_3$ + 0.8 N KNO_3, two electrocapillary curves are indeed obtained as seen from Fig. 1 which is borrowed from the work of Frumkin and Polyanovskaya [39, 40]. In this case the measurements were carried out under conditions not corresponding to the premises of the thermodynamic derivation, viz., while passing a perceptible current through the system and with concentration gradients of thallium in the amalgam phase and of Tl^+ ions in the aqueous phase when the potentials were sufficiently negative; however, the results obtained can all the same serve as a qualitative illustration that the treatment is correct.†

It must be noted that such a clear separation of the two electrocapillary curves of a redox system as shown in the figure is only possible when there is a large difference between the values $\varphi_{Q'=0}$ and $\varphi_{Q''=0}$. Thus, such a separation is not realized in the cathodic polarization of mercury in cadmium salt solution [39] although the adsorption behaviors of Cd^{2+} and Tl^+ ions are in many respects similar.

Let us consider in some detail the problem of the relation between Q and ε and of the form of the Lippmann equation for the frequency case where the composition of the metal phase is given. According to (17) or (21) one can write in this case

$$\frac{\partial \sigma}{\partial \varphi} = -Q = -\Gamma_{Me^{n+}} = -\varepsilon - A_{Me^{n+}}, \tag{22}$$

where $\Gamma_{Me^{n+}}$ expresses the overall adsorption of Me^{n+} ions, and $A_{Me^{n+}}$ is the part of Me^{n+} ions disappearing from the solution when new surface area is created without supplying electricity from outside, and

*It follows from [39-41] that in the presence of complex-forming anions, Tl^+ is adsorbed on mercury primarily in the form of anionic complexes. The quantity which we have labeled A_{Tl^+} accounts for the amount of Tl^+ on the ionic side independently of the form in which the thallium ions are adsorbed.

†At sufficiently negative potentials a thallium amalgam electrode in KNO_3 solution is practically ideally polarizable. The Lippmann equation for this kind of electrode was derived starting from Gibbs' equation for the reversible system in an earlier paper of Frumkin where the mercury electrode was discussed [31]. This derivation was later subjected to criticism with particular reference to the fact that the concentrations of Hg^{2+} ions with which we are dealing in this case at not very high positive potentials are vanishingly small [11, 42]. Such criticism would be founded if the kinetics of double layer formation were discussed but it cannot affect the correctness of the derivation of equilibrium conditions. In the present paper the possibility was also shown of treating the platinum-hydrogen electrode as an ideally polarizable electrode; however, it will hardly be disputed that the system Pt, H_2, H^+ can rightly be considered as a reversible system in the potential range indicated above, on the basis that, e.g., at 0.48 V against a hydrogen electrode in the same solution the concentration of H_2 in the solution is reduced to 10^{-20} mole/liter. The concept of an ideally polarizable electrode made it possible to cast the derivation of the fundamental equation of electrocapillarity into an elegant form; however, an overly profound differentiation between ideally polarizable and reversible electrodes led later to false conclusions, which may be exemplified by the suggestion that there exist in the case of reversible electrodes some Billiter null point which is different from the Lippmann null point characteristic for the ideally polarizable electrodes [44, 45]. Actually it is not reflected in the structure of the electric double layer if the ideally polarizable mercury electrode is endowed with the property of reversibility so long as this is achieved by introducing sufficiently small amounts of a more electronegative components, as shown by experiment [45].

