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The Estance Method

A.Ya.Gokhshtein

A method based on the measurements of estance—the derivative of the surface tension of a conducting solid with respect to an electrical variable—is proposed for the investigation of surface phenomena. The basis of the method involves two mutually opposed effects—the change in the surface tension of the solid when its potential relative to a flowing medium is altered and the change in the potential on elastic deformation of the solid. The experimental technique, certain problems of the theory of the method, and examples of its employment are described.
The bibliography includes 35 references

CONTENTS

I. INTRODUCTION

The dependence of the interfacial tension between two liquids on the potential jump at the interface is known as the phenomenon of electrocapillarity[1]. As a result of research by Frumkin and his school[2-4], this phenomenon has become one of the principal sources of information about the structure of the electrode–electrolyte boundary. The large volume of information obtained by measuring the surface tensions of liquid electrodes stimulated the search for a method which would permit the measurement of the influence of the potential on the surface tensions of solid electrodes too.

II. THE SURFACE TENSIONS OF SOLID ELECTRODES

1. Principle of the Method

The variation of the surface tensions of solid electrodes with potential could not be measured previously because of the extremely slight deformation of the solid electrode and the appreciable side effects. An increase of the surface tension by 1 dyn cm^{-1} shortens a silver plate 1 cm long and 0.1 cm thick only by 0.001 Å. Appreciable internal stresses within the material of the electrode arise owing to the diffusion of extraneous species into the bulk of the electrode. Under the conditions of the example quoted, the result of the measurements may be distorted when the temperature of the electrode changes by only 10^{-6} K. In the method proposed these difficulties have been eliminated.

The essence of the method can be described briefly as follows[5-11]. If the surface tension of the solid electrode γ depends in some way on the electrode potential φ relative to the solution, then the oscillations in φ with an amplitude $\Delta\varphi$ should lead to oscillations in the surface tension with an amplitude $\Delta\gamma$. The variation of $\Delta\gamma$ with φ is recorded, the following procedure being used. The solid electrode, for example an L-shaped electrode, is clamped in a specified manner to a piezoelectric element (Fig. 1) and forms with the latter a mechanical system possessing a series of resonance frequencies. These frequencies are used in the measurements. The length of the working section of the L-shaped electrode is about 1 cm. The lower surface of the electrode is wetted by the electrolyte. It is raised somewhat above the level of the electrolyte, which makes it possible to refer to it as a suprameniscus electrode. An alternating current at a specified frequency is passed through the electrode and the potential oscillations received from the piezoelectric element are amplified at the same frequency. After rectification, this signal is applied to the vertically deflecting plates of a cathode ray tube. The horizontal scan of the beam is proportional to the average electrode potential.

Measurements can be made under two sets of conditions depending on whether one keeps constant the amplitude of the electrode charge density q (by specifying the alternating current amplitude) or the amplitude of the electrode potential φ. Under the first set of conditions, $\Delta\gamma$ is proportional to the derivative $\partial\gamma/\partial q$ and under the second set to $\partial\gamma/\partial\varphi$, which we call respectively the q-estance and the φ-estance or simply the estance (when there is no possibility of a misunderstanding). The term "estance" is modelled on the term "impedance" using as a basis the word "elastic" in connection with the study of elastic materials. The variables $\partial\gamma/\partial q$ and φ have definite advantages over others, since both these quantities have the same dimensions. They are used in the oscillograms in Figs. 2–5, where the modulus of estance $|\partial\gamma/\partial q|$, abbreviated to $|\gamma_q|$ is plotted against φ, expressed relative to the potential of the normal hydrogen electrode.

The introduction of the quantity $\partial\gamma/\partial q$ also follows naturally from a number of observed phenomena. One of these is the independence of the estance $\partial\gamma/\partial q$ of frequency in slow localised adsorption of charged species (Fig. 2*a*, on the right). This striking feature cannot be obtained by plotting $\partial\gamma/\partial\varphi$ or γ against φ.

The loss of information due to the differentiation of the $\gamma-\varphi$ relation in the process described is small. Static measurements, where there is no differentiation, nevertheless cannot yield the absolute value of γ. It is measured to within an arbitrary constant, which disappears on differentiation.

Yet another problem is important. In principle, static measurements can yield the variation of γ not only with φ

but also with the chemical potential μ of the adsorbed substance. The derivative $\partial\gamma/\partial\mu$ contains information about the concentration of this substance on the surface. However, $\partial\gamma/\partial\varphi$ can also be measured at different values of μ.

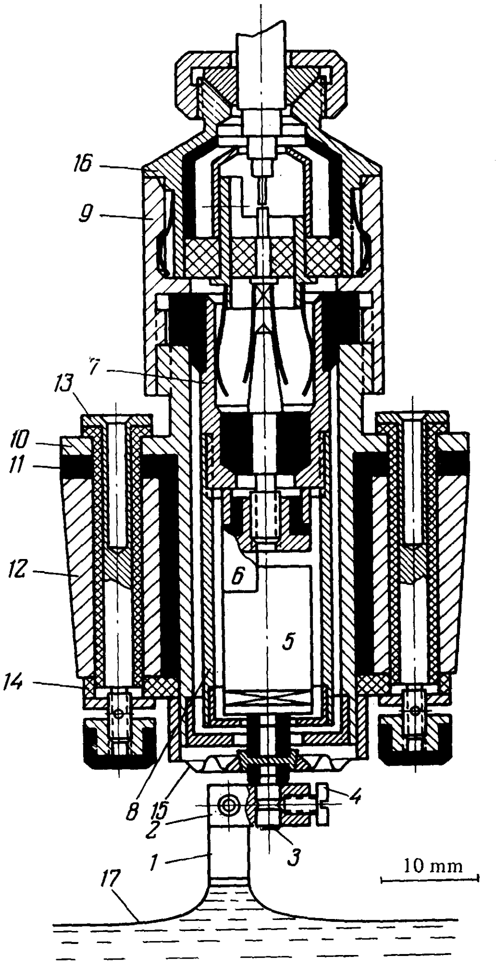

Figure 1. Unit for the transformation of surface tension: 1) L-shaped suprameniscus electrode; 2) holder; 3) shaft; 4) focussing screw; 5) piezoelectric element; 6) bush; 7) cartridge; 8) inner screen; 9) lock nut; 10) outer screen; 11) insulating beaker; 12) ground collar; 13) terminals; 14) insulating ring; 15) protective membrane; 16) coaxial plug; 17) electrolyte.

