THE NONEQUILIBRIUM COMPONENT OF SURFACE TENSION

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In addition to the surface tension (S.T., γ) of solid bodies under conditions close to equilibrium, the method I have described previously [1] enables S.T. to be determined directly when nonequilibrium conditions exist, which is a matter of interest on its own. At a constant area of the interfacial boundary measurements are made of the oscillations of the S.T. of this boundary (Fig. 1) caused by oscillations of the potentials in the phases, basically (of the jump) of the electric potential (at the boundary) $\psi = \psi_m + \Delta\psi \exp i\omega t$ (Δ is the symbol of a low complex amplitude or increment and t is the time). The degree of deviation from equilibrium (between the layer and the phases) is regulated by: 1) the frequency ω of the oscillations; and 2) the rate of change $d\psi_m/dt$ of the mean potential ψ_m. In a sufficiently general case, the state of the interfacial layer is determined by the specific surface extensive parameters Γ_q (for example, the density of the adsorbed particles) and by the corresponding intensive parameters in the phase close to the boundary μ_q (chemical potential of the particles), $q = 1, \ldots, h$, $\mu_h = \psi$. The number a of independent Γ_q's may be less than h, for example, because of the condition of electroneutrality

$$\varepsilon + z_1\Gamma_1 + \ldots + z_{h-1}\Gamma_{h-1} = 0,$$

where z_q are the charges of the particles in the solution and ε is the charge imparted to the electrode. Let b of the h types of particles by adsorbed so rapidly that their Γ_g's ($g = h - b + 1, \ldots, h$) are determined by the remaining parameters and do not depend explicitly on t. Let us put $n = \min\{a, h - b\}$. Let us introduce three pairs of running indices: $r,\ q = 1, \ldots, h$; $s,\ p = 1, \ldots, n$; $f,\ g = h - b + 1, \ldots, h$. Subsequently, brackets [...] represent a column, row, or matrix if they contain, respectively: the first running index (r; s; f), the second (q; p; g), or both (s, p; s, q; ...); $[\Gamma_p]$ is the column $\{\Gamma_1, \ldots, \Gamma_n\}$; $[\partial\Gamma_s / \partial\mu_p]$; and $[\partial\Gamma_s / \partial\mu_q]$ are the matrices $n \times n$ and $n \times h$.

Surface kinetics. Let Γ_s be the mean stationary values ($\Delta\mu_q = 0$), Γ_{s0} be the stationary values that would become established at constant μ_q's equal to those that are realized at a given moment t in the process of oscillations ($\Delta\mu_q \neq 0$) and $\tilde{\Gamma}_s$ the true values at the given moment t. Let us find the change in Γ_s caused by a known change in μ_q with time. In the general case, $d\tilde{\Gamma}_s / dt = F_s([\tilde{\Gamma}_p], [\mu_q])$. Hence n of the equations for Γ_{s0} (and Γ_s): $F_s([\Gamma_{s0}], [\mu_q]) = 0$. At small values of $|\Gamma_{p0} - \tilde{\Gamma}_p|$ $[d\tilde{\Gamma}_s / dt] = [\partial F_s / \partial\Gamma_p][\Gamma_{p0} - \Gamma_p]$, or $[\partial\tilde{\Gamma}_s / \partial t] = [k_{sp}][\Gamma_{p0} - \tilde{\Gamma}_p]$, where $K = [k_{sp}]$ is the matrix of the surface kinetics, and $k_{sp} = \partial F_s/\partial\Gamma_p$ (the value of $\partial F_s/\partial\Gamma_p$ at $\tilde{\Gamma}_p = \Gamma_p$). Since $\Gamma_{s0}(\Gamma_s)$ depends only on μ_q, the given increment $[\Delta\mu_r]$ corresponds to $[\Delta\Gamma_{s0}] = [\partial\Gamma_{s0} / \partial\mu_q][\Delta\mu_r]' = [\partial\Gamma_s / \partial\mu_q][\Delta\mu_r]$. Because of the retardation of the establishment of the stationary state, the true increment $[\Delta\tilde{\Gamma}_s]$ differs from $[\Delta\Gamma_{s0}]$, $[\Delta\tilde{\Gamma}_s] = (I - A_\nu)[\Delta\Gamma_{s0}]$, where $I = [\delta_{sp}]$ is the unit matrix and $A_\nu = [\alpha_{sp}^\nu]$ is the matrix of the inequality corresponding to a definite (index ν) law of the change of μ_r with time, $\mu_r = \mu_{rm} + \Delta\mu_r^\nu f_\nu(t - t_r)$. A_ν is expressed in terms of K. For periodic $\mu_r = \mu_{rm} + \Delta\mu_r^\omega$ $\exp i\omega t$, hence: $\Gamma_{s0} = \Gamma_s + \Delta\Gamma_{s0} \exp i\omega t$, $\tilde{\Gamma}_s = \Gamma_s + \Delta\tilde{\Gamma}_s \exp i\omega t$, $d\tilde{\Gamma}_s / dt = i\omega\Delta\tilde{\Gamma}_s \exp i\omega t$; $i\omega[\Delta\tilde{\Gamma}_s] = [k_{sp}]([\Delta\Gamma_{s0}] - [\Delta\tilde{\Gamma}_s])$. Hence $[\Delta\tilde{\Gamma}_s] = (i\omega[\delta_{sp}] + [k_{sp}])^{-1}[k_{sp}][\Delta\Gamma_{s0}]$. Thus,