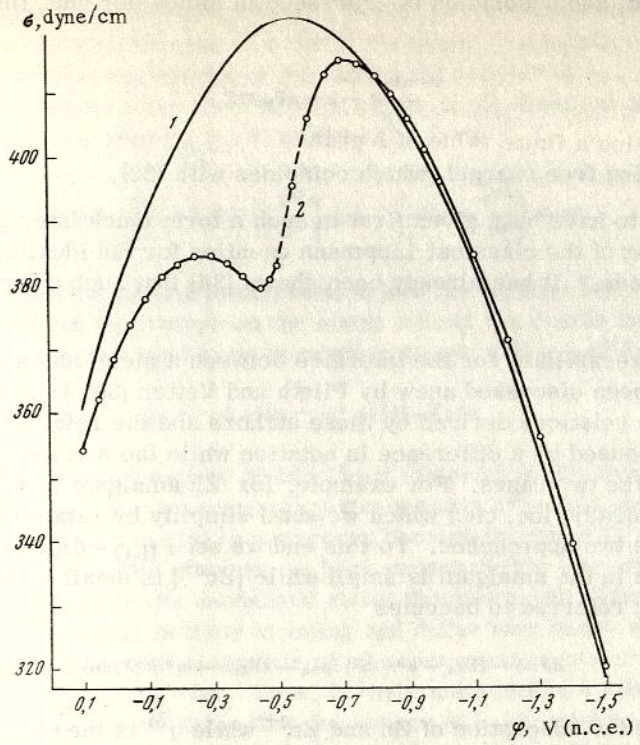

Fig. 1. Potential dependence of interfacial tension: 1) Mercury, 1 N KNO_3; 2) mercury, 0.2 N $TlNO_3$ + 0.8 N KNO_3 (according to the data of [39]).

which remains in the ionic part of the double layer and does not give off its charge to the metal surface. The subscript at $\partial\sigma/\partial\varphi$ can be dropped because the potential of a reference electrode reversible with respect to the anion remains constant at constant anionic composition of the solution, and φ can thus be referred to any constant reference electrode. It has already been shown that the introduction of the nonthermodynamic quantity ε into (22) is only justified when it is assumed that covalent bonds between the metal surface and the ions of the ionic side of the double layer are absent.

The noncoincidence between total and free charge for reversible mercury and amalgam electrodes had long been clear though it had not been formulated in these terms. Kruger already [46] proposed as an explanation for the asymmetry of the electrocapillary curve in halide-ion-containing solutions that on the positively charged mercury surface complex anions of mercury are adsorbed which become part of the ionic side of the double layer. Kruger put the Lippmann equation into the form

$$\frac{\partial\sigma}{\partial\varphi} = \varepsilon + F(k-1)c\delta, \tag{23}$$

where c is the concentratior of mercury in the solution, k is the distribution coefficient of mercury salt between the surface layer and the bulk of the solution, and δ is the thickness of the surface layer; the potential was reckoned from the solution to the electrode.

The hypothesis of a direct connection between the second term on the right-hand side of Eq. (23) and the asymmetry of the electrocapillary curve was erroneous [31] but this does not affect the thermodynamic correctness of Kruger's deduction [34].* If only those ions which do not give off their charge to the metal

*A hypothesis similar to Kruger's, although with a different motivation, was recently put forth by Barker [43].

surface are called adsorbed, and adsorption is expressed in moles per cm^2, then (23) can be written in the form

$$\frac{\partial \sigma}{\partial \varphi} = -\varepsilon - n\Gamma_{Me^{n+}}F \tag{24}$$

(the "charge," ε, really being free charge), which coincides with (22).

This equation seems to have been given first in such a form much later [31]; it was derived anew by Mohilner [47] as the "analog of the classical Lippmann equation for the ideally polarizable electrode in the case of a reversible electrode." It has already been shown [34] that such a formulation is historically unjustified.

