SURFACE TENSION OF SOLID ELECTRODES AND THE NULL CHARGE POINT

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The slope of the stance-potential curve at zero stance is an index of the effect of an elastic deformation on the charge density at constant potential. It is equal to one if this effect is absent. The coincidence of the zero stance with the null charge point in lead, bismuth, cadmium, and thallium indicates the absence of this effect at null potential. In dilute solutions, the second harmonic of the potential for a given alternating current passes through zero at the null charge point. This was used for comparison with zero stance. Near zero, the slope of the curve for cadmium in 0.01 N NaF is greater than three, which indicates elastic adsorption of water with the formation of bonds between the water molecules and the individual electrode atoms. Near zero stance, hysterisis is characteristic for a number of metals. The effect of a deformation on the charge density is the result of the action of geometrical, dielectric, dipole, and energetic factors. The stance of the oxidized surface is positive at sufficiently anodic potentials in platinum and a number of other metals due to deformation of the dipoles in the oxide monolayer.

The charge on the electrode, which is one of the two facings of the interphase layer, can be determined by integrating the electrical capacitance of the interphase boundary. In dilute solutions, the capacitance passes through a minimum at the null charge potential [1], and this gives the integration constant. The null charge potential (electrocapillary maximum) can also be found from the maximum on the electrocapillary curve [2], but electrocapillary measurements can be made only in the case of liquid metals.

The dependence of the surface tension of solid electrodes on the potential [3-7] contains information which differs in principle from that which is given by purely electrical measurements, particularly the capacitance method. In a solid, the surface tension γ, the relative area ϑ, the surface charge density ε, and the potential φ are related by the equation

$$\frac{\partial \gamma}{\partial \varphi} = -\varepsilon - \frac{\partial \varepsilon}{\partial \vartheta}, \tag{1}$$

in which the second argument of the partial derivatives is constant, $\partial\gamma/\partial\varphi \equiv (\partial\gamma/\partial\varphi)_\vartheta$, $\partial\varepsilon/\partial\vartheta \equiv (\partial\varepsilon/\partial\vartheta)_\varphi$; $\Delta\vartheta = \Delta\Omega/\Omega$, where Ω is the electrode area. Equation (1) is valid under both equilibrium and nonequilibrium conditions.

Area as a State Parameter of the Surface of a Solid Electrode. Equation (1) is derived from thermodynamic conformity between the mutually opposite effects of surface tension and elastic charging [6]

$$\frac{\partial \gamma}{\partial \Theta} = \frac{\partial \varphi}{\partial \Omega}, \tag{2}$$

where Θ is the charge of the entire electrode. This conformity has been experimentally confirmed [6]. The essential point of derivation (2) is the question whether the surface area Ω will serve as a state param-

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eter. The same change in the area $\Delta\Omega$ can be geometrically obtained by various deformations, e.g., by unilateral and bilateral stretching of a solid. The two states obtained in this way have different lattice geometries. Can one then consider them to be identical? Yes, if, in these states, following $\Delta\Omega$, the increments in the remaining values of Eq. (2), viz., $\Delta\varphi$, $\Delta\Theta$, and $\Delta\gamma$, are the same. This condition is satisfied if there is a fourth-order axis of symmetry in the solid which is perpendicular to the surface. This holds true for all polycrystalline materials as well as single crystals with various types of cubical lattices (Pt, Pb, Cd, etc.).

Canonical Coordinates. Multiplication by Ω using the smallness of deformations (2) leads to the form

$$\frac{\partial\gamma}{\partial\varepsilon}=\frac{\partial\varphi}{\partial\vartheta}, \tag{3}$$

where $\partial\gamma/\partial\varepsilon \equiv (\partial\gamma/\partial\varepsilon)_{\vartheta}$, $\partial\varphi/\partial\vartheta \equiv (\partial\varphi/\partial\vartheta)\Theta$. The amplitude of the vibrations of the surface tension $\Delta\gamma$, caused by fluctuations of the charge of fixed amplitude $\Delta\varepsilon$, which is obtained by assignment of an alternating current [3, 4], is recorded for the direct measurement of $\partial\gamma/\partial\varepsilon$. The variations in the potential of a solid electrode, periodically deformable during open (with respect to alternating current) circuit [5, 6], are recorded for the direct measurement of $\partial\varphi/\partial\vartheta$. The $\gamma_{\varepsilon} \equiv \partial\gamma/\partial\varepsilon$ value, designated here as the stance or ε-stance [7], is related to $\gamma_{\varphi} \equiv \partial\gamma/\partial\varphi$, designated here as φ-stance, by the electrode capacitance $C = \partial\varepsilon/\partial\varphi$

$$\frac{\partial\gamma}{\partial\varepsilon}=\frac{\partial\gamma}{\partial\varphi}\frac{\partial\varphi}{\partial\varepsilon}=\frac{1}{C}\frac{\partial\gamma}{\partial\varphi}. \tag{4}$$

Since $C \neq 0$, $\partial\gamma/\partial\varepsilon$, and $\partial\gamma/\partial\varphi$ pass through zero simultaneously. The coordinates $\partial\gamma/\partial\varepsilon$ and φ in which the results of this investigation are presented, have advantages over the coordinates $\partial\gamma/\partial\varphi$ and φ. The dimensions of $\partial\gamma/\partial\varepsilon$ and φ are the same: both values are measured in volts. This makes it possible to call the $\partial\gamma/\partial\varepsilon$ and φ coordinates canonical.

Specially pure metals, twice-recrystallized reagents, and twice-distilled water, alcohol, and acid were used in the experiments. The electrodes were 0.2-0.4-cm^2 supermeniscus electrodes [3, 4]. The $|\partial\gamma/\partial\varepsilon| - \varphi$ oscillograms (Figs. 1 and 2) were obtained for electropolished cadmium (current 0.1-0.5 A/cm^2 in 50% orthophosphoric acid), lead [8], bared (with a glass edge) bismuth, tin, indium, thallium, and nickel, purified (by cathodic and anodic polarization) platinum, palladium, iridium, and rhodium, and solidified gallium. Treatment of the electrode does not introduce distortions: the results, obtained on cadmium and lead processed by the various methods—electropolishing, chemical polishing [8], and baring with a glass edge — coincided. The oscillograms were repeatedly reproduced during repeated scanning over the same range of potentials. The scan time was 15 (Fig. 2a-c), 31 (Fig. 1a-p, Fig. 2d, f, h, and l-p), and 62 sec (Fig. 2e, g, and i-k). The time lag at initial φ after return from the final φ (τ_0) was 10 sec (Fig. 1c-g, m-p), and 1 min (Fig. 2a, b, e-k, m-p). The curves are reproducible at any τ_0 in the absence of hysteresis (Fig. 1a and b) and when they are plotted from the cathode to anode potentials (Fig. 1e, i-l). A number of solutions were acidified with H_2SO_4: 0.002 (Fig. 1d and l), 0.001 (Fig. m-p), and 0.01 N (Fig. 2o). Magnetization of the given Ni sample is the reason for the setting which causes a rise in the zero line in Fig. 2p. The current amplitude and the setting are constant along the curve and can be eliminated by compensation. The potentials are indicated on a normal-hydrogen-equivalent scale.

