PHYSICAL METHODS OF INVESTIGATION

RADIOFREQUENCY RECORDING OF THE SURFACE TENSION OF A SOLID ELECTRODE

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The variation of the surface tension of solids, γ [1, 2], provides a control* to check the surface state and the reactions in the layer between the phases. An alternating potential difference is applied to the interface of the solid electrode with the electrolyte. This potential difference generates oscillations in the surface tension of the solid electrode which are picked up by a piezoelectric element. The dependence of their amplitude on electrode potential φ is recorded as a plot of γ_ε against φ or of γ_φ against φ, where ε is the charge density of the electrode, $\gamma_\varepsilon \equiv \partial\gamma/\partial\varepsilon$, and $\gamma_\varphi \equiv \partial\gamma/\partial\varphi$. We call the quantity $\partial\gamma/\partial\varepsilon$ estance (in analogy to impedance). The method is more effective the wider the working frequency range. It is fortunate, therefore, that this method is free from the frequency limitations arising when measuring the interfacial capacity.

The unequal accessibility of the electrode in the form of a rectangular plate causes an insignificant loss in amplitude (in practice, less than 1%) and insignificant dispersion in phase (less than 10%), and this only near two particular values of frequency f, related to the geometry of the space around the electrode f_{ma}, and to the roughness f_{mi}. For Pt in 1 N H_2SO_4 at $\varphi = +0.1$ V (vs nhe), $f_{ma} \approx 1$ kHz and $f_{mi} \approx 10$ MHz. The shift in meniscus due to the connection between the angle of contact and φ is a slow process, and at 20 Hz already it is no longer necessary to insulate the electrode at the level of the meniscus.

In the measurements made, the piezoelectric element was connected to an over-meniscus electrode, which had the form of an L-shaped plate, and was touching the solution beneath it. The resonance frequencies of such a mechanical system spread over a region from low acoustical to radio frequencies: 0.3, 0.7, 1.0, 1.9, 2.6, 4.1, 7.4, 16.0, 22.5, 54, 108, 147, 209, and 256 kHz with half-widths from 0.3 to 2%. It is interesting that the resonance frequency and half-width are practically independent of the electrode material and of the height to which it is raised above the solution level; the electrode sets in vibrations the remainder of the system but does not itself participate in the resonance.

Experimental Results. The oscillographic traces of the estance, $|\gamma_\varepsilon|$, as function of potential φ, are given in Fig. 1, a–l, for smooth Pt in various media (aqueous solutions of H_2SO_4 and $HClO_4$) and at different frequencies (from 0.7 to 209 kHz) at 20°C. The sheet thickness of the electrode was 0.35 mm, the dimensions of the planar working surface were 4 × 10 mm. Curves a, d, and e were recorded in one scan at two frequencies simultaneously (superposition of the oscillations): 2.6 and 54 kHz (a), 0.7 and 22.5 kHz (d), and 0.7 and 7.4 kHz (e); part i compares the curves $|\gamma_\varepsilon|$ against φ and j against φ. (j is the charging current.)

Prior to an experiment the electrode was subjected to alternating anodic and cathodic polarization in order to clean its surface; this was achieved by scanning many times between +1.45 and 0 V; parts k and l show curves of $|\gamma_\varepsilon|$ against φ before (first scan: k) and after (tenth scan: l) such a treatment. The scanning rate (in V/sec) was: 0.01 (a, b, c, k, and l), 0.03 (d and e), 0.05 (f and g), 0.09 (i), and 0.17 (h). The length of time for which the electrode was kept at the initial potential was: 2 min (a, b, c, k, and l), 1 min (f, g, and h), and 18 sec (i). The last two parameters have no effect on the curve in the hydrogen region of φ. The curve $|\gamma_\varepsilon|$ against φ is reversible in this region (g). The arrows in Fig. 1 give the direction of the curve. The sensitivity of the instrument at a frequency

