Some Aspects of the Thermodynamics of the Platinum Hydrogen Electrode

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ABSTRACT

The presence of adsorbed hydrogen results in essential differences in the thermodynamics of the surface phenomena on the platinum electrode compared to the mercury one. Thus in this case the point of zero charge (in the conventional sense) does not coincide with the maximum of the electrocapillary curve. The value of the potential difference between the electrode and the solution depends not only on the surface charge but also on the amount of adsorbed hydrogen. Additional complications arise in the presence of specifically adsorbed cations and anions in the solution. The experimental data used in this paper have been obtained by the charging curves method, by direct determinations of anion and cation adsorption, and by the measurements of the potential shift with changing composition of the solution under isoelectric conditions.

A platinum electrode obtained by platinization or activation of smooth platinum by alternating anodic and cathodic polarization in the potential range of ψ_r from $\psi_r = 0$ to $\psi_r = 0.5$-0.6, as referred to hydrogen electrode in the same solution, can be considered a reversible system in acid solutions. Therefore, in interpreting its surface properties, it is possible to make use of Gibbs thermodynamics. Thereby, it should be taken into consideration that, in addition to free charges and ions forming the electric double layer, there is adsorbed hydrogen on the electrode surface. It can be assumed that within the potential range indicated no adsorbed oxygen is present on the electrode surface. In the presence of strongly adsorbed anions or cations (I^-, Cd^{2+}), the condition of reversibility of adsorption processes may be violated. In that case a thermodynamic treatment would give only approximate results.

In the case of alkaline solutions, the above assumptions seem to be valid only within a narrower potential range and only for solutions containing singly charged cations of alkali metals. In the presence of doubly charged cations, such as Ba^{2+}, complications may arise (1)

Let us consider first the case of an acidified or alkalized solution of a binary electrolyte (2), assuming the concentration of the H^+ or OH^- ions to be small compared to that of the salt ions.[1] At constant temperature and pressure, the state of the system is determined by the chemical potentials of hydrogen μ_H, of the hydrogen ion μ_{H+} and of the salt ions μ_s, which we shall express in electric units. We shall set the interface in such a way that the Gibbs adsorption of water $\Gamma_{H_2O} = 0$. Then for $d\sigma$, where σ is the surface density of the free energy, we shall have

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{H+} d\mu_{H+} - (\Gamma_{C+} + \Gamma_{A-}) d\mu_s \quad [1]$$

where Γ_H, Γ_{H+}, Γ_{C+}, and Γ_{A-} are Gibbs surface densities of hydrogen, hydrogen ion, cation and anion of the salt, respectively, also expressed in electric units.

Evidently

$$\psi_r = (\mu_H)_o - \mu_H \quad [2]$$

where $(\mu_H)_o$ is the value of μ_H in equilibrium with molecular hydrogen at given temperature and pressure. Now

$$\Gamma_{H+} = \Gamma_{A-} - \Gamma_{C+} \quad [3]$$

The quantity Γ_{H+} can be considered to be the density of the electrode surface charge ϵ, assuming that with an excess of C^+ cations, the presence of H^+ ions in the ionic part of the double layer can be neglected (see footnote 1) and that being adsorbed, all hydrogen ions give off their charges to the metal and change to H atoms. In other words, we assume that the potential determining H^+ ions are not adsorbed specifically or that jointly the specifically adsorbed H^+ ion and the negative surface charge can be identified with an H atom. Equating Γ_{H+} with ϵ is somewhat conditional. In fact, specifically adsorbed ions, such as I^- or Cd^{2+}, are shown by experiment to form covalent bonds with the electrode surface (4). Therefore, it could be assumed that in Cd^{2+} adsorption, some of the Cd^{2+} ions change to atoms, giving off positive charges to the surface. Hence two separate quantities Γ_{Cd+} and Γ_{Cd} could be introduced, just as it was done in considering the electrocapillarity of thallium amalgams (5). However, since in the case under consideration we cannot vary independently μ_{Cd} and μ_{Cd2+}, such separation would be aimless. Therefore, within the frame of the thermodynamic treatment it would be reasonable to consider formally all ions disappearing from the solution, except the H^+ ions, to be adsorbed as ions, although such an assumption would have to be essentially corrected in developing a molecular theory of the electric double layer on the Pt electrode (see below).

Let us designate by A_H the amount of hydrogen adsorbed per unit surface. The quantity A_H is not identical with Γ_H, as part of the hydrogen disappearing from the bulk of the solution, when a unit surface is formed, is ionized and expended in its charging. Obviously the following relationship exists between A_H and Γ_H

$$\Gamma_H = A_H - \Gamma_{H+} = A_H - \epsilon \quad [4]$$

From Eq. [1], [2], [3], and [4] it is possible to deduce some relationships between measurable quantities (2, 6). No allowance will be made for hydrogen solubility in the metal and the possible effect of dissolved hydrogen on the electrode process. We shall also assume the quantity μ_{H+} to remain constant with changing ψ_r, that is that the changes in the value of

[1] In practice, the last condition was often not fulfilled, since in an experimental determination of ionic adsorption the use of solutions with a low concentration of H^+ or OH^- ions makes it difficult to keep the pH of the solution constant. However, at least in the case of Cs^+ ions, this could not lead to a significant error in the determination of the charge of adsorbed cations, since when the ratio $[H^+]:[Cs^+]$ is decreased 10 times, adsorption of Cs^+ from $0.01N$ Cs_2SO_4 solution at $\psi_r = 0$ increases only by 30% (3), as it follows also from Fig. 1. Even at the same concentration, the Cs^+ ions seem to displace considerably the H^+ ions from the ionic side of the double layer.

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$[H^+]$ caused by those in A_H are small compared to $[H^+]$.[2]

Let us consider the case of a solution of a constant salt composition (μ_s = const). Since

$$\left(\frac{\partial\Gamma_H}{\partial\mu_{H+}}\right)_{\mu_H} = \left(\frac{\partial\Gamma_{H+}}{\partial\mu_H}\right)_{\mu_{H+}} \quad [5]$$

or

$$\left(\frac{\partial\Gamma_H}{\partial\mu_{H+}}\right)_{\psi_r} = -\left(\frac{\partial\Gamma_{H+}}{\partial\psi_r}\right)_{\mu_{H+}} \quad [5a]$$

$$\left(\frac{\partial\Gamma_{H+}}{\partial\psi_r}\right)_{\mu_{H+}} = \left(\frac{\partial\psi_r}{\partial\mu_{H+}}\right)_{\Gamma_H}\left(\frac{\partial\Gamma_H}{\partial\psi_r}\right)_{\mu_{H+}} \quad [6]$$

The quantity Γ_{H+} can be determined experimentally directly from the change in the hydrogen ion concentration in the solution in contact with the electrode polarized to the potential ψ_r, or, according to Eq. [3], from the difference between the anion and cation adsorptions. Some examples of the dependence of Γ_{H+} upon ψ_r are given in Fig. 1 and 2 (7).

The curves in these figures, as well as in others, are extended into the oxygen region, which, however, will not be discussed in the present paper. Now, evidently

$$\left(\frac{\partial\Gamma_H}{\partial\psi_r}\right)_{\mu_{H+}} = -\left(\frac{\partial Q}{\partial\psi_r}\right)_{\mu_{H+}} \quad [7]$$

where Q is the quantity of electricity to be supplied to the electrode per unit surface to shift its potential from some initial value to the value ψ_r, assuming that the quantity of hydrogen dissolved in the bulk of the solution, which is in equilibrium with the electrode, can be neglected compared to the amount of adsorbed hydrogen. Finally, the quantity $\left(\frac{\partial\psi_r}{\partial\mu_{H+}}\right)_{\Gamma_H}$ is determined from the change in the electrode potential, as referred to hydrogen electrode in the same solution, with changing $[H^+]$ under isoelectric conditions, *i.e.*, at open circuit (constant Γ_H).[3] Thus Eq. [6] can be verified quantitatively. A roughly approximate verification of this kind has already been carried out (2). There the quantity $\left(\frac{\partial\psi_r}{\partial\mu_{H+}}\right)_{\Gamma_H}$ was determined from the change in ψ_r when passing from acidified to alkalized solutions, *i.e.*, μ_{H+} was changed within too wide limits. The values of the derivatives in Eq. [6] were equated with the half-sum of the values obtained experimentally for the lowest and the highest *p*H. At present similar measurements are made using improved technique.[4]

Of interest is another deduction from Eq. [1] and [4]. With the solution composition constant

$$\frac{\partial\sigma}{\partial\psi_r} = \Gamma_H = A_H - \epsilon \quad [10]$$

Thus, the maximum of the "electrocapillary curve" of the platinum hydrogen electrode lies not at $\epsilon = 0$, but at $A_H - \epsilon = 0$ and does not coincide with the point of zero charge in the usual sense of this term, *i.e.*, the potential at which the quantity $\epsilon = \Gamma_{A-} - \Gamma_{C+}$ vanishes. According to (2), the point of zero charge of platinum in solution of N NaCl + 0.01N HCl lies at $\psi_r = 0.16$, whereas the quantity $A_H - \epsilon$ vanishes at $\psi_r \approx 0.3$. Such a discrepancy may seem to be unexpected if we proceed from the derivation of Lippman's equation, suitable for the concept of an ideal polarizable mercury electrode, *e.g.*, in the form given by Grahame (10) or Parsons (47). However, Lippman himself understood perfectly well that what the right-hand side of his equation expresses is the capacitance of a unit surface at constant potential (11). Evidently, in the case of a hydrogen-adsorbing metal, the last quantity cannot coincide with the surface charge in the sense of the electrostatic theory of the double layer. In 0.01N Cs_2SO_4 + 0.01N H_2SO_4 the point of zero charge lies at $\psi_r = 0.30$ (3, 7) (0.19 *vs.* NHE) and is close to the potential of the maximum of σ. This coincidence is, however, an accidental one.

The platinum electrode potential ψ, measured against a constant reference electrode, such as the normal hydrogen electrode, depends not only on Γ_{H+}, but on A_H as well. In fact

[2] When the above conditions are fulfilled, the state of the system at a given initial solution composition is completely determined by the quantity of electricity Q supplied to the electrode from some initial moment of time. In this sense, the behavior of the electrode does not differ from that of an ideal or completely polarized electrode, although in this case, the condition of the absence of the exchange of charges between the electrode and the solution, which is usually considered to be the criterion of ideal polarizability, is not fulfilled.

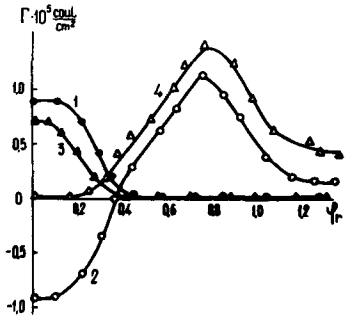

Fig. 1. Dependence of Γ_{Cs+} (1) and Γ_{H+} (2) in 0.018N Cs_2SO_4 + 0.002N H_2SO_4 and Γ_{Cs+} (3) and $\Gamma_{SO_4 2-}$ (4) in 0.01N Cs_2SO_4 + 0.01N H_2SO_4 on ψ_r.

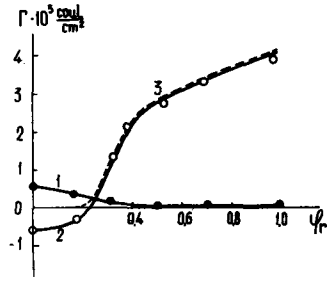

Fig. 2. Dependence of $\Gamma_{Na}{}^+$ (1), Γ_{H+} (2) and Γ_{Br-} (3) in 10^{-3}N NaBr + 10^{-3}N H_2SO_4 on ψ_r.

[3] Changes in the electrode state in which the quantity Γ_H, determining the total amount of electricity stored on the electrode, remains constant were suggested to be called isoelectric (8). Isoelectric measurements can be carried out readily in the case of electrodes with developed surface (platinized platinum, activated carbon), for which the condition Γ_H = const. can be fulfilled easily in practice when replacing the solution. These measurements have something in common with the coulostatic method developed by Delahay and collaborators (46), since in both cases changes in the electrode potential at open circuit are observed. The problems to be solved in the two cases were, however, different.

[4] From Eq. [6] by simple transformations (9) it is possible to obtain the relationship

$$\left(\frac{\partial\psi_r}{\partial\mu_{H^+}}\right)_{\Gamma_H} = 1:\left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} - 1\right] \quad [8]$$

or

$$\left(\frac{\partial\psi}{\partial\mu_{H^+}}\right) = \left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}}:\left[\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}} - 1\right] \quad [9]$$

where ψ is the potential measured against normal hydrogen electrode.

Equations [8] and [9] determine the dependence of the hydrogen electrode potential on the *p*H of the solution with Γ_H remaining constant, *i.e.*, under isoelectric conditions. The quantity $\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}}$ is negative in most cases; if $\left|\left(\frac{\partial A_H}{\partial\Gamma_{H^+}}\right)_{\mu_{H^+}}\right| >> 1$, Eq. [9] turns into the usual relationship for the reversible hydrogen electrode.