Slope of the Stance-Potential Curve near Zero. We differentiate the dependence of $\partial\gamma/\partial\varepsilon$ on φ using Eqs. (4) and (1):

$$\frac{\partial}{\partial\varphi}\left(\frac{\partial\gamma}{\partial\varepsilon}\right)=\frac{\partial}{\partial\varphi}\left[-\varepsilon-\frac{\partial\varepsilon}{\partial\vartheta}\right]\frac{\partial\varphi}{\partial\varepsilon}+\frac{\partial\gamma}{\partial\varphi}\frac{\partial}{\partial\varphi}\left(\frac{\partial\varphi}{\partial\varepsilon}\right)=-1-\frac{1}{c}\frac{\partial c}{\partial\vartheta}+\frac{\partial\gamma}{\partial\varphi}\frac{\partial}{\partial\varphi}\left(\frac{\partial\varphi}{\partial\varepsilon}\right).$$

Since $\partial\gamma/\partial\varphi = 0$ at the zero point of the $(\partial\gamma/\partial\varepsilon) - \varphi$ curve, introducing $\zeta = \ln C$, we then obtain

$$\frac{\partial}{\partial\varphi}\left(\frac{\partial\gamma}{\partial\varepsilon}\right)=-1-\frac{\partial\zeta}{\partial\vartheta} \text{ when } \frac{\partial\gamma}{\partial\varepsilon}=0. \tag{5}$$

The $\partial\zeta/\partial\vartheta$ term characterizes the relative change in capacitance caused by a relative change in area, $\partial\zeta/\partial\vartheta = (\Omega/C)\,(\partial C/\partial\Omega)$. The $\partial\varepsilon/\partial\vartheta$ term in Eq. (1) is the change in charge density during elastic deformation. If $\partial\varepsilon/\partial\vartheta = 0$, $\partial\zeta/\partial\vartheta = 0$. Then, in accordance with Eq. (5), in the vicinity of zero

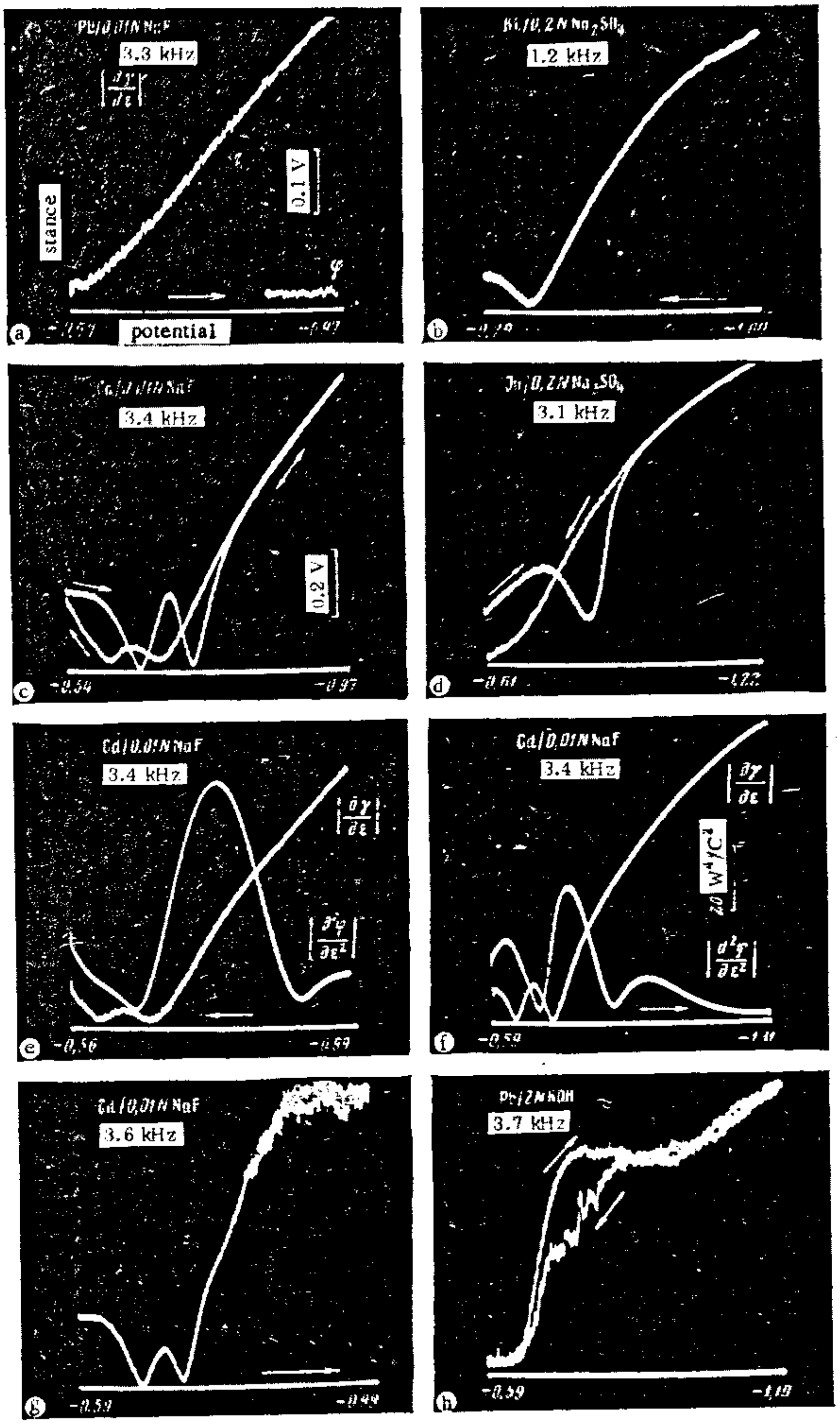

Fig. 1a-h

$$\frac{\partial}{\partial\varphi}\left(\frac{\partial\gamma}{\partial\varepsilon}\right) = -1, \tag{6}$$

i.e., the $(\partial\gamma/\partial\varepsilon) - \varphi$ curve passes through zero at 45° if the scales of the $\partial\gamma/\partial\varepsilon$ and φ axes are the same (Fig. 1a, Pb in 0.01 N NaF). In the process, the stance-potential curve is symmetrical relative to zero even when the capacitance changes in the vicinity of the null potential and disturbs the symmetry of the φ-stance-potential curve.

