HYDROGEN ADSORPTION AND THE SURFACE TENSION OF PLATINUM

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The platinum electrode is one of the most studied solid electrodes [1]. In aqueous solutions, the density ε of total charge is the sum of the density α spent for discharging H^+ to the state of adsorbed atoms, and the density ρ of free charge: $\varepsilon = \alpha + \rho$ [2]. A number of new results were obtained [3] by measuring the "estance" (the term was earlier introduced by us for the derivative of the surface tension γ of a solid with respect to ε: $\gamma_\varepsilon = \partial\gamma/\partial\varepsilon$).* We have interpreted these data as follows. On Pt in aqueous solutions of acids (H_2SO_4, $HClO_4$) there exists the effect of an internal transition of adsorbed H: the sharp estance peak found at a potential $\varphi = 0.1$ V (everywhere vs rhe) survives at frequencies $f > 200$ kHz on account of the transition of H from the state H_e (apparently above each Pt atom) into the state H_m (inside the lattice cube, beneath every second Pt atom). The transition is caused by changing φ and is described by an internal capacity $(\partial\alpha_1/\partial\varphi)_\alpha = -(\partial\alpha_2/\partial\varphi)_\alpha$, where α_1 and α_2 are the surface densities of H_m and H_e (expressed through the expenditure of charge on H^+ discharge) and $\alpha = \alpha_1 + \alpha_2$.

As the frequency increases from zero, a peak (see Fig. 1) rises from the bottom of the estance trough whose limits, which are a distance $\Phi = 0.15$ V apart, are frequency-independent (the theory of these phenomena is given below). It follows that the occupancy with H_m covers an interval of 0.15 V with the center near $\varphi = 0.1$ V; i.e., it begins later and stops earlier than the occupancy with H_e. With H_m situated over the Pt atom, a monolayer would be required therein which would not comprise all hydrogen ($H_m + H_e$) at $\varphi > 0$. Hence the limiting occupancies: $\max \alpha_1 = Q = 104\ \mu C/cm^2$, $\max \alpha_2 = 2Q$. The adsorption of H_m terminates at an H_e occupancy close to one-half the limiting value. The trough of equilibrium estance at 0.1 V and the estance step at 0.04 V are caused by the adsorption break detected here; when φ changes cathodically, the adsorption of H_e is interrupted by the adsorption of H_m, owing to the mutual effect of H_m and H_e, and turns into desorption, but is resumed after H_m occupancy and continues at $\varphi < 0$, which is also shown by the estance rise setting in [3] past -0.1 V at high f.

For the estance maximum near 0.2 V, which increases with frequency (despite cessation of H^+ discharge), we have no other explanation than dechemisorption of water caused by the cathodic shift of φ, regardless of whether H occupies the sites vacated on the Pt surface (capacity maximum at low f) or not (high f). This conclusion is confirmed by the fact that at $\varphi < 0.2$ V, the effect of water on H adsorption is not important; the estance peak, the trough, its edges, and the low level of heat evolved ($|T\Delta S| < 1$ kcal/faraday, where T is the temperature, ΔS the entropy of adsorption) persist when the acid concentration is strongly raised [3].

The Intensive and the Extensive Component of Estance. At constant electrode area Ω it follows from $\gamma = \gamma(\alpha, \varphi)$ for the estance that

$$\partial\gamma/\partial\varepsilon = (\partial\gamma/\partial\alpha)_\varphi d\alpha/d\varepsilon + (\partial\gamma/\partial\varphi)_\alpha d\varphi/d\varepsilon = \mathrm{Ext}\,\gamma_\varepsilon + \mathrm{Int}\,\gamma_\varepsilon, \quad (1)$$

where Ext and Int are the extensive and intensive component whose separation is assured by their different dependence on f, for example, $d\alpha/d\varepsilon \to 0$ when $f \to \infty$. Hence

$$(\partial\alpha/\partial\vartheta)_\varphi = -\alpha - (1+\tau)^{-1}(d\varepsilon/d\varphi)\,\mathrm{Ext}\,(\partial\gamma/\partial\varepsilon) \quad (2)$$

is the change of α with the relative elastic deformation of the surface ϑ. Here $\tau = (\partial\rho/\partial\alpha)_\varphi$.