By integrating the derivative $\partial^2\gamma/\partial\mu\partial\varphi$ obtained in this way with respect to φ and starting with the desorption region (the potential φ_d at which there is no adsorbate on the electrode surface), we arrive at the following expression for $\partial\gamma/\partial\mu$:

$$\frac{\partial\gamma}{\partial\mu}=\int_{\varphi_d}^{\varphi}\frac{\partial}{\partial\mu}\left(\frac{\partial\gamma}{\partial\varphi}\right)d\varphi. \qquad (1)$$

Vanishingly small deformations of the solid electrode as a whole, occurring in measurements of the surface tension, have the same physical significance as the appreciable deformations caused by large forces. However, our aim was not to observe such vanishingly small deformations but to measure the forces under conditions where the deformations due to these forces are virtually absent.

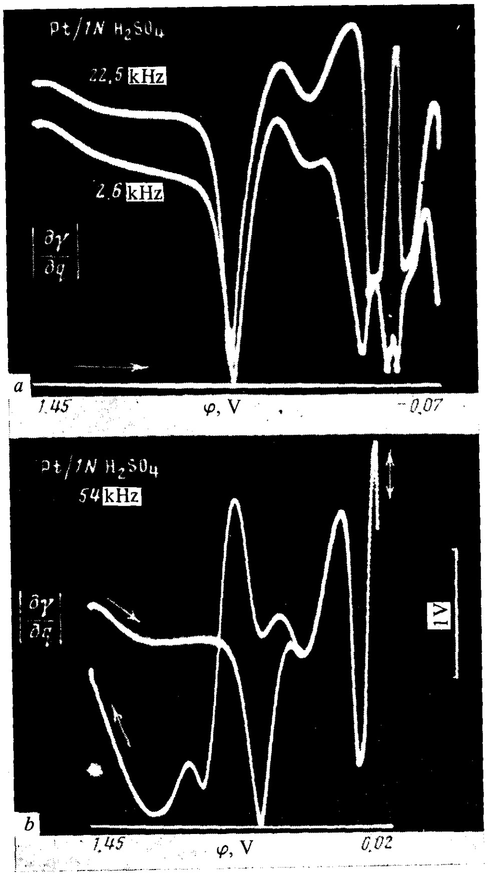

Figure 2. Estance–potential oscillograms for platinum in sulphuric acid: *a*) curves obtained by a single scan at two frequencies simultaneously; *b*) the merging of the forward and reverse curves in the hydrogen potential range

The measurements were made by comparing the surface tension with an independent standard tension, which is applied to the same surface and therefore simulates exactly the required quantity. The deformation does not have to be measured. As a result of this, the estance method is not restricted to any special shape of the electrode or to any specific mode of vibration of the electrode at different frequencies. The abandonment of deformation as the object of measurement is also natural because, when appreciable inertial forces act on the electrode, the deformation cannot serve as a unique measure of the surface tension forces.

The requirement of a small deformation is significant in the measurement of oscillating surface tensions of solids under equilibrium conditions and even more so under non-equilibrium conditions. This is because of the influence of elastic deformation on the state of the solid and of its surface. The process of measurement can distort the surface tension if the latter is able to execute a large amount of work in altering the surface.

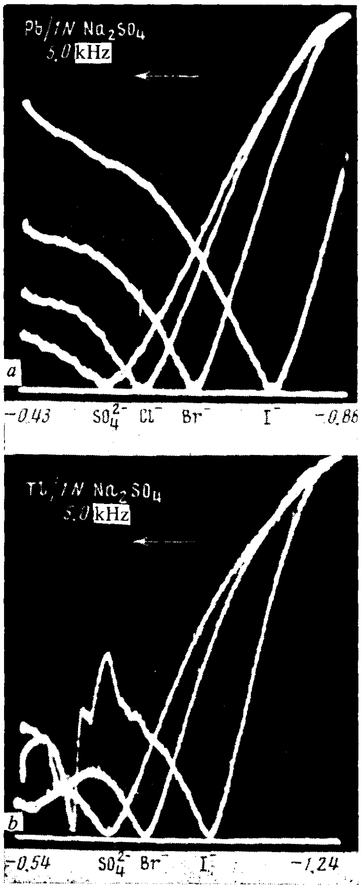

Figure 3. The influence of surface-active anions on the position of the zero estance point; electrodes: *a*) lead; *b*) thallium.

The estance method ensures a sensitivity to within not more than 0.01 dyn cm^{-1} with respect to the oscillating surface tension. It is more than enough to record exactly all the details of the dependence of the surface tension of the solid electrode on the potential. At the same time there is a capacity for a further improvement of sensitivity.

2. Experimental Technique

The results of estance measurements do not depend on the shape of the electrode. In the first experiments the electrode employed consisted of a strip of foil, which had been stretched beforehand, immersed vertically in a liquid electrolyte[5,6]. The lower end of the strip was attached to the bottom of the vessel and the upper end to a piezoelectric element built into the shell of the apparatus. With increase of the surface tension of the strip, the force applied to the piezoelectric element changes. The greater the rigidity of the piezoelectric element the smaller the shortening of the strip and the more complete the transmission of the increment in surface tension to the piezoelectric element. Thus, in measuring the force it is necessary to reduce the deformation. This constitutes the fundamental difference between the measurements of the force and deformation. The former can be achieved in general without altering the dimensions of the specimen; for this purpose, it is sufficient to balance the measured force by another force. Thermodynamically this is the most correct method of measurement. Under the given conditions, the balancing force is provided by the response of the piezoelectric element (if its rigidity is much greater than that of the foil). This device is suitable for measurements both under oscillatory and quasistatic conditions when the curve relating γ to φ is recorded directly for a linear variation of the electrode potential[5].

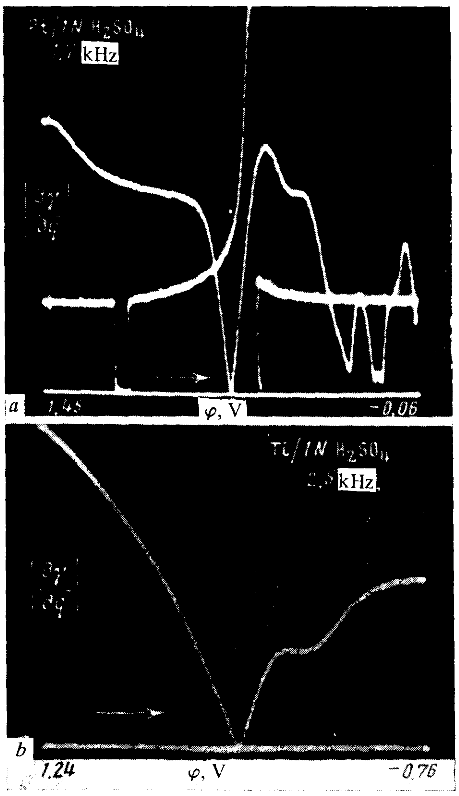

Figure 4. Estance–potential oscillograms: *a*) platinum, scale determined by thermal simulation; *b*) titanium, stepwise variation of estance in the hydrogen potential range.

