CHANGES IN SURFACE TENSION IN NONEQUILIBRIUM CONDITIONS

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The author discusses the laws characterizing surface tension during deviation from equilibrium between phases and the layers separating them. In the general case, the change in surface tension is not proportional to the change in surface free energy. The author gives oscillograms of the "surface tension amplitude" versus the mean potential for Pt and Ir in 1 N H_2SO_4.

As well as direct experimental investigation of surface tension (ST, γ) of solids by the methods in [1-3], we can also use a different approach to study ST when there is disequilibrium between the phases and the layers separating them. We measure the amplitude and phase of ST oscillations generated by oscillations of ψ, the potential drop at the phase boundary. The degree of deviation from equilibrium increases with the frequency ω of oscillation of ψ and with $d\psi_m/dt$, the rate of change of the mean value ψ_m. Information on surface tension phenomena obtained in this way is wider in scope than that given by measurements made only at equilibrium. In order to interpret it, we must elucidate how the laws governing ST in equilibrium conditions change when we deviate from equilibrium.

Internal Energy of Interphase Layer As a Source of Surface Tension Work in Nonequilibrium Conditions. By "interphase layer" I shall denote a spatial formation, at the boundary between two phases, which is not itself a phase, i.e., which is of nonuniform composition in one direction (perpendicular to the layer) and which has nonuniform distribution of opposite charges. The ST is determined by the state of the interphase layer. Deviations from equilibrium in a system of phases can be expressed as disturbance of equilibrium between the layer and the phases, or as disturbance of equilibrium within the phases. Both processes may occur together. The fact that these processes are physically different and spatially separated gives us grounds for analyzing each of them separately, regarding the other as an external condition. The features of nonequilibrium ST, in particular the inapplicability of Gibbs' equation, are due to disturbance of equilibrium between the layer and the phases. In all cases the ST is the force acting per unit length of the contour bounding any region of the interphase surface, and directed tangentially to the surface along the internal normal to the contour [4]. The ST force can always be defined as the ratio of the infinitely small mechanical work done by the interphase layer on an infinitely small displacement of the contour to the area swept out by the contour in its displacement.

The change in the intersurface effected by the ST in counteracting the internal forces can be represented as the sum of two processes: 1) the change in area due only to the change of the internal energy of the layer as if there were no exchange of energy between the layer and the phases (as a result of this, the ST itself changes somewhat); 2) the gradual restoration of the original values of the relative internal energy and other parameters of the layer owing to exchange with the phases. In equilibrium conditions, i.e., for sufficiently slow surface changes, the second process scarcely lags behind the first, and therefore the ST is practically constant for any finite increment of the surface. This is used in the derivation of Gibbs' equation. If equilibrium is absent (which in the simplest case is equivalent to the absence of the second process), then the first process goes on just the same—the ST executes work in displacing the boundary surface—but only at the expense of the free energy of the layer, which is only enough for a very small displacement. The ST itself will change during the displacement, and its value after the displacement may be quite different from that before the displacement: in nonequilibrium conditions, information is lost during the displacement.

Condition of Constancy of Interface Area. Information can be retained by securing constancy of the interphase boundary area. The "constant area" condition, like the equilibrium condition, is ideal. In an experiment it is sufficient to satisfy it to a given degree of accuracy. For example, if the ST changes by 1 dyn/cm owing to elastic deformation in the interphase layer 10^{-6} cm thick, then this change in tension can be measured only if during the measurement the surface area is constant to within 10^{-7}, because the relative deformation causing the tension is about 10^{-6}. In research on ST by the methods in [1-3], the area was kept constant to within 10^{-11}. This would suffice

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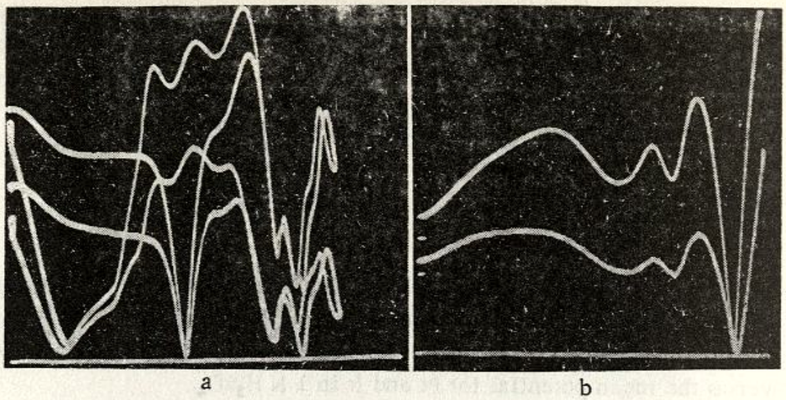