* The term "estance" is given thus in English by the author himself – Publisher.

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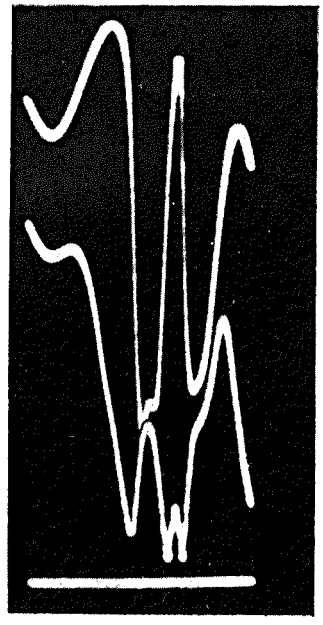

Fig. 1

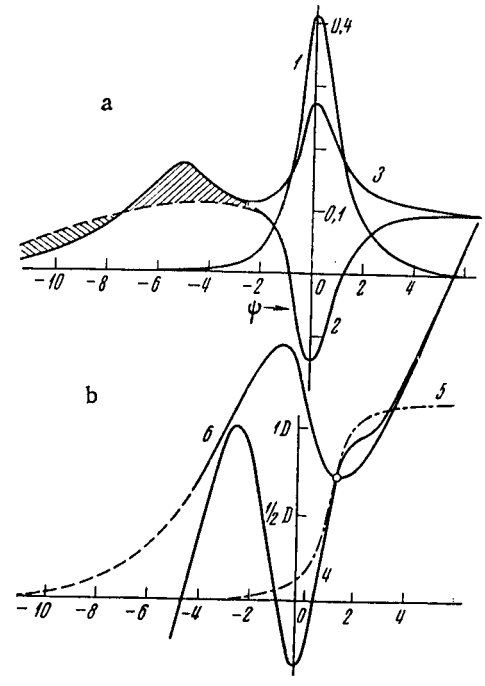

Fig. 2

Fig. 1. Oscillographic traces of estance vs potential on platinum in 1 N H_2SO_4 obtained with one potential sweep at the two frequencies 2.6 (lower trace) and 22.5 kHz (upper trace; amplification 1.27 times higher than for the lower trace) from −0.47 to −0.09 V (from left to right).

Fig. 2. a) Adsorption capacities of hydrogen in the states H_m ($d\theta_1/d\psi$) (curve 1) and H_e ($d\theta_2/d\psi$) (curve 2); curve 3 gives the total capacity ($d\theta/d\psi$). b) The equilibrium estance ($\partial\gamma/\partial\alpha$) (curve 4) and the specific contributions of H_m ($\partial\gamma/\partial\alpha_1$) (curve 5) and H_e ($\partial\gamma/\partial\alpha_2$) (curve 6) to the surface tension. Chemisorption of water deforms the anodic branch of the isotherm for the outer hydrogen H_e (dashed line).

Let us introduce $\omega = 2\pi f$, $\lambda = \omega/k$, where k is the equilibration constant, and $\varkappa = (\partial\rho/\partial\varphi)_\alpha/(d_\varepsilon/d\varphi)_0$ is the ratio between the capacity at $f \to \infty$ and that at $f \to 0$. For $\varphi = \Delta\varphi \exp i\omega t$ + const, where t is the time, it follows from $d\alpha/dt = k[\alpha_0(\varphi)-\alpha]$ that $d\alpha/d\varphi = (d\alpha/d\varphi)_0/(1 + i\lambda)$, $d\alpha/d\varepsilon = (1-i\lambda)/[1 + \varkappa(1 + \lambda^2) - i\lambda](1 + \tau)$, and $d\varphi/d\varepsilon = (1 + \lambda^2)/[1 + \varkappa(1 + \lambda^2) - i\lambda](1 + \tau)(d\alpha/d\varphi)_0$. The independence of estance on f in the audiofrequency range ($d\alpha/d\varepsilon \approx 1$) over ranges of φ near 0 and 0.16 V (Fig. 1) implies that in these ranges one practically has Ext $\gamma_{\varepsilon 0} = \gamma_{\varepsilon 0}$ (likewise for Ir; for Rh, this holds over the entire H region of φ; the sharp break in the $\gamma_\varepsilon - \varphi$ curve for Rh at 0.06 V [3] points to a superficial transformation involving H, though not the same as on Pt).