$$A_\omega = [\alpha_{sp}^\omega] = I - (i\omega I + K)^{-1}K. \tag{1}$$

For example, at n = 2, (I) is equivalent to the following:

$$\begin{aligned} \alpha_{11}^\omega &= (\omega^2 - i\omega k_{22}) / [\omega^2 - k_{11}k_{22} + k_{12}k_{21} - i\omega(k_{11} + k_{22})], \\ \alpha_{12}^\omega &= i\omega k_{12} / [\omega^2 - k_{11}k_{22} + k_{12}k_{21} - i\omega(k_{11} + k_{22})], \\ \alpha_{21}^\omega &= i\omega k_{21} / [\omega^2 - k_{11}k_{22} + k_{12}k_{21} - i\omega(k_{11} + k_{22})], \\ \alpha_{22}^\omega &= (\omega^2 - i\omega k_{11}) / [\omega^2 - k_{11}k_{22} + k_{12}k_{21} - i\omega(k_{11} + k_{22})]. \end{aligned} \tag{2}$$

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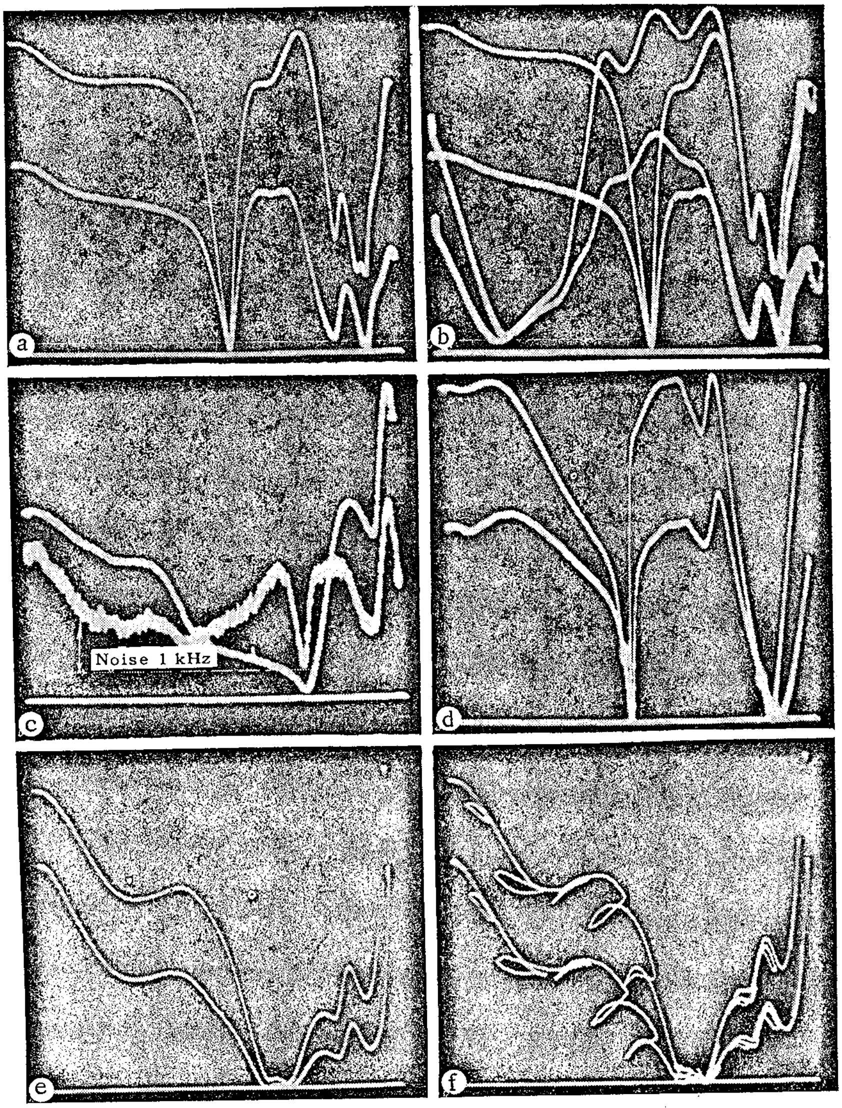