The equation of electrocapillary for the interface between a metal and a solution containing the ions of that metal has recently been discussed anew by Plieth and Vetter [36, 48]. It can readily be shown that the differences between the relations derived by these authors and the relations given here and partially in our earlier papers are caused by a difference in notation while the mathematical content of the derivations actually coincides in the two cases. For example, for Zn amalgam in $KCl + ZnCl_2$ solution an expression is given in [36] (Eq. (29) loc. cit.) which we shall simplify by retaining only the terms which are essential for comparing the two approaches. To this end we set $\Gamma_{H_2O} = 0$ and $\mu_{KCl} = \text{const}$ and assume that the concentration of Zn in the amalgam is small while $[Zn^{2+}]$ is small as compared to $[K^+]$. With these simplifications the equation referred to becomes

$$d\sigma = -(\Gamma_{Zn} - q^M / 2F)\, d\mu_{Zn} - (\Gamma_{Zn^{2+}} + q^M / 2F)\, d\mu_{Zn^{2+}}. \tag{25}$$

Here Γ_{Zn} and $\Gamma_{Zn^{2+}}$ denote the adsorption of Zn and Zn^{2+} while q^M is the charge (in our teminology the free charge) of the metal surface. When comparing (25) with the relations deduced by us one must keep in mind that Plieth and Vetter use the electrons and ions of the metal phase as well as particles in the red- and ox-form when constructing the surface layer. Therefore the quantities Γ in [36] correspond to our A but not to our Γ. One must further remember that the quantities Γ and μ in [36] are not translated into electrical units, in contrast to the present paper. Retaining the notation of (25) and taking into account that

$$d\mu_{Zn^{2+}} = d\mu_{Zn} + 2F d\varphi,$$

we obtain from (25)

$$d\sigma = -(\Gamma_{Zn} + \Gamma_{Zn^{2+}})\, d\mu_{Zn} - (q^M + 2\Gamma_{Zn^{2+}}F)\, d\varphi. \tag{26}$$

Taking into account what was said above concerning the physical meaning and dimension of the quantities Γ in (26) and also taking into account the condition $\mu_{KCl} = \text{const}$ we see that Eq. (26), which is not derived in [36], is equivalent to our Eq. (19). As from (19), one can obtain from (26) the equation of the electrocapillary curve under the condition $\mu_{Zn} = \text{const}$

$$\left(\frac{\partial \sigma}{\partial \varphi}\right)_{\mu_{Zn}} = -(q^M + 2\Gamma_{Zn^{2+}}F).$$

In spite of the identity of the mathematical relations there seems to exist some difference in the understanding of their physical meaning. In fact, the suggestion is made in [36] that the values of $\Gamma + q^M/zF$ obtained from equations of the type (25) can be corrected for the value of $q^M/2F$ by a determination with the aid of electrocapillary and capacity measurements, without saying that such a correction can only be accomplished when introducing additional, nonthermodynamic assumptions.* In [48] Plieth and Vetter consider the case where red- and ox-components of the solution are indistinguishable in the adsorbed state. Following the ideas of Lorenz [5, 6] it is proposed that the material in the adsorbed state bears a charge

*According to our terminology the quantity $q^M + 2\Gamma_{Zn^{2+}}F$ in Eq. (26) is the total electrode charge at μ_{Zn} equals const. At least with an electrode of the platinum-hydrogen type, a separation of the components of total charge by measuring the capacity at high frequencies also cannot be realized for the reason that on such an electrode the value of q^M determined at high frequencies differs from the equilibrium value.

differing by λn from the charge of the red-component, n being the difference in charge between ox- and red-components, and $0<\lambda<1$.* In the special case of a metal electrode in a solution containing ions of charge z it is correspondingly assumed that the charge of the adsorbing species is λz. For this case Plieth and Vetter deduce equations of electrocapillary ((54) in [48]) which, if all chemical potentials except μ_M and $\mu_M{}^{z+}$ are taken as constant and one sets $\Gamma_{H_2O}=0$, assume the form

$$d\sigma = -\left[(1-\lambda)\Gamma_{ad} - \frac{q^M}{zF}\right] d\mu_M - \left[\lambda\Gamma_{ad} + \frac{q^M}{zF}\right] d\mu_M{}^{z+}. \tag{27}$$