At +0.16 V, $\gamma_\varepsilon \approx 0.1$ V, $d\varepsilon/d\varphi = 5 \cdot 10^{-4}$ F/cm^2, $\alpha = -1 \cdot 10^{-4}$ C/cm^2, and $|\tau| < 0.1$. Then from (2) $(\partial\alpha/\partial\vartheta)_\varphi \approx -2.5 \cdot 10^{-4}$ C/cm^2. Since $\gamma = \gamma(\alpha_1, \alpha_2, \varphi)$,

$$\partial\gamma/\partial\varepsilon = (\partial\gamma/\partial\alpha_1)\,d\alpha_1/d\varepsilon + (\partial\gamma/\partial\alpha_2)\,d\alpha_2/d\varepsilon + (\partial\gamma/\partial\varphi)_{\alpha_1,\alpha_2} d\varphi/d\varepsilon, \tag{3}$$

$$(\partial\gamma/\partial\varphi)_{\alpha_1,\alpha_2} = -(\partial\rho/\partial\varphi)_{\alpha_1,\alpha_2} \sum_j \delta\varphi_j\,[1 + (\partial\zeta_j/\partial\vartheta)]. \tag{4}$$

Here the interfacial layer is broken down into elementary double layers contributing $\delta\varphi_j$ to the total drop φ across the interface and possessing an effective integral capacity $C_{j0}\,\partial\zeta_j/\partial\vartheta = (\partial C_j/\partial\vartheta)/C_j$. It follows from experiments at $f \to \infty$ that in the H region of φ, the contribution of the last term of (3) to the equilibrium estance is small, of the order of magnitude of 0.01 V. From (1) and (3)

$$(\partial\gamma/\partial\alpha)_\varphi = (\partial\gamma/\partial\alpha_1)(\partial\alpha_1/\partial\alpha)_\varphi + (\partial\gamma/\partial\alpha_2)(\partial\alpha_2/\partial\alpha)_\varphi, \tag{5}$$

$$(\partial\gamma/\partial\varphi)_\alpha = (\partial\alpha_1/\partial\varphi)_\alpha[\partial\gamma/\partial\alpha_1 - \partial\gamma/\partial\alpha_2] + (\partial\gamma/\partial\varphi)_{\alpha_1,\alpha_2}. \tag{6}$$

Double-Parameter Hydrogen Adsorption Isotherm. We shall write a system of isotherms for the localized adsorption of l substances in n states ($r = 1, \ldots, l$; $s = 1, \ldots, n$):

$$\mu_r - \nu_s(\theta_1, \ldots, \theta_n; \psi) = \ln(\theta_s/\theta_{sm} - \theta_s), \quad \partial\nu_s/\partial\theta_j = \partial\nu_j/\partial\theta_s, \tag{7}$$

where in concept each is close to the Frumkin isotherm [4] for the adsorption of one substance; θ_s and ν_s are the occupancy and energy level of the s-th state; $\theta_{sm} = \max\theta_s$; μ_r is the electrochemical potential of the r-th substance (μ_r and ν_s are in units of RT); $\psi = -\varphi F/RT$; $RT/F = 0.0253$ V at $T = 293°K$. In the simplest case $\nu_s = a_{s1}\theta_1 + \ldots + a_{sn}\theta_n + a_{\psi s}\psi + a_{s0}$, $a_{js} = a_{sj}$.

