THE EXCHANGE BETWEEN THE TWO TYPES OF ADSORBED HYDROGEN

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In [1] we discovered that, within the interphase, adsorbed H transfers quickly under the surface of a Pt electrode when the potential φ is changed. At $\varphi < 0.17$ V (rhe), increasing the H_2SO_4 concentration has no effect on the estance-potential curve [1] or the heat evolving during H adsorption ($T\Delta S < 1$ kcal/faraday, where ΔS is the entropy of adsorption, and T the temperature). These data imply: 1) At $\varphi < 0.17$ V, the mechanism of H adsorption is independent of water being adsorbed or not on the Pt. 2) The estance maximum at +0.24 V signifies the chemisorption of water during anodic shift of φ; the equilibrium-capacity maximum at +0.24 V signifies expulsion of adsorbed H by water. 3) The estance peak at +0.1 V is preserved at frequencies $f > 200$ kHz on account of the transfer of the H adsorbed upon the Pt surface (H_e, over each Pt atom) under it (H_m, inside the cube of the lattice, beneath every second Pt atom), and on account of the low value for the energy of activation of the exchange $H_e \rightleftharpoons H_m$. 4) The maximum coverages: $\max \Gamma_e = 2 \max \Gamma_m = 208\ \mu C/cm^2$, where Γ_e and Γ_m are the charge densities connected with H_e and H_m. 5) The adsorption of H_m is limited to an interval of 0.15 V, with the center of $\varphi = 0.1$ V. 6) In this interval, $\Gamma_e < 0.5 \max \Gamma_e$. 7) The minimum capacity $\partial\Gamma_e/\partial\varphi$ at the φ of maximum $\partial\Gamma_m/\partial\varphi$ is the result of the interaction between H_e and H_m, which is described by the isotherm $\varphi = \alpha\Gamma_m + \beta\Gamma_e$, where α and β are constants. 8) In each of the states, H_e and H_m, the repulsion between the H adatoms increases with coverage. 9) A varying part of $\partial\Gamma/\partial\varphi$ ($\Gamma = \Gamma_m + \Gamma_e$) is proportional to $\partial\Gamma_m/\partial\varphi$. 10) at +0.1 V and $f > 200$ kHz, the capacity of the internal transition $(\partial\Gamma_m/\partial\varphi)_\Gamma = -(\partial\Gamma_e/\partial\varphi)_\Gamma = 0.3\,(\partial\Gamma/\partial\varphi)_{f=0}$. 11) Because of the different contributions of H_e and H_m to the dipole potential drop χ, the transition $H_e \rightarrow H_m$ absorbs part (one-half at $f \rightarrow \infty$) of the increase in φ, lowering thus (by a factor of two) the rate of H^+ discharge and the equilibration rate constant k; $k(\varphi) = k_0[1-\psi_{em}\sigma(\varphi)]$, $\sigma(\varphi) = (\partial\Gamma_m/\partial\varphi)_\Gamma RT/F \max \Gamma_m$, $\psi_{em} = \varphi_{em}\ F/RT$, $\varphi_{em} \approx -0.2$ V being the change in χ, referred to $\max \Gamma_m$, during the transition $H_e \rightarrow H_m$. 12) $\sigma(\varphi) = b_0/[b_1 + \theta_m^{-1}(1-\theta_m)^{-1}]$, $\theta_m(\varphi) = \Gamma_m(\varphi)/\max \Gamma_m$; k_0, b_0, and b_1 being constants. 13) The energy consumption for the processes discovered here at 0.10 and 0.24 V causes an excess double-layer capacity C_{de} in the form of two peaks which do not disappear at $f > 200$ kHz; $C_{de}(\varphi) \propto \sigma(\varphi)$ around $\varphi = 0.1$ V. 14) $\partial\Gamma_e/\partial\varphi$ $(-0.1 < \varphi < 0) \approx \partial\Gamma_e/\partial\varphi$ $(\varphi = +0.2$ V).

LITERATURE CITED

1. A. Ya. Gokhshtein, Élektrokhimiya, 6, 979 (1970); 7, 3 (1971).

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