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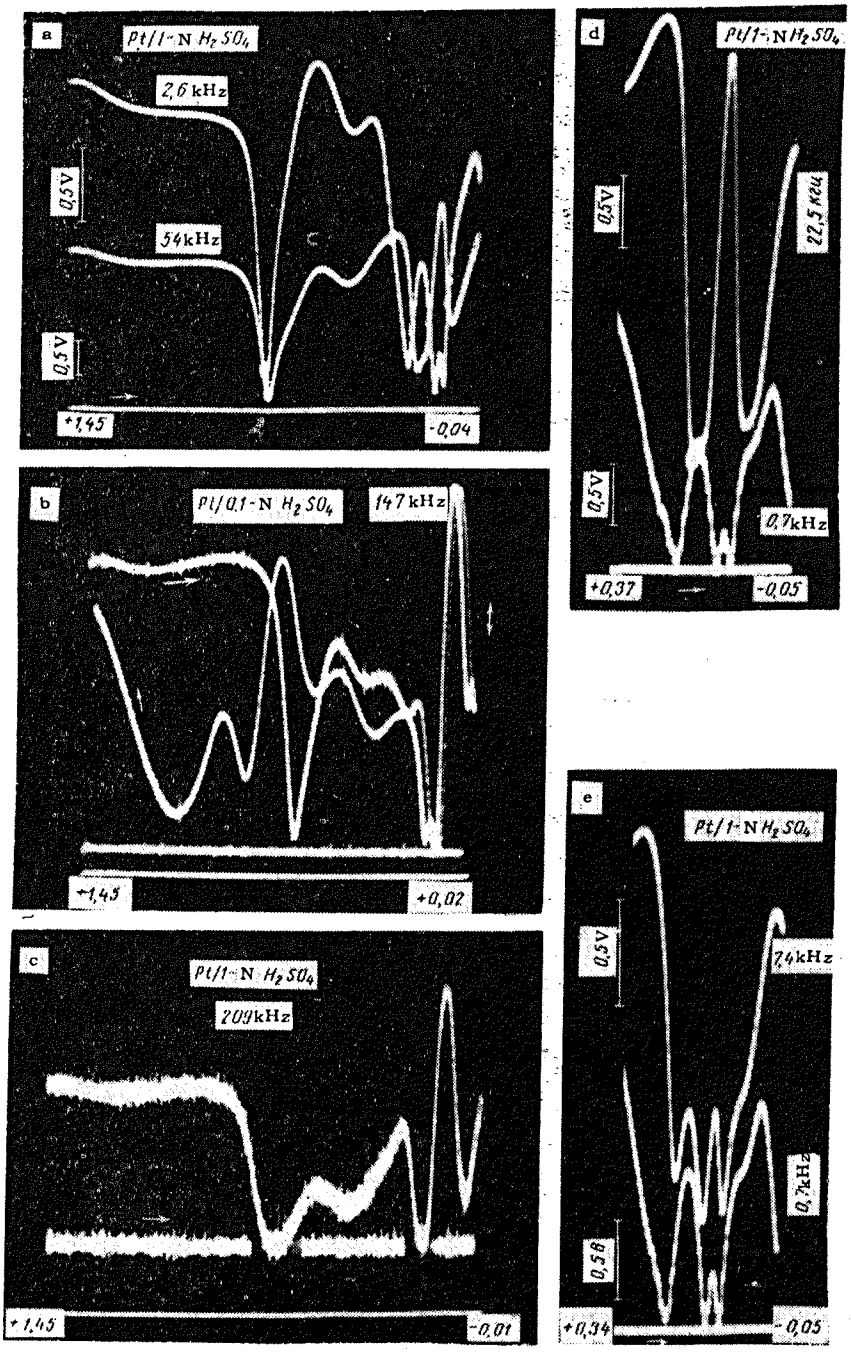


Fig. 1. (a = 1) oscillographic traces $\left|\partial\gamma/\partial\xi\right|^{vs}\varphi$