In this case, too, Plieth and Vetter separate the transition into the surface layer from the potential-determining adsorption which brings out the charge on the metal side of the double layer, so that the quantities Γ_{ad} must be compared with our A. Using Nernst's relation $d\mu_M{}^{z+} = d\mu_M + zFd\varphi$ we obtain from (27)

$$d\sigma = -\Gamma_{ad} d\mu_M - (q^M + \lambda z\Gamma_{ad}F)\, d\varphi. \tag{28}$$

The quantity Γ_{ad} expresses the overall excess of adsorbing material in the surface layer and corresponds to the quantity $(A_{Tl}+A_{Tl^+})$ in (19). In our terminology the quantity $q^M+\lambda z\Gamma_{ad}F$ is the total surface charge of the electrode at $\mu_M=\text{const}$,† which in (19) is expressed through the quantity $\varepsilon+A_{Tl^+}$. The term $\lambda z\Gamma_{ad}F$ gives the charge of the adsorbed species whereas we have proposed that any adsorbed Tl not included into A_{Tl^+} is present in the surface layer in the uncharged state; therefore, the quantities $\lambda z\Gamma_{ad}F$ and A_{Tl^+} for the case considered by us are identical in their meaning and differ only in the way in which they are presented. Since we have taken the chemical potentials of all other components of the solution to be constant, we have further in (19) $d\mu_{CA}=0$ and $d\varphi_A=d\varphi$. Thus, in their mathematical substance (28) and (19) are identical. However, Plieth and Vetter's conclusion that the charge $\lambda z\Gamma_{ad}F$ must be referred to the ionic side of the double layer to us appears unfounded because the problem of referring any charge whatever in a reversible redox system to the metal or ionic side of the double layer cannot at all be solved within the framework of a purely thermodynamic treatment; rather its solution requires a detailed clarification of the structure of the double layer. Likewise the definition of some quantity such as the total surface charge of the electrode is in no way equivalent to saying that this charge actually resides on the surface of the metal.

One can hardly agree with the method of determining λ as proposed in [48]. According to Plieth and Vetter one has in the case of a strongly adsorbing substance in the presence of excess inert electrolyte

$$\lambda \approx \frac{\partial\sigma}{\partial\mu_O} \Big/ \left(\frac{\partial\sigma}{\partial\mu_O} + \frac{\partial\sigma}{\partial\mu_R}\right) = \frac{-Q''}{Q'-Q''}, \tag{29}$$

where μ_O and μ_R are the chemical potentials of oxidant and reductant [the meaning of the quantities Q' and Q'' is given in (20) and (21)]. Relation (29) follows directly from (27) if one assumes that the free charge is small as compared to the quantity $zF\Gamma_{ad}$. It can be demonstrated at the example of the system Hg, Tl, K^+, A^-, H_2O discussed above that such an assumption is inapplicable in the general case. In fact, it can be seen from Fig. 1 that at potentials more positive than the left-hand electrocapillary maximum, (29) gives $\lambda>1$, while at potentials more negative than the right-hand electrocapillary maximum, $\lambda<0$, which is devoid of physical meaning. In the potential range between these maxima, λ varies from 1 to 0, according to (29). Salie and Lorenz [50] used other methods whose unequivocal meaning cannot be agreed to either [7], and came for the same system to precisely the opposite conclusion, viz., that the fraction of charge transferred is independent of φ. These results prove that it is in principle impossible to define partial charge transfer during adsorption by purely thermodynamic methods.

The case of Zn amalgam in Zn salt solution, e.g., $ZnSO_4$, is an interesting example for the difference between free and total charge. Since the ionic part of the double layer is made up of Zn^{2+} and $SO_4{}^{2-}$ ions we have

$$\varepsilon = -(A_{Zn^{2+}} - \Gamma_{SO_4{}^{2-}}), \tag{30}$$

*In contrast to Lorenz, Plieth and Vetter denote through λ the fraction of charge remaining on the adsorbed particle rather than that transferred to the electrode. The quantity λ in Plieth and Vetter's notation corresponds to the quantity $(1-\lambda)$ in Lorenz' notation.