Subsequently it was found that short (1 cm) and relatively thick (about 1 mm) plates can be used as the electrodes. One end of such an electrode is attached to the piezoelectric element and the other is free and immersed in the electrolyte[8]. The piezoelectric element records the inertial force of the plate oscillating under the influence of the variable surface tension. The response of the thick (and therefore rigid) plate to the shrinking tendency of its surface layer constitutes the balancing force under these conditions. With increase of the thickness of the plate, its deformation diminishes. However, as in the previous case, the residual capacity for the improvement of sensitivity is great. Furthermore, the mass of the plate increases with its thickness, which partly compensates the loss of inertial force caused by the decrease of deformation.

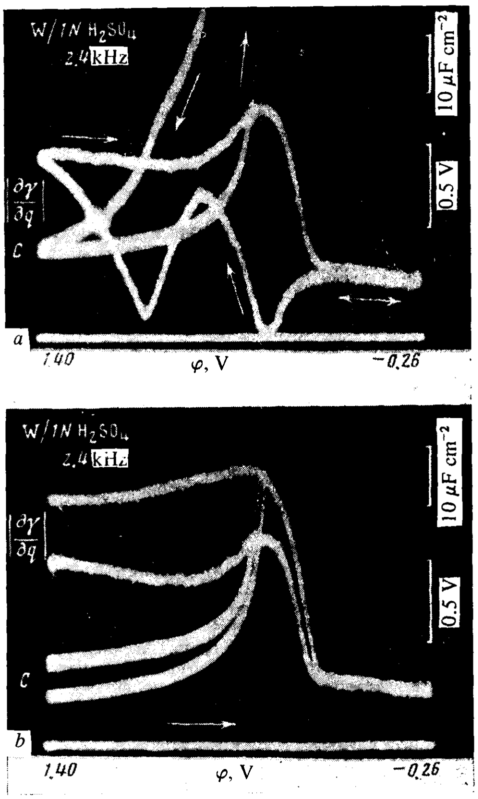

Figure 5. The variation of the estance $|\partial\gamma/\partial q|$ and the capacitance C recorded simultaneously as a function of the potential for tungsten in sulphuric acid: *a*) forward and reverse curves; *b*) different degrees of oxidation of tungsten.

A fully immersed electrode (foil strip), with both its sides operative to the same extent, was used in the first experiments because of the necessity to prevent possible distortions caused by pressure at right angles to the electrode during the passage of the alternating current[5-7]. The magnitude of this pressure was not known previously. In the course of the investigation it was found that, under the conditions of estance measurements, the above pressure is negligibly small (we shall return to its estimation at the end of this review). This made it possible to employ also electrodes with only one side operative. An example is provided by the suprameniscus electrode. Other types of electrodes were also proposed for studies of this kind[9], for example a dipolar electrode consisting of parallel plates with the electrolyte in the gap between them and an electrode with a vertical meniscus and a non-wettable frame.

3. The Influence of Side Effects

An interesting feature of the method described is virtually complete absence of an influence by side effects, as a result of which the oscillograms recorded are identical with the estance–potential curves and do not require a preliminary treatment. The internal stresses within the bulk of the electrode are isolated because diffusion in the solid is unable to follow the oscillations of the potential jump on its surface. The Joule heating of the electrolyte is quadratic in terms of the current and varies at twice the alternating current frequency, so that it is not recorded at the frequency of the estance measurement.

The shift of the electrolyte meniscus relative to the solid electrode, caused by the effect of the potential on the wetting angle[12], is slow at frequencies in excess of 10 Hz. Insulation of the electrode at the level of the meniscus (coating of the lateral faces of the suprameniscus electrode with glass, insulation of straight plates and foil strips at the sites where they emerge from the solution) does not influence the results of estance measurements in the above frequency range. Consequently such insulation is not necessary in the experiments under consideration.

4. The Standard Tension

For polarisable electrodes, which are the main object of study in the investigation of the structure of the interfacial layer, the alternating current is consumed in charging the sides of this layer, which leads to a change in surface tension. The evolution of heat on the surface of the electrode is then negligibly small.

On the other hand, in a concentrated oxidation-reduction system at moderate frequencies the alternating current is almost wholly consumed in the electrochemical reaction which is accompanied by the evolution of an appreciable amount of Peltier heat (of the order of 0.1 cal C^{-1}). On the other hand, the interfacial layer and the surface tension hardly change under these conditions. Depending on the direction of the current, the heat of reaction is evolved or absorbed at the electrode–solution boundary. Variable thermal and mechanical stresses, which induce oscillations in the electrode plate of exactly the same type as in the oscillating surface tension at the same frequency, develop in the electrode near this boundary. It is therefore sufficient to record the readings of the apparatus in the experiment with the oxidation-reduction system to be able to assess its sensitivity to surface tension[9].

The estance–potential curve for platinum in sulphuric acid is superimposed in Fig. 4*a* on the curve for the thermal vibrations of the same platinum electrode after the replacement of sulphuric acid by a solution of the 0.2 M $K_3Fe(CN)_6$–0.2 M $K_4Fe(CN)_6$ oxidation-reduction system with a Peltier coefficient $\Pi = 0.43$ V at 20°C. Exact formulae for thermal calibration, taking into account thermal waves in the bulk of the electrode, have been published[11]. It is interesting that for platinum the coefficient in these formulae is found to be close to unity, so that the level of the horizontal section of the calibration curve on the left-hand side of Fig. 4*a* approximately corresponds to $\Pi = 0.43$ V (we may note that the estance $\partial\gamma/\partial q$, plotted along the ordinate axis, is also measured in volts).

In order to calibrate in this way electrodes made of other metals, after the main experiments they were coated with a thin layer of gold (0.5 μm) in an electroplating bath, which protects them from disintegration in the above oxidation-reduction medium.

