LETTERS TO THE EDITOR

EQUATION FOR NONEQUILIBRIUM SURFACE TENSION COMPONENTS

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The constant area and the variable frequency (ω) in the measurement process make the method of [1] useful for the study of surface tension (γ) at any deviation from equilibrium, independent of frequency. Let Γ_q be the equilibrium specific surface extensive parameters (for example, the density of adsorbed particles), and μ_q be the corresponding intensive parameters in the phases near their boundaries (the chemical potentials of the particles). Let [. . .] denote a row, column, or matrix (m by m or m by h), depending on whether it encloses either one of the indices p(q) or s(r), or both of them – p(q) and s(r); r, q = 1, . . . , h; s, p = 1, . . . , m: $[\Gamma_q] = \{\Gamma_1, \ldots, \Gamma_h\}$ is a row. The Gibbs equation becomes $\Delta\gamma_0 = [\Gamma_q][\Delta\mu_r]$. Let m of the Γ_q be independent, m ≤ h. If Γ_s are the nonequilibrium values of the parameters, then at small $|\Gamma_s - \tilde{\Gamma}_s|$, $[d\tilde{\Gamma}_s / dt] = [k_{sp}][\Gamma_s - \tilde{\Gamma}_s]$ is valid. The surface kinetics matrix $K = [k_{sp}]$ characterizes the rates of adsorption and conversion in the interphase layer.

I. Systems in which $\gamma = \gamma([\Gamma_p])$. Under nonequilibrium conditions, to small increments (complex amplitudes) in $\Delta\mu_r^{\nu}$ accomplished over a time t according to the relation $\mu_r = \mu_{ro} + \Delta\mu_r^{\nu} f_{\nu}(t - t_r)$, corresponds $\Delta\gamma^{\nu} = \Delta\gamma_o^{\nu} + \Delta\gamma_n^{\nu}$,

$$\Delta\gamma_n^{\nu} = [\Gamma_p][\partial\Gamma_s / \partial\mu_p]^{-1}[a_{sp}^{\nu}][\partial\Gamma_s / \partial\mu_q][\Delta\mu_r^{\nu}], \tag{1}$$

$A^{\nu} = [\ _{sp}^{\nu}]$ is the nonequilibrium matrix. For $\mu_r = \mu_{ro} + \Delta\mu_r^{\omega} \exp i\omega t$,

$$[a_{sp}^{\omega}] = A^{\omega} = I - (i\omega I + K)^{-1} K, \tag{2}$$

where I is the unit matrix. For h = m + 1: $[\Gamma_p][\partial\Gamma_s / \partial\mu_p]^{-1}[\partial\Gamma_s / \partial\mu_h] - \Gamma_h = 0$.

II. Systems in which $\gamma = \gamma([\mu_q], [\Gamma_p])$. Example. Let the solution consist of one surface-active substance $\Gamma_1 = \Gamma$, $\mu_1 = \mu$, $d\Gamma / dt = k[\Gamma - \tilde{\Gamma}]$) and let the rest of the electrolyte be of any composition. If ε and ψ are the charge and potential of the electrode ($\varepsilon + z_1\Gamma_1 + \ldots + z_m\Gamma_m = 0$, where z_s are the charges of the particles in the solution) and $\psi = \psi_0 + \Delta\psi \exp i\omega t$, then for a given ψ_0,

$$\Delta\gamma^{\omega} = \Delta\gamma_0^{\omega} + \Delta\gamma_n^{\omega} = \left[-\varepsilon + \Gamma\left(\frac{\partial\Gamma}{\partial\psi} \Big/ \frac{\partial\Gamma}{\partial\mu}\right) \frac{\omega}{\sqrt{\omega^2 + k^2}}\, e^{i \operatorname{arctg}(k/\omega)}\right]\Delta\psi. \tag{3}$$

If the diffusion rate of particles for which s = 1 is also important (coefficient D and concentration c in the solution), then

$$\Delta\gamma^{\omega} = \left[-\varepsilon + \Gamma\left(\frac{\partial\Gamma}{\partial\psi} \Big/ \frac{\partial\Gamma}{\partial\mu}\right) \frac{(\lambda + \varkappa)^2 + \varkappa(1 + \varkappa) + i(\lambda + \varkappa)}{(\lambda + \varkappa)^2 + (1 + \varkappa)^2}\right]\Delta\psi, \tag{4}$$

$\lambda = \omega/k$, and $\varkappa = (\partial\Gamma / \partial c)\sqrt{\omega / 2D}$. From Eqs. (1)-(4) it follows that with an increase in $|\Delta\gamma|$ the displacement of the zero (minimum) of the curve ψ_0 from one point on the zero line to another occurs by a rise over the zero line at intermediate values of ω. This is actually observed (Pt in 1 N H_2SO_4, a sharp rise of the zeros +0.21, +0.10, and +0.08 V NHE during the transition from 1 to 5 kHz; oscillograms of $|\Delta\gamma| - \psi_o$ were recorded simultaneously at both frequencies).

LITERATURE CITED

1. A. Ya. Gokhshtein, Zavod. Lab., 32, 815 (1966); Élektrokhimiya, 2, 1318 (1966); Dokl. Akad. Nauk SSSR, 174, 394 (1967); Fiz. i Tekh. Poluprov., 1, 1486, 1787 (1967).

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