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$$d\psi = d\mu_{H+} - d\mu_H \quad [11]$$

Now, let us put (2)

$$d\psi = \left(\frac{\partial\psi}{\partial A_H}\right)_{\Gamma_{H+}} dA_H + \left(\frac{\partial\psi}{\partial\Gamma_{H+}}\right)_{A_H} d\Gamma_{H+}$$

$$= X dA_H + Y d\Gamma_{H+} \quad [12]$$

From [11] and [12] it follows

$$X\left(\frac{\partial A_H}{\partial\mu_H}\right)_{\mu_{H+}} + Y\left(\frac{\partial\Gamma_{H+}}{\partial\mu_H}\right)_{\mu_{H+}} = -1 \quad [13]$$

$$X\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H} + Y\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_H} = 1 \quad [14]$$

From [13], [14], [4], and [5] we obtain

$$X = -\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H} : Z \quad [15]$$

$$Y = \left[\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H} + \left(\frac{\partial A_H}{\partial\mu_H}\right)_{\mu_{H+}}\right] : Z \quad [16]$$

where

$$Z = \left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_H}\left(\frac{\partial A_H}{\partial\mu_H}\right)_{\mu_{H+}} - \left(\frac{\partial\Gamma_{H+}}{\partial\mu_H}\right)_{\mu_{H+}}\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H}$$

$$= \left(\frac{\partial\Gamma_H}{\partial\mu_H}\right)_{\mu_{H+}}\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_H} - \left(\frac{\partial\Gamma_H}{\partial\mu_{H+}}\right)^2_{\mu_H} \quad [17]$$

If $\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H} = 0$, *i.e.*, atomic hydrogen adsorption does not depend on the composition of the solution, according to Eq. [15], $X = 0$. In this case, the presence of adsorbed hydrogen has no effect on the potential difference. In actual fact, however, the value of A_H depends on pH, increasing when passing from acid to alkali at small and medium coverages and decreasing at large coverages (2, 6). As all the quantities appearing in the right-hand sides of Eq. [15], [16], and [17] are measurable, it is possible to calculate from these equations the contribution of atoms and ions to the potential difference at the electrode-solution interface. Unfortunately, there are no sufficiently accurate values of the quantities $\left(\frac{\partial A_H}{\partial\mu_{H+}}\right)_{\mu_H}$ and $\left(\frac{\partial\Gamma_{H+}}{\partial\mu_{H+}}\right)_{\mu_H}$ available at present. The results of a roughly tentative calculation from the data obtained in (2) are presented in Fig. 3. Since in this case the measurements of Γ_{H+} were made in N NaCl + 0.01N HCl and in N NaCl + 0.05N KOH, the results of the calculation can give an approximate idea of the quantities X and Y for the intermediate value of pH, *i.e.*, for a neutral solution. More accurate measurements of this kind are to be made at a later date. In spite of the tentative nature of the data in Fig. 3, it is possible to draw some conclusions from them regarding the mechanism of the appearance of the potential difference on the platinum hydrogen electrode. At small coverages, the quantity X is positive, *i.e.*, in the atomic hydrogen coverage the negative dipole end is turned toward the solution. With increasing coverage, the sign of polarity changes, the effect continuing to increase in absolute value as $\psi_r = 0$ is approached. As already pointed out in the literature,

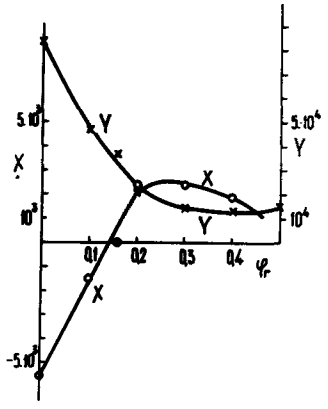

Fig. 3. Dependence of the quantities $X = \left(\frac{\partial\psi}{\partial A_H}\right)_{\Gamma_{H+}}$ and $Y = \left(\frac{\partial\psi}{\partial\Gamma_{H+}}\right)_{A_H}$ on ψ_r in N NaCl solution. Ordinates in farads^{-1} x cm^2.

the change in polarity with increasing coverage is in agreement with the results of the work function measurements (12). It follows from a comparison of the X and Y curves that the contribution of the adsorbed hydrogen atom to the establishment of the potential difference is approximately by an order of magnitude less than that of the adsorbed ion. The quantity Y^{-1} is the electrode capacitance at constant A_H. At ψ_r = 0.3-0.5, it is equal to *ca.* 70 μf/cm^2 and decreases to 12 μf/cm^2 with ψ_r approaching zero. The decrease in capacitance can be partially due to the substitution of cations for anions in the ionic side of the double layer, but the effect of the increasing surface coverage with adsorbed hydrogen on the capacitance should be taken into consideration as well. In actual fact, as is clear from Fig. 3, the increase in Y with decreasing ψ_r becomes appreciable beginning with ψ_r = 0.3, whereas the point of zero charge, as is evident from Fig. 6 in Frumkin and Slygin's work, in neutral N NaCl should lie at ψ_r = 0.18. It should be noted that within the range of ψ_r = 0.3-0.5 the capacitance values are high. Numerous a-c measurements on smooth electrodes at sufficiently high frequencies give capacitance values of 15-20 μf/cm^2 in the double layer region. It is possible that this value should be even smaller if allowance is made for the roughness factor. The reliability of the values obtained from the adsorption measurements depends on the correct estimation of the platinized electrode surface. The calculation of adsorption per cm^2, and hence of the quantities X and Y, given in this paper is based on the assumption that at $\psi_r = 0$, there is one H atom for each Pt atom, and 1.31 x 10^{15} atoms/1 cm^2 of the Pt surface.[5] The determination of the surface area by this method leads to values which are in agreement with the Pt surface measurements by the BET method (14, 15). Thus, the discrepancy between the results of the capacitance determination from adsorption measurements and from impedance is a real one. The most probable explanation would be to suppose the establishment of equilibrium between the adsorbed anion and the platinum surface to be a slow process, which is in agreement with the covalency of the Pt-anion bond under equilibrium conditions. It should be noted that the capacitance of the Pt electrode in the double layer region in a 0.1N H_2SO_4 solution, determined from adsorption measurements (without control however of the condition A_H=const being

[5] There are some discrepancies in the estimation of the latter value. Thus, Fisher, Chon, and Aston (13) give the value 1.195 x 10^{15}. These discrepancies are too small, however, to account for those between the results of the two methods of the capacitance determination.

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observed) amounts to as little as 36 ± 5 μf/cm² (3), *i.e.*, is much less than in solutions of halides.

If the establishment of the potential difference at the platinum electrode-solution interface cannot be understood without taking into account the contribution of the atomic coverage, it is not possible either to assume, as Bowden and Rideal (16) did some time ago, the total potential difference established to be determined by the dipole moment of the adsorbed atoms. As pointed out by Frumkin (17), it is impossible to fulfill the conditions of equilibrium between electrode, solution, and adsorbed gas at a given electrode potential without taking into consideration the electric double layer. Let us explain this for the simplest case of the equilibrium hydrogen electrode. Under the assumption made, the quantity A_H depends only on μ_H and hence on ψ_r

$$A_H = f(\psi_r) \qquad [18]$$

On the other hand, if we designate the effective dipole moment of the Pt-H bond as d, we shall have

$$\psi = \psi_r - (\mu_{H+})_o + \mu_{H+} = \frac{4\pi A_H d}{e} + \text{const} \qquad [19]$$

where e is the elementary charge and $(\mu_{H+})_o$ the value of μ_{H+} at molar concentration of the H^+ ions. It is evident that the quantity A_H, determined from [19], in the general case cannot be the solution of Eq. [18]. This conclusion remains valid if, under the assumption about the equilibrium state of the system, we assume O_{ads} to be present on the surface along with H_{ads}. At the first glance, the results of the adsorption measurements of the cations from dilute NaOH and CsOH solutions seem to be at variance with this conclusion (18) (Fig. 4). In this case the cation adsorption practically does not depend on ψ_r. In other words, the change in the potential difference seems to be due to that in the atomic coverage, a decrease in the amount of adsorbed H and an increase in that of adsorbed O. In actual fact, however, the constancy of Γ_{C+} is probably of a random nature, since the adsorption effect in alkaline solutions is made up of two items: cation adsorption, associated with H_{ads} ionization, and adsorption by hydrated surface oxide groups, which are of a weakly acid nature and take up cations in alkaline solutions. With increasing ψ_r, the first effect decreases, whereas within a certain potential range, the second effect increases, resulting in the approximate constancy of Γ_{C+}. Such an explanation is supported by the following observations. In the presence of Br^- or I^- ions (as well as of Cl^- ions at higher concentrations, which displace oxygen from Pt surface) in alkaline solutions at not too small ψ_r, Γ_{C+} decreases with increasing ψ_r (Fig. 5) (7, 18, 19). In $Ca(OH)_2$ and $Ba(OH)_2$ solutions containing doubly charged cations Ca^{2+} and Ba^{2+}, which seem to be strongly chemisorbed by hydrated surface oxides, with increasing ψ_r in the hydrogen region Γ_{C+} increases (Fig. 6) (1). Of particular interest is the approximate constancy of Γ_{C+} in the hydrogen region, which is also observed, although within a narrower range of ψ_r values, in

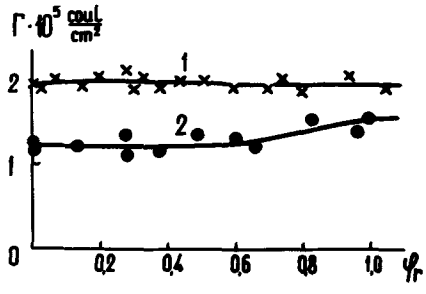

Fig. 4. Dependence of Γ_{Cs+} (1) and Γ_{Na+} (2) in 10^{-2}N CsOH and 10^{-2}N NaOH on ψ_r.

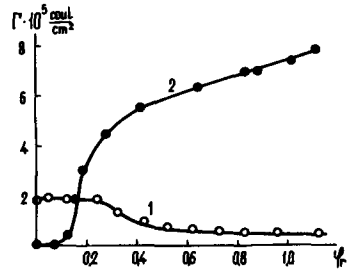

Fig. 5. Dependence of Γ_{Cs+} (1) and Γ_{I-} (2) in 10^{-2}N CsOH + 10^{-2}N CsI on ψ_r.

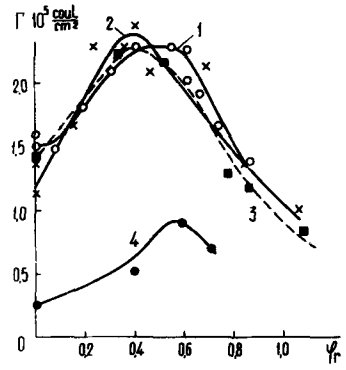

Fig. 6. Dependence of adsorption values on ψ_r: 1, Ca^{2+} in 10^{-3}N $Ca(OH)_2$; 2, Ba^{2+} in 10^{-3}N $Ba(OH)_2$; 3, Ba^{2+} in 10^{-3}N $Ba(OH)_2$ + 1N NaOH; 4, Ca^{2+} in 10^{-3}N $Ca(OH)_2$ + 1N NaOH.

acidified solutions of sulfates (Fig. 1). In this case, the change in ψ_r at a practically constant Γ_{C+} is partly determined by that in the effective dipole moment of the Pt-H bond. As pointed out earlier, at small coverages the dipole of this bond is turned toward the solution with its negative, at large coverages—with its positive end. Another factor leading to an increase in the absolute value of the negative potential difference at constant Γ_{C+} in the range of small ψ_r, which we have also mentioned earlier, is the decrease in the capacitance of the electric double layer with increasing A_H.

The thermodynamic theory outlined here can be extended to other hydrogen adsorbing metals. As shown by Tyurin and Tsybulevskaya (20), who studied the dependence of the charging curves of disperse rhodium on the pH of the solution, an empiric relationship is valid in the case of the rhodium electrode

$$A_H = f_1 (pa^{-0.52}) \qquad [20]$$

where p is the equilibrium pressure of molecular hydrogen, a is the activity of hydroxonium ion, and f_1 is some functional dependence. Equation [20] can also be written as

$$A_H = f_2 (\mu_H - 0.26\,\mu_{H+}) \qquad [21]$$

whence from [11], [15], and [16] it follows

$$\left(\frac{\partial A_H}{\partial \Gamma_{H+}}\right)_\psi = -\left(\frac{\partial \psi}{\partial \Gamma_{H+}}\right)_{A_H} : \left(\frac{\partial \psi}{\partial A_H}\right)_{\Gamma_{H+}}$$

$$= \left[\left(\frac{\partial A_H}{\partial \mu_H}\right)_{\mu_{H+}} + \left(\frac{\partial A_H}{\partial \mu_{H+}}\right)_{\mu_H}\right] : \left(\frac{\partial A_H}{\partial \mu_{H+}}\right)_{\mu_H}$$

$$= -\frac{1 - 0.26}{0.26} = -2.8$$

The relatively low value of $\left|\left(\frac{\partial A_H}{\partial \Gamma_{H+}}\right)_\psi\right|$ (com-

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pared to platinum) can be partly due to the Rh surface which apparently always carries a positive charge in the hydrogen region (21). It also points to a considerable and constant polarity of the Rh-H bond, with the negative dipole end turned toward the solution.