The heat evolved in the reversible electrochemical dissolution of the electrode itself in a specially selected medium can be employed similarly. In another method of thermal simulation of surface tension, use is made of the Peltier heat evolved at the boundary between two metals. The end of a narrow strip of platinum foil is lightly welded to the rear side of the suprameniscus electrode. For calibration, an alternating current is passed through this junction. The simulation effect is the same as for evolution of heat on the working electrode surface. This method permits calibration in the course of the main experiment. A simplification is introduced by replacing the welded foil by a drop of liquid metal (gallium or mercury). The drop is placed on the rear surface of the electrode and is connected to the current generator via a rigid conductor. If the junction between the two metals occupies an insignificant proportion of the rear electrode surface, the nature of the distribution of current in this junction is immaterial.

Another procedure for the thermal simulation of surface tension involves the passage of a high-frequency amplitude-modulated current. The surface of the electrode is periodically heated by the Joule heat evolved in the electrolyte. This operation is performed during the main experiment without changing the solution. However, it is necessary to take precautions in order to eliminate the influence of the thermal expansion of the electrolyte; in dilute aqueous solutions this can be achieved, for example, by making measurements near 4 °C (when a surface source of heat such as the heat of reaction, is employed, the bulk of the electrolyte is not heated and this precaution is of course unnecessary).

For rectangular high-frequency sinusoidal current pulses with a tracking frequency $\omega/2\pi$ and the reciprocal of the Q-factor π/α, the amplitude of the standard thermal tension at the frequency $\omega/2\pi$ is

$$\Delta\gamma_r = \frac{\sin\alpha}{\pi}\Delta j^2 r D_\tau^{1/2}\omega^{-3/2}\cdot\frac{1}{1-\nu}\cdot\frac{\varkappa Y}{\zeta\rho}|M|, \tag{2}$$

where Δj is the amplitude of the current density; parameters of the electrolyte: r is the resistivity and L_T the thermal diffusivity; parameters of the electrode: ν is the Poisson coefficient, Y the modulus of elasticity, κ the coefficient of linear thermal expansion, ζ the specific heat, and ρ the density; the quantity M takes into account the loss of heat from the electrode surface; in the upper part of the audiofrequency range $|M|$ is usually close to unity; the formula for M has been published[11].

5. Thermal Tension in Adsorption on the Electrode

Apart from its main purpose, the estance method can be used also to estimate the heat evolved on the electrode during adsorption, which was apparently difficult to achieve by other methods in earlier investigations. In those rare cases where the thermal and surface tensions act simultaneously, they can be readily separated by virtue of the phase difference caused by the loss of heat to the bulk of the electrode[11]. Measurements have shown that the heat evolved in adsorption is usually negligibly small against the background of the estance values. Thus, according to an estimate made by the estance method, the evolution of heat in the adsorption reaction $H^+ + e \rightleftharpoons H_{ads}$ on platinum does not exceed 1 kcal faraday^{-1} or 0.05 V.

6. Examples of the Interpretation of the Oscillograms

Fig. 6 illustrates the estance–potential curves for platinum in sulphuric acid obtained simultaneously at frequencies of 2.6 and 22.5 kHz (they correspond to the oscillograms in Fig. 1*a* adjusted to the same vertical scale). A study was made of the range of potentials in which hydrogen is adsorbed on platinum. Therefore all the details of these curves are associated with the characteristics of the adsorption of hydrogen.

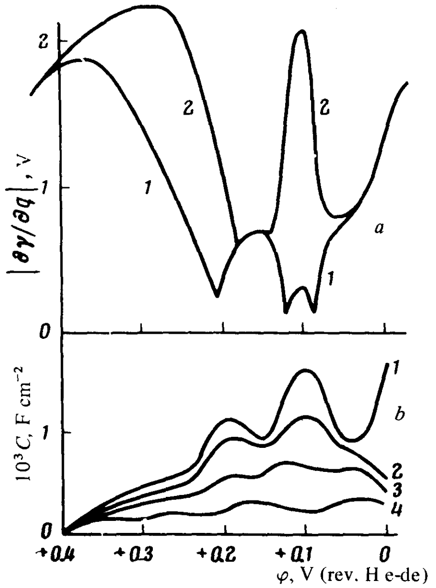

Figure 6. The influence of frequency on the variation of the estance (*a*) and the capacitance (*b*) with potential for platinum in sulphuric acid; frequency (kHz): *a*) [1) 2.6; 2) 22.5]; *b*) [1) 0.03; 2) 1.7; 3) 4; 4) 10].

The influence of frequency on estance is unexpected; sections corresponding to a strong dependence of estance on frequency alternate along the potential axis with sections where estance is almost independent of frequency and two such sections are located within the region corresponding to the adsorption of hydrogen. As the potential shifts in the cathodic direction, the sections alternate as follows: (1) from +0.50 to +0.30 V—the section where the potential is independent of frequency due to the absence of hydrogen from the platinum surface (the adsorption of hydrogen begins near +0.30 A); (2) from +0.30 to +0.18 V—the section of a strong dependence on frequency; (3) from +0.18 to +0.14 V—the section with potentials independent of frequency; (4) from +0.14 to +0.04 V—the section of a strong dependence on frequency (there is a dip in the curve at 2.6 kHz and a peak at 22.5 kHz); (5) below +0.04 V—the section where the potential is independent of frequency[13].

For comparison, Fig. 6*b* presents the known capacitance curves for the same system at different frequencies[14]. In contrast to estance, the capacitance decreases monotonically with frequency at all the potentials in the hydrogen adsorption region. Under these conditions, the capacitance is almost wholly due to the discharge of hydrogen ions from the electrolyte before their adsorption on platinum in the form of atoms. The discharge stage is slow[3] regardless of the final state of the adsorbed atom. At high frequencies the discharge lags behind the change in periodic component of the potential, which leads to a decrease of the capacitance with frequency.

In contrast to this, the variation of estance with frequency is directly related to the *final* state of the adsorbed hydrogen atoms. It has no bearing on the discharge stage and its rate, since in the estance method the current amplitude and hence the number of hydrogen atoms which reached the surface *after* the discharge are specified beforehand. Thus the sections where estance is and is not independent of frequency separate along the potential axis adsorption regions with different final states of the hydrogen atoms.

This quite definite result follows immediately from the estance–potential oscillograms without any need for their quantitative interpretation. Another problem, i.e. the problem of the adsorption mechanisms along each of the differentiated sections, requires special study, which has been carried out[13]. Here we shall enumerate some of the results obtained here. It had been known previously that hydrogen can exist on platinum in two states (which shall be designated conventionally by H_e and H_m), but the limits of the regions corresponding to adsorption in these states had not been known. It was assumed that H_e is adsorbed initially and then H_m. It follows from the estance data that along the sections where estance is independent of frequency H_e is adsorbed (the third and fifth sections), while in the intermediate region with a strong dependence of estance on frequency H_m is adsorbed (the fourth section). Along this section, the dip in the estance curve at 2.6 kHz is due to an interruption in the adsorption of H_e and the estance peak at 22.5 kHz is caused by the internal transition $H_e \rightleftharpoons H_m$ when the potential is altered. The fact that the internal transition influences the estance markedly and is not manifested in the capacitance measurement is due to the difference between force (estance method) and energy (capacitance method). A large change in the force can be caused by an arbitrarily small energy. In this case an appreciable alteration of the surface tension is caused by a small expenditure of energy in changing the state of the interfacial layer. This is the reason for the enhanced sensitivity of the estance method to a number of processes which cannot be detected by "energy" methods.