Fig. 1. Oscillograms of the amplitude $|\Delta\gamma|$ of the surface tension of a solid electrode versus the potential ψ_m for smooth platinum, iridium, and palladium electrodes taken simultaneously performs vibrations with the two frequencies; the two beams move simultaneously: the upper one (in the sequence on the left) at 5 kHz and the lower one at 1 kHz; the zero line is shown below the curves); $\Delta\psi$ is superposed by applying an alternating current with an amplitude of 0.01 A/cm^2 at 1 kHz and 0.05 A/cm^2 at 5 kHz; ψ_m on the SHE scale, on the left the more anodic values; the dimensions of the working part of the electrode in mm were: 8 × 4 × 0.35 (Pt), 6 × 2 × 0.10 (Ir), and 8 times 4 × 0.50 (Pd); treatment of the electrodes before the experiment – a succession of pulses ψ_m in the range studied; maximum values of $|\Delta\gamma|$ of the order of 1 dyne/cm. a) Pt in 1 N H_2SO_4, ψ_m varies (from left to right) from +1.38 to −0.02 V, time at the initial ψ_m: $\tau_0 = 40$ sec (this affects ψ_m of the oxygen zero near +0.06 V), $|d\psi_m/dt| = 0.04$ V/sec, scale at 5 kHz 1.7 times greater than at 1 kHz; b) Pt in 1 N H_2SO_4, ψ_m from +1.38 to −0.02 V and then back again, $\tau_0 = 60$ sec, $|d\psi_m/dt| = 0.04$ V/sec; c) Ir in 1 N H_2SO_4, ψ_m from +1.23 to −0.02 V, $\tau_0 = 30$ sec, $|d\psi_m/dt| = 0.03$ V/sec; d) Pd in 1 N Na_2SO_4 + 0.01 N H_2SO_4, ψ_m from +1.31 to −0.25 V, $\tau_0 = 23$ sec, $|d\psi_m/dt| = 0.07$ V/sec; f) Pt in 1 N KCl, pH = 5, $\tau_0 = 23$ sec $|d\psi_m/dt| = 0.07$ V/sec, ψ_m varies from +0.74 to −0.50 V in zigzag fashion in order to determine the degree of reversibility of the system at any value of ψ_m large loops on the left the result of the irreversible elimination of adsorbed oxygen, 25°C.

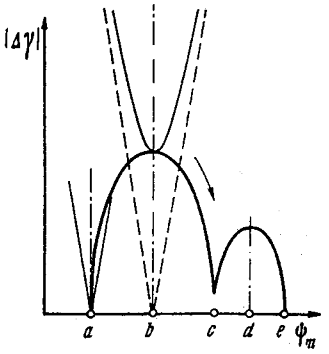

Fig. 2. Trajectory described by the zero of the relationship $|\Delta\gamma|$ versus ψ_m with an increase in ω. Case of the slow adsorption of two types of particles with $k_{11}(\psi m) << k_{22}(\psi m)$; the points marked off on the ψm axis correspond to: $\omega a/k_{11}(\psi ma) << 1$, $\omega b \approx k_{11}(\psi mb)$. $I << \omega c/k_{11}(\psi mc) >> \omega c/k_{22}(\psi mc) << 1$, $\omega d \approx k_{22}(\psi md)$, $\omega e/k_{22}(\psi me) >> 1$.

At $n = 1$ $(k_{11} = k,\ \alpha_{11} = \alpha)$ $\alpha = i/[i + (k/\omega)]$. For linear $\mu_r = \mu_{r0} + (\Delta\mu_r^{\tau}/\tau)t$, $t \leqslant \tau$: $A_\tau = [I - \exp(\tau K)](\tau K)^{-1}$. Thus, $[\Delta\widetilde{\Gamma}_s] - [\Delta\widetilde{\Gamma}_{s0}] = -[\alpha_{sp}^{\nu}][\partial\Gamma_s/\partial\mu_q][\Delta\mu_r^{\nu}]$.