Let us consider some other possible changes in the composition of the solution.

Adsorption of cations and anions of the electrolyte, on one hand, and hydrogen adsorption, on the other, exert a mutual influence (6). It follows from [1], [3], and [4] that

$$\left(\frac{\partial A_H}{\partial \mu_s}\right)_{\psi_r,\mu_{H^+}} = \left(\frac{\partial(\Gamma_{A^-} - \Gamma_{C^+})}{\partial \mu_s}\right)_{\psi_r,\mu_{H^+}} - \left(\frac{\partial(\Gamma_{A^-} + \Gamma_{C^+})}{\partial \psi_r}\right)_{\mu_s,\mu_{H^+}} \quad [22]$$

Equation [22] can be verified experimentally, although this has not been done yet. In fact, adsorption of cations and anions on platinum can be directly estimated from experiment, primarily by the method of radioactive tracers (7). Then, by the charging curves method, it is possible to find the quantity $\left(\frac{\partial \Gamma_H}{\partial \mu_s}\right)_{\psi_r,\mu_{H^+}}$, and hence $\left(\frac{\partial A_H}{\partial \mu_s}\right)_{\psi_r,\mu_{H^+}}$. From [22], by elementary transformations, we obtain

$$\left(\frac{\partial \psi}{\partial \mu_s}\right)_{\epsilon,\mu_{H^+}} = -\left[\frac{\partial(\Gamma_{A^-} + \Gamma_{C^+})}{\partial \epsilon}\right]_{\mu_s,\mu_{H^+}} - \left(\frac{\partial \psi}{\partial \epsilon}\right)_{\mu_s,\mu_{H^+}} \left(\frac{\partial A_H}{\partial \mu_s}\right)_{\psi_r,\mu_{H^+}} \quad [23]$$

With $\frac{\partial A_H}{\partial \mu_s} = 0$, Eq. [23] changes to a relation which is well known from the thermodynamics of electrocapillary phenomena (22, 27).

At the present time, experimental data are available on the adsorption on platinum of the cations Na^+, Cs^+, Ca^{2+}, Ba^{2+}, Cd^{2+}, Tl^+ and the anions SO_4^{2-}, $H_2PO_4^-$, Cl^-, Br^-, I^- from acid and partly from alkaline solutions (1, 3, 4, 7, 18, 19, 23) which, however, will not be presented here. Let us consider briefly only a few of the specific features of this adsorption.

The behavior of adsorbed Na^+ and Cs^+, as well as of Ca^{2+} and Ba^{2+} in acid solutions is on the whole similar to their behavior at the mercury-solution interface.[6] But the difference in their adsorptivities, which increases in the sequence: $Na^+ < Cs^+ < Ca^{2+} < Ba^{2+}$ is much greater. The maximum charge of adsorbed cations remains within 5 — 10 x 10^{-6} coul/cm^2 for acid and 10 — 25 x 10^{-6} coul/cm^2 for alkaline solutions at the bulk concentrations of the order of 10^{-2} mol. The cations Cd^{2+} and Tl^+ show a pronounced specific adsorptivity (to a lesser degree also Zn^{2+} and Pb^{2+}). In the case of Cd^{2+} the maximum charge reaches the value 60 x 10^{-6} coul/cm^2, and the coverage reaches large fractions of a monolayer. The adsorptivity of anions increases in the sequence $SO_4^{2-} < Cl^- < Br^- < I^-$; the maximum charge of adsorbed anions increases in this sequence from 15 to 140 x 10^{-6} coul/cm^2. Some specific adsorptivity is observed also in the case of the least adsorbable ion SO_4^{2-}, since the adsorption of SO_4^{2-} and Cs^{2+} maintains a small, but still measurable, value at the point of zero charge in acidified Cs_2SO_4 solution as well. One of the characteristic differences between specific adsorption of ions on Pt and that on mercury is that in the former

[6] Added in proof: New data show that the difference in the behavior of Ba^{2+} at both interfaces is much greater than it was supposed earlier.

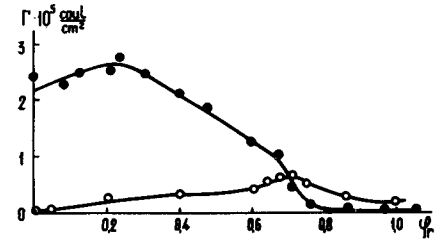

Fig. 7. Dependence of $\Gamma_{Cd^{2+}r}$ and $\Gamma_{SO_4^{2-}}$ in 10^{-2}N $CdSO_4$ + 10^{-2}N H_2SO_4 on ψ_r.

case the phenomenon of superequivalent adsorption is much less pronounced. Considerable adsorption of halogen ions on platinum is accompanied over a wide potential range by slight adsorption of cations only (Fig. 2). The same holds true in the case of adsorption of the anion SO_4^{2-} in the presence of the Cd^{2+} ion (Fig. 7). In the latter case, however, it is this small quantity of adsorbed anions and the positive charges on Pt corresponding to them which determine the ultimate positive sign of the potential difference between metal and solution to be observed at potentials more positive than the point of zero charge of platinum in absence of specific adsorption. Hence it follows that the effective charge of specifically adsorbed cations Cd^{2+} must be very small. It would be possible to estimate this charge quantitatively by measuring, *e.g.*, $\left(\frac{\partial \psi}{\partial \Gamma_{Cd}}\right)_{\Gamma_{A^-}}$ and $\left(\frac{\partial \psi}{\partial \Gamma_{A^-}}\right)_{\Gamma_{Cd}}$ in $CdSO_4$ + H_2SO_4 solutions with varying concentration of both components. At the present time, however, such data are not available. The results of an attempt to estimate the effective charge of adsorbed Tl^+ ions in (23) cannot be agreed with.

Adsorptivity of ions can also be determined from the potential shift on introduction of an ion under isoelectric conditions into a solution containing only weakly, or not at all, specifically adsorbable ions.[7] Such "adsorption" potentials of anions (24) (Cl^-, Br^-, I^-) and cations (25) (Tl^+, Cd^{2+}, Zn^{2+}, Pb^{2+}) were determined by Obrucheva on platinized and smooth platinum [see also (26)]. A supporting electrolyte was used, *e.g.*, *N* H_2SO_4. Let us designate the chemical potential and the surface density of the surface active ion by μ_i and Γ_i, respectively. We assume its concentration to be so small, compared to that of other ions in the solution, that it can be varied, maintaining the chemical potentials of the other ions in the solution practically constant. Under these conditions, the variables to be taken into consideration are μ_H and μ_i. From the relation

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_i d\mu_i \quad [24]$$

it follows

$$\left(\frac{\partial \Gamma_H}{\partial \mu_i}\right)_{\mu_H} = \left(\frac{\partial \Gamma_i}{\partial \mu_H}\right)_{\mu_i} \quad [25]$$

whence

$$\left(\frac{\partial \psi_r}{\partial \mu_i}\right)_{\Gamma_H} = -\left(\frac{\partial \psi_r}{\partial \Gamma_H}\right)_{\mu_i} \left(\frac{\partial \Gamma_H}{\partial \mu_i}\right)_{\mu_H} = \left(\frac{\partial \psi_r}{\partial \Gamma_H}\right)_{\mu_i} \left(\frac{\partial \Gamma_i}{\partial \psi_r}\right)_{\mu_i} = \left(\frac{\partial \Gamma_i}{\partial \Gamma_H}\right)_{\mu_i} \quad [26]$$

Taking into consideration Eq. [4], Eq. [25] can be written as

$$\left(\frac{\partial \psi_r}{\partial \mu_i}\right)_{\Gamma_H} = 1 : \left[\left(\frac{\partial A_H}{\partial \Gamma_i}\right)_{\mu_i} - \left(\frac{\partial \epsilon}{\partial \Gamma_i}\right)_{\mu_i}\right] \quad [27]$$

[7] Evidently, the isoelectricity condition cannot be fulfilled at potentials which are so close to the reversible hydrogen potential that the hydrogen content in the bulk of the solution becomes comparable to the amount of hydrogen adsorbed on the electrode surface.

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We shall assume the adsorptivity of the ion i to be so large that, in spite of small concentration, it will displace from the ionic part of the double layer other ions with charges of the same sign. Then in the case of the surface-active anion

$$\epsilon = \Gamma_{i-} - \Gamma_{C+} \qquad [28]$$

and the surface-active cation

$$\epsilon = \Gamma_{A-} - \Gamma_{i+} \qquad [28a]$$

where C^+ and A^- are cation and anion which do not show significant specific adsorptivity. From [27], [28], and [28a], it follows for the case of anion adsorption[8]

$$\left(\frac{\partial\psi_r}{\partial\mu_i}\right)_{\Gamma_H} = 1 : \left[\left(\frac{\partial A_H}{\partial\Gamma_{i-}}\right)_{\mu_i} - 1 + \left(\frac{\partial\Gamma_{C+}}{\partial\Gamma_{i-}}\right)_{\mu_i}\right] \qquad [29]$$

and for the case of cation adsorption

$$\left(\frac{\partial\psi_r}{\partial\mu_i}\right)_{\Gamma_H} = 1 : \left[\left(\frac{\partial A_H}{\partial\Gamma_{i+}}\right)_{\mu_i} + 1 - \left(\frac{\partial\Gamma_{A-}}{\partial\Gamma_{i+}}\right)_{\mu_i}\right] \qquad [29a]$$

The expressions in square brackets determine the sign and value of the potential shift under isoelectric conditions with increasing concentration of the i ion, assuming the adsorption equilibrium to be maintained all the time. These expressions differ from those obtained in the case of the mercury electrode not only in that they contain the term $\left(\frac{\partial A_H}{\partial\Gamma_i}\right)_{\mu_i}$, but also in that the quantity $\left(\frac{\partial\Gamma_{C+}}{\partial\Gamma_{i-}}\right)_{\mu_i}$ and, accordingly, $\left(\frac{\partial\Gamma_{A-}}{\partial\Gamma_{i+}}\right)_{\mu_i}$ are small (unless the potential lies in the immediate vicinity of the point of zero charge). The latter fact is due to the insignificance of the value of superequivalent adsorption on the Pt electrode, already mentioned earlier.[9] In the expression in square brackets in Eq. [29] all items are always negative. Therefore, the quantity $\left(\frac{\partial\psi_r}{\partial\mu_i}\right)_{\Gamma_H}$ should be negative, as would be expected in the case of anion adsorption, and less than unity in absolute value, approaching unity on complete displacement of adsorbed hydrogen by the anion. The last conclusion is at variance with some results of Obrucheva (24), since, when the concentration of Br^- and I^- was increased ten times, with H_2SO_4 used as a supporting electrolyte, under certain conditions adsorption shifts of the potential in the direction of more negative values equal to 0.12v or even larger were observed, which would correspond to $\left(\frac{\partial\psi_r}{\partial\mu_i}\right)_{\Gamma_H} \sim -2$. It is possible, however, that in more dilute solutions adsorption equilibrium was not established. In the case of cation adsorption (Eq. [29a]), the second and the third items in square brackets are always positive. Usually, the first item is also positive, and the positive value of the sum determines in the case of cation adsorption the shift of ψ_r in the direction of higher values. In some cases, however, *e.g.*, in adsorption of Cd^{2+} from acid solution of $CdSO_4$, at small values of ψ_r, Γ_{i+} increases with increasing ψ_r (7). Probably, this is the result of the competition between Cd^{2+} and H for sites on the platinum surface (Fig. 7). At large enough negative values of $\left(\frac{\partial A_H}{\partial\Gamma_{i+}}\right)_{\mu_i}$, the quantity $\left(\frac{\partial\psi_r}{\partial\mu_{i+}}\right)_{\Gamma_H}$ may become negative, and the adsorption of the cation may cause a potential shift toward more negative values. Such effects were actually observed in the case of the adsorption of the Tl^+ ion in the vicinity of the reversible hydrogen potential and were explained by the displacement of adsorbed hydrogen (25). It should be emphasized, however, that these data are of a strictly qualitative nature, and the verification of the quantitative theory of adsorption shifts of potential in the case of specific ion adsorption on platinum necessitates further study.

Measurements of adsorption shifts of potential also give an independent method of determination of the changes in the shape of the charging curve with changing composition of the solution since all the values of ψ_r obtained in passing from the values $\mu_i = (\mu_i)_1$ to $\mu_i = (\mu_i)_2$ at Γ_H = const. evidently can give a charging curve corresponding to the solution with $\mu_i = (\mu_i)_2$, provided the charging curve of the solution with $\mu_i = (\mu_i)_1$ is known (28).

Recently much attention has been given to adsorption of organic substances on electrodes of the platinum type, and valuable results have been obtained by Bockris and co-workers (29). Assuming that this kind of adsorption can be considered to be a reversible process, which does not seem to be true in all cases, the following relation can be used for a system with constant concentration of all components except adsorbed hydrogen and organic substance

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{org} d\mu_{org} \qquad [30]$$

where Γ_{org} and μ_{org} are adsorbed amount and chemical potential of the organic substance (30).