Fig. 1. Surface tension amplitude $|\Delta\gamma|$ of platinum versus potential ψ_m, recorded simultaneously for two frequencies. The electrode oscillates simultaneously with frequencies 5 kHz (upper trace) and 1 kHz (lower trace); zero line is below; $\Delta\psi$ is superimposed by feeding ac with amplitude of 0.01 A/cm^2 at 1 kHz and 0.05 A/cm^2 at 5 kHz; 25°C; ψ_m rel. to NHE. To the left: anode values of over-meniscus electrode [1] sized 8 × 4 × 0.35 mm: a) Pt in 1 N H_2SO_4, ψ_m varies at first from +1.38 to −0.07 V (left to right), then in the reverse direction, $|d\psi_m/dt| = 0.08$ V/sec, retention at initial ψ_m $\tau_0 = 50$ sec; scale of $|\Delta\gamma|$ at 5 kHz 1.6 times larger than at 1 kHz; b) Pt in 1 N KI, pH = 5; ψ_m: from −0.16 to −0.71 V, $|d\psi_m/dt| = 0.01$ V/sec, $\tau_0 = 20$ sec.

to register any nonequilibrium changes in ST. The methods usually used to measure ST in liquids cannot in general be used to make measurements in nonequilibrium conditions—they allow too much change in the interface area during the measurements and the apparatus has marked inertia. Nevertheless, even in the case of an interface between liquid phases it is in principle possible to measure ST at constant area. This could, for example, be achieved by measuring the variable pressure inside a dropping mercury electrode, with small dimensions so as to ensure sphericity (or freely falling under gravity together with the solution), or by applying the methods of [1-3] to a liquid electrode [1] at sufficiently high frequencies.

Disproportion between Tension and Surface Free Energy. In nonequilibrium conditions at constant interface area, the change in ST may be incomparably greater than the change in surface free energy. An example is the interface in a single-crystal semiconductor which forms a p−n junction. Here the nonequilibrium is due to the fact that not all the elements of the interphase layer take part in exchange with the phases—a circumstance which is important when the whole interphase layer (or most of it) is in the solid state. In the simplest case, when we can neglect the piezoelectric and electrostrictive effects and regard the semiconductor as mechanically isotropic, the ST amplitude of the p−n junction is made up of two components [2]: $\Delta\gamma = \Delta\bar{\gamma} + \Delta\bar{\bar{\gamma}}$; $\Delta\bar{\gamma} = -(\varepsilon/2)\Delta\psi$, $\Delta\bar{\bar{\gamma}} = -(\varepsilon/2)[\sigma/(1-\sigma)]\Delta\psi$. Here ε is the charge on one face of the interphase layer, and σ is Poisson's ratio; $\Delta\bar{\gamma}$ is due to repulsion between like electric charges in a direction parallel to the p−n junction layer, and $\Delta\bar{\bar{\gamma}}$ is due to transverse mechanical stresses arising by unidirectional compression of the layer in a direction perpendicular to the layer. The components $\bar{\gamma}$ and $\bar{\bar{\gamma}}$ and their sum γ correspond to $\bar{A}$, the energy expended on charging the interphase layer, $\bar{\bar{A}}$, the energy expended on elastic deformation of the layer, and $A = \bar{A} + \bar{\bar{A}}$.

Assuming small deformations, we get $\Delta A = (\psi + \text{const})d\varepsilon$,

$$\Delta\bar{\bar{A}} = [\pi(1+\sigma)(1-2\sigma)/D(1-\sigma)](\varepsilon^2/Y)(\psi + \text{const})\,d\varepsilon,$$

where Y is the modulus of elasticity and D the dielectric constant in the layer. Let us compare the ratios $\Delta\bar{\bar{\gamma}}/\Delta\bar{\gamma} = \sigma/(1-\sigma)$ and

$$\Delta\bar{\bar{A}}/\Delta\bar{A} = [\pi(1+\sigma)(1-2\sigma)/D(1-\sigma)](\varepsilon^2/Y).$$

Since $\sigma \approx 0.2$-0.3 and $D \approx 10$, $\Delta\bar{\bar{\gamma}}/\Delta\bar{\gamma}$ is of the order 1 and $\Delta\bar{\bar{A}}/\Delta\bar{A}$ is of order ε^2/Y. If the p−n junction is 1μ thick and the acceptor concentration is $10^{16}/\text{cm}^{-3}$, $\varepsilon = -1.6 \cdot 10^{-7}$ C/cm^2 $= -4.8 \cdot 10^2$ esu/cm^2. In the conditions of [2], $Y \approx 0.8 \cdot 10^{12}$ dyn/cm^2. Hence $\varepsilon^2/Y = 3 \cdot 10^{-7}$, i.e., the ratios $\Delta\bar{\bar{\gamma}}/\Delta\bar{\gamma}$ and $\Delta\bar{\bar{A}}/\Delta\bar{A}$ differ by seven orders of magnitude. Thus, if we select two specimen p−n junctions differing in mechanical characteristics