Amplitude of the surface tension as a function of the frequency. A constant interfacial layer $\{[\Gamma_p], [\mu_q]\}$ corresponds to $\gamma = \gamma([\Gamma_p], [\mu_q])$. An increment (amplitude) $|\Delta\mu_q^{\nu}|$ leads to an increment (amplitude) $\Delta\gamma = [\partial\gamma/\partial\Gamma_p][\Delta\widetilde{\Gamma}_s] + [\partial\gamma/\partial\mu_q][\Delta\mu^{\nu}]$. Under ordinary conditions $\Delta\gamma_0 = [\partial\gamma/\partial\Gamma_p][\Delta\Gamma_{s0}] + [\partial\gamma/\partial\mu_q][\Delta\mu_r^{\nu}]$. Thus, the nonequilibrium component of the S.T. $\Delta\gamma_n = \Delta\gamma - \Delta\gamma_0 = [\partial\gamma/\partial\Gamma_p]([\Delta\widetilde{\Gamma}_s] - [\Delta\Gamma_{s0}])$, or

$$\Delta\gamma_n = -[\partial\gamma/\partial\Gamma_p][\alpha_{sp}^{\nu}][\partial\Gamma_s/\partial\mu_q][\Delta\mu_r^{\nu}]. \tag{3}$$

From $\Delta\gamma = \Delta\gamma_0 + \Delta\gamma_n$ and Eq. (3), we obtain

$$\Delta\gamma(\omega) = \Delta\gamma_0 + \sum_{s,p}\alpha_{sp}^{\omega}(\omega)\Delta\chi_{sp}, \tag{4}$$

where $\Delta\gamma_0$ and $\Delta\chi_{sp}$ are material linear functions of the magnitudes $\partial\gamma/\partial\Gamma_p$, $\partial\Gamma_s/\partial\mu_q$, $\Delta\mu_r^{\omega}$ and do not depend on ω. It follows from Eqs. (1) and (4) that $\Delta\gamma(\infty) = \Delta\gamma_0 + \Delta\chi_{11} + \Delta\chi_{22} + \ldots + \Delta\chi_{nn}$.

Case of surface tension independent of the potentials of the slowly adsorbed particles. Let n = 1: of the solutes, only one (Γ, μ, z) is slowly adsorbed onto the electrode. Then γ is unambiguously determined by three independent parameters, $\gamma = \gamma(\Gamma, \mu, \psi)$. The other parameters are constant or are given by these three, for example, $\varepsilon = \varepsilon(\Gamma, \mu, \psi)$. The properties of the function $\gamma(\Gamma, \mu, \psi)$ also appear in the conditions of equilibrium when the Gibbs equation is valid, $\Delta\gamma_e = -\varepsilon\Delta\psi - \Gamma\Delta\mu$. Can it be used to determine the derivatives in the expansion of $\Delta\gamma = (\partial\gamma/\partial\Gamma)_{\mu,\psi}\Delta\widetilde{\Gamma} + (\partial\gamma/\partial\mu)_{\Gamma,\psi}\Delta\mu + (\partial\gamma/\partial\psi)_{\Gamma,\mu}\Delta\psi$? No, because $(\partial\gamma/\partial\Gamma)_{\mu,\psi}$ is taken at μ = const and ψ = const, while at equilibrium Γ cannot change if both μ and ψ are constants. If, however, γ does not then depend on μ, $\gamma = \gamma(\Gamma, \psi)$, the position changes – in the expansion of $\Delta\gamma = (\partial\gamma/\partial\Gamma)_{\psi}\Delta\widetilde{\Gamma} + (\partial\gamma/\partial\psi)_{\Gamma}\Delta\psi$ the derivatives can be calculated from the Gibbs equation: $(\partial\gamma/\partial\Gamma)_{\psi} = (\partial\gamma_e/\partial\Gamma)_{\psi} = \Gamma/(\partial\Gamma/\partial\mu)_e$ with given values of μ and ψ, while for equilibrium (index e) the function $\Gamma = \Gamma_e(\mu, \psi)$ is known. If the stationary state is the equilibrium state and of μ and ψ, only ψ varies, then, taking Eqs. (1) and (3) into account, at n = 1 we can write

$$\Delta\gamma(\omega) = \left[-\varepsilon + \Gamma\left(\frac{\partial\Gamma}{\partial\psi}\Big/\frac{\partial\Gamma}{\partial\mu}\right)\frac{\omega}{\sqrt{\omega^2 + k^2}}e^{i\arctan(k/\omega)}\right]\Delta\psi. \tag{5}$$

Cases where γ does not depend on μ are widespread: the specific adsorption of molecules and also of ions if the content of the latter in the diffuse part of the interfacial layer is far lower than in the bulk.