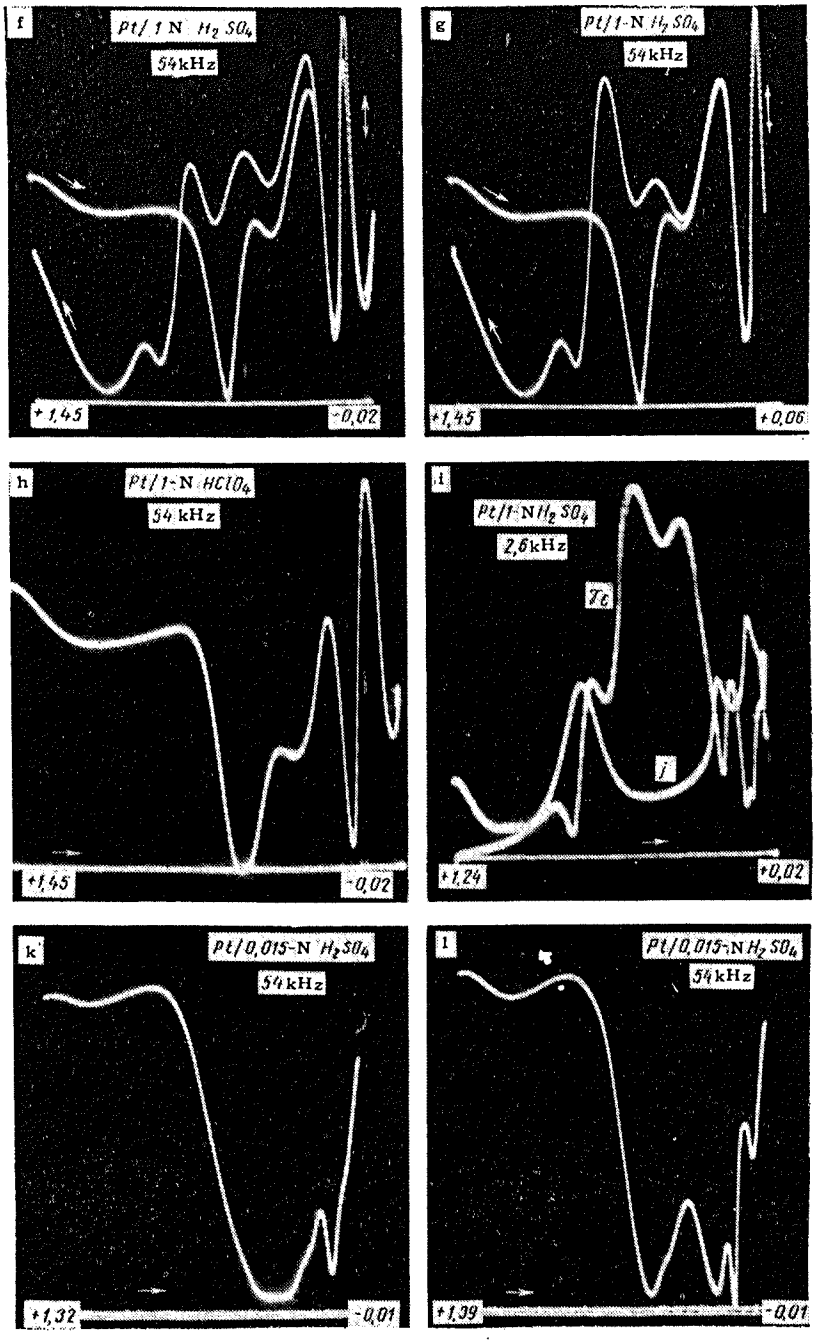


Fig. 1 (continued)