Taking into consideration Eq. [4], it follows from [30] that

$$\left(\frac{\partial A_H}{\partial\mu_{org}}\right)_{\psi} - \left(\frac{\partial\epsilon}{\partial\mu_{org}}\right)_{\psi} = -\left(\frac{\partial\Gamma_{org}}{\partial\psi}\right)_{\mu_{org}} \qquad [31]$$

whence

$$\left(\frac{\partial\mu_{org}}{\partial\psi}\right)_{\Gamma_{org}} = -\left(\frac{\partial\mu_{org}}{\partial\Gamma_{org}}\right)_{\psi}\left(\frac{\partial\Gamma_{org}}{\partial\psi}\right)_{\mu_{org}} = \left(\frac{\partial A_H}{\partial\Gamma_{org}}\right)_{\psi} - \left(\frac{\partial\epsilon}{\partial\Gamma_{org}}\right)_{\psi} \qquad [32]$$

Equation [32] can also be written in the form

$$\left(\frac{\partial\Delta G_{org}}{\partial\psi}\right)_{\Gamma_{org}} = -\left(\frac{\partial\epsilon}{\partial\Gamma_{org}}\right)_{\psi} + \left(\frac{\partial A_H}{\partial\Gamma_{org}}\right)_{\psi} \qquad [33]$$

where ΔG_{org} is the standard free energy of adsorption of organic substance. In the case of the mercury electrode, the change in adsorptivity of organic substance with the potential is determined by the first term in the right hand side of Eq. [33]. To compare the values of the first and of the second terms, let us put it as it is usually done (31)

$$\epsilon = \epsilon_1\left(1 - \frac{\Gamma_{org}}{\Gamma_\infty}\right) + \epsilon_2\frac{\Gamma_{org}}{\Gamma_\infty} \qquad [34]$$

where Γ_∞ is the limiting adsorption of organic substance and ϵ_1 and ϵ_2 the charge per unit surface on uncovered and covered parts of the surface, respectively. Similarly, we can put

[8] If $A_H = 0$, Eq. [29], as it is easy to show, becomes identical with the relation deduced recently by Dutkievicz and Parsons (48) (*loc. cit.*, Eq. [14]) to determine the shift of the potential of a mercury electrode in a KF solution, caused by the adsorption of I- ions at constant charge.

[9] For the mercury electrode in the case of specific adsorption of anions, the quantity $\left(\frac{\partial\Gamma_{C^+}}{\partial\Gamma_{i^-}}\right)_{\mu_i}$ is close to 0.3 (27).

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$$A_H = (A_H)_1 \left(1 - \frac{\Gamma_{org}}{\Gamma_\infty}\right) + (A_H)_2 \frac{\Gamma_{org}}{\Gamma_\infty} \quad [35]$$

It follows from [34] and [35] that

$$\frac{\partial \epsilon}{\partial \Gamma_{org}} = \frac{1}{\Gamma_\infty} (\epsilon_2 - \epsilon_1) \quad [36]$$

$$\frac{\partial A_H}{\partial \Gamma_{org}} = \frac{1}{\Gamma_\infty} [(A_H)_2 - (A_H)_1] \quad [37]$$

For many organic substances and over a wide potential range, in the case of the mercury electrode $|\epsilon_2|$ is known to be several times less than $|\epsilon_1|$, which fact determines the desorbing action of the electric field. Judging by the few experimental data available (32), a similar relation should exist between $(A_H)_2$ and $(A_H)_1$. Thus, the relative importance of the first and the second terms in the right-hand side of Eq. [33], as the factors determining the value of $\left(\frac{\partial \Delta G_{org}}{\partial \psi}\right)_{\Gamma_{org}}$, depends in order of magnitude on the ratio of A_H and $|\epsilon|$. Taking into consideration that the maximum value of A_H in the hydrogen region is $\sim 2 \times 10^{-4}$ coul/cm^2, and the maximum value of ϵ for the Pt electrode, *e.g.*, in acid sulfate solutions, is of the order of 10^{-5} coul/cm^2, it is evident that the second term in the right-hand side of Eq. [36] is of great importance. Even at the positive boundary of the hydrogen region and within the so-called "double layer" region, in which in the case of solutions without surface-active anions the amount of hydrogen adsorbed on platinum surface, small as it is, is not equal to zero, ϵ and A_H can be of the same order of magnitude and the presence of the term $\left(\frac{\partial A_H}{\partial \Gamma_{org}}\right)_\psi$ should be taken into consideration in determining the dependence of ΔG_{org} on ψ. Hence it follows that the relations deduced for the mercury electrode are not applicable for the determination of the position of the adsorption maximum of neutral molecules relative to the point of zero charge in the case of the platinum electrode. Whereas the point of zero charge of platinum at low pH values lies in the hydrogen region, due to the desorbing action of hydrogen, the potential of maximum adsorption should be shifted into the double layer region. The magnitude of this shift is limited by the appearance on the platinum surface not only of positive charges, but also of adsorbed oxygen. The mutual influence of adsorption of organic substance and oxygen cannot be considered using thermodynamic methods owing to the irreversibility of oxygen adsorption, but there is no doubt that the presence of the latter also reduces the adsorption of organic molecules. The shift of the potential of maximum adsorption in the direction of more positive values relative to the point of zero charge must decrease in the presence of surface-active anions, since at not too small ψ_r the latter decrease A_H and increase ϵ.

It should be noted that in considering the thermodynamics of adsorption of organic substances on the Pt electrode, we assumed the molecule to be adsorbed without dissociation. In actual fact, the adsorption of many compounds, e.g., aliphatic alcohols, involves dehydrogenation (33), which makes the treatment of the process somewhat more complicated. This case should be considered separately.

A suggestion was made to determine the point of zero charge of platinum from the potential at which adsorption of organic substance does not depend on the electrolyte concentration (34). This conclusion could be considered to be justified only if the quantity A_H were proved to remain unchanged with changing electrolyte concentration.

Finally, it should be noted that Eq. [33] is applicable not only to adsorption of a neutral molecule, but also to that of the surface active cations and anions, present as an addition to the supporting electrolyte, provided their concentration is so small that it can be varied, keeping the concentration of the supporting electrolyte practically constant. In this case, the quantity Γ_{org} in Eq. [33] should be substituted by the surface density of the ion being adsorbed Γ_i.

ADDENDUM

Of essential importance for the development of the theory of the double layer on platinum is the determination of the potential of zero charge $\psi_{\epsilon=0}$. The following methods were used for this purpose: direct determination of the quantity Γ_{H^+} from the changes of the hydrogen ion concentration caused by the adsorption process (I); determination of the potential at which anion and cation adsorptions, expressed in electric units, become equal (II); determination of the deviation of a thin platinum wire in an electric field (III); determination of the dependence of the force which must be applied in order to establish a contact between two crossed platinum wires on the potential (IV); determination of the potential corresponding to the maximum contact angle (V). The last method is a roughly approximate one. Some results obtained by the above methods are listed in Table I.

As it is evident from Table I, the data obtained by different methods are in fair agreement. In the case of minimum specific adsorption $\psi_{\epsilon=0} = 0.16$-0.19. This quantity shifts in the direction of more negative values in adsorption of the anions Cl^- and Br^- and in the direction of more positive values in adsorption of the ion Cd^{2+}.

In addition to investigations by the above mentioned methods, attempts have been made to determine the value of $\psi_{\epsilon=0}$ from the position of the minimum on the differential capacitance-potential curve, this minimum being assumed to correspond to the maximum diffusivity of the electric double layer. The use of this method, which gives reliable results for metals that do not adsorb hydrogen, such as mercury (38), gallium (39), silver (40), lead, tin, etc. (41, 42), involves, however, considerable difficulties in the case of the platinum electrode, on whose surface adsorbed hydrogen and oxygen are present, since in this case the pseudocapacity of ionization of these gases is superimposed on the double layer capacity. Additional difficulties arise due to the slowness of the process of adsorption equilibrium establishment during the formation of the double layer on platinum, which was discussed earlier. Although, in principle, measurements carried out in dilute solutions at sufficiently high frequencies should give correct values of $\psi_{\epsilon=0}$, the difficulties arising in such measurements do not seem to have been overcome as yet. The values of $\psi_{\epsilon=0}$, obtained by various investigators from the capacitance measurements of the Pt electrode (43, 44), show great divergences. Moreover, the potential corresponding to the minimum observed on the differential capacitance curve greatly depends on pH, which has been recently confirmed by Gileadi, Rubin, and Bockris (45). As already shown by Frumkin and Slygin, due to the polarity of the Pt-H bond, a dependence of $\psi_{\epsilon=0}$ on pH should exist. But the linear rela-

Table I. Zero charge potential of platinum in different solutions

Solution	$\psi_{\epsilon=0}$, v, NHE	Method of measurements, reference	
$2 \cdot 10^{-5}N$ H_2SO_4	0.16	III	(35)
N Na_2SO_4 + $10^{-2}N$ H_2SO_4	0.11	I	(19)
$10^{-3}N$ Na_2SO_4 + $10^{-3}N$ H_2SO_4	0.18	II	(7)
$10^{-2}N$ Cs_2SO_4 + $10^{-2}N$ H_2SO_4	0.19	II	(3)
$1.8 \cdot 10^{-2}N$ Cs_2SO_4 + $2 \cdot 10^{-3}N$ H_2SO_4	0.19	II	(3)
$2 \cdot 10^{-5}N$ HCl	0.19	III	(35)
N NaCl + $10^{-2}N$ HCl	0.06	I	(19)
$10^{-3}N$ NaCl + $10^{-3}N$ HCl	0.10	II	(7)
$10^{-3}N$ NaBr + $10^{-3}N$ H_2SO_4	0.04	II	(7)
N NaBr + $10^{-2}N$ HBr	−0.02	I	(19)
$10^{-2}N$ $CdSO_4$ + $10^{-2}N$ H_2SO_4	0.65	II	(7)
N NaBr + $5 \cdot 10^{-2}N$ NaOH	−0.26	I	(19)
$10^{-2}N$ CsI + $10^{-2}N$ CsOH	−0.58	II	(7)
$10^{-2}N$ KCl	0.20	IV	(37)
$10^{-3}N$ KCl	0.20	IV	(37)
N Na_2SO_4 + $10^{-2}N$ H_2SO_4	0.27	V	(36)

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tionship between the supposed value of $\psi_{\epsilon=0}$ and *p*H, established in (45), cannot be explained on the basis of the theory and makes it probable that the minimum observed reflects to some extent the minimum coverage of the surface with adsorbed hydrogen and oxygen rather than the maximum diffusivity of the double layer (44). This is in agreement with the relation between the slopes of the $\Gamma_{H^+,\psi}$ and the $\Gamma_{H,\psi}$ curves in solution containing the SO_4^{2-} ion (3, 7), which shows that in this case, in the so-called double layer region the amount of adsorbed hydrogen and oxygen on the surface is commensurable with the double layer charge. Thus, in 0.1*N* H_2SO_4, within the potential range 0.3-0.8, the value of $\partial\Gamma_{H^+}/\partial\psi$ is equal to 36 ± 5 μf/cm^2, whereas the value of $-\partial\Gamma_H/\partial\psi$, determined from the slope of the charging curve, is ~70 μf/cm^2 at ψ = 0.3-0.5 and 150 μf/cm^2 at ψ = 0.5-0.8 (3). An even greater discrepancy is observed at higher *p*H (2). Only in the presence of specifically adsorbed anions, such as Cl^- and Br^-, the capacitance values, determined from the adsorption measurements and the charging curves coincide over some potential range, *i.e.*, the surface is practically free of adsorbed H and O.

It should be also kept in mind that a certain lowering of the differential capacitance values with increasing dilution is not necessarily connected with increased diffusivity of the double layer and can be caused by an exclusion of a part of the surface, which is especially pronounced if the surface is not perfectly smooth or markedly inhomogeneous.

On the whole we think that the capacitance minimum of the platinum electrode, corresponding to the maximum diffusivity of the double layer, has not yet been established. It appears therefore doubtful whether the value of $\psi_{\epsilon=0}$ equal to 0.48 at *p*H = 3 obtained by capacity measurements (45) really corresponds to the point of zero charge of platinum. The question of the relationship between the potential of zero charge and that of maximum adsorption of neutral molecules in the case of the Pt electrode was discussed earlier.