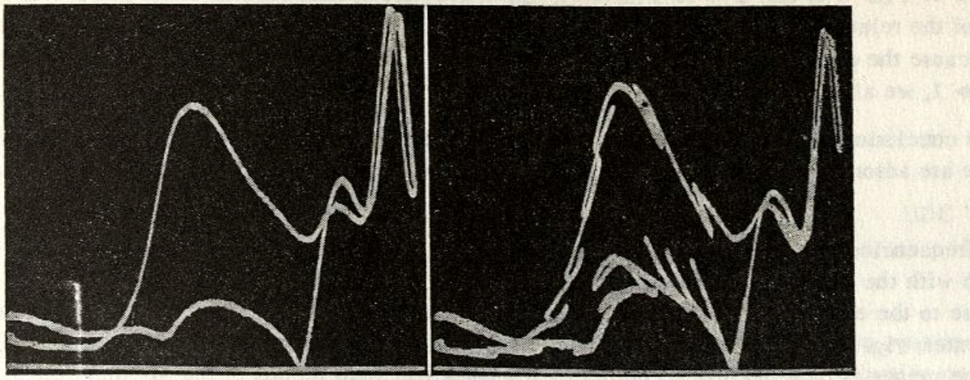

Fig. 2. $|\Delta\gamma|$ versus ψ_m for iridium in 1 N H_2SO_4, frequency 1 kHz. $\Delta\psi$: amplitude of imposed current 0.02 A/cm²; 25°C; ψ_m rel. to NHE, $|d\psi_m/dt|$ = 0.07 V/sec, τ_0 = 60 sec; over-meniscus electrode 9 × 2 × 0.10 mm: a) ψ varies linearly from + 1.18 to − 0.04 V (left to right), then in the reverse direction; b) the same, but ψ_m varies in a zigzag fashion so as to reveal the degree of reversibility of the system for any ψ_m as the latter changes; from (b) we see that the difference between the forward and reverse curves near +0.31 V (rise from zero on reverse curve) occurs only after ψ_m has made an excursion into the hydrogen adsorption region.

(even if only in σ), we may get markedly different $\Delta\gamma$ values with practically the same ΔA (which coincides quite accurately with $\Delta\overline{A}$) and the same electrical capacitance C. In a more complex-structured nonequilibrium interphase layer the mechanical characteristics (strictly speaking their analogs) will depend on the potential ψ. In a given range of ψ they may in principle vary, and hence the ST may vary, even if there are no appreciable changes in the free energy and capacitance of the layer in the same range of ψ. This must be taken into account in comparing $\gamma-\psi$ curves with $A-\psi$ and $C-\psi$ curves.

Surface Tension Amplitude. Equilibrium between the layer and the phases will be disturbed if the rate of change of potential by some $\Delta\psi$ becomes so high that the state of the layer cannot change as much as it does for the same $\Delta\psi$ in equilibrium conditions. Can we say of the ST that, if for slow $\Delta\psi$ the change in ST is $|\Delta\gamma_0|$, for rapid $\Delta\psi$ the ST will not be able to change by $|\Delta\gamma_0|$ and will change by a smaller amount, $|\Delta\gamma| < |\Delta\gamma_0|$? Calculations show that this is not so: according to the conditions, $|\Delta\gamma| < |\Delta\gamma_0|$ and $|\Delta\gamma| > |\Delta\gamma_0|$ are equally possible. Suppose, for example, that only one surface-active substance is slowly adsorbed from the electrolyte on to the electrode, with chemical potential μ in the solution near the electrode, and surface density Γ on the electrode-solution interface. Suppose that the steady state is equilibrial. If μ = const (the case when diffusion in the solution is not limiting) and if ψ is periodic with low amplitude $\Delta\psi$ [$\psi = \psi_m + \Delta\psi \exp(i\omega t)$], the complex amplitude $\Delta\gamma$ will be [3]

$$\Delta\gamma(\omega) = \left[-\varepsilon + \Gamma\left(\frac{\partial\Gamma}{\partial\psi} \Big/ \frac{\partial\Gamma}{\partial\mu}\right)\frac{\omega}{\sqrt{\omega^2+k^2}}\, e^{i\,\mathrm{arctg}(k/\omega)}\right]\Delta\psi, \tag{1}$$