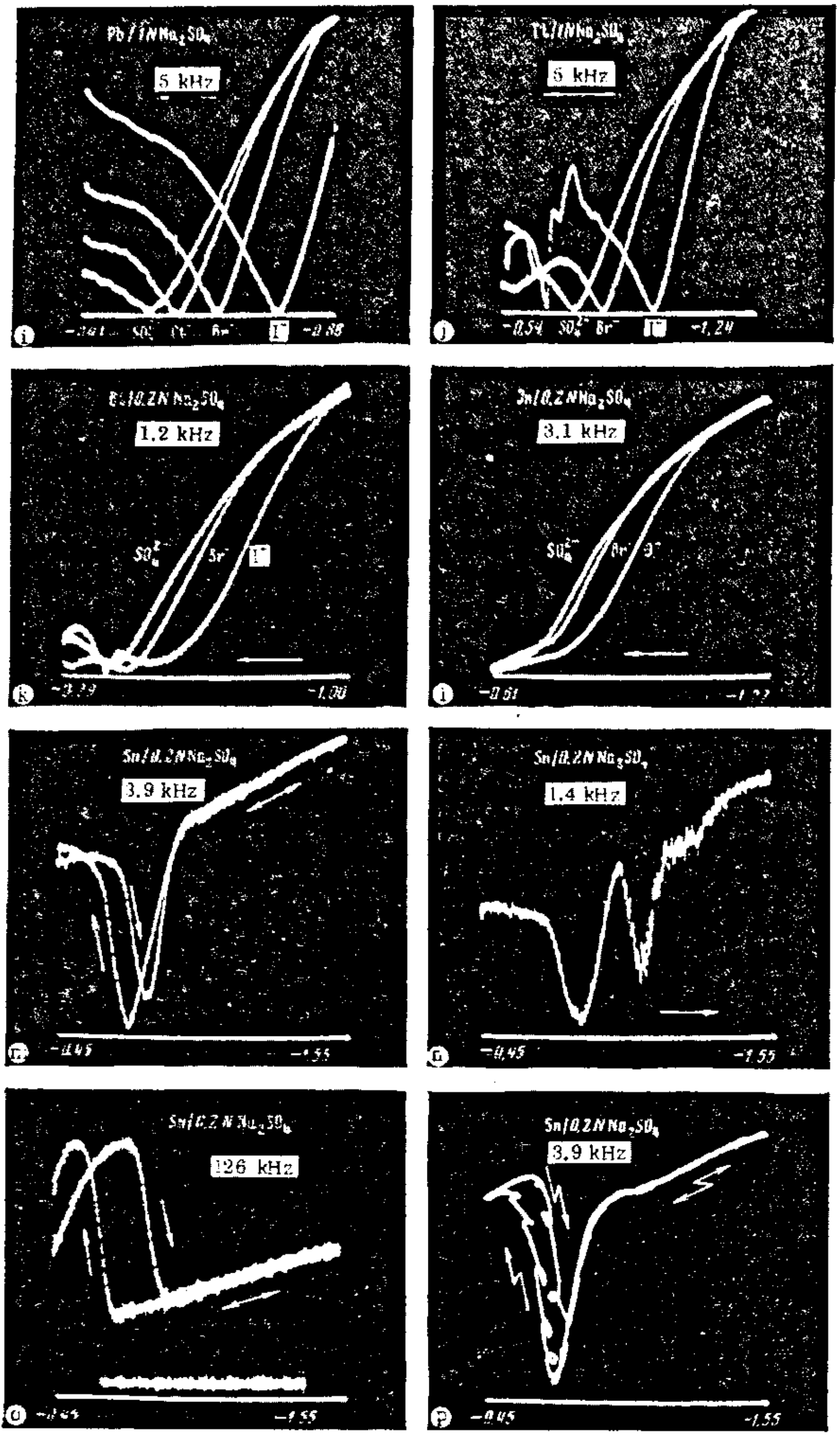

Fig. 1. i-p

Formula (6) enables one to determine immediately from the slope of the curve how and to what extent elastic deformation affects the current density. None of the methods known up to now can answer this question. The stance method does this without relying on any supplementary data.

Shift in the Null Charge Point during Elastic Deformation. The work function in vacuo and the null charge potential are different in different metals. A metal is also to some degree two different metals before and after deformation. Consequently, the null charge point is shifted somewhat during elastic deformation. This is equivalent to a shift in the potential of the undeformed electrode with respect to the degree of the effect on the charge. The energy introduced into an electrode during elastic deformation is extremely small (in comparison, for example, with an equidimensional thermal deformation). This provides a basis to expect that $\partial \varphi_0/\partial \vartheta \geq 1$ V for the null charge potential φ_0 if the change in the work function in vacuo is the sole source of the effect of the elastic deformation on φ_0. In any case, the shift in the null charge potential during elastic deformation is determined by the formula

$$\frac{\partial \varphi_0}{\partial \vartheta} = \frac{\partial \varphi}{\partial \vartheta}\bigg|_{\varphi=\varphi_0} = \frac{\partial \gamma}{\partial e}\bigg|_{\varphi=\varphi_0}, \tag{7}$$

i.e., it is the stance when $\varphi = \varphi_0$. It is zero if the zero stance coincides with the null charge point. Within the limits of error in the measurements (0.03 V), such coincidence is observed in a number of metals. For example, consider the following zero stances: −0.56 V for Pb in 0.01 N NaF (Fig. 1a), −0.39 V for Bi in 0.2 N Na_2SO_4 (Fig. 1b), −0.68 V (anodic reversible branch of the stance-potential curve) and −0.72 (cathodic branch) for Cd in 0.01 N NaF (Fig. 1c), and −0.74 V for Tl in 1 N Na_2SO_4 (Fig. 1j). The null charge potentials of these electrodes, found from the capacitance minimum, are: −0.56 V for Pd [9], −0.40 V for Bi [10], −0.72 V for Cd [11], and from −0.70 to −0.75 V for Tl [12]. Thus, here, $\partial \varphi_0/\partial \vartheta < 0.03$ V. This indicates that the change in the work function during elastic deformation is insignificant. In addition, it is substantially independent of the electrode potential and, as a constant, does not affect $\partial \gamma_\varepsilon/\partial \varphi$. In many cases, this effect can be disregarded.

The chief reasons for the change in the charge density during elastic deformation are the change in the adsorption capacity of the deformable electrode with respect to definite particles and deformation of the layer of adsorbed dipoles. For example, stretching of platinum in 1 N H_2SO_4 in the vicinity of +0.16 V increases its capacity to adsorb hydrogen: its surface density increases. In the same system, measured $\partial \varphi/\partial \vartheta$ values more positive than +1 V are determined chiefly by deformation of a −Pt−O− dipole layer, the overall quantity of which does not change during deformation. When the surface is stretched, the number of dipoles per unit area decreases as does the number of atoms of platinum itself. The shift in the null complete-charge point [1] is considerable on platinum: $\partial \varphi_0/\partial \vartheta \approx -2$ V when $\varphi = \varphi_0 = +0.3$ V.