REFERENCES

1. N. Balashova and M. Kulesneva, *Elektrokhimiya*, **1**, 155 (1965).
2. A. Frumkin and A. Slygin, *Acta physicochim. URSS*, **5**, 819 (1936).
3. V. Kazarinov and N. Balashova, *Doklady Akad. Nauk SSSR*, **157**, 1174 (1964).
4. N. Balashova and V. Kazarinov, *Elektrokhimiya*, **1**, 512 (1965).
5. A. Frumkin and A. Gorodetzkaya, *Z. physik. Chem.* (*A*), **136**, 451 (1928); A. Frumkin and A. Titievskaya, *Zhur. Fiz. Khim.*, **31**, 485 (1957); **32**, 157 (1958); A. Frumkin, "Surface Phenomena in Chemistry and Biology," p. 189, J. Danieli, K. Pankhurst and A. Riddiford, Editors, Pergamon, London (1958).
6. A. Frumkin, "Advances in Electrochemistry," vol. 3, p. 328, P. Delahay, Editor, Interscience, New York (1963).
7. N. Balashova and V. Kazarinov, *Uspekhi Khim.*, **31**, 1721 (1965); *Collec. Czech. Chem. Comm.*, **30**, 4184 (1965); A. Frumkin, G. Mansurov, V. Kazarinov, and N. Balashova, *ibid.*, **31**, 806 (1966); G. Mansurov, V. Kazarinov, and N. Balashova, *Elektrokhimiya*, In press.
8. E. Ponomarenko, A. Frumkin, and R. Burshtein, *Isvest. Akad. Nauk SSSR, Ser. Khim.*, 1549 (1963).
9. A. Frumkin, *Elektrokhimiya*, **2**, 387 (1966).
10. D. Grahame, *Chem. Revs.*, **41**, 441 (1947).
11. G. Lippman, *Ann. chim. phys.*, (5), **5**, 494 (1875).
12. J. Mignolet, *J. chim. phys.*, **52**, 19 (1957).
13. R. Fisher, H. Chon, and J. Aston, *J. phys. Chem.*, **68**, 3420 (1964).
14. G. Chomchenko, A. Pletyushkina, and G. Vovchenko, "Catalytic reactions in the liquid phase" Akad. Nauk Kaz. SSR, Alma Ata, 1963.
15. M. Tarasevich, K. Radyushkina, and R. Burshtein, *Elektrokhimiya*, In press.
16. P. Bowden and E. Rideal, *Proc. Roy. Soc.*, (A), **120**, 59 (1928); P. Bowden, *ibid.*, **125**, 446 (1929).
17. A. Frumkin, *Sov. Phys.*, **4**, 260 (1933).
18. V. Kazarinov, N. Balashova, and M. Kulesneva, *Elektrokhimiya*, **1**, 975 (1965).
19. A. Slygin, A. Frumkin, and V. Medvedovsky, *Acta physicochim. URSS*, **4**, 911 (1936).
20. Yu. Tyurin and A. Tsybulevskaya, *Doklady Akad. Nauk SSSR*, **159**, 1140 (1964).
21. G. Chomchenko, A. Lunev, and K. Bogdanovskaya, *Elektrokhimiya*, **1**, 1352 (1965).
22. A. Frumkin, *Z. physik. Chem.*, **103**, 55 (1923).
23. B. J. Bowles, *Electrochim. Acta*, **10**, 717, 731 (1965).
24. A. Obrucheva, *Zhur. Fiz. Khim.*, **32**, 2155 (1958); *Doklady Akad. Nauk SSSR*, **141**, 1413 (1961); **142**, 859 (1962).
25. A. Obrucheva, *ibid.*, **120**, 1072 (1958).
26. A. Frumkin, "Transactions of the Symposium on Electrode Processes," p. 1, E. Yeager, Editor, Wiley & Sons, Inc., New York (1961); *Electrochim. Acta*, **5**, 266 (1961).
27. A. Frumkin, *Zhur. Fiz. Khim.*, **30**, 2066 (1956); R. Parsons, Proc. Sec. Congr. Surf. Act., Electrical Phenomena, p. 38, Butterworths, London (1957).
28. A. Frumkin, G. Mansurov, N. Balashova, and V. Kazarinov, *Elektrokhimiya*, In press.
29. H. Dahms and M. Green, *This Journal*, **110**, 1075 (1963); J. O'M. Bockris, and D. Swinkels, *ibid.*, **111**, 736 (1964); J. O'M. Bockris, D. Swinkels, and M. Green, *ibid.*, **111**, 743 (1964).
30. A. Frumkin, *Doklady Akad. Nauk SSSR*, **154**, 1432 (1964).
31. A. Frumkin and B. Damaskin, "Modern Aspects of Electrochemistry," J. O'M. Bockris and B. Conway, Editors, Vol. 3, p. 149 (1964).
32. M. Breiter and S. Gilman, *This Journal*, **109**, 622 (1962); O. Khasova, Yu. Vasiliev, and V. Bagotsky, *Elektrokhimiya*, **1**, 84 (1965).
33. O. Petry, B. Podlovchenko, A. Frumkin, and Hira Lal, *J. Electroanal. Chem.*, **10**, 253 (1965); B. Podlovchenko, O. Petry, A. Frumkin, and Hira Lal, *ibid.*, **11**, 12 (1966).
34. H. Dahms and M. Green, *This Journal*, **110**, 466 (1963).
35. N. Balashova and A. Frumkin, *Doklady Akad. Nauk SSSR*, **20**, 449 (1938).
36. A. Gorodetzkaya and B. Kabanov, *Phys. Ztschr. Soviet Union*, **5**, 419 (1934).
37. T. Voropaeva, B. Deryaguin, and B. Kabanov, *Dokl. Akad. Nauk SSSR*, **128**, 881 (1959); *Zhur. Koll. Khim.*, **24**, 396 (1962).
38. M. Vorsina and A. Frumkin, *Doklady Akad. Nauk SSSR*, **24**, 918 (1939).
39. A. Frumkin, N. Grigoryev and I. Bagotskaya, *Elektrokhimiya*, **2**, 329 (1966).
40. D. Leikis, *Dokl. Akad. Nauk SSSR*, **135**, 1429 (1960); I. Dagaeva, D. Leikis, and E. Sevastyanov, *Elektrokhimiya*, **2**, 820 (1966).
41. T. Borisova, B. Ershler, and A. Frumkin, *Zhur. Fiz. Khim.*, **22**, 925 (1948); T. Borisova and B. Ershler, *ibid.*, **24**, 337 (1950).
42. A. Frumkin, *Svensk. Kim. Tid.*, **77**, 300 (1965).
43. V. Kheifets and B. Krasikov, *Zhur. Fiz. Khim.*, **31**, 1992 (1952).
44. T. Birintseva and B. Kabanov, *Doklady Akad. Nauk SSSR*, **132**, 868 (1960); *Zhur. Fiz. Khim.*, **37**, 2600 (1963).
45. E. Gileadi, B. Rubin, and J. O'M. Bockris, *J. Phys. Chem.*, **69**, 3335 (1965).
46. P. Delahay and D. Mohilner, *J. Am. Chem. Soc.*, **84**, 4247 (1962); P. Delahay, *J. Phys. Chem.*, **67**, 135 (1963); **68**, 981 (1964).
47. R. Parsons, "Modern Aspects of Electrochemistry," Vol. 1, p. 103, J. O'M. Bockris, Editor, Butterworths, London (1954).
48. E. Dutkiewicz and R. Parsons, *J. Electroanal. Chem.*, **11**, 100 (1966).

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Discussion

M. W. Breiter: The paper stresses the important aspects in which the adsorption of inorganic and organic species on platinum differs from that on mercury because of simultaneous adsorption of hydrogen atoms or oxygen atoms. The general predictions of the thermodynamic treatment given first by Frumkin and Slygin[1] are in good agreement with the numerous results of direct measurements of ion adsorption on platinum by the above authors. The influence[1] of the composition of the electrolyte on hydrogen adsorption is also reflected by the heats of hydrogen adsorption[2,3] at the same coverage in different electrolytes. The heat decreases with increasing adsorbability and concentration of the anion. The decrease of the heat is paralleled[4,5] by less negative values of the corresponding entropy change at small hydrogen coverage ($\theta < 0.1$). If organic species are chemisorbed, the resulting decrease of hydrogen adsorption may be used as a measure of the coverage with organic species. A quantitative method was suggested recently.[6]

An attempt was made some time ago to apply the thermodynamic treatment[1] to the determination of halide ion adsorption from the measurements[7] of hydrogen adsorption on smooth platinum in 1M $HClO_4$ with additions of HCl or HBr at halide ion concentrations of 10^{-3} and 10^{-2}M. However the changes of Q (see Eq. [7] in the paper) with the chemical potential of HCl and HBr, respectively, were not large enough to warrant a computation under the condition of having the same surface state at different anion concentrations. The technique developed by Gilman[8] appears useful for the study of halide ion adsorption on platinum.

S. Schuldiner: This paper gives an excellent thermodynamic treatment of the Pt hydrogen electrode. Many useful relations are derived which are of value. The initial assumption of the authors that the potential range from 0 to 0.5-0.6v *vs.* the hydrogen electrode in the same solution can be considered as a reversible system in acid solution is open to question. Work at the U. S. Naval Research Laboratory has shown that the reversible H^+/H_2 reaction determines potential on a Pt electrode in acid solution only up to 0.18v *vs.* NHE. Furthermore this work and others has shown that a large part of the hydrogen associated with a Pt electrode is irreversibly sorbed. Thus, the potential range Frumkin, Balashova, and Kazarinov assume to be valid for the reversible hydrogen electrode appears to be much less than claimed.

A. N. Frumkin (communicated): It is not important for the theory developed by us whether the equilibrium of the reaction H^+/H_2, to which Dr. Schuldiner's remark refers, is realized in practice. The theory presumes only the existence of an equilibrium for the ionization reaction of adsorbed hydrogen. The existence of this equilibrium is proved by the complete reversibility of the charging curves in the potential range indicated and by the independence of the length and shape of the charging curves from the time of measurement, which varied from 10 to 100 min, when employing our method (platinized platinum electrodes with 5-10 mg Pt-black/cm^2 of visible surface).[9] Apparently, owing to the wide use of fast pulse methods in recent years it has become unusual to treat the surface of the platinum hydrogen electrode as an equilibrium system.

F. G. Will: In Eq. [7] of the thermodynamic treatment, it is assumed that the amount of charge supplied to the electrode to shift its potential from one to another value in the hydrogen adsorption region is not substantially affected by molecular hydrogen in the electrolyte. With the lightly platinized electrodes used in this study, this assumption can lead to significant errors, depending on the particular conditions of charging. Recent, still unpublished calculations show that an even more significant error may be introduced by neglecting the diffusion of atomic hydrogen from the surface of the electrode into its interior. The magnitude of this error will again depend on transition times, surface roughness, and the size of the platinum black grains.

With regard to the relative contributions of adsorbed atomic hydrogen and of hydrogen ions to the potential difference at the platinum solution interface, it seems surprising that the contribution of the ions should be an order of magnitude larger. While it is granted that this would be true for the particular electrolytes (1N NaCl + 0.01N HCl and 1N NaCl + 0.05N KOH) considered in this study, it appears highly unlikely that it is also true for many acid electrolytes. In the case of the latter, a near 1:1 ratio between surface platinum atoms and adsorbed hydrogen atoms is found. From studies in the gas phase[10,11] it is known that the work function of platinum is changed by as much as 1 electron volt when hydrogen is adsorbed. Certainly, then, the effect of adsorbed ions cannot be one order of magnitude larger.

E. Gileadi: I would like to agree with Dr. Will that the surface area measured from a hydrogen charging curve at very low current densities may be substantially in error due to hydrogen diffusion from the bulk of the metal. On the other hand, the authors find agreement between their area measurement and B. E. T. measurement so that their hydrogen charging method probably cannot be very much in error.

A. N. Frumkin (communicated): Contrary to Dr. Will's comments, the data presented by Marvet and Petry[12] also show that hydrogen solubility in the electrolyte and the metal could not affect the results obtained. The question as to how the presence of dissolved hydrogen could be taken into consideration in the equations derived by us, should this be necessary, will be dealt with elsewhere.

Dr. Will's remark regarding the relationship between the quantities designated by us X and Y seems to be founded on a misunderstanding. The contribution of the adsorbed H atoms to the potential difference set up at the interface is by an order of magnitude less than that of the adsorbed Na^+ and Cl^- ions per one adsorbed particle. The maximum amount of adsorbed Na^+ and Cl^- ions is, however, in about the same proportion less than the maximum amount of adsorbed hydrogen atoms. As the result, the contribution of the ions and of the atoms to the potential difference being set up become comparable, which deter-

[1] A. Frumkin and A. Slygin, *Acta Physicochim. URSS.*, **5**, 819 (1936).

[2] W. Böld and M. Breiter, *Z. Elektrochem.*, **64**, 897 (1960).

[3] M. Breiter and B. Kennel, *ibid.*, **64**, 1180 (1960).

[4] M. Breiter, *Elektrochim. Acta*, **7**, 25 (1962).

[5] M. W. Breiter, *Ann. N. Y. Acad. Sci.*, **101**, 709 (1963).

[6] M. W. Breiter and S. Gilman, *This Journal*, **109**, 622 (1962).

[7] M. W. Breiter, *Electrochim. Acta*, **8**, 925 (1963).

[8] S. Gilman, *J. Phys. Chem.*, **68**, 2098, 2112 (1964).

[9] R. Marvet and O. Petry, *Elektrokhimiya*, **1**, 1225 (1965).

[10] Ref. (12) of the paper.

[11] Sachtler, Rootsaert, and Van Reijen.

[12] R. Marvet and O. Petry, *Elektrokhimiya*, **1**, 1225 (1965).