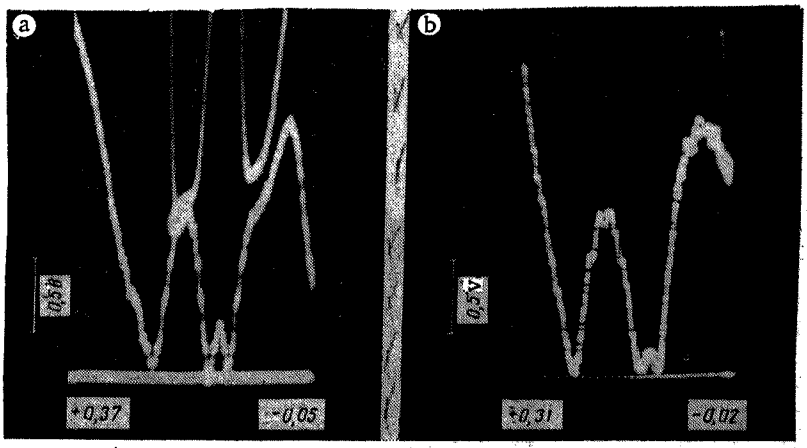


Fig. 2. Comparison of the oscillographic traces $|\partial\gamma/\partial\varepsilon|$ vs φ (surface tension method: a) and $|\partial\varphi/\partial\vartheta|$ vs φ (elastic charging of the interphase layer: b) for Pt in $1\,N\,H_2SO_4$; a) over-meniscus electrode in the form of a plate of 0.35 mm thickness, 660 Hz (at the top there are portions of the curve at 22.5 kHz, cf. Fig. 1 d); b) electrode in the form of a ribbon of foil of 10 μ thickness, 38 Hz.

of 2.6 kHz: oscillations of γ having an amplitude of $2.3 \cdot 10^{-2}$ dyne/cm produce a voltage of 1 μV amplitude on the piezoelectric element.

Method of Calibration. In order to define the scale of the oscillographic traces $|\gamma_\varepsilon|$ against φ, the oscillations of the surface tension are represented by alternating thermal strains near the electrode surface. After the main experiment the electrode is transferred into the solution of a redox system, and an alternating current is passed through it which has the same frequency as before. In this process heat is developed on the electrode surface, which is of an intensity W. With electrodes made of unstable materials, a thin layer of gold (0.1 μ) is plated on prior to calibration in order to protect them from chemical attack. For the surface tension γ_0 and the charge ε_0 on a flat surface (the true surface or the mean surface representative for a rough surface) we have

$$\frac{\partial\gamma_0}{\partial\varepsilon_0} = \frac{\partial\gamma_r}{\partial\varepsilon_r}\,\frac{\Delta I_r}{\Delta I_c}\,\frac{\Delta v_c}{\Delta v_r}. \tag{1}$$

Four amplitudes (Δ) are entering here: ΔI_c and ΔI_r are the given amplitudes of current, Δv_c and Δv_r are the amplitudes of the voltage at the piezoelectric element in the basic (c) and calibrating (r) experiments, respectively. The derivative of the thermal strain γ_r, with respect to the amount of electricity ε_r, in the calibrating experiment is calculated from known parameters:

$$\frac{\partial\gamma_r}{\partial\varepsilon_r} = \frac{W}{1-\nu}\,\frac{\varkappa Y}{\zeta\rho}\,M(\xi), \tag{2}$$

$$\xi = \lambda\sqrt{\frac{\omega\zeta\rho}{8k}}, \tag{3}$$

where $\varkappa$ is the coefficient of linear thermal expansion, Y is the elastic module, ν is Poisson's coefficient, ζ is the heat capacity, ρ is the density, k is the thermal conductivity, λ is the thickness of the electrode plate, and $\omega = 2\pi f$.