Cases where the density of the adsorbed particles remains practically constant during elastic deformation are also common. Particles (ions in the diffusion portion of the double layer, ions which are contact-adsorbed [13] due to the described forces and some polar molecules) which are purely electrostatically adsorbed and sense the electrode as a half-space with high electrical conductivity and not as an aggregate of individual atoms behave in this way.

Elastically and Plastically Adsorbed Particles. We will consider particles which do not belong to the electrode but which enter into the composition of the interphase layer. Those whose state depends directly on elastic deformation of the electrode we will call elastically adsorbed particles. The remaining particles will be called plastically adsorbed particles. If the deformation affects the state of the particles of one sort, this is indirectly reflected in the state of the other particles. For example, deformation of locally adsorbed dipoles is accompanied by a change in the electrode capacitance and the charge density of the diffusion portion of the interphase layer. The effect by means of a change in the work function of the electrode material in vacuo is also indirect. Thus, the effect of the elastic deformation is spread indirectly to the plastically adsorbed particles. Elastic adsorption is also possible on a liquid electrode. However, it does not manifest itself since a liquid electrode is not elastically deformed under the usual conditions.

Localized adsorbed particles are also elastically adsorbed. The reverse is not always true. In the example given involving hydrogen it is apparent that the geometry of the covering is not so important as the energy of interaction of the electrode with adsorbed hydrogen which increases due to elastic stretching of the platinum. Moreover, the adsorbed hydrogen is capable of moving along the surface. There are representatives of each of the two forms of adsorption (elastic and plastic) among ions which can be contact-adsorbed. It follows from elastic adsorption that interaction between the electrode and the particles does not reduce to electrostatic attraction of the particles by a homogenous, conducting, half-space and that the properties and discrete structure of the electrode substance are not reflected in the particle state.

One of the major components of the interphase layer on the electrode −solution boundary are solvent molecules, eg., water. Their adsorption has not been studied to any great degree. Even among the most investigated solid metals such as Cd, Pb, and Bi, there are no data on whether the water molecules behave only as dipoles electrostatically attracted and oriented by the charged electrode surface acting as a homo-

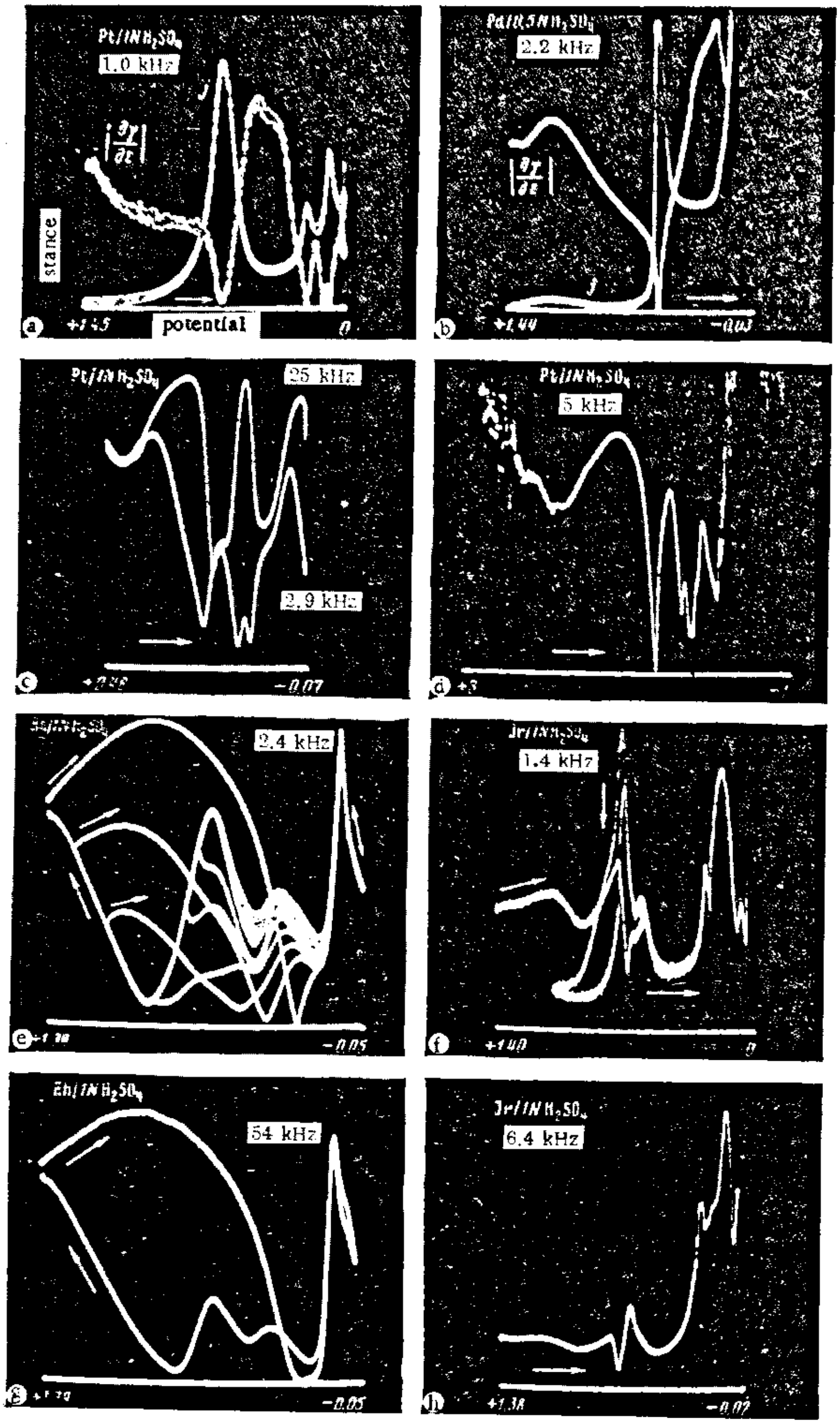

Fig. 2a-h

genous plane, or whether they form bonds with the individual electrode atoms and thereby relinquish their preference for definite sites on the surface. In the first of the indicated cases, water is plastically adsorbed while in the second case it is elastically adsorbed; this is a difference which the stance method should detect.