As n > 1, $\Delta\gamma = \gamma([\Gamma_p + \Delta\widetilde{\Gamma}_p], [\mu_g + \Delta\mu_g]) - \gamma([\Gamma_p], [\mu_g])$, where the values of $\Delta\mu_g$ are given and those of $\Delta\widetilde{\Gamma}_p$ are defined above. Let us find the values of $\delta\mu_p$ by which μ_p should change under equilibrium conditions for μ_g to change from Γ_p to $\Gamma_p + \Delta\widetilde{\Gamma}_p$ at given increments. Let us substitute the values of $\delta\mu_p$ found in the Gibbs equation and obtain a result which must coincide with the value of $\Delta\gamma$ sought. To determine $\delta\mu_p$ there are exactly n equations (s, p = 1, ..., n):

$$\left(\frac{\partial\Gamma_s}{\partial\mu_1}\right)_e\delta\mu_1 + \ldots + \left(\frac{\partial\Gamma_s}{\partial\mu_n}\right)_e\delta\mu_n + \left(\frac{\partial\Gamma_s}{\partial\mu_{h-b+1}}\right)_e\Delta\mu_{h-b+1} + \ldots + \left(\frac{\partial\Gamma_s}{\partial\mu_h}\right)_e\Delta\mu_h = \Delta\widetilde{\Gamma}_s. \tag{6}$$

However, since the increments of all the arguments γ are predetermined, to exclude contradictions, none of $\mu_1, \ldots, \mu_n$ (or any of the n potentials upon which $\Gamma_1, \ldots, \Gamma_n$ depend) can be present among the arguments of γ. This naturally eliminates the case in which the composition of the interfacial layer is independent of n or more potentials. It follows from the definition of n that this case is actually realized if the state does not depend on the potentials of the slowly adsorbed particles. Finally,

$$\Delta\gamma_n^{\nu} = [\Gamma_p][\partial\Gamma_s/\partial\mu_p]_e^{-1}[\alpha_{sp}^{\nu}][\partial\Gamma_s/\partial\mu_q][\Delta\mu_r^{\nu}]. \tag{7}$$

If the stationary state is a nonequilibrium state, $[\Gamma_p]$ and $[\partial\Gamma_s/\partial\mu_q]$ are taken at the given stationary state and $[\partial\Gamma_s/\partial\mu_p]_e$ - at the equilibrium state with given values of Γ_p and μ_g (which can be done by selecting μ_p). If.

however, the stationary state is an equilibrium state, the index e in Eqs. (6) and (7) is omitted. A state of non-equilibrium within the phase (diffusion) is taken into consideration by calculating $\Delta \mu_r^{\nu}$ and substituting the values found in Eqs. (3) and (7) in [1].

The adsorption-potential-determining particles. Equations (3) and (5) are valid. At $n = 1$, the simplified Eq. (5) is true here only at $\omega = \infty$, which is necessary for μ to be constant when ψ changes; the function $\Gamma = \Gamma_e(\mu, \psi)$ remains meaningful (although its calculation from experimental results becomes more complicated): the equality $\mu = -z\psi$ at equilibrium, maintained here automatically, can also be maintained (artificially) for particles with μ not connected by a natural relationship with ψ. In the general case, $\partial\Gamma / \partial\psi \neq -z(\partial\Gamma / \partial\mu)$, which does not contradict $\mu = -z\psi$. Consequently, in general $\Delta\gamma(\infty) \neq -(\varepsilon + z\Gamma)\Delta\psi$. Following Frumkin, the magnitude $\varepsilon + z\Gamma$ can be regarded as the free charge of the electrode, which is responsible for the electrostatic adsorption.

Trajectories of the zeros. With an increase in ω the displacement of the zeros (minima of $|\Delta\gamma|$ in the neighborhood of the points $\mathrm{Re}\Delta\gamma = 0$) takes place by means of their rising above the ψm axis (Fig. 2). In the case of Ir, there is a zero in the double-layer region of ψ at +0.31 V, which shows the equilibrium nature of this system.

The curves for platinized Pt are similar. However, on smooth Pt in the hydrogen region the equilibrium is disturbed if the initial potential exceeds 1 V (Fig. 1a, b).

LITERATURE CITED

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