The function

$$M(\xi) = \left[1 - \frac{\operatorname{th} z}{z}\right]/[1 + \tau \operatorname{cth} 2z] \tag{4}$$

accounts for the loss of heat into the solution (denominator) and into the interior of the plate (numerator). Here $z = (1 + i)\,\xi$ and $\tau = \sqrt{k_s\zeta_s\rho_s/k\zeta\rho}$; values with the index s refer to the solution, those without index refer to the electrode. The plot of $P(\xi) = |1-(1/z)\tanh z|$ is given in [3]; $P(0) = 0$, $P(\infty) = 1$. At $\xi \geq 2$

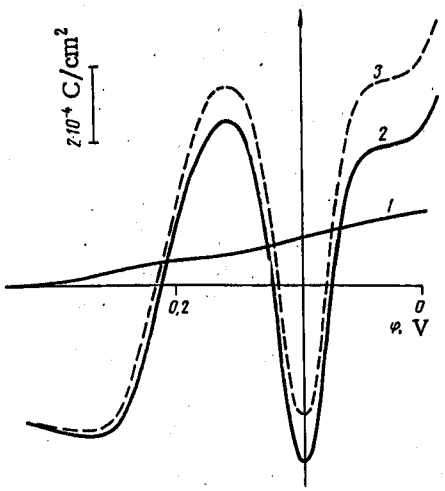


Fig. 3. The quantities $-\varepsilon$ (1), $-\partial\varepsilon/\partial\vartheta$ (2), and $\partial\gamma/\partial\varphi$ (3) in the hydrogen region of φ for a Pt electrode in 1 N H_2SO_4.

$$|M(\xi)| = \frac{1}{1+\tau}\sqrt{1-\frac{1}{\xi}+\frac{1}{2\xi^2}}, \tag{5}$$

$$\arg M(\xi) = \operatorname{arctg}\frac{1}{2\xi-1}. \tag{6}$$

For platinum $(\varkappa Y/\zeta\rho)/(1-\nu) = 1.0$; with a plate thickness of 0.35 mm and $f = 3$ kHz, $\xi = 3.46$. In dilute aqueous solutions $1/(1+\tau) = 0.9$. With the system 0.3-M $K_3Fe(CN)_6$ + 0.3-M $K_4Fe(CN)_6$, W = +0.4 V.

Effect of Roughness. With an isotropic, rough surface having a roughness factor α, the true value of the estance, $\partial\gamma/\partial\varepsilon$, is connected with its planar equivalent $\partial\gamma_0/\partial\varepsilon_0$, by

$$\frac{\partial\gamma}{\partial\varepsilon} = \alpha^{\frac{1+\nu}{1-\nu}}\frac{\partial\gamma_0}{\partial\varepsilon_0}. \tag{7}$$

Elastic Charging of a Solid Electrode. In a method recently developed [4], $\partial\varphi/\partial\vartheta$ is recorded as the change in the electrode potential φ, upon elastic deformation at constant total charge; ϑ is the relative change in electrode area. It turns out that

$$\frac{\partial\gamma}{\partial\varepsilon} = \frac{\partial\varphi}{\partial\vartheta}. \tag{8}$$

This equation was derived thermodynamically and confirmed experimentally. It holds for a smooth as well as for a rough surface.

In Fig. 2, the oscillographic traces of $\partial\gamma/\partial\varepsilon$ against φ and $\partial\varphi/\partial\vartheta$ against φ are compared for Pt in 1 N H_2SO_4. In spite of the fact that they have been obtained by principally different methods and on different samples, their proportions are the same, and the characteristic points (a null point at +0.21 V, a maximum at +0.16 V, and a maximum between two adjacent null points at +0.10 V) lie at the same potentials to within 0.01 V. This confirms, in particular, that the influence of the roughness factor appears as change in the proportionality coefficient between $\partial\gamma_0/\partial\varepsilon_0$ and $\partial\gamma/\partial\varepsilon$.

The results of the two methods were also compared on electrodes having the same α. At $\alpha = 1.5$ and φ = +0.16 V, the values of $\partial\gamma_0/\partial\varepsilon_0$ and $\partial\varphi_0/\partial\vartheta_0$ coincide to within 10% and are +0.4 V. Hence according to Eq. (7) $\partial\gamma/\partial\varepsilon \approx +1$ V at $\varphi = +0.16$ V (here φ is everywhere given against a hydrogen electrode in the medium compared).