To solve this problem, the stance was measured on different metals in aqueous NaF solutions. It is well known that Na^+ and F^- are not specifically adsorbed because of their small radii, i.e., they preserve their hydrated shells and do not disturb the hydrated electrode shell. Under these conditions, water may be the only elastically adsorbed component. For lead in 0.01 N NaF (Fig. 1a), the slope $(\partial\gamma_\varepsilon/\partial\varphi)$ of the

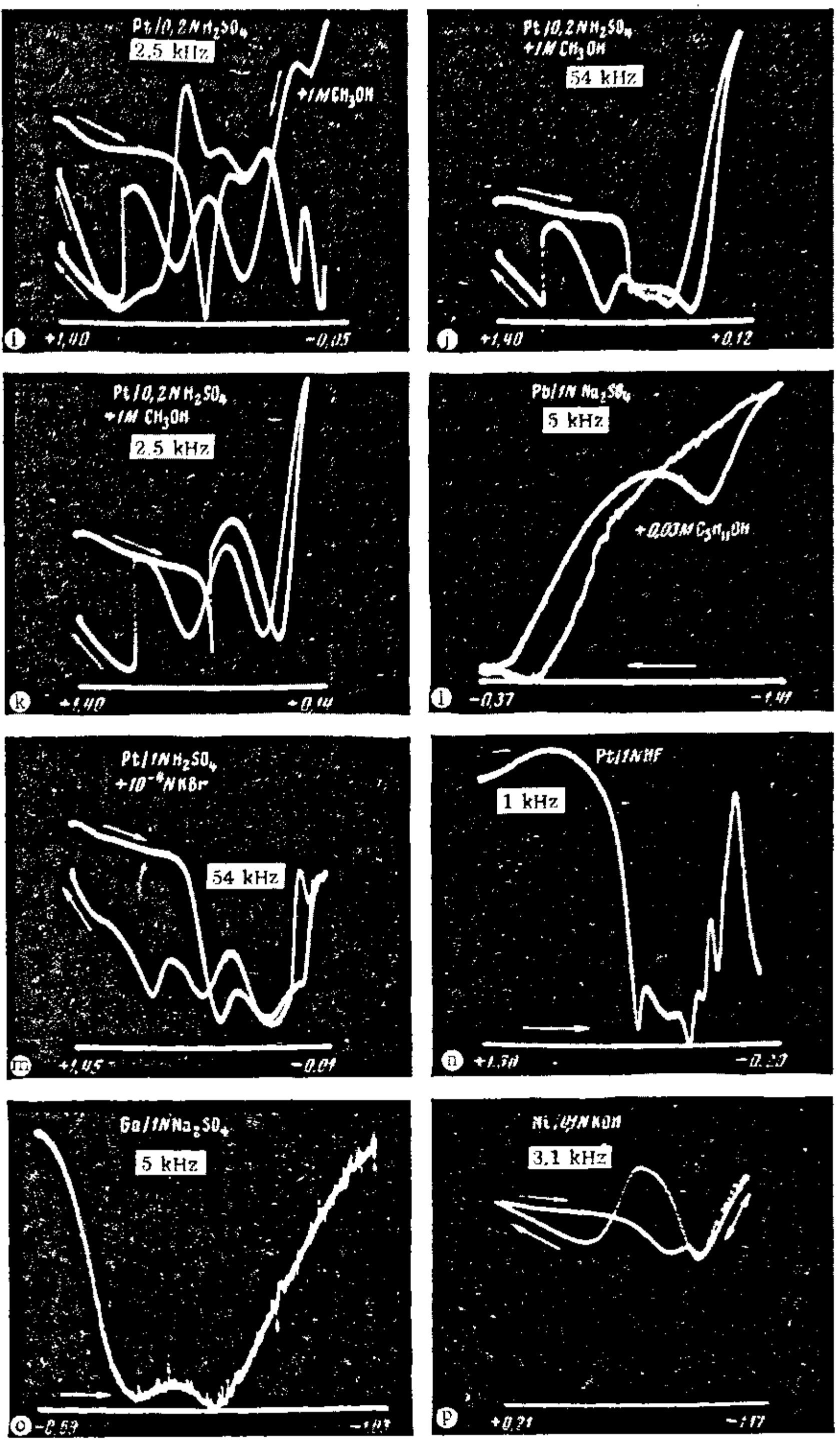

Fig. 2i–p

stance-potential curve near the null potential is equal to one with an accuracy, ensured by calibrations, of 20%. The zero stance coincides with the null charge point. Thus, for lead in 0.01 N NaF, no signs of the elastic adsorption of water are detected. The picture is quite different for cadmium in 0.01 N NaF (Fig. 1c). The slope $(\partial\gamma_\varepsilon/\partial\varphi)$ near the zero point is close to three here. It hence follows that water is elastically adsorbed on cadmium. In conjunction with this, the coincidence of the zero stance with the null charge point of cadmium appears strange: the elastic adsorption effect exists everywhere except for this point.

Elastic Components of Stance. By relying on the $\partial\varepsilon/\partial\vartheta$ term in Eq. (1), we will clarify which form of elastic adsorption affects the stance.

1. The geometrical factor is the change in the thickness of the elastic interlayer between the ionic and metallic facings of the interphase layer. When the electrode is stretched along the surface, the thick-

ness of the interlayer decreases and the capacitance therefore increases. At constant potential, this leads to an increase in the charge density of each of the facings. The $\partial\varepsilon/\partial\vartheta$ term has the same sign as ε. This factor does not shift the zero stance from the null charge point but increase the slope of the stance-potential curve at this point in comparison with unity. If the elastic medium between the facings were isotropic, the decrease in the thickness of the interlayer h would be determined by the Poisson coefficient ν, $0 \leq \nu \leq 0.5$. Introducing $\delta = \ln h$, we obtain in relative values $\partial\zeta/\partial\vartheta = -\partial\delta/\partial\vartheta = \nu/(1-\nu)$ and $0 < \partial\zeta/\partial\vartheta < 1$. Then from Eq. (5),

$$\left|\frac{\partial}{\partial\varphi}\left(\frac{\partial\gamma}{\partial\varepsilon}\right)\right| \leqslant 2. \tag{8}$$

However, the medium of the interlayer is substantially anisotropic, and, in the case of cadmium, is oriented water molecules. The contribution of the geometrical factor may therefore significantly exceed unity.

2. The dielectric factor is the change in the dielectric permeability of the interlayer. An increase in the dielectric permeability during stretching has the same effect as decreasing the thickness of the interlayer: it increases the capacitance but does not shift the zero stance: $\partial\zeta/\partial\vartheta > 0$, $\varepsilon(\partial\varepsilon/\partial\vartheta) \geq 0$. Both factors act simultaneously.

3. The dipole factor is the change in the dipole moment and position of the dipoles in the interphase layer during deformation of the electrode. The decrease in the contribution of the dipoles to the interphase potential difference is compensated for by a charge influx. The dielectric factor differs from the dipole factor in that it reflects the change in the displaceability of charges by the applied field. The dipole factor is independent of this displaceability. The contribution of the dipole factor in the general case does not reduce to zero when $\varepsilon = 0$. Therefore, in contrast to the dielectric factor, it shifts the zero stance relative to the null charge point.