†The total charge at $\mu_M{}^{z+}=\text{const}$ is determined from the expression

$$d\sigma = -\Gamma_{ad} d\mu_M{}^{z+} - [q^M - (1-\lambda)zF\Gamma_{ad}]\, d\varphi. \tag{28a}$$

where $A_{Zn^{2+}}$ is that part of the quantity of Zn^{2+} ions adsorbed which enters the ionic side of the double layer.

The total charge Q, in agreement with (21), is

$$Q = \varepsilon + A_{Zn^{2+}} = \Gamma_{SO_4^{2-}}. \tag{30a}$$

Since at a sufficiently negative potential the negative adsorption of the anion is small as compared to the absolute value of negative surface charge, therefore, according to (30a), the total charge of Zn amalgam in $ZnSO_4$ solution is only a small fraction of the free charge [32]. Equations of the type (30a) have later again repeatedly been deduced [10, 12, 36], partly with the use of zinc amalgam as an example, too. The example given illustrates the necessity of distinguishing free and total surface charge; however, the difference between these quantities can in this case be removed by adding a sufficient excess of foreign electrolyte, and has no principal significance since we have not suggested the presence of covalent bonds in the double layer.

The General Case of a Reversible Redox System

After analyzing two examples of applying the theory of electrocapillary to reversible systems we shall limit ourselves to discussing briefly the general case of the simplest reversible redox system

$$O + ne^- \rightleftarrows R, \tag{31}$$

assuming that the chemical potentials of all components other than O and R are practically constant.

The Nernst equation for such a system can be written in the form

$$d\varphi = d\mu_O - d\mu_R, \tag{32}$$

and the Gibbs equation as

$$d\sigma = -\Gamma_O d\mu_O - \Gamma_R d\mu_R, \tag{33}$$

where the symbols Γ, μ, and φ retain their former significance. It will be clear from (34), (35), (43), and (44) that the value of n from (31) is taken into account when expressing the quantities Γ and μ in electrical units.

Assuming, in agreement with (33), that the electric double layer is created without introducing electricity from outside we obtain for the relation between the value of charge and the adsorption of the oxidant particles an expression

$$\Gamma_O = A_O + \varepsilon, \tag{34}$$

and similarly for the adsorption of reductant particles

$$-\Gamma_R = -A_R + \varepsilon, \tag{35}$$

where the symbols A and ε also have their former meaning.

At $\mu_O = \text{const}$ we have $d\mu_O = 0$, $d\varphi = -d\mu_R$, and $d\sigma = \Gamma_R d\varphi$, whence with (35) we find

$$-\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_O} = -\Gamma_R = \varepsilon - A_R = Q', \tag{36}$$

where Q', as shown earlier, is the total (thermodynamic) charge of the surface at constant oxidant activity. At $\mu_R = \text{const}$ we have $d\mu_R = 0$, $d\varphi = d\mu_O$, and $d\sigma = -\Gamma_O d\varphi$, whence with (34) we find

$$-\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_R} = \Gamma_O = \varepsilon + A_O = Q'', \tag{37}$$

where Q'' is the total (thermodynamic) charge of the surface at constant reductant activity.

The charge Q', which is defined as $\varepsilon - A_R$, expresses with inverted sign the quantity of electricity which one can extract per cm^2 of electrode surface during exhaustive oxidation upon stopping the exchange between the electrode and the bulk of the solution, i.e., when bringing ε to zero and converting the entire reserve of A_R into A_O. Likewise the charge Q'', which is defined as $\varepsilon + A_O$, expresses the quantity of electricity which one can extract per cm^2 of electrode surface during exhaustive reduction, i.e., when bringing ε to zero under the same conditions and converting the entire reserve of A_O into A_R. Thus, the definition of "charge" given here is entirely analogous to the definition of elecdrode charge for a source of current which is generally accepted in applied electrochemistry. This confirms the basic position taken in the present work which entails that in a rational definition of the concept of "charge," the Lippmann equation will remain valid both for ideally polarizable and for reversible electrodes.