where $k = k(\psi_m)$ is a kinetic constant which indicates the rate of approach of the nonequilibrium value $\tilde{\Gamma}$ to the equilibrium value Γ for a given ψ_m, $d\tilde{\Gamma}/dt = k(\Gamma - \tilde{\Gamma})$. The equilibrium $\Delta\gamma_0 = \Delta\gamma(0) = -\varepsilon\Delta\gamma$; the limiting nonequilibrium $\Delta\gamma(\infty) = \{-\varepsilon + \Gamma[(\partial\Gamma/\partial\psi)/(\partial\Gamma/\partial\mu)]\}\Delta\psi$. Since always $\partial\Gamma/\partial\mu > 0$ and $\Gamma > 0$, it depends on the sign of $\partial\Gamma/\partial\psi$ whether $|\Delta\gamma(\infty)| < |\Delta\gamma(0)|$ or $|\Delta\gamma(\infty)| > |\Delta\gamma(0)|$. We know [5] that many surface-active substances, in particular high-atomic alcohols, are adsorbed in a limited range of potentials ψ, including the zero charge point, i.e., the value ψ_0 at which $\varepsilon = 0$ and the sign of ε are different in either side, $\varepsilon'(\psi_0) > 0$. This means that on both sides of ψ_0, possibly at some distance from it, are regions of desorption in which the sign of $\partial\Gamma/\partial\psi$ is opposite to the sign of ε. From (1) it follows that in these regions $|\Delta\gamma(\infty)| > |\Delta\gamma(0)|$. This "less natural" inequality is apparently more often found.

Together with the modulus of the complex amplitude $|\Delta\gamma|$ we experimentally measured [1] the phase γ, equal to arg $\Delta\gamma$. By (1), the phases γ are the same when $\omega = 0$ and $\omega = \infty$: $\Delta\gamma(0)$ and $\Delta\gamma(\infty)$ are real quantities.

When $\omega / k \ll 1$ ($\omega \approx 0$) and $\omega / k \gg 1$ ($\omega \approx \infty$), $\Delta\gamma$ is practically independent of frequency. Experimental investigations of the relation between $\Delta\gamma$ and ω always begin with $\omega_0 > 0$ (measurements cannot be performed at $\omega = 0$, because the duration of the experiment cannot be much shorter than the period, $2\pi/\omega$, which is infinite). If $\omega_0/k \gg 1$, we already have $\Delta\gamma(\omega_0) \approx \Delta\gamma(\infty)$.

The conclusions here drawn as consequences of (1) remain valid in the more general case when several types of particle are adsorbed simultaneously, both the kinetics and diffusion are slow, and the stationary state is nonequilibrial [3].

At frequencies between 1 and 5 kHz, $\Delta\gamma$ is close to the limiting nonequilibrial value, and therefore does not vary much with the frequency in the systems Pt in 1 N H_2SO_4 at $\psi_m > 0.8$ V (Fig. 1a, left), Pt in 1 N KI (Fig. 1b); $\Delta\gamma$ is close to the equilibrial value at 1 kHz for Ir in 1 N H_2SO_4 for $0.2 < \psi_m < 0.4$ V (the double-layer potential region, center, Fig. 2). Before each experiment the electrodes were treated in the solution by repeated ψ_m pulses in the same ranges as those used in recording the oscillograms. For metals of the platinum group—Pt, Ir, Pd, Rh (all smooth specimens)—the curves of $|\Delta\gamma|$ versus ψ_m are very similar to each other. For Pt and Ir in 1 N H_2SO_4, as ψ_m changes in the range limited by evolution of O_2 and H_2, the phase γ changes four times by π. The minima of $|\Delta\gamma|$, near which this happens, we shall call zeros (near them Re γ passes through zero). For movement in the cathode direction (left to right in Figs. 1a, 2a), the zeros are as follows: The first is the oxygen zero, due to nonequilibrium recording of adsorbed oxygen (1-5 kHz: ≈ 0.6 V for Pt and ≈ 0.7 V for Ir; ψ_m of the zero depends on the initial ψ_m at which oxidation occurs, and on the oxidation time). The second zero occurs on transition from the double-layer to the hydrogen region of ψ_m (1 kHz: 0.22 V for Pt, 0.31 V for Ir). The third and fourth are double zeros in the hydrogen region (5 kHz: + 0.10 V and +0.08 V for Pt); they can coalesce into one minimum without phase reversal (1 kHz: +0.09 V for Pt, + 0.17 V for Ir); independently of the degree of superimposition, they are equivalent to a local fall in γ near the given ψ. The curves of $|\Delta\gamma|$ versus ψ_m for Rh and Pd are similar, except that in the hydrogen region the Pd curve is complicated, apparently by a polymorphic transition. The formation of an oxide phase film on the metal and other transitions of this kind have effects on the curve of $|\Delta\gamma|$ versus ψ_m similar to those occasioned by exchanging an electrode of one substance for an electrode of another. In nonequilibrium conditions, the zeros of $|\Delta\gamma|$ may fail to coincide with the zero charge point. For the simplest case this follows from (1).

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