Some of the effects detected by the estance method in the adsorption of hydrogen on platinum are illustrated in Fig. 7, which represents schematically the surface layer of platinum.

Effect of the interruption of adsorption. As the potential varies in the cathodic direction, the adsorption of external hydrogen (H_e) is interrupted by the adsorption of internal hydrogen (H_m), but begins anew after vacancies in the internal hydrogen have been largely filled.

Effect of the internal transition. There is a discrete change in the state of adsorbed hydrogen when the potential is altered. In a pure form the effect is observed at high frequencies when the supply of hydrogen from the electrolyte ceases and the overall amount of adsorbed hydrogen does not vary with potential. The transition is possible at potentials where the vacancies in both external and internal hydrogen are far from being completely filled.

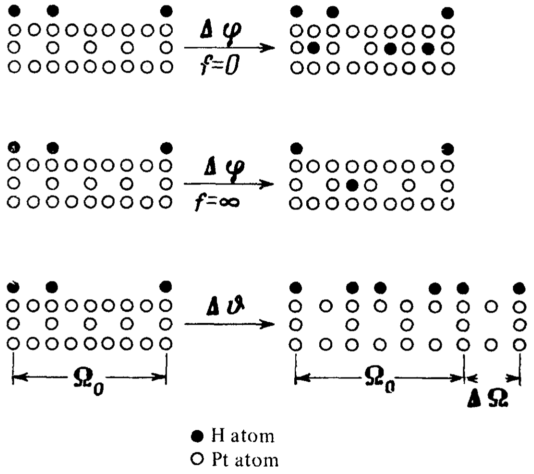

Figure 7. Schematic illustration of the effects observed by the estance method in the adsorption of hydrogen on platinum: *a*) the interrupted adsorption effect; *b*) the internal transition effect; *c*) the effect involving an increase of the surface density of adsorbed hydrogen on elastic extension of platinum; Ω_0 = initial area of the electrode; f = frequency.

Effect of the increase of adsorbed hydrogen density during elastic extension of platinum. The number of surface platinum atoms and the number of adsorbed atoms per unit surface area vary in opposite directions. With increase of the distance between the surface platinum atoms, the average distance between the hydrogen atoms diminishes. This shows that, as the platinum atoms move apart, their affinity for external atomic hydrogen rises.

The first two effects are caused by the change in electrode potential and the third is due only to the elastic deformation at a constant potential. Thus information about the events on the electrode when the potential is varied under conditions without deformation can also be obtained with equal success from the same estance–potential oscillogram.

The dual nature of estance-potential oscillograms will be considered further.

III. ELASTIC CHARGING OF THE INTERFACIAL LAYER

1. The Change in the Potential of the Polarisable Electrode on Elastic Deformation

An electrode in the form of a stretched foil strip immersed in the electrolyte undergoes periodic elastic extension and contraction with an elongation amplitude of the order of 10^{-6} at a definite frequency to which the measuring apparatus is tuned. Under the conditions of a constant charge, the potential of this electrode oscillates with an amplitude of the order of 1 μV. For a specified relative deformation amplitude, the potential oscillations are independent of the dimensions of the electrode. The results are recorded oscillographically in terms of a plot of $|\partial\varphi/\partial\theta|$ against φ, where $\theta = \Delta\Omega/\Omega$ is the relative change in the area of the electrode Ω on elastic deformation.

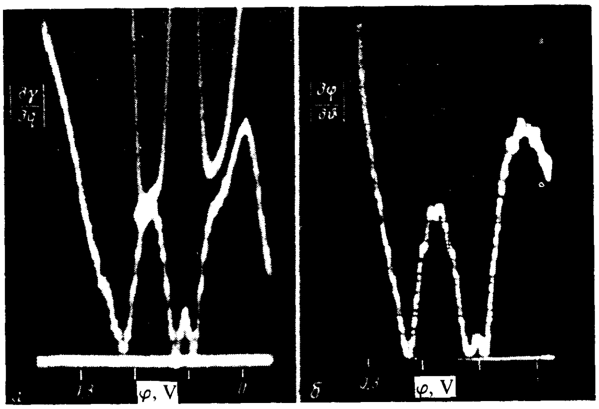

Figure 8. Comparison of oscillograms for estance (*a*) and the elastic charging of the interfacial layer (*b*); the potential is given relative to that of the reversible hydrogen electrode.

2. Mutually Opposed Effects

The $|\partial\varphi/\partial\theta|-\varphi$ oscillogram obtained in a reversible system (for example for platinum in 1 *N* sulphuric acid solution in the hydrogen potential range) is of exactly the same form as the $|\partial\gamma/\partial q| -\varphi$ oscillogram (Fig. 8). The significance of this agreement, which appeared unexpected in the very first experiment on elastic charging, is that the surface tension varies with the charge in the same way as the potential varies with the surface area[15,16]

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

(the derivative $\partial\varphi/\partial\theta$ is obtained for a constant overall electrode charge). Hence follows also the equation

$$\frac{\partial\gamma}{\partial\varphi} = -q - \frac{\partial q}{\partial\vartheta}. \tag{4}$$

After Eqn. (3) had been suggested by experiment, it became clear that it should follow from thermodynamics. However, until the elastic charging effect had been observed there was no reason to compare the two derivatives. Furthermore, in the thermodynamics of surface phenomena it is simpler to formulate the equation than to elucidate the significance of the quantities involved in it. An example is provided by Young's simple equation for the angle of wetting of a solid by a liquid, which was proposed in 1805.[17] However, controversy concerning the physical significance of its variables is still continuing, namely whether these are forces acting along three interfaces or whether they represent the work of formation of these interfaces[18,19].

In the absence of experiments on elastic charging the significance of the quantity θ in Eqn. (3) would have remained obscure, i.e. it would not have been known whether it represents elastic or plastic deformation. On the other hand, if one could imagine an effect opposite to that of the potential on the wetting angle, the significance of the quantities in Young's equation would become clearer.