The Change in Charge Density During Elastic Deformation. From (8) we have

$$\frac{\partial\gamma}{\partial\varphi} = -\varepsilon - \frac{\partial\varepsilon}{\partial\vartheta}. \tag{9}$$

To the left ϑ is constant; to the right, φ is constant. Equations (8) and (9) also hold true under nonequilibrium conditions, viz., at high frequencies (the derivatives involved then become complex), as well as for the metal–vacuum interface. At $f = 0$ and $\varphi = +0.16$ V, the charge and capacity of the platinum electrode are, respectively, $\varepsilon = -1\cdot10^{-4}$ C/cm^2 and $C = 5\cdot10^{-4}$ F/cm^2. Hence $\partial\gamma/\partial\varphi = C\,\partial\gamma/\partial\varepsilon = 5\cdot10^{-4}$ C/cm^2. From (9) we find $\partial\varepsilon/\partial\vartheta = -4\cdot10^{-4}$ C/cm^2; i.e., stretching the electrode at $\varphi = +0.16$ V increases the density of negative charge. The effect is so large that if it were possible to elastically stretch the electrode to twice its length (which, of course, is impossible), its charge would increase by an order of magnitude. The φ-dependence of $\partial\varepsilon/\partial\vartheta$ is given in Fig. 3.

Change in the Density of Adsorbed Hydrogen. The charge ε consists of a charge ε_a, which was spent on the transition of hydrogen ions from the solution into the state of adsorbed atoms, and a charge ε_i, which is balancing the electrostatic adsorption of ions from the solution [5]. Hence also $\partial\varepsilon/\partial\vartheta = \partial\varepsilon_a/\partial\vartheta + \partial\varepsilon_i/\partial\vartheta$.

The frequency dependence of the estance aids in finding the contribution of each term to this sum. At $\Delta\varepsilon = \Delta\varepsilon_a + \Delta\varepsilon_i = \text{const}$ (a condition which is fulfilled in the experiments described), the amplitudes $\Delta\varepsilon_a$ and $\Delta\varepsilon_i$ vary

with frequency in opposite directions. From 0 to 54 kHz, $\Delta\varphi$ and together with it $\Delta\varepsilon_i$ increase by an order of magnitude, while conversely the amplitude $\Delta\varepsilon_a$ decreases, although not significantly since $\Delta\varepsilon_a \gg \Delta\varepsilon_i$ at $f = 0$. It turns out that at $\varphi = +0.16$ V the amplitude of γ follows $\Delta\varepsilon_a$, not $\Delta\varphi$, when the frequency changes (Fig. 1d).

Thus, practically the entire change in $\gamma(\partial\gamma/\partial\varepsilon)$ is here the direct consequence of H^+ ions going over from the solution into the atomic state on the platinum surface; i.e., the decrease in surface tension of the platinum is proportional to the increase in the amount of hydrogen on its surface. It then follows from (9) that the observed $\partial\varepsilon/\partial\vartheta$, too, is practically completely to be attributed to the adsorption of hydrogen; the density of hydrogen adsorbed on the platinum surface at +0.16 V increases substantially when the platinum is stretched. The same is observed near 0 V (Fig. 1d). The effect has the opposite sign around +0.1 V. This difference is due to different arrangements of the hydrogen atoms adsorbed at different potentials. We shall denote the state of hydrogen adsorbed at +0.16 V and 0 V as H_e, and that at +0.1 V as H_m. It follows from these data that an increase in the separation of the surface atoms of platinum brings about a strengthening of their bond with the hydrogen adsorbed at +0.16 V.