According to the above one can realize electrocapillary curves of two kinds in such a redox system: at μ_O=const and at μ_R=const. These curves only coincide under the condition $A_O = A_R = 0$. The connection between Q, and Q'' follows from (36) and (37):

$$Q'' = Q' + A_O + A_R. \tag{38}$$

At the conclusion of this section it must once again be stressed that, as discussed before, in considering reversible systems we have for simplicity excluded any possibility of charge transfer in the adsorbed layer except as expressed by Eq. (31). Therefore, in the equations expressing the total charge of a reversible electrode, we were able to consider the quantity ε as the free charge.

Organic Redox System

It is of interest to apply the treatment given here to organic redox systems. In a paper of Plieth published recently [49], which is concerned with the adsorption of quinone and hydroquinone on a Hg electrode, equilibrium between three components is considered:

$$QH_2 \rightleftarrows Q + 2H^+ + 2e^-$$

(Q being quinone), while accounting for the intermediate formation of semiquinone, QH. Plieth arrives at three relations [(13), (14), and (15) of the paper cited], which in our notation should be written as

$$\left(\frac{\partial\sigma}{\partial\mu_{QH_2}}\right)_{\mu_Q,\,\mu_{H^+}} = -A_{QH_2} - {}^1/_2 A_{QH} + \varepsilon, \tag{39}$$

$$\left(\frac{\partial\sigma}{\partial\mu_{Q}}\right)_{\mu_{QH_2},\,\mu_{H^+}} = -A_{Q} - {}^1/_2 A_{QH} - \varepsilon, \tag{40}$$

$$\left(\frac{\partial\sigma}{\partial\mu_{H^+}}\right)_{\mu_{QH_2},\,\mu_{Q}} = -\varepsilon - A_{H^+}. \tag{41}$$

However, in the right-hand side of Plieth's Eq. (15), from which (41) is obtained, a term corresponding to A_{H^+} is omitted under the assumption that this quantity is small as compared to ε. Thanks to this nonthermodynamic assumption, whose justification we shall not discuss here, it becomes possible for Plieth not only to determine the overall adsorption $A_{QH_2} + A_{QH} + A_Q$ but also to separate the surface concentrations of the red- and ox-component from ε. At μ_{H^+}=const the left-hand sides of (39) and (40) become, respectively, equal to $-(\partial\sigma/\partial\varphi)_{\mu_0}$ and $(\partial\sigma/\partial\varphi)_{\mu_R}$, and these equations lead to the form of (36) and (37). The introduction of a third variable, μ_{H^+}, allows one more electrocapillary curve to be constructed, as follows from (41). In the general case the number of characteristic electrocapillary curves, i.e., curves satisfying the generalized Lippmann equation, equals the number of independent variables in the Nernst equation. In [49] the concentrations of QH_2, Q, and H^+ have not been varied in sufficiently wide limits so as to be able to actually construct electrocapillary curves.

Let us now consider the electrocapillary relation obtained when the condition

$$[O] + \gamma[R] = \text{const} \tag{42}$$

is fulfilled, where γ is a constant. With $\gamma = (D_R/D_O)^{1/2}$ where D_R and D_O are the diffusion coefficients of the red- and ox-form, respectively, Eq. (42) portrays the variation of the concentration of ox- and red-

form at the surface of a drop electrode if removal of material adsorbed at the drop surface can be neglected, and if the concentration of hydrogen ions can be taken as constant where the latter participate in the electrode process. Equation (42) also represents an approximate relation betwen [O] and [R] under the conditions where the $\sigma-\varphi$ curve of Fig. 1 was obtained.