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mines the shape of the charging curves observed. In the case of ions with pronounced specific adsorptivity, such as Tl^+ ions, when maximum ion adsorption becomes comparable with hydrogen adsorption owing to the covalent bond between the metal and the adsorbed ion, Y should approach X.

E. Gileadi: I would like to refer to two of the topics mentioned in this paper, namely, the position of the potential of zero charge on Pt and the interpretation of the potential dependence of organic adsorption on Pt.

The potential of zero charge on platinum has been investigated in our laboratory in some detail by two methods.[13] One method depends on the study of the effect of natural salt concentration on the potential dependence of organic adsorption[14] and the other is the well-known measurement of differential double layer capacity as a function of potential in highly purified dilute solutions of $HClO_4$. Results obtained by the two methods were found to be in good agreement, and I would like to concentrate on those obtained by the capacitance method.

Fig. EG 1 shows a typical C-V plot in highly purified, dilute $HClO_4$ solution. The pretreatment of the electrode was found to be of very great importance, and in particular the absorption of hydrogen into the bulk of the metal must be controlled. The curve marked "without H" in Fig. EG 1 was obtained on an electrode which has been treated for 3 hr at 450°C in an atmosphere of purified argon. Calculations based on independent measurement of the diffusion coefficient of hydrogen in Pt carried out in our laboratory[15] confirmed that under these conditions all the hydrogen was eliminated from the metal. Prolonged heating (overnight) had no further effect. The curve marked "with H" was obtained after keeping the electrode at a potential of 0.2v r.h.e. for 5 min, allowing for hydrogen diffusion into the metal. Figure EG 2 gives similar results in alkaline solutions.

[13] E. Gileadi, S. D. Argade, and J. O'M. Bockris, *J. Phys. Chem.*, 70, 2044 (1965).

[14] H. Dahms and M. Green, *This Journal*, 110, 466 (1963).

[15] E. Gileadi, M. A. Fullenwider, and J. O'M. Bockris, *This Journal*, in press.

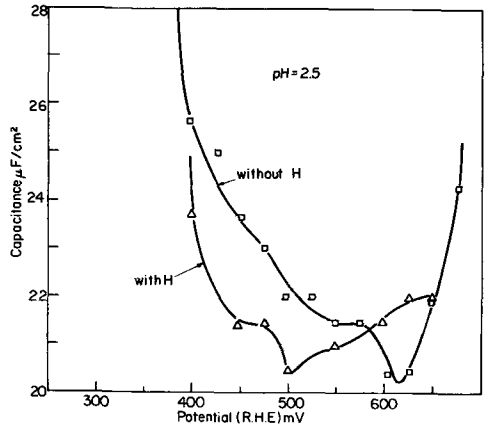

Fig. EG 1. Capacitance-potential relationship in dilute $HClO_4$ solution.

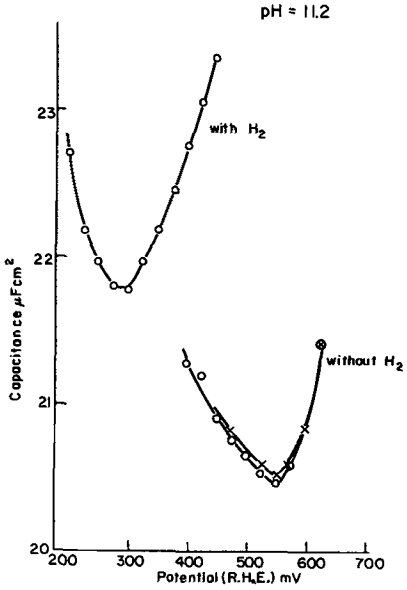

Fig. EG 2. Capacitance-potential relationship in dilute $NaClO_4$ + NaOH solution at high pH.

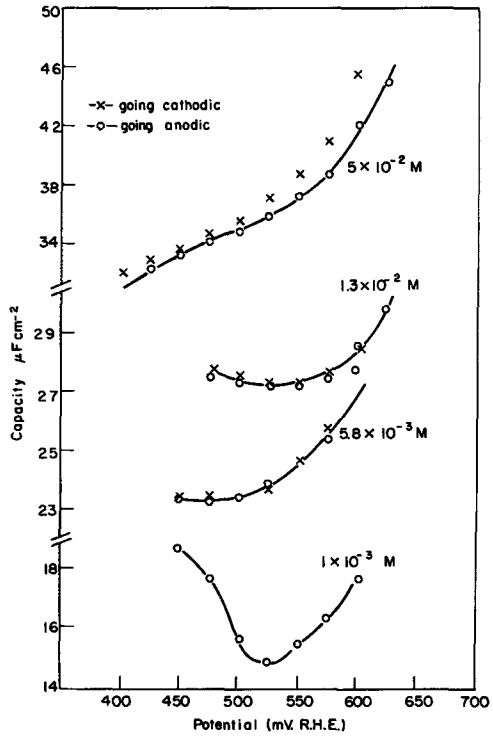

Fig. EG 3. Variation of the shape of the C-V plots with increasing $HClO_4$ concentration.

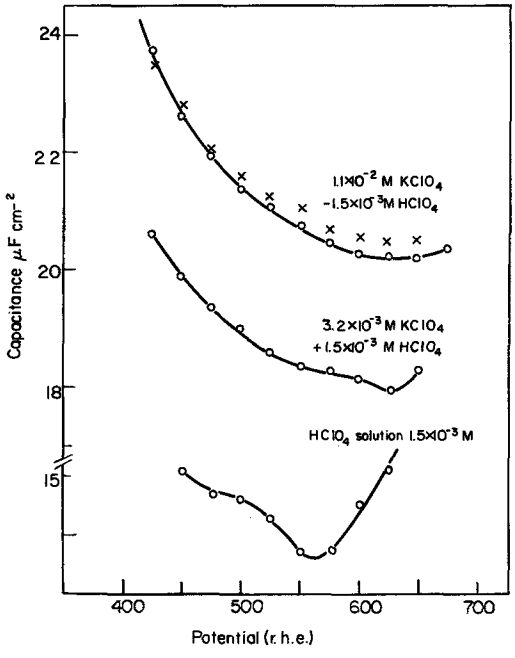

Fig. EG 4. Effect of addition of increasing amounts of $KClO_4$ on the shape of the C-V curves.

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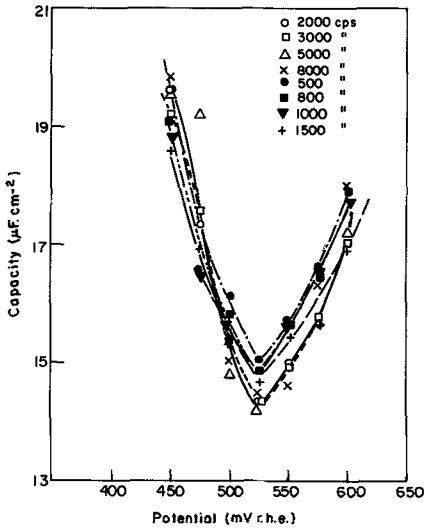

Fig. EG 5. Differential capacity measurements on platinum in 0.001N $HClO_4$ solution as a function of frequency.

Two types of experiments were performed to prove that the capacitance minimum observed here does in fact correspond to the maximum diffusivity of the double layer, *i.e.*, to the potential of zero charge. Figure EG 3 shows the variation of the shape of the C-V plot with increasing concentration of $HClO_4$. In Fig. EG 4, the effect of increasing the total ionic strength by addition of $KClO_4$ is shown. In both cases the capacitance minimum characteristic of the potential of zero charge in dilute solutions disappears as soon as the total concentration of electrolyte exceeds $5 \times 10^{-3}N$.

In Fig. EG 5, the effect of frequency on the C-V plot in the vicinity of the potential of zero charge is given for a frequency range of 0.5×10^3 to 8×10^3 cps. A very small frequency variation is observed, which can be attributed to the lack of complete symmetry between the working and counter electrode, and to a certain extent to a possible slight roughness of the surface.

On the basis of the effect of concentration and frequency on the C-V plot we then conclude that the capacitance minimum observed in our measurements in very dilute solution corresponds to the potential of zero charge. The value of the potential of zero charge, measured *vs.* a constant reference electrode, varies linearly with pH to an extent of 60 mv/pH unit and has a value of $V_{pzc} = 0.56 \pm 0.025$v independent of pH when measured *vs.* a reversible hydrogen electrode in the same solution.

The disagreement between the results presented by Frumkin *et al.* in this paper and our own recent result may be at least in part due to the different pretreatment of the electrode. Our values refer to a "hydrogen free" Pt electrode, while the results of Frumkin *et al.* and probably all other results reported so far refer to a "hydrogen loaded" electrode. Figures EG 1 and EG 2 indicate that the effect of hydrogen in the metal is at least in the right direction to resolve this discrepancy.

I would like to turn now to the question of the interpretation of the potential dependence of adsorption of neutral organic molecules on Pt. In several publications from our laboratory in recent years[16-19] this dependence has been interpreted in terms of a "competition with water" model while according to the present papers of Frumkin *et al.*, this is more likely due to essentially a competition with hydrogen and oxygen adsorbed on the surface.

We are in agreement with the relevant Eq. [33] in this text, which gives the variation of the free energy of adsorption of organic with potential at constant Γ_{org} as a function of the derivatives of the charge and the hydrogen coverage A_H with respect to Γ_{org} at constant potential

$$\left(\frac{\partial \Delta G_{org}}{\partial \psi}\right)_{\Gamma_{org}} = -\left(\frac{\partial \epsilon}{\partial \Gamma_{org}}\right)_{\psi} + \left(\frac{\partial A_H}{\partial \Gamma_{org}}\right)_{\psi}$$

The relative importance of the two terms on the r.h.s. of this equation for the Pt system is, however, disputed. Moreover, to explain the decrease of coverage with potential above 0.5v a similar equation would have to be assumed for adsorbed oxygen. It is doubtful if such an equation would be valid, due to the irreversible nature of oxygen adsorption, as pointed out by Frumkin in a previous publication.[20]

Several experimental facts do not seem to be in agreement with the theory proposed here by Frumkin.

1. Peak adsorption on Pt occurs at about 0.45v (NHE) in $1N$ H_2SO_4. The coverage decreases roughly symmetrically on either side of V_{max}, yet at 0.2v, $\theta_H = 0.5$ while at 0.7v (*i.e.*, at an equal distance on the anodic side of V_{max}) the coverage by oxygen is probably not more than 0.05.

2. In a study of hydrocarbon adsorption on Pt on open circuit it was found[21] that ethylene displaced hydrogen from the electrode surface. On the other hand, it was found to have essentially no effect on oxygen coverage in the same system.[22] Thus

$$|(\partial A_H/\partial \Gamma_{org})_{\psi}| >> |(\partial A_o/\partial \Gamma_{org})_{\psi}|$$

and an unsymmetrical $\theta - \psi$ relationship would be predicted.

3. In the adsorption of naphthalene and n-decylamine on Ni an increase of coverage with increasing cathodic potential occurred in a region where coverage by hydrogen also increased.

In conclusion, we agree that hydrogen adsorption may have an effect on the potential dependence of organic adsorption in certain systems. However, it appears highly unlikely that our results for *e.g.*, ethylene[17] and benzene[18] adsorption can be interpreted even partially on this basis.

The pH dependence of the potential of zero charge and the effect of pH on organic adsorption are consistent with our interpretation of the $\theta - V$ relationship. Figure EG 6 shows $\theta - V$ plots for the adsorption of benzene on Pt from mixtures of H_2SO_4 and Na_2SO_4 maintaining a constant concentration of $SO_4^=$ ions.[18] A plot of the potential of zero charge and the potential of maximum adsorption *vs.* pH is given in

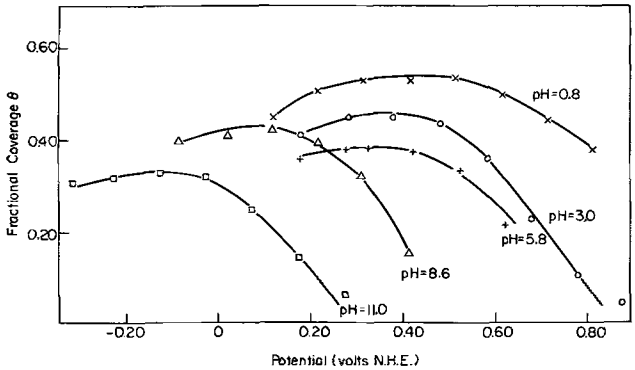

Fig. EG 6. The adsorption of benzene on Pt as a function of potential and pH.

[16] J. O'M. Bockris, M. Green, and D. A. J. Swinkels, *This Journal*, 111, 736, 743 (1964).

[17] E. Gileadi, B. T. Rubin, and J. O'M. Bockris, *J. Phys. Chem.*, 69, 3335 (1965).

[18] W. Heiland, E. Gileadi, and J. O'M. Bockris, *ibid.*, 70, (1966).

[19] E. Gileadi, *J. Electroanal. Chem.*, 11, 137 (1966).