3. The Equation for the Wetting of Solid Electrodes

Frumkin and coworkers[20-22] have made systematic studies on the influence of the potential on the wetting of liquid electrodes. At the boundary between the electrode and a gas bubble a conducting electrolyte film was observed[21]. The publication of studies specially devoted to the wetting of solid electrodes began recently. A series of detailed studies by Morcos, in which measurements were made of the wetting angle for a planar solid electrode as a function of potential[23-26], and the investigation of Bonnemay et al.[27] are noteworthy.

Below we shall describe an approach to the problem based on the relation between the forward and reverse effects. Consider a solid electrode of arbitrary shape partly immersed in a liquid electrolyte solution (for example a half-immersed rectangular plate). Suppose that z is the vertical coordinate of the electrode (the depth of immersion is reckoned from the horizontal level of the liquid solution), $\mathscr{P}$ the weight of the partly immersed electrode for a fixed z (the force experienced by the object from which the electrode is suspended), Q the overall charge of the electrode, and φ the potential of the electrode relative to a reference electrode immersed in the same electrolyte. If the remaining parameters of the system are kept constant, the total differential of its free energy is

$$dF = -\mathscr{P}dz + \varphi dQ \quad . \tag{5}$$

Hence we obtain the fundamental equations

$$\frac{\partial\mathscr{P}}{\partial Q} = -\frac{\partial\varphi}{\partial z}, \tag{6}$$

$$\frac{\partial\mathscr{P}}{\partial\varphi} = \frac{\partial Q}{\partial z} \tag{7}$$

representing the change in the weight of the partly immersed electrode when the change in potential corresponds to the change in the charge of the electrode on immersion.

Suppose further that the electrode has a cylindrical surface with a vertical generatrix and directrix of arbitrary form (for example, a vertical plate). The contour of the horizontal section through the electrode at the level of the solution at a point remote from the meniscus will be called the water line of the electrode. The wetting boundary does not coincide with this line and is not in the general case a two-dimensional curve. For example, at the edges of the plate the meniscus is below its position in the central part of the plate. We introduce the following notation: s is the length of the water line and, what amounts to the same thing, the perimeter of the electrode cross-section and q_i and q_n are the charge densities on the immersed and unimmersed parts of the electrode respectively. If the electrode is not smooth, then q_i and q_n must be replaced in the corresponding formulae by αq_i and αq_n, where α is the roughness factor. The overall charge of the electrode is $Q = s[zq_i + (H - z)q_n]$, where H is the height of the electrode. Since the densities q_i and q_n are independent of z, it follows that $(\partial Q/\partial z)/s = q_i - q_n$. On substituting this in Eqn.(7), we obtain the equation for the wetting of solid electrodes:

$$\frac{1}{s}\frac{\partial \mathscr{P}}{\partial \varphi} = q_i - q_n. \tag{8}$$

This is the fundamental equation. It makes it possible to determine $q_i - q_n$ directly from the dependence of the weight of the electrode on the potential. No restrictions are then imposed on the form of the electrode cross-section and the shape of the meniscus. The non-uniformity of the wetting line is permissible, for example the fall of the meniscus at the edges of the plate.

The following formula was obtained similarly:

$$\frac{1}{s}\frac{\partial \mathscr{P}}{\partial \mu} = \Gamma_i - \Gamma_n, \tag{9}$$

where μ is the chemical potential of the adsorbable substance and Γ_i and Γ_n are the relative surface amounts of this substance on the immersed and unimmersed parts of the electrode respectively (relative to the simultaneous adsorption of the solvent).

Under conditions where q_n is independent of φ, the differential equation (8) yields

$$\frac{1}{s}\frac{\partial^2 \mathscr{P}}{\partial \varphi^2} = C, \tag{10}$$

where $C = \partial q_i/\partial \varphi$ is the differential capacitance of the electrode. The minimum weight $\mathscr{P}$ is reached when $q_i = q_n$.

A force equal to the weight of the meniscus is applied to the electrode along the wetting line. We project a small section of this line on to the water line. The ratio of the corresponding fraction of the weight of the meniscus to the length of the projection will be called the weight tension $\mathscr{C}$. The weight tension is the same at all points on the water line for any shape of the latter. Thus the weight of the meniscus is $s\mathscr{C}$. For this reason Eqn.(8) can be rewritten as follows:

$$\frac{\partial \mathscr{C}}{\partial \varphi} = q_i - q_n. \tag{11}$$

Formulae referring to special types of electrodes follow from Eqn.(8). Suppose, for example, that the electrode consists of a thin layer of metal deposited on the inner surface of a capillary with radius a and that the capillary contains a column of electrolyte with a height h and density ρ. Then $s = 2\pi a$ and $\mathscr{P} = \pi a^2 h\rho$ (the weight of the liquid in the capillary) to within constant terms. Eqn.(10) immediately yields the following result:

$$\frac{\rho a}{2}\frac{\partial^2 h}{\partial \varphi^2} = C, \tag{12}$$

which agrees with the formula obtained previously by Bonnemay by differentiating Young's equation and by examining the geometry of the meniscus in the capillary[27]. Measurement of the height of the rise of the liquid by an optical method (involving the passage of X-rays through the liquid[27]) is associated with errors comparable to the radius of the capillary.

However, it follows from the general equation (8) that there is no need to consider the geometry of the meniscus, to make separate calculations for each shape of the electrode, and to measure a specific parameter characteristic of each given electrode. It is sufficient to measure the influence of the potential on a parameter common to all electrodes, namely their weight. This greatly simplifies the experiment, increasing its accuracy and sensitivity.

The weight tension $\mathscr{C}$ is related to the wetting angle θ and the surface tension of the liquid by the expression

$$\mathscr{C} = \sigma_0 \cos\theta. \tag{13}$$

Hence we obtain from Eqn.(11)

$$q_i - q_n = -\sigma_0 \sin\theta \frac{\partial \theta}{\partial \varphi}. \tag{14}$$

Eqns.(8) and (11) are applicable to isotropic and anisotropic surfaces. The charge densities on the right-hand side of Eqn.(11) are independent of the orientation of the anisotropic surface following immersion. Consequently $\mathscr{C}$ is a scalar quantity. It characterises the work of wetting and has no bearing on the surface tension of the solid, which is a tensor. The quantities entering into Young's equation are also scalar and cannot be identified with forces. On the other hand, owing to the term $\partial q/\partial \theta$, which depends on the direction of deformation, Eqn.(4) defines a tensor—the surface tension γ.