Analysis of the Frequency Dependence of the Estance. On Pt at $\varphi = +1.45$ V in 1 N H_2SO_4, the estance is practically independent of frequency at $f > 1$ kHz. Four maxima stand out on the $|\gamma\varepsilon| - \varphi$ curve in the range from 54 to 256 kHz: at +0.10 V (a peak), +0.24 V, +0.77 V, and +1.0 V (the latter two only with increasing $\varphi > 0$). At the first three maxima $\gamma_\varepsilon < 0$, and at the last one $\gamma_\varepsilon > 0$. It is important that the capacity maxima (which are also close to +0.10 and +0.24 V) already disappear at $f > 5$ kHz. The peak of $\partial\gamma/\partial\varepsilon$ at +0.10 V, which is measured from the zero line, increases with frequency like $\partial\varphi/\partial\varepsilon$, a quantity which is the converse of an impedance. At $f = 54$ kHz the peak is 11.5 times higher than at $f = 0$. Beyond 54 kHz it increases more slowly. The peak is enclosed between two portions of the curve (near 0 and +0.16 V) where the frequency dependence of the estance is weak (Fig. 1d, e).

Other components of the interphase layer are involved, too, in the adsorption of hydrogen. Therefore, the adsorption into each of the states H_e and H_m, is here considered as one process. The contributions of H_e and H_m to the change in γ are different. The peak at +0.1 V (hydrogen appears in the state H_m) is not due to discharge of H^+ ions from the solution. In fact, at $\Delta\varepsilon$ = const the peak increases by more than an order of magnitude as the frequency rises from 0 to 209 kHz while the consumption of electricity in the discharge of H^+ falls by more than a factor of two over the same frequency range (because of the slowness of H^+ discharge).

Thus, the cause for the peak (the source of hydrogen) may lie, either in the H_e already adsorbed, or in chemisorbed water. However, within the scheme $H_e \rightleftharpoons H_m$ the increase of the peak with frequency would have to occur much faster than it actually does. For example, this scheme predicts an increase by a factor of seven for 5 kHz, rather than the observed rise by a factor of 2.2. The potential of +0.17 V where, towards the negative side, the estance suddenly ceases to depend on frequency (in this point, the curves for 0.7 and 22.5 kHz practically flow together, cf., Fig. 1d) coincides with the potential where the free electrode charge goes to zero [5]. Replacing the H_2SO_4 solution by an $HClO_4$ solution does not alter the $\gamma_\varepsilon - \varphi$ curve in the hydrogen and oxygen regions of φ (Fig. 1f, h); i.e., the nature of the anion is not important in the phenomena described. The estance peak and the depression enclosing it are preserved on the $\gamma_\varepsilon - \varphi$ curve up to 36 N H_2SO_4.

The $\gamma_\varepsilon - \varphi$ curves are not distorted by side effects. The evolution of heat on the electrode surface, when H^+ ions from the solution go over into the state of H atoms adsorbed on the platinum, is insignificant (less than 1 kcal/Faraday). This has been established in three ways: a) by measurements on plates of different thicknesses (going from $\lambda = 0.5$ to $\lambda = 0.1$ mm does not change the observed $\partial\gamma/\partial\varepsilon$, while the thermal effect $\partial\gamma_T/\partial\varepsilon_T$ would have to decrease strongly then, viz., by a factor of four at 1 kHz); b) by measurements on the foil (Fig. 2b), where a thermal effect is practically excluded because of the fast dissipation of heat into the solution; c) by measuring the height of the null points of estance above the zero line. Because of the phase difference between $\partial\gamma/\partial\varepsilon$ and $\partial\gamma_T/\partial\varepsilon_T$ (75° at $\lambda = 0.1$ mm and $f = 1$ kHz), the vector sum of these quantities can only go to zero (it does so three times in the hydrogen region of φ, cf., Fig. 2a) when each of these quantities goes to zero. On the oscillographic traces γ_ε vs φ for iridium, the same peculiarities are observed as on the traces for platinum (cf., Fig. 1).

The experiments performed show:

1. On platinum there is locally adsorbed an overall neutral compound containing the atoms O and H (a product of the adsorption of water).

2. The changes in the state of this compound with φ are primary with regard to the adsorption of H from the solution and stimulate this adsorption; they also occur at high frequencies where the adsorption is inhibited.