For the adsorption of H on Pt, $l = 1$, $\mu_1 = \mu_2 = \mu$; $n = 2$, $\theta_1 = \alpha_1/Q$, $\theta_2 = \alpha_2/Q$; $\theta = \theta_1 + \theta_2 = \alpha/Q$. At equilibrium $\mu = \psi$. Of the two equations (7), the second ($s = 2$) is open to linearization, by the following indications: 1) similarity of the slopes $d(\partial\gamma/\partial\varepsilon)/d\varphi$ and also the capacities $d\varepsilon/d\varphi$ before and after adsorption of H_m, 2) the closeness of θ_2 to $0.5\,\theta_{2m}$ in the region of H_m adsorption, so that $\ln[\theta_2/(2-\theta_2)] \approx 2(\theta_2 - 1)$.

The second equation (7) then assumes the form $\psi = a\theta_1 + b\theta_2 + \text{const}$.

Let $p = \theta_{1m}/\max(d\theta_1/d\psi)$ be the effective width of the capacity peak at 0.1 V, $g = 1/\max(d\theta/d\psi)$, $\delta = \max(d\alpha_1/d\varphi)/\max(d\alpha/d\varphi) = \theta_{1m}g/p$.

Hence $b = (QF/RT)/(\partial\alpha_2/\partial\varphi)_{\alpha_1}$, $a = q/\theta_{1m}$, where $q = p[1 + (b/g)(\delta - 1)]$.

From experiment $p = 2.4$, $g = 3.6$, and $b/g = 2.7$. Since $\theta_{1m} = 1$, we have $\delta = 1.5$, $a = 5.6$ (close to $\Phi F/RT = 6$), and $b = 9.7$.

Thus, from (7)

$$\frac{d\theta_2}{d\psi} = \frac{1}{b} - \frac{a}{b}\frac{d\theta_1}{d\psi}, \quad \frac{d\theta}{d\psi} = \frac{1}{b} + \left(1 - \frac{a}{b}\right)\frac{d\theta_1}{d\psi}, \tag{8}$$

where the dependence of $d\theta_1/d\varphi$ on ψ is determined by eliminating θ_2 from the two equations (7). From (8) follow: 1) experimentally observed peak of the capacity $d\theta/d\psi$, after subtraction of the constant component, resembles the peak of $d\theta_1/d\psi$, which can thus be found from experiment; 2) a minimum in the capacity $d\theta_2/d\psi$ corresponds to the maximum in the capacity $d\theta_1/d\psi$, which is a consequence of the interruption of adsorption (Fig. 2).

At equilibrium $\partial\gamma/\partial\varepsilon \approx \partial\gamma/\partial\alpha$; from (3) $\partial\gamma/\partial\alpha = \partial\gamma/\partial\alpha_2 - [\partial\gamma/\partial\alpha_2 - \partial\gamma/\partial\alpha_1](d\theta_1/d\theta)$.

Knowing $\partial\gamma/\partial\alpha$ and $d\theta_1/d\theta$ from experiment, and assuming that in the interval Φ, $\partial\gamma/\partial\alpha_2$ is linear in θ_1 and θ_2 and, synonymously, in θ_1 and ψ, we calculate $\partial\gamma/\partial\alpha_1$ as a function of ψ (Fig. 2; $\psi = 0$ was chosen at $\varphi = +0.1$ V, in the point of max $d\theta_1/d\psi$). In each of the states H_m and H_e, the contribution of a newly adsorbed H atom to the decrease in γ (repulsion) increases with occupancy. The estance trough at +0.1 V reflects the minimum in $d\theta_2/d\psi$. The convergence of $\partial\gamma/\partial\alpha_1$ and $\partial\gamma/\partial\alpha_2$ towards the end of H_m occupancy explains the estance step at +0.04 V. The contributions of $\partial\gamma/\partial\alpha_1$ and $\partial\gamma/\partial\alpha_2$ are functions of α_1 and α_2, wherein $\partial(\partial\gamma/\partial\alpha_2)/\partial\alpha_1 = \partial(\partial\gamma/\partial\alpha_1)/\partial\alpha_2$. The asymmetry of the peak in $d\theta_1/d\psi$ (max $d\theta_1/d\psi$ is at $\theta_1 \approx 0.4$) indicates that ν_1 increases with θ_1 as θ_1^z, where $z > 1$.