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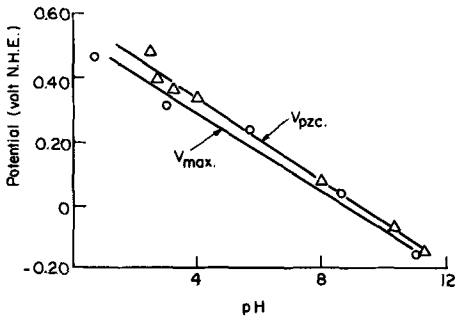

Fig. EG 7. pH dependence of the potential of zero charge and the potential of maximum adsorption on Pt.

Fig. EG 7. The two lines are parallel within experimental error with V_{max} slightly cathodic to V_{pzc} at all pH values as expected according to the water competition model.[16]

A. N. Frumkin (Communicated): A number of attempts have been made at the Institute of Electrochemistry to use for the platinum-hydrogen electrode the method of the point of zero charge determination from the capacitance minimum in dilute solutions, first proposed by one of the authors.[23] Although Birintseva and Kabanov[24] observed at $\psi = 0.18$v the appearance of a minimum on the C, ψ curves in 0.01 and 0.001N H_2SO_4, which disappeared with increasing concentration (C, the capacitance per unit electrode surface; other designations, the same as in our paper), *i.e.*, in agreement with the point of zero charge determination, in our paper we pointed out with good reason, as it seems to us, that the difficulties involved in these measurements have not yet been overcome. Recently Burshtein, Pshenichnikov, and Shevchenko, of the same Institute, apparently obtained more reliable results. The experiments were carried out with a smooth Pt electrode, which after reduction in hydrogen at 450°C and outgassing *in vacuo* at 900°, had been activated in the solution by the application of sawtooth cathodic and anodic pulses in the interval of ψ_r values from 0.0 to 1.6v. As can be seen from Fig. AF 1, at higher concentrations a minimum is observed at $\psi \sim 0.55$v, which is, undoubtedly, a pseudocapacity minimum due to ionization of adsorbed hydrogen and oxygen. As the solution is diluted, however, a deeper minimum appears at $\psi = 0.23$v, *i.e.*, close enough to the pzc determined by direct adsorption measurements. The position of this minimum on the ψ-axis does not change when the concentration of the acid is changed from 0.01 to 0.002N and appears therefore to be pH independent. Further measurements will show how far this result can be considered conclusive.

Comparing the results of his measurements by the differential capacitance method with the data on the pzc given in our paper, Dr. Gileadi suggests that the difference in the surface state of the electrode is one of the reasons for the discrepancy observed. In Dr. Gileadi's opinion, his own data refer to a "hydrogen free" electrode, whereas our data are for a "hydrogen loaded" one. In this connection, we would like to make two observations. The term "hydrogen loaded" does not correctly describe the surface state of the electrodes used by us, as under cathodic polarization the electrode can be loaded with hydrogen to various degrees. In actual fact, our aim was to establish the conditions for the equilibrium relative to the ionization reaction of adsorbed hydrogen as given by Eq. [2]. Such conditions, as will be shown below, really can be established. As regards the surface treatment carried out by Dr. Gileadi, there is no doubt that no equilibrium is established on the surface of a smooth electrode deactivated by prolonged heating at 450°C without subsequent activation by alternating anodic and cathodic polarizations. Measurements of the electronic work function of platinum, however, performed at the Institute of Electrochemistry by Fokina, Shurmovskaya, and Burshtein have shown that in order to remove strongly adsorbed or dissolved gases from the surface of solid smooth platinum it is necessary to carry out degassing *in vacuo* at 900°C. In addition, as it follows from a series of studies by Bagotsky and collaborators,[25] previously degassed platinum absorbs appreciable amounts of oxygen from the solution already at the potential $\psi_r \sim 0.4$v. Therefore, we suppose that the minimum observed by Dr. Gileadi in the experiments with 0.001N $HClO_4$ is likely to be connected with the position of the pzc of a somewhat oxidized platinum surface. In fact, according to the data of Balashova and Frumkin,[26] in dilute H_2SO_4 the pzc of oxidized platinum lies at $\psi \sim 0.5$v, *i.e.*, it is strongly shifted in the positive direction.

At any rate, the shift in the minimum on the capacitance curve along the ψ-axis with changing pH of the solution, observed by Dr. Gileadi, as well as by Kheifets and Krasikov,[27] shows adsorbed oxygen (or hydrogen) to be present on the metal surface, since otherwise it would be impossible to account for this pH dependence by means of any theory. Unfortunately, Dr. Gileadi does not mention whether he observed the dependence of the depth of this minimum

[20] A. M. Franklin, *Doklady Akad. Nauk. SSSR*, 154, 1432 (1964).

[21] L. W. Niedrach, *This Journal*, 111, 1309 (1964).

[22] J. O'M. Bockris, H. Wroblowa, E. Gileadi, and B. J. Piersma, *Trans. Faraday Soc.*, 61, 2531 (1965).

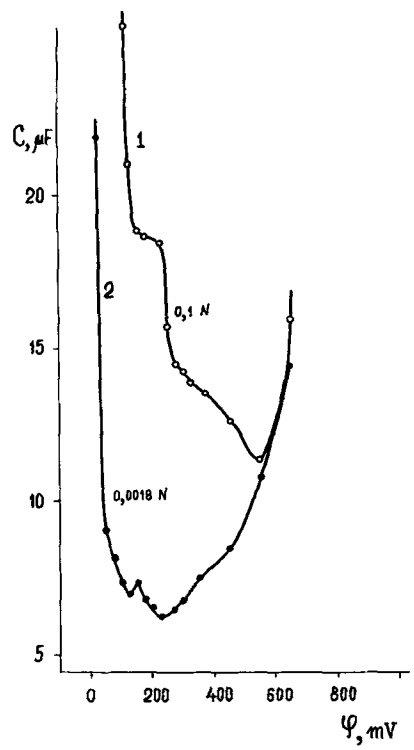

Fig. AF 1. Dependence of the capacitance of an activated Pt electrode on the potential vs. NHE in dilute solutions (Burshtein, Pshenichnikov and Shevchenko). 1. 0.1N H_2SO_4; 2. 0.0018 NH_2SO_4; frequency: 1. 10,000; 2. 5100 cps.

[23] T. Borisova, B. Ershler, and A. Frumkin, *Zhur. Fiz. Khim.*, 22, 925 (1948).

[24] T. Birintseva and B. Kabanov, *Zhur. Fiz. Khim.*, 37, 2600 (1963).

[25] V. Lukianycheva and V. Bagotsky, *Doklady Akad. Nauk SSSR*, 155, 160 (1964); V. Lukianycheva, V. Tikhomirova, and V. Bagotsky, *Elektrokhimya*, 1, 262 (1965).

[26] N. Balashova and A. Frumkin, *Doklady Akad. Nauk SSSR*, 20, 449 (1938).

[27] V. Kheifets and B. Krasikov, *Zhur. Fiz. Khim.*, 31, 1992 (1952).

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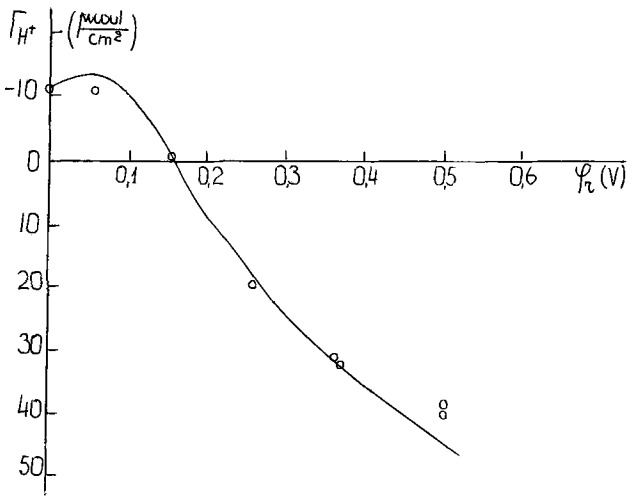

Fig. AF 2. Dependence of Γ_{H+} on ψ_r for a platinized platinum electrode in *N* KCl + 0.01*N* HCl. The full drawn curve has been calculated from Eq. [6]; the circles represent experimental values (Frumkin, Petry, and Marvet).

on the concentration of the solution only in acid solutions or at other *p*H as well. This point is an important one.

From our point of view, it was most important to show that under the conditions of our experiments, the surface of the platinum electrode could really be treated as an equilibrium system, so that Gibbs thermodynamics could be applied to it. At present, Frumkin, Petry, and Marvet have been able to prove experimentally the correctness of this assumption, at any rate for the case of a platinized platinum electrode. In Fig. AF 2 the values of Γ_{H+} in the function of ψ_r determined experimentally in *N* KCl + 0.01*N* HCl solution are compared with those calculated by means of Eq. [6] of our paper from the values of $\left(\frac{\partial \Gamma_H}{\partial \psi_r}\right)_{\mu_{H+}}$ and $\left(\frac{\partial \psi_r}{\partial \mu_{H+}}\right)_{\Gamma_H}$.

The calculated values were obtained by the integration of the $\left(\frac{\partial \Gamma_{H+}}{\partial \psi_r}\right)_{\mu_{H+}}$ curve determined from Eq. [6] using the value of Γ_{H+} at $\psi_r = 0$ found experimentally. Good agreement between calculated and experimental values corroborates the correctness of our assumption as well as of the determination of the pzc by the method designated in our paper as method I.

In the second part of his discussion, Dr. Gileadi presents some arguments against the thermodynamic treatment of the dependence of the adsorption of organic substances on the potential, which was suggested by one of the authors.[28] According to Dr. Gileadi, the relations like our Eq. [33] are quantitatively inapplicable to the oxygen region of the charging curve owing to the irreversibility of oxygen adsorption. This is quite correct and was emphasized in our paper. It is not clear, however, how a model based on "competition with water" can be quantitatively used in this potential range when the measurements of the anion adsorption show that in the case of anions, which are not adsorbed specifically, the tension of the electric field of the double layer, due to positive surface charges and negative charges of adsorbed anions, decreases rather than increases with rising ψ_r.[29] The increase in the latter quantity depends completely on that in the number of adsorbed oxygen atoms and on the dipole nature of the Pt — O bond.

Our treatment refers to the idealized case of organic substance adsorption when an equilibrium relative to adsorption of all components is established on the surface. Naturally in the case of chemisorption of such substances as ethylene, when adsorbed hydrogen [30,31] appears on the platinum surface and methane and ethane can be detected in the gas phase,[31] it is not possible to explain all the phenomena observed in terms of a thermodynamic theory. The general parallelism, however, between the position of the potential of maximum adsorption and the supposed pzc determined as it has been done by Dr. Gileadi, follows from our interpretation of the physical significance of this potential and the relationship between the adsorption of organic substances and that of electrochemically active gases.

Hideaki Kita: 1. According to the statement on the fourth paragraph, the H^+ ions in the ionic part of the double layer are adsorbed giving off their charges to the metal and changing to H atoms. Thus, the quantity Γ_{H+} is identified with the charge density on the electrode.

If we extend this identification further, Γ_{H+} can also be the quantity of adsorbed hydrogen atoms thus formed. Since Γ_H is the symbol for the surface density of hydrogen atom, these quantities, Γ_{H+} and Γ_H, appear not to be separated definitely from each other.

On the other hand, if we understand the quantity Γ_{H+} as the surface density of hydrogen ion as defined in paragraph 3, the charge density of electrode surface would be negligibly small according to the statement in paragraph 4 that the presence of H^+ ions in the ionic part of the double layer can be neglected at the conditions of an excess of C^+ cations.

2. Equation [2] can be taken as applicable only for the case where the step, $H^+ + e^- = H(ads)$, is in equilibrium, since the hydrogen electrode reaction occurs irreversibly at the polarization of ψ_r. Hence, the quantity A_H, which is understood to be the amount of hydrogen disappeared from the bulk of solution according to the statement in paragraph 5 cannot be the equilibrium quantity and must not be introduced in the thermodynamical equations.

In short, interrelations among Γ_{H+}, Γ_H, and A_H do not seem to be clear enough.

A. N. Frumkin (Communicated): 1. The quantities Γ_H and Γ_{H+} may become equal (but opposite in sign) if no measurable amount of adsorbed hydrogen in the atomic form is present on the electrode surface. Such case was considered by one of the authors earlier.[32]

2. The exchange current of the reaction $H^+ + e^- \rightleftarrows H_{ads}$ at $[H^+] = 10^{-2}N$ is of the order of 10^{-1} amp/cm^2. The maximum current density, used by us in the measurements of the charging curves, calculated per cm^2 of true electrode surface, did not exceed 10^{-6} amp/cm^2. Thus, the equilibrium conditions for the above reaction were realized.

S. Gilman: It was suggested that the discrepancy between the results of capacitance determination from adsorption measurements and from the impedance might be explained on the basis of slow establishment of equilibrium between the adsorbed anion and the platinum surface. While the observation need not be general for all anions, evidence has been found[33]

[28] A. Frumkin, *Doklady Akad. Nauk SSSR*, 154, 1432 (1964).

[29] A. Slygin, A. Frumkin, and V. Medvedovsky, *Acta physicochim. URSS*, 4, 911 (1936); N. Balashova and V. Kazarinov, *Usp. Khim.*, 34, 1721 (1965).