4. The energetic factor is the change in the affinity of the electrode for adsorbed particles during elastic deformation. If these particles are ions, their charge participates in the total influx of charge induced by the deformation. If, however, they are dipoles, the charge increases due to an increase in the quantity of electrostatically adsorbed particles. This factor also shifts the zero stance.

The mutual independence of the enumerated factors and the small character of the deformation make it possible to represent the charge increment during deformation in the form of a sum, each term of which is the contribution of the corresponding factor

$$\Delta\varepsilon = \Delta\varepsilon_g + \Delta\varepsilon_d + \Delta\varepsilon_p + \Delta\varepsilon_e. \tag{9}$$

Plasticization of the Adsorbed Layer. The fact that the zero stance for cadmium coincides with the null charge point is permitted by the geometrical and dielectric factors but is not compatible with the dipole factor. This coincidence may indicate either that the dipole potential difference does not change during deformation of the layer of elastically adsorbed water molecules, or that the water molecules cease to be elastically adsorbed at the null charge potential. The dependence of the stance on frequency introduces certainty.

It turns out that at 100 kHz the zero stance for cadmium in 0.01 N NaF is shifted markedly in a positive direction from the site where it was found at frequencies below 10 kHz. A similar phenomenon is observed for tin (see Figs. 1m and 1o) and for a number of other metals. These results indicate that the dipole factor operates for cadmium even at the null charge potential. The location of the zero stance at the null charge point at low frequencies can be explained by plasticization of the layer of adsorbed water, viz., by a peculiar thawing of the layer on passing from high to low current densities. The orientation and deformation of water molecules in a strong field apparently promote fixing of the molecules on the electrode and hardening of the layer of adsorbed water. This layer reveals the properties of the viscous-elastic medium whose relaxation time increases on intensifying the field. At weak fields (near the null charge point), this time is of the order of 10^{-5} sec. At 1 kHz, the layer of water molecules on the electrode therefore behaves as a liquid, but, at 100 kHz, it behaves as a solid. In the process, it is not absolutely necessary that each of the molecules form a strong bond with the electrode. The size effect depends on the fraction of such molecules in the total number and on their bond with the remaining molecules. Some of the molecules are localized on the lattice defects which, however, occupy only an insignificant portion of the electrode surface.

The sign of the dipole factor for cadmium is such that at sufficiently high frequencies

$$\left(\frac{\partial\varphi}{\partial\vartheta}\right)_{\bullet} > 0, \left(\frac{\partial\varepsilon}{\partial\vartheta}\right)_{\bullet} < 0 \text{ when } \varphi = \varphi_{\bullet}, \tag{10}$$

i.e., stretching of the surface shifts the electrode potential to the positive side during open circuit.

Near-Zero Stance Hysteresis. For lead and bismuth, the trend of the stance-potential curve is reversible on both sides of zero (Fig. 1a and b). For cadmium, tin, indium, and several other metals, hysteresis is observed for potentials which are more positive than the zero stance (Fig. 1c, d, m, and o). In these cases, it follows from experiments with a zigzag change in potential (Fig. 1p) that the trend of the curve is more negatively reversible than the zero stance. The relationship to the null charge points and the absence of a significant change in the pH of the solution indicate the decisive role of the sign of the electrode charge in this process. This phenomenon is apparently the result of irreversible reorientation of the adsorbed water molecules.

Null Point of the Second Harmonic of the Potential. In addition to changes in the capacitance, another path can be obtained to determine the null charge points of the same object, viz., by measuring the second harmonic of the potential for a fixed sinusoidal current. In the process, the $(\partial^2\varphi/\partial\varepsilon^2) - \varphi$ curves are recorded (Fig. 1e, f; the $\partial\gamma/\partial\varepsilon$ and $\partial^2\varphi/\partial\varepsilon^2$ curves were plotted successively on one frame). The $\partial\varphi/\partial\varepsilon$ value reaches a maximum and $\partial^2\varphi/\partial\varepsilon^2$ reduces to zero at the null charge point where the capacitance $\partial\varepsilon/\partial\varphi$ passes through a minimum. In dilute solutions, where such measurements are possible, the resistance drop, which is proportional to the current, is the predominant portion of the voltage on the electrodes. Since it contains only the first harmonic, it is completely excluded during recording of the voltage at a frequency which is twice the current frequency. Here, recording of $\partial^2\varphi/\partial\varepsilon^2$ is carried out for 1 kHz (Fig. 1e and f). The null potentials $\partial\gamma/\partial\varepsilon$ and $\partial^2\varphi/\partial\varepsilon^2$ differ by no more than 0.02 V on the oscillogram in Fig. 1e which does not enter into the strongly cathodic region. The hysteresis observed on the $(\partial\gamma/\partial\varepsilon) - \varphi$ curves also exists on the $(\partial^2\varphi/\partial\varepsilon^2) - \varphi$ curves.

Effect of the Nature of the Anion. For cadmium and tin, increasing the solution concentration (from 0.01 N to 1 N) and replacing the F^- anion by the SO_4^{2-} anion does not significantly change the shape of the stance-potential curve.

In a number of solutions containing SO_4^{2-}, Cl^-, Br^-, and I^-, the zero stance in lead and thallium is shifted to the negative side (Figs. 1i and j) in a manner similar to that which occurs with the electrocapillary maximum for mercury. This effect is manifested more weakly in bismuth and indium (Fig. 1k and l). The oscillograms presented were obtained by successive addition of anions to the same solution (1 N Na_2SO_4 + 0.15 N KCl + 0.15 N KBr + 0.15 N KI in Fig. 1i and j; 0.2 N Na_2SO_4 + 0.1 N KBr + 0.1 N KI in Fig. 1k and l; the curve for Tl with Cl^- is not shown since it coincides with the original curve). Similar results are obtained for solutions containing anions separately. The difference in the slopes at which the curves of the different anions pass through zero indicates the deviation from plastic adsorption under the given conditions: during plastic adsorption the slopes at the zero points should be the same (and equal to unity) regardless of the solution composition.

Electrode Noise. In contrast to electropolished lead, noise is superimposed on the stance-potential curve for mechanically processed lead but does not change the trend of the curve. The noise is caused by movement of the disolocations in the surface layer of lead. It is less in KBr than in KCl. This is associated with the greater surface activity of the Br^- anion, whose adsorption localizes the dislocations to a large degree. High-frequency noise (100 kHz) is observed under certain conditions for electropolished cadmium.