Since $\mu_O - \mu_R = \varphi - \varphi_{1/2} + \text{const}$ where $\varphi_{1/2}$ is the potential where $[O]=\gamma[R]$ (under polarographic conditions this is the half-wave potential of the electroreduction reaction), it follows from (42) that

$$\mu_O = (\varphi - \varphi_{1/2}) - \frac{RT}{nF} \ln\left[1 + \exp\frac{nF}{RT}(\varphi - \varphi_{1/2})\right] + \text{const} \tag{43}$$

and

$$\mu_R = -\frac{RT}{nF} \ln\left[1 + \exp\frac{nF}{RT}(\varphi - \varphi_{1/2})\right] + \text{const}\,. \tag{44}$$

From (33), (34), and (35) follows

$$d\sigma = -(\varepsilon + A_O)\,d\mu_O + (\varepsilon - A_R)\,d\mu_R \tag{45}$$

whence, with (43) and (44),

$$\frac{\partial\sigma}{\partial\varphi} = -\varepsilon + \frac{-A_O + A_R \exp\frac{nF}{RT}(\varphi - \varphi_{1/2})}{1 + \exp\frac{nF}{RT}(\varphi - \varphi_{1/2})} \tag{46}$$

At $\varphi \gg \varphi_{1/2}$ (46) goes over into (36), at $\varphi \ll \varphi_{1/2}$ it goes over into (37), i.e., into the Lippmann equations corresponding to the conditions $\mu_O = \text{const}$ and $\mu_R = \text{const}$. Equation (46) has already been derived in the literature [51-53] but without consideration of the problems with which the present communication is concerned. It is easy to prove that the second term on the right-hand side of (46) vanishes in the Henry region at all values of φ and at arbitrary coverages at $\varphi = \varphi_{1/2}$ if the O- and R-form have equal adsorbabilities. If A_R can be neglected at $\varphi > \varphi_{1/2}$, and A_O at $\varphi < \varphi_{1/2}$, then adsorptive factors affect the shape of the $\sigma-\varphi$ dependence only through their influence on ε, and the electrocapillary curve corresponding to the differential equation (46) can to a first approximation be composed from two ordinary electrocapillary curves as observed with the curve in Fig. 1. However, strong adsorption of R at $\varphi > \varphi_{1/2}$, which takes place when prewaves appear [54] and which may be due to the formation of a surface complex RO [55], must lead to a strong drop in σ. Conversely, the adsorption of O at $\varphi < \varphi_{1/2}$ must lead to a rise in σ. Joint adsorption of O and R must in the general case occur in some potential range around $\varphi_{1/2}$, especially if they form a strongly adsorbing intermediate compound of the type OR or $\frac{1}{2}$ OR without splitting of the wave; therefore, on the electrocapillary dependence one must expect near $\varphi_{1/2}$ the appearance of a more or less asymmetric dip whose depth depends on the strength with which these adsorption processes appear.

In the polarographic literature numerous "electrocapillary curves" are reported which express the dependence of drop time (or weight) on the potential applied to the drop electrode [53-58]. The shape of these curves confirms the thoughts presented here in many cases. However, these curves have so far not been subjected to a proven theoretical discussion. Barker [43] points out that under polarographic conditions two maxima can appear on the electrocapillary curve; however, he does not interpret the potential of the second maximum as the pzc. The approach developed here can, we believe, serve as a basis for interpreting polarographic "electrocapillary curves" including also more complex cases of multi-step reactions. Unfortunately the results of determining the $\sigma-\varphi$ dependence from the time for drop formation are distorted because of tangential motions of the mercury surface which arise when current is passed and which are complicated by the adsorption processes.

So far as we know, the only determination of the $\sigma-\varphi$ dependence for an organic redox system with the aid of the capillary electrometer, i.e., with the same method as used for measuring the curve in Fig. 1, was carried out by Bezuglyi and Korshikov [59]. On an electrocapillary curve of 0.01 M 2-iodo-anthraquinone + 5% H_2SO_4 solution in dimethyl formamide, these authors observed two clearly developed maxima and a strong drop of σ when approaching the potential where reduction of the anthraquinone begins.

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