[30] R. Burshtein, V. Tiurin, and A. Pshenichnikov, Proc. 14th Internat. Symp., Brighton, September 1964, p. 315, D. Collins, Editor, Pergamon Press (1965); *Doklady Akad. Nauk SSSR*, 160, 629 (1965); V. Tiurin, A. Pshenichnikov, and R. Burshtein, *Electrokhimiya*, In press.

[31] L. Niedrach, *This Journal*, 111, 1309 (1964).

[32] B. Bruns and A. Frumkin, *Z. physik. Chem.* (A), 147, 125 (1930).

[33] S. Gilman, *J. Phys. Chem.*, 68, 2098, 2112 (1964).

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that (at potentials below *ca.* 0.8v in acid solution) the adsorption-desorption of chloride and phosphate ions is rapid and reversible. An alternative explanation for low capacitance is naturally surface contamination,[34] although it is not altogether certain that the high values measured at clean smooth Pt electrodes [34,35] are entirely free of pseudocapacitance.

A. N. Frumkin (Communicated): Our paper was concerned with the discrepancy between the calculated value of $Y^{-1} = \left(\frac{\partial \Gamma_{H^+}}{\partial \psi}\right)_{A_H}$ and the capacitance determined by the a-c measurements at a high enough frequency, the former quantity proving to be much larger than the latter. Since the presence of pseudocapacity of the ionization reaction of adsorbed hydrogen could have affected only the second quantity, taking it into consideration would have resulted only in the increase in this discrepancy.

In the case of I^- adsorption from NaI solutions on a platinized Pt electrode, it takes hours for the equilibrium to be established.[36] Such a delay was not observed in the case of ions without specific adsorptivity, which shows that it cannot be caused by the diffusion difficulties or by the presence of impurities in the solution. The effect of the latter moreover could not be of great importance in the case of platinized electrodes with a highly developed surface. The adsorption process of such anions as I^- on platinum is in many respects similar to that of oxygen chemisorption from the solution. Slow establishment of the equilibrium in this case is a well known fact and has been the object of a number of investigations (*e.g.*[37]). In the case of the chlorine anion, these phenomena are much less pronounced, but hardly absent altogether. The technique used by Dr. Gilman is probably not quite suitable for the investigation of very slow processes.

G. C. Barker: I do not question any of the experimental facts reported by Professor Frumkin and his co-workers. I merely wish to point out that the specific adsorption of certain metals on platinum is an effect far more striking than might be suspected from adsorption potential measurements. Our unpublished work, based largely on studies of the rate of increase of the part of the interfacial impedance connected with the reduction of hydrogen ions and the oxidation of adsorbed hydrogen atoms, suggests that hydrogen adsorption sites are readily occupied by adsorbed metal atoms sometimes even when the solution concentration of the ion metal is as low as 10^{-8}M. The adsorption for potentials in the range in which hydrogen is adsorbed is very marked for Cd and Tl and strong adsorption of the ions of Pb, Bi, and Sn in the same potential region is also observed with strongly acid solutions (HCl, $HClO_4$). Generally the adsorbed metal is displaced when the platinum electrode is anodically polarized and this displacement (due to oxygen adsorption) rather than the oxidation of organic matter is usually the main reason why platinum electrodes are "activated" by anodic polarization. Often the solutions used in studies of the kinetics of the formation and oxidation of molecular hydrogen contain copper and lead ions at concentrations up to 10^{-7} — 10^{-6}M and such concentrations are sufficient to rapidly displace a substantial amount of the adsorbed hydrogen from a smooth platinum electrode and so greatly lower the activity of the electrode. The fall in activity is generally accelerated in stirred solution as the adsorption usually seems to be a diffusion-controlled process. It might also be mentioned that, if a smooth platinum electrode is suspended in a sealed glass cell lined with platinum, the surface of which has been platinized, after saturating the solution with hydrogen and subjecting the electrode to brief anodic polarization occasionally during the first few days, the activity of the electrode (studied by a-c means) remains almost constant for months without further activation. This shows clearly that if adequate precautions are taken to remove from the solution organic matter and ions tending to be strongly adsorbed, a spontaneous fall in activity such as has been suggested from time to time in the literature does not occur. Clearly such falls are due to faulty experimental techniques. Professor Frumkin states that adsorbed Cd is covalently bound to the electrode, and it seems likely that the same may be true in other cases where almost complete coverage (judging from the effect on the impedance) is obtained at potentials considerably more positive than that for bulk deposition of the metal. As has been suggested earlier by Professor Frumkin, the strong adsorption is presumably connected with the formation of a two-dimensional intermetallic compound. Mössbauer studies of the bonding of specifically adsorbed tin on platinum made recently by Bowles and Cranshaw at Harwell suggest that the adsorbed tin is very strongly bound to the electrode.

Reply by *M. W. Breiter*: Study of the deposition of copper ions on smooth platinum from acidic solutions (1M $HClO_4$) was carried out by me at potentials more anodic than the potential of copper deposition about two years ago. The results were not published because of the presence of small amounts of organic impurities leading to an anodic wave in the oxygen region during an anodic sweep. It was observed that copper ions may be deposited at potentials up to 0.25v more anodic than the deposition potential. The layer formed is less than a monolayer and considered by me as an adsorbed layer of Cu atoms. Thicker layers are formed at the potential of copper deposition. The layers can be removed by anodic stripping.

H. D. Hurwitz: Without using the original method of Gibbs, it seems to me that we may formulate the problem of the nonideal polarized interphase in an equivalent manner starting from the equation of Gibbs-Duhem and the electroneutrality condition

$$\Gamma'_{H^+} + \epsilon = \Gamma_{A^-} - \Gamma_{C^+} \qquad [1]$$

At constant T one has

$$(d\sigma)_T = -\Gamma_{A^-} d\mu_{A^-} - \Gamma_{C^+} d\mu_{C^+} - \Gamma'_{H^+} d\mu_{H^+} - A_H d\mu_H - \epsilon d\psi \qquad [2]$$

In [1] and [2] one has stated that the Gibbs surface defined by $\Gamma_{H_2O} = 0$ is permeable to H^+ and H. The quantities Γ_{A^-}, Γ_{C^+}, A_H and the charge ϵ have been defined in the paper. As for Γ'_{H^+}, the surface excess of H^+, it has been assumed to vanish in the model of Frumkin *et al.* in order to fit with the interpretation of the value of ϵ.

For the condition of electrochemical equilibrium respectively at the working electrode and at the reference electrode, one has

$$\mu_{H^+} - F\psi = \mu_H \qquad [3]$$

$$\mu_{H^+} - F\psi^{ref} = (\mu_H)_o \qquad [4]$$

and

$$\psi_r = \psi + \frac{(\mu_H)_o - \mu_{H^+}}{F} \qquad [5]$$

with ψ_r the cell potential.

From Eq. [2] and [3] one deduces easily that

$$(d\sigma)_T = -\Gamma_{A^-} d\mu_{A^-} - \Gamma_{C^+} d\mu_{C^+} - [\Gamma'_{H^+} + \epsilon] d\mu_{H^+} - [A_H - \epsilon]\, d\mu_H \qquad [6]$$

[34] S. Gilman, *Electrochim. Acta*, 9, 1025 (1964).

[35] M. Breiter, *J. Electroanal. Chem.*, 7, 38 (1964).

[36] N. Balashova and V. Kazarinov, *Elektrokhim.*, 1, 512 (1965).

[37] V. Nesterova and A. Frumkin, *Zhur. Fiz. Khim.*, 26, 1178 (1952).

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Another way to write [2] is obtained in making use of [1], [3], and [4], thus

$$(d\sigma)_T = -\Gamma_{A-}d\mu_{AH} - \Gamma_{C+}d\mu_{COH} - F[\epsilon - A_H]d\psi_r \quad [7]$$

in which

$$d\mu_{AH} = d\mu_{A-} + d\mu_{H+};\ d\mu_{COH} = d\mu_{C+} - d\mu_{H+}$$

According to the definition $\epsilon = \Gamma_{H+}$ and assumption $\Gamma'_{H+} = 0$, Eq. [6] transforms into Eq. [1] of Frumkin *et al.*, and relations [3] and [4] of this work are readily inferred and may be extended to the case where H^+ is not only in state of contact adsorption ($\Gamma'_{H+} \neq 0$).

From [6] it is observed that at μ_{A-} and μ_{C+} constant, $[\Gamma'_{H+} + \epsilon]$ and $[A_H - \epsilon]$ are thermodynamically independent variables. Therefore, by exact differential property, $d\psi$ could be written in terms of these coordinates, or by introducing an analytical change of coordinates* in terms of either $[A_H + \Gamma'_{H+}]$ and $[\Gamma'_{H+} + \epsilon]$ or A_H and Γ_{H+}, according to the approximation of Frumkin. Equation [12] of Frumkin with X^{-1} the pseudocapacitance of adsorption and Y^{-1} a capacitance of the double layer suggests that such change of coordinates has been used.

Equation [10] of Frumkin *et al.* may be easily shown to follow from Eq. [7] given above.

* With $X = [A_H - \epsilon]$; $Y = [\Gamma'_H + \epsilon]$ and $U = X + Y$; $V = Y$ the Jacobian $J(X,Y/U,V)$ of the transformation $X,Y \rightarrow U,V$ is unity.

Ion Pairing Mechanisms in Electrode Processes

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ABSTRACT

The influence of "bulk" ion pairing on electrode processes is easily detected when its main effect is to decrease the activity of the depolarizer. On the other hand, when association with the adsorbed ions of the supporting electrolyte forms a more electroactive entity, it is known that it can be more difficult to distinguish between direct discharge, or via ion pairs. However, a broad intercomparison (under strictly identical experimental conditions) of the influence of the nature and concentration of the supporting cation (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) on depolarizers of various electronic charge, allows to detect the abnormal behaviors, which are not determined by the pure "static" ψ effect. An indirect method has also been used, which essentially consists in modifying the double layer profile by adding, at constant concentration, increasing amounts of tensioactive ions having the same charge as the electrode, *e.g.*, iodide at not too negative charge densities.

The occurrence of chemical ion pairing as a concomitant rate-determining factor in electrode processes is generally easily detected from the effect of suitable composition changes at constant double layer structure: a typical case is the action of the sulfate ion on cation reduction, recently studied in our laboratory (15). However, it has been pointed out (1, 2) that, in the case of anion reduction proceeding at sufficiently negative potentials in not too concentrated solutions, the variations of the apparent rate constant produced by changing the concentration of the supporting electrolyte can be referred either to the usual ψ effect acting on the "bulk" species or to a prior charge-decreasing process involving ion-pairing with the supporting cations, which helps to circumvent the repulsive interaction with the electrode. In some cases, sudden changes in α_0 values (for want of more definite proof) seem even to suggest that each mechanism could be rate-determining within separate potential ranges (3).

Exact diagnosis of the type of mechanism unfortunately is made more difficult by the conjunction of three circumstances:

1. Since no double layer model of sufficient accuracy is available (if it should be, it would probably be hardly adaptable to electrode kinetics), the fact that a given electrochemical reaction follows closely the predictions derived from the Frumkin relation coupled with for instance the Gouy-Chapman theory, does not constitute in itself an overwhelming argument (2).

2. There is some tendency to focus the investigations on electrochemical reactions which present quite abnormal characteristics, without paying enough interest to reactions more apt to bring clearer information. Some of these latter reactions have occasionally received only superficial attention, or have been investigated with inadequate methodology, enough however to hinder their reexamination.

3. Most of the available data cannot be directly compared, since experimental conditions (such as drop time, compositions, temperature) and measured quantities (average or instantaneous currents, 45° tangent of half-wave potentials, etc. . . .) are highly variable.

The method adopted here consists in reassessing the basic characteristics of a sufficient number of these reactions, under strictly standardized conditions.[2]

The systematic intercomparison of the results obtained allows the identification of the various types of behavior and relates them specifically to their corresponding rate-determining mechanisms. Additional evidence may be gained from a more general comparison considering other data relative to behaviors which are known to be affected by ion pairing.

The present study is limited to concentrated solutions (0.1 and 1*N*) of supporting electrolytes with the most common mono- and divalent cations. As far as the charge of the depolarizer is concerned, it is worthwhile to distinguish: (*a*) the "formal" charge z^0 calculated from valencies and stoichiometry; (*b*) the "bulk" charge z_B which prevails in solution and may vary with the concentration of the supporting electrolyte [for highly charged anions, z_B is generally close to −2 in 1*N* solutions (8)]; (*c*) the "apparent" charge z_K which best fits the Frumkin equation if it is assumed that there is no prior labile association with the supporting cation, and when ψ is controlled by the supporting electrolyte concentration; (*d*) the "actual" charge z_δ of the electroactive entity itself.

[1] Excerpts from dissertations to be submitted to the Faculty of Sciences as partial fulfillment of the requirements for Ph.D. degree.

[2] Since no claim for originality is made, the extended list of references pertaining to each of the various depolarizers used has been deliberately omitted. Such references are easily available in systematic polarographic surveys (6, 7).

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