Fluctuation Anomaly of the Stance. The outwardly similar stance fluctuations differ from noise. They are observed in a number of cases in cadmium, lead, and tin and are characterized by the following features. 1) The appearance of fluctuation is accompanied by a change in the shape of the curve, often by a decrease in the stance in the region of potentials encompassed by the fluctuations (Fig. 1g and n). 2) For lead and tin, a decrease in stance exists at low frequencies (1 kHz and below) but does not exist under the same conditions at frequencies above 3 kHz (Fig. 1m and n). 3) The phenomenon is nonstationary, is accompanied by hysteresis, and is sensitive to the electrode's previous history.

For cadmium, a curve with fluctuations (Fig. 1g) is obtained after prolonged electropolishing (5 min). The fluctuations occur only at a certain more negative potential (−0.8 V in Fig. 1g). After several scannings, the fluctuations disappear and the normal shape of the curve is restored. Thus, foreign particles which penetrate the metal and then are removed during polarization of the electrode apparently manifest themselves. Introduction of alkali metals [14] also gives the fluctuation anomaly.

Relationship between the Sign and the Space-Charge Region. If the double layer is formed only by electrostatically adsorbed particles, the metal charge on the boundary with the electrolyte is created by an excess or insufficiency of electrons in the surface layer of the metal. In the first case, the metal is negatively charged, while in the second case it is positively charged. The position of the space-charge region does not change on passing through the null charge point. If, however, a layer of strongly adsorbed particles exists on the electrode, this layer, depending on the nature of the particles, may be a dielectric, conductor, or semiconductor. In the latter case, charged particles of various sorts and different regions of arrangement of these particles may correspond to different signs of the electrode charge. It is well known [15] that, in a p-type semiconductor at fixed current-carrier concentrations, a negative surface charge is created by the labile electrons, while a positive surface charge is set up by the localized lattice ions. The monatomic layer of substance on the metal naturally has different properties than the homogenous semiconductor. For example, it may be a dielectric during positive electrode charge but a conductor during negative charge, i.e., it serves as an extension of the metal. On passing from positive to negative charge, the space-charge region is then promoted from a solid to a liquid. The change in the structure of the interphase layer corresponds to this.

An interesting phenomenon, observable on platinum in aqueous acid solutions (e.g., 1 N H_2SO_4), is apparently caused by such a departure of the space-charge region from the solid portion of the interphase layer: an abrupt cessation of the dependence of the stance on the frequency on passing through a point at which the free electrode charge is reduced to zero (+0.17 V, in agreement with [16]). This is expressed in the fact that the stance-potential oscillograms obtained simultaneously at two frequencies (2.9 and 25 kHz in Fig. 2c) differ markedly at potentials more positive than +0.17 V but are virtually confluent at potentials more negative than + 0.17 V in a certain neighborhood of this potential.

Because of the slow character of hydrogen adsorption on platinum, the same amplitude $\Delta\varepsilon$ of the electricity consumed in the discharge of hydrogen ions is obtained at high frequency due to the large potential amplitude $\Delta\varphi$. Near +0.17 V, $\Delta\varphi$ is five times larger at 25 kHz than at 2.9 kHz. So long as the solid portion of the interphase layer, which here includes the adsorbed water and hydrogen, is found in the electrical field zone, its deformation amplitude increases with increasing $\Delta\varphi$. This leads to an increase in the stance with increasing frequency. The deformation component of the stance vanishes as the space-charge region emerges from the solid electrode. The contribution of hydrogen atoms, which is proportional to the amount of them adsorbed per half-period ($\sim 2 \cdot 10^{-12}$ dyn/cm per 1 H atom), remains. Like $\Delta\varepsilon$, it is the same at different frequencies. The difference in $\Delta\varphi$ is preserved, but it has virtually no effect on the stance value.

These conclusions are valid for frequencies from 0 to 10-20 kHz, so long as the major fraction of $\Delta\varepsilon$ accounts for the discharge of hydrogen ions up to the state of adsorbed atoms. As the frequency is further increased, an even greater portion of $\Delta\varepsilon$ is consumed in charging the double layer; the hydrogen fraction decreases and, in accordance with this, the stance near +0.17 V gradually decreases.

The merging of the curves at 2.9 and 25 kHz is interrupted by the stance peak near +0.1V. The peak height is proportional to $\Delta\varphi$ [7]. This is associated with the fact that, near +0.1 V, an increase in the potential difference on the platinum–solution boundary is reached due to a change in state of hydrogen in the adsorbed layer itself. Because of this, an alternating electrical field temporarilty reverts to the solid portion of the interphase layer until all the vacancies corresponding to the new state are filled. On the potential axis, this process occupies a 0.1 V long interval with center at $\varphi = +0.1$ V. The stance is independent of frequency on both sides of it. Similar phenomena were observed for iridium in the same media (Fig. 2f and h). They were not observed for palladium and rhodium (Fig. 2b, e, and g).

Oxygen Branch of the Stance. The zero stance, which corresponds to the null charge point (but is not necessarily coincident with it), divides the stance-potential curve into cathodic and anodic branches. At sufficiently negative potentials, the stance is positive

$$\frac{\partial\gamma}{\partial e} > 0 \text{ when } \varphi < \varphi_n, \tag{11}$$

where φ_z is the null potential (the most cathodic if there are several nulls for the stance). As the potential is increased, the stance passes through zero and becomes negative. The electrode is oxidized in aqueous solutions above a certain potential. The stance on the oxidized surface is generally positive

$$\frac{\partial\gamma}{\partial\varepsilon} > 0 \text{ when } \varphi > \varphi_{ox}, \tag{12}$$

where φ_{ox} is the potential of the oxygen zero stance. This experimental fact was established for Pt, Ir, Pd, Rh, Cd, Pb, Sn, In, Ga, Zn, Ni, and Co (Ag and Au are exceptions). Thus, if $\varphi_{ox} > \varphi_z$, the stance passes through zero at least twice with increasing potential. The number of zeros is even. The dependence of the stance modulus (which contains all the zeros) on potential takes on the shape of the letter W (Fig. 1e, 2o and p) or several successively joined W's (Fig. 2a). The oxygen zero for the cathodic curves of platinum and palladium is situated under the maximum of the current consumed in the reduction of the oxide (Fig. 2a and b; the stance modulus $|\partial\gamma/\partial\varepsilon|$ is compared with current j).

If φ_z and φ_{ox} coincide, both zeros merge (Sn, In). If, however, $\varphi_{ox} < \varphi_z$, the cathodic and oxygen branches of the stance are superimposed and the stance is positive everywhere (Zn).

The stance of the oxygen branch is determined by the deformation of the solid layer of dipoles formed due to addition of hydrogen atoms to the surface metal atoms. On can draw definite conclusions regarding the structure of this layer from the sign and value of the stance. The fact that, at sufficient anodic potentials, the stance of the oxygen branch is anomalously positive for various metals indicates the similarity of the structure of the surface oxides of these metals. According to Eq. (3), from $\partial\gamma/\partial\varepsilon > 0$ it follows that $\partial\varphi/\partial\vartheta > 0$, as is also given directly by experiments with respect to elastic charging [6]. This indicates that the elastic increase in the electrodes area ($\Delta\vartheta > 0$) during open circuit leads to an increase in its potential ($\Delta\varphi > 0$).