4. The Surface Tension and the Work of Formation of the Surface of a Solid Electrode

The difference between the surface tension of a solid γ and the reversible work of formation of its unit surface σ, noted 100 years ago by Gibbs[28], has not so far been confirmed experimentally owing to the lack of data for the surface tensions of solids. The results of the present study permit such a comparison at the level of derivatives of these quantities with respect to the potential.

Fig. 9 illustrates the variation of $\partial\gamma/\partial\varphi$ and $\partial\sigma/\partial\varphi$ with potential φ for platinum in 1 N H_2SO_4; $\partial\gamma/\partial\varphi$ was measured by the estance method and $\partial\sigma/\partial\varphi$ is equal, according to Lippman's equation, to the total charge density q of the platinum electrode, the dependence of which on the potential was measured for the first time by Frumkin and coworkers[3]. The difference between the two quantities is large: like the charge, $\partial\sigma/\partial\varphi$ varies monotonically with potential, while $\partial\gamma/\partial\varphi$ passes through zero three times in the hydrogen potential range. Accordingly the integrated relation between the surface tension of the platinum electrode and the potential has three extrema—two maxima at +0.1 and +0.2 V (relative to the potential of the reversible hydrogen electrode) with an intervening minimum.

After substracting q from the φ-estance in accordance with Eqn.(4), we obtain $\partial q/\partial\theta$—the change in charge density as a result of elastic deformation at a constant potential. The variation of $\partial q/\partial\theta$ with φ is indicated by a dashed line; hence it is clear that, in the system under consideration, the term $\partial q/\partial\theta$ in Eqn.(4) predominates over the term q and largely determines the variation of γ with φ.

Thus the experimental data obtained by the estance method demonstrate a difference between the surface tension of a solid and the reversible work of formation of its unit surface and also that this difference obtains in the region of electrocapillary phenomena. The latter had been overlooked until the present investigation.

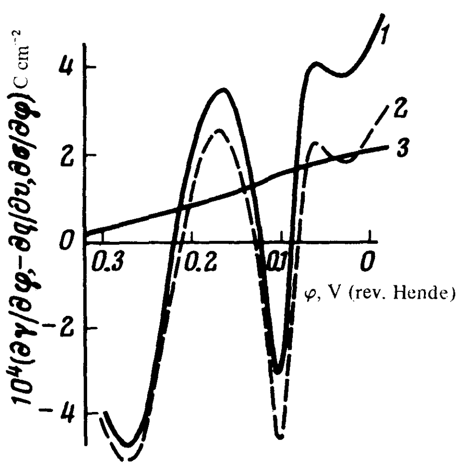

Figure 9. The difference between the surface tension γ and the work of formation of unit surface area σ of a solid electrode at the level of derivatives of these quantities with respect to the potential φ for platinum in 1 *N* H_2SO_4:
1) $\partial\gamma/\partial\varphi$; 2) $-\partial q/\partial\theta$; 3) $\partial\sigma/\partial\varphi$.

5. The Surface Tension of a Rough Surface

Suppose that the rough interface coincides with one of the sides of the plate and that α is the roughness factor: the ratio of the area of the rough surface Ω to the area of its average plane Ω_0 is $\alpha = \Omega/\Omega_0$. The surface tension γ directed along rugosities deforms the plate as a whole in a specific manner. It is necessary to find γ_0, acting uniformly, which when directed along the plane would give rise to the same deformation. For each specific electrode, the results of the surface tension and elastic charging methods should coincide regardless of whether the electrode surface is smooth or rough. Hence, and also on the basis of the principle of the reciprocity of the displacements, it was found that the increments in the tensions γ_0 and γ refer to the increments of the areas Ω and Ω_0 on elastic deformation. We call the ratio

$$\beta = \Delta\Omega/\Delta\Omega_0 = \Delta\gamma_0/\Delta\gamma \tag{15}$$

the differential roughness factor. In many cases the model of a rough surface with rugosities in the form of parallel ridges with a symmetrical triangular cross-section is applicable. For an isotropic surface, consisting of sections with ridges running in random directions[13], we have

$$\beta = \frac{1}{2}[(1-\nu)\alpha + (1+\nu)\alpha^{-1}]. \tag{16}$$

For example, for lead ($\nu = 0.44$) the deviation of β from unity on such a surface does not exceed 11% in the range $1 \leq \alpha \leq 3$.

The knowledge of β permits the determination of the true estance from its planar equivalent (subscript 0) measured experimentally. For φ- and q-estance, we have

$$\frac{\partial\gamma_0}{\partial\varphi} = \beta\frac{\partial\gamma}{\partial\varphi}; \frac{\partial\gamma_0}{\partial q_0} = \frac{\beta}{\alpha}\frac{\partial\gamma}{\partial q}. \tag{17}$$

6. Discrepancies Between the Forward and Reverse Effects

Among the irreversible processes which disturb the correspondence between the results of surface tension and elastic charging measurements, the Faraday diffusion current, caused by the presence of traces of electrochemically active substances in solution, is encountered most frequently. Stirring is known to increase this current. A strip undergoing longitudinal deformation stirs the solution much less than a transversely vibrating suprameniscus electrode. This in fact dictated the choice of a strip for recording elastic charging.

It is interesting that the diffusion current does not influence at all the result of measurements of oscillating surface tension (it is smaller by several orders of magnitude than the specified charging current amplitude). This is the reason for the discrepancies and demonstrates at the same time the advantages of the surface tension method. Hence it is also seen that the agreement between the surface tension and elastic charging data is not predetermined beforehand and that even the discrepancies between these data can lead to useful conclusions about the test object.

Noting the similarity between the data derived by the two methods, we began with the first harmonics of the quantities recorded by them—the surface tension and the potential. At the level of the highest harmonics the two methods yield different information even in reversible systems.

IV. SOME PROBLEMS OF THE THEORY OF ESTANCE

1. The Surface Tension Increment

Consider a solid electrode in a solution containing, together with a solvent, m components which are electrically neutral overall. The electrode potential φ is specified relative to a reference electrode, which is reversible with respect to one of the ions forming part of the electrolyte. In the general case the change in the surface tension of the solid electrode γ is described by the equation[15]:

$$d\gamma = -\left[q + \left(\frac{\partial q}{\partial\vartheta}\right)_{\varphi,\mu_k}\right]d\varphi - \sum_{s=1}^{m}\left[\Gamma_s + \left(\frac{\partial\Gamma_s}{\partial\vartheta}\right)_{\varphi,\mu_k}\right]d\mu_s, \tag{18}$$

where q is the electrode charge density, Γ_s and μ_s are the excess amounts on the surface relative to the solvent and the chemical potentials of the solution components, θ is the relative change in the area of the electrode during its elastic deformation, and $k, s = 1, \ldots, m$.