Effect of the Internal Transition. Eliminating μ from the two equations (7) we find the isotherm for the internal transition

$$\nu_{21}(\theta_1, \theta - \theta_1; \psi) = \ln[\theta_1(2 - \theta + \theta_1)/(1 - \theta_1)(\theta - \theta_1)], \tag{9}$$

where $\theta = \theta_1 + \theta_2 = \text{const}$, $\nu_{21} = \nu_2 - \nu_1$. The internal capacity $\sigma(\psi) = (\partial\theta_1/\partial\psi)_\theta = -(\partial\theta_2/\partial\psi)_\theta$ as function of ψ (through θ_1) is:

$$\sigma(\psi) = (\partial\nu_{21}/\partial\psi)/[\partial\nu_{21}/\partial\theta_2 - \partial\nu_{21}/\partial\theta_1 + h + \theta_1^{-1}(1 - \theta_1)^{-1}], \tag{10}$$

where $h = 2\,\theta_2^{-1}(2-\theta_2)^{-1} \approx 2$; $\sigma(\psi) = \partial\alpha_1/\partial\varphi)_\alpha(RT/QF)$, $(\partial\alpha_1/\partial\varphi)_\alpha = (d\alpha_1/d\varphi)_{f\to\infty}$. The maxima in σ and $d\theta_1/d\psi$ are attained at different but rather close ψ. Therefore max $\sigma(\psi)$ can be calculated from the data for $\psi = 0$. By separation of Int γ_ε and Ext γ_ε (at 0.6 and 147 kHz) it was found for $\psi = 0$ that $(\partial\gamma/\partial\varphi)_\alpha = -0.16$ D $(d\varepsilon/d\varphi)_0$ and $(\partial\gamma/\partial\alpha)_\varphi = -0.21$ D, where D $= \partial\gamma/\partial\varepsilon$ (0.16 V) ≈ 0.7 V. From Fig. 2 at $\psi = 0$: $\partial\gamma/\partial\alpha_1 = 0.13$ D, $\partial\gamma/\partial\alpha_2 = 1.23$ D. Then from (6) for the height of the peak of the internal capacity: max $(\partial\alpha_1/\partial\varphi)_\alpha = 0.15$ max $(d\varepsilon/d\varphi)_0 \approx 1.7 \times 10^{-4}$ F/cm^2, and max $\sigma(\psi) = 0.04$.

The estance at the maximum near +0.16 V, which is here adopted as the conventional unit D, was found by thermal calibration [3]. Transition to the surface tension γ from its planar equivalent γ_0 is accomplished via the formula $\gamma = \gamma_0/\beta$, where $\beta = \partial\Omega/\partial\Omega_0$ is the differential roughness factor, Ω is the area of rough surface, Ω_0 is the area of the plane averaging it.

$$\beta = {}^1/_2[(1-\nu)\alpha + (1+\nu)\alpha^{-1}], \quad (11)$$

$\alpha = \Omega/\Omega_0$ is the roughness factor, and ν is the Poisson ratio of the electrode. The expenditure of energy on fast processes, observed here at +0.1 V (internal transition) and +0.2 V (chemisorption of water), causes an excess double-layer capacity C_{de} in the form of two separate peaks which do not vanish at $f > 200$ kHz. Near +0.1 V, $C_{de}(\varphi)$ is proportional to $\sigma(\varphi)$; $\varkappa \approx 0.04$ at +0.1 V.

LITERATURE CITED

1. A. N. Frumkin, in: Adv. Electrochem. Electrochem. Eng., Vol. 3, New York (1963), p. 287.
2. A. N. Frumkin, O. A. Petrii, and R. V. Marvet, J. Electroanal. Chem., 12, 504 (1966).
3. A. Ya. Gokhshtein, Élektrokhimiya, 6, 979 (1970); 7, 3 (1971); 2, 1318 (1966).
4. A. N. Frumkin, Z. Physik. Chem., 116, 466 (1925); Z. Physik, 35, 792 (1926).