The dipole potential difference χ is put together from the χ_0 portion created by immobile dipoles of $-\mathrm{Pt}-\mathrm{O}-$type and the χ_e portion created by the surface electronic cloud. Elastic deformation affects both χ_0 and χ_e. Under fixed conditions, χ_0 changes more significantly with deformations than does χ_e, and $\partial\chi_0/\partial\vartheta \gg \partial\chi_e/\partial\vartheta$. χ_0 is proportional to the number of dipoles per unit surface and to the dipole moment. their number per unit surface decreases. The dipole moment also decreases: the dipole layer becomes thinner, if it is deformed, just as an elastic body (this can be taken for granted, considering the similarity of the phenomenon on different metals).

We now consider the results of experiments based on the assumption that $\partial\chi_e/\partial\vartheta \ll \partial\chi_0/\partial\vartheta$ for platinum. The result $\Delta\varphi > 0$ is then compatible with a decrease in the dipole potential difference χ_0 only if this difference is negative, i.e., the negative end of the dipoles is turned to the metal while the positive end is turned to the solution: in the oxide monolayer on the metal, the oxygen atoms are deposited more deeply than the surface metal atoms. One of the possible methods of such an arrangement is coating of the monolayer of oxygen atoms with a monolayer of metal atoms.

For platinum, palladium, and rhodium (Fig. 2), the stance of the oxygen branch changes relatively slightly with potential if the surface oxide is formed at sufficiently anodic potentials (from +1.4 to +1.8 V for platinum), which is equivalent to the formation of a monolayer. For platinum, moreover, $\partial\gamma/\partial\varepsilon = \partial\varphi/\partial\vartheta \approx +3\mathrm{V}$. The slight effect of the potential is the result of the slight change in the oxide parameters on changing the electrical field. The electrostriction contribution to $\partial\gamma/\partial\varepsilon$, which depends linearly on the potential, is small here. The certain increase in the stance with a decrease in the anodic potential (Fig. 2d, to the left) is the effect of the double layer charge, which is relatively small here.

Under the conditions under examination, where all the factors except the dipole factor are insignificant, the stance is determined by the expression

$$\frac{\partial\gamma}{\partial\varepsilon} = -\chi_0\left[1 - \frac{\partial\rho}{\partial\theta}\right], \tag{13}$$

where $\partial\rho/\partial\vartheta$ is the derivative of the relative change of the dipole shoulder in the projection on the normal to the surface with respect to the relative change in area. In any case, apparently, $\partial\rho/\partial\vartheta < 0$. From Eq. (13), the estimate

$$|\chi_0| < \left|\frac{\partial\gamma}{\partial\varepsilon}\right|. \tag{14}$$

then follows. For platinum, this indicates that $|\chi_0| < 3$ V.

If platinum is oxidized when $1.1 > \varphi > 0.9$ V (intermediate stage oxidation), at low frequencies (less than 3 kHz), $\partial\gamma/\partial\varepsilon \approx 0$. It follows from (14) that, in this case, $\chi_0 \approx 0$, i.e., the layer is made up of oppositely oriented dipoles which compensate for each other. With increasing frequency (above 50 kHz), this compensation is disrupted, apparently due to the slowness of the relaxation of one of these types of dipoles (with positive end toward the metal). Since the work function on the oxidized surface is determined by the change in the individual components of the dipole difference, comparison of the stance with the data on the work function may be used to compare the χ_0 and χ_e, $\partial\chi_0/\partial\vartheta$ and $\partial\chi_e/\partial\vartheta$ fractions in the total χ and $\partial\chi/\partial\vartheta$ values.

Stance during Adsorption of Organic Substances. If, at a certain potential, the electrode is gradually covered with an adsorbed substance or freed of it, the stance experiences a difference at the same potential. The stance differences arise during adsorption of methanol on platinum (Fig. 2i, the cathodic and anodic curves up to the addition of methanol in 0.2 N H_2SO_4 and the anodic curve after addition of methanol at +0.5 V are shown; Fig. 2j and k). The discontinuity on the cathodic curve is due to adsorption of methanol, while that on the anodic curve is due to its removal.

The adsorption of high-molecular-weight alcohols on metals of the lead type shifts the zero stance to the positive side. A minimum, caused by the pseudocapacitance maximum at the same potentials, arises on the boundary of the adsorption region (Fig. 2l).

Energy and Surface Tension of Solid Electrodes. In solving the Lippman equation

$$\frac{\partial\sigma}{\partial\varphi} = -\varepsilon \tag{15}$$

the aggregate state of the electrode is not used explicitly anywhere. Thus, this equation is valid not only for liquid but also for solid electrodes. The σ value is the energy of formation of a unit surface, coinciding with the surface tension only in the case of liquids but not identical to it. Even in liquids under definite conditions the energy of formation of the surface is not equal to the surface tension.

At equilibrium, Eqs. (1) and (15) are simultaneously applicable to solid electrodes. This cannot raise doubts as does the fact that for solid electrodes there simultaneously exist both the surface tension (γ) and the energy of formation of the surface (σ) which, in the general case, are not equal [17].

We will clear up two questions: 1) Why cannot the information which is contained in the $\partial\varepsilon/\partial\vartheta$ term be extracted from the electrocapillary measurements – is it because it does not exist, or, if it does, is it because there is no method by which it can be accomplished ? 2) Why cannot electrocapillary measurements be made for solid electrodes – is it because there is not yet a method for accomplishing this, or is it because the electrocapillarity phenomenon does not exist in solids ?

Electrocapillarity is important as a means for nonelectrical verification of electrical measurements. A property of electrocapillary measurements is reiteration of the results of purely electrical measurements, similar to the property of a liquid of taking on the shape of the vessel in which it is placed. Information regarding the internal structure, which, for example, is contained in the crystal form when the substance is a solid, is not included in this shape. Nevertheless, the liquid structure is similar to the solid structure. Many phenomena which can be observed distinctly by measuring the stance but which cannot be detected directly from experiments with electrocapillarity are also possible in liquid electrodes, particularly localization of the adsorbed particles relative to the surface metal atoms.

Crystalline solids do not take on the shape of the miniscus and are not drawn up into a capillary, not so much because their rigidity prevents this but because it is energetically unfavorable. In contrast to a liquid, the equilibrium form of a solid at any potential is not a sphere but a crystal with plane faces which occupy a significant portion of the surface. Equilibrium conditions are therefore really feasible even on solid electrodes. It is not the slowness involved in setting up the equilibrium form but the relationship between this form and the crystal structure which make strictly electrocapillary phenomena impossible in solids.

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