3. The estance maximum at +0.77 V corresponds to a strengthening of the bond of the adsorbed compound with the platinum surface. Electrical measurements do not reveal this process because it involves no electrooxidation, and the consumption of electricity in it is low.

4. The null points of estance at +0.91 and +1.13 V (Fig. 1b, f, and g; the minima on the anodic curves) indicate that the electrooxidation of platinum consists of two consecutive stages which are irreversible and set in only when potentials of +0.9 V (first stage) and +1.1 V (second stage) are reached; two types of sites on the platinum surface enter the process successively (at different φ). Between the null points the state of platinum changes reversibly with potential.

5. The change in γ with φ in the oxygen region is caused by the deformation of dipoles, which is essentially nonlinear because of the high values of the field (on the order of 10^7 V/cm), and which is therefore, accompanied by a change in $\partial\gamma/\partial\varphi$.

The strong fields are the reason why the reversible (at +0.8 and +1.0 V) deformation reaches (at +0.9 and +1.1 V) a critical level and goes to completion as an irreversible transformation (formation of oxide).

6. The sharp drop in the frequency dependence of the estance when going through the point of zero charge (+0.17 V) is caused by the drop in the deformation component of γ and indicates that the space-charge region is displaced outwards from the surface layer of platinum. The positive charge is accumulated in this layer, but the negative charge is outside this layer (except for the vicinity of +0.1 V).

7. The estance peak at +0.1 V is the manifestation of a hitherto unknown fast process confined to the interphase layer. The fact that $\partial\gamma/\partial\varepsilon$ on the peak increases with frequency like $\partial\varphi/\partial\varepsilon$ is equivalent to saying that $\partial\gamma/\partial\varphi$ does not depend on frequency. Thus, at $\Delta\varphi$ = const the peak does not depend on the H^+ions from the solution being able to discharge (low frequencies) or not (high frequencies).

8. The transition of adsorbed hydrogen from one state (H_e in the adsorption near 0 and +0.16 V) to another (H_m in the adsorption near +0.10 V) is either absent or insignificant under these conditions.

9. To each of the two types of hydrogen adsorption—in the H_e state and the H_m state—corresponds a definite region of the interphase layer where the potential drop is localized which is responsible for this type of adsorption. These regions do not overlap. Near +0.1 V the entire increase in φ is expended on the change of potential in the H_m region (the electrode layer next to the surface). For this reason, the potential drop in the H_e region (the electrolyte layer next to the surface) ceases to change, and the adsorption of hydrogen into the H_e state is suspended. The reduction in the contribution of H_e adsorption to $\Delta\gamma$ is the reason for the dip near +0.1 V on the $\gamma_\varepsilon-\varphi$ curve at low frequencies. A saturation of the H_e layer or a passivation of the H_e sites does not occur here, because hydrogen is adsorbed into the H_e state both before and after the dip. With increasing frequency the estance peak grows out from this dip (Fig. 1e) and fills it (Fig. 1d).

10. Near +0.16 V the estance $\partial\gamma/\partial\varepsilon$ diminishes with frequency like $\partial\varepsilon_a/\partial\varepsilon$, i.e., that part of the charge amplitude which is expended on the discharge of H^+ ions from the solution. The decrease in γ during the transition of H^+ from the solution into the H_e state on the platinum surface (about $2\cdot10^{-12}$ dyne/cm per H atom) is the main component of estance in this region of φ. The decrease of estance with frequency is faster in more dilute solutions.

11. The elastic stretching of platinum strongly increases the density of hydrogen adsorbed by it at φ = +0.16 V and at φ = 0 V.

12. As the frequency increases from 0 to 22 kHz, the potential where H recombination begins (the maximum γ_ε at $\varphi < 0$ V) moves away from 0 to −0.05 V, i.e., at fixed φ the fraction of ac which is expended on H_2 evolution decreases with increasing frequency.

13. The evolution of heat in the reaction $H^+ + e \rightleftharpoons H_{ads}$ on platinum does not exceed 1 kcal/Faraday.

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