2. Indication of Localised Adsorption

The slope of the estance–potential curve is characterised by the derivative $\gamma_{q\varphi} = \partial(\partial\gamma/\partial q)/\partial\varphi$. The amplitude of the second harmonic of the potential at a specified sinusoidal current is proportional to the derivative $\varphi_{qq} = \partial^2\varphi/\partial q^2$. On metallic electrodes in the absence of localised adsorption, $\gamma_{q\varphi} = -1$ both at the zero-charge point and at the zero points of the second harmonic:

$$\gamma_{q\varphi} = -1 \text{ when } q = 0 \text{ or } \varphi_{qq} = 0. \tag{19}$$

Under the same conditions, $\gamma_{q\varphi}$ at zero estance is

$$\gamma_{q\varphi} = -1 + \frac{\partial\varphi_0}{\partial\vartheta}\frac{1}{C}\frac{\partial C}{\partial\varphi} \text{ when } \gamma_q = 0, \tag{20}$$

where C is the differential capacitance of the electrode and

$$\frac{\partial\varphi_0}{\partial\vartheta} = \frac{\partial\gamma}{\partial q}\bigg|_{\varphi=\varphi_0} \tag{21}$$

is the shift of the zero-charge potential φ_0 on elastic deformation of the electrode. For non-localised adsorption, this quantity does not exceed 0.03 V [29] and the property $\gamma_{q\varphi} = -1$ therefore persists to within at least 10% also at zero estance.

The deviation of the slope $\gamma_{q\varphi}$ from unity at the above points is a sufficient indication of localised adsorption. For cadmium in 0.01 M NaF, the slope of the estance–potential curve at zero estance (and at the point where $q = 0$) is close to -3. Hence we conclude that water is locally adsorbed on cadmium [29].

3. The Estance of the Diffuse Double Layer

If the fluidity of the liquid electrolyte persists up to its boundary with the dense part of the double layer, elastic deformation does not alter the parameters of the diffuse layer. Under these conditions, at the zero-charge point and a low electrolyte concentration a, the following relation holds:

$$\gamma_{q\varphi} = -1 - B\sqrt{a} \text{ when } \varphi = \varphi_0, \tag{22}$$

where B is a constant independent of a. On dilution and therefore on increase of the thickness of the diffuse part of the double layer, the slope $\gamma_{q\varphi}$ tends to unity regardless of the structure of the dense part of the double layer.

The fluidity condition probably does not hold in all systems. On dilution, an appreciable decrease of the slope should occur for cadmium in aqueous NaF solutions. However, up to a concentration of 0.001 M, this effect is not observed, which suggests that on cadmium there is a locally adsorbed polymolecular film of water in which the diffuse part of the double layer adjoining the electrode is accommodated; this film has an ordered structure but retains the defects characteristic of the liquid in the form of migrating vacancies, which permits the motion of ions at the electrode and preserves nearly normal capacitance values.

4. The Estance of a Solid *in Vacuo*

Consider a planar condenser consisting of identical plates *in vacuo*, whose electron work function is φ_{0v}. When an alternating current is passed through the condenser and the average stress applied to its plates is zero (for example the plates are connected to the secondary winding of a transformer), the oscillations of the surface tension γ of each plate at the current frequency can be measured. Then [30]

$$\frac{\partial\gamma}{\partial q} = \frac{\partial\varphi_{0v}}{\partial\vartheta}, \tag{23}$$

i.e. the estance is equal to the change in the electron work function on elastic deformation of the specimen.

5. The Introduction of Elastic Deformation into the Adsorption Isotherm

When electrically neutral species are adsorbed from the solution, their chemical potential in solution μ is independent of the electrode potential φ. At a constant value of φ the surface concentration of these species Γ is a function of μ and of the relative change in the area of the electrode on elastic deformation θ: $\Gamma = \Gamma(\mu, \theta)$. In its usual sense [4], the adsorption isotherm defines the variation of Γ with μ in the absence of deformation (when $\theta = 0$):

$$\Gamma = \Gamma(\mu, 0) = f(\mu). \tag{24}$$

Suppose that

$$\xi(\mu, \vartheta) = \frac{\partial\gamma}{\partial\Gamma}(\mu, \vartheta) \tag{25}$$

is the contribution of the adsorbed species to the surface tension known on the basis of experimental data to be a function of both μ and θ. Then expansion of Γ in powers of θ is

$$\Gamma(\mu, \vartheta) = f - \vartheta(f + f'\xi) + \frac{1}{2}\vartheta^2[f + f'(2\xi + \xi\xi_\mu - \xi_\vartheta) + f''\xi^2], \tag{26}$$

where

$$f' = \mathrm{d}f/\mathrm{d}\mu,\ f'' = \mathrm{d}^2f/\mathrm{d}\mu^2,\ \xi_\mu = \partial\xi/\partial\mu,\ \xi_\vartheta = \partial\xi/\partial\vartheta.$$

6. The Increase of Estance with the Thickness of the Polarised Layer

In many systems, for example on platinum and tungsten, in aqueous solutions at fairly anodic potentials the estance increases with the degree of oxidation of the surface (the capacitance curves corresponding to different degrees of oxidation are superimposed in Fig. 5*b* on the estance curves; a decrease of the capacitance curve is accompanied by a rise of the estance curve). The increase of estance with the thickness of the coating, in the given instance an oxide coating, is a sign of the existence of an intrinsic dipole moment of the coating and is described by the expression [31]

$$\frac{\partial\gamma}{\partial q} = \left(-1 + \frac{\partial\delta}{\partial\vartheta} - \frac{\partial w}{\partial\vartheta}\right)(\varphi - \varphi_n) + \left(\frac{\partial\delta_0}{\partial\vartheta} - \frac{\partial\delta}{\partial\vartheta}\right)\frac{P}{\varepsilon}\mathfrak{h} + \frac{\partial\varphi_n}{\partial\vartheta}, \tag{27}$$

where P is the intrinsic polarisation of the coating (the dipole moment per unit volume), ϵ the effective dielectric constant of the coating, θ the relative change in the area of the electrode on elastic deformation, w, δ, and δ_0 are the relative values of the dielectric constant, the thickness of the coating, and the length of one arm of the dipole respectively, φ_n is the zero-charge potential of the oxidised electrode extrapolated to zero thickness of the oxide film, and $\mathfrak{h}$ the effective thickness of the coating, whose significance is retained at coverages less than the monolayer value, equal to the ratio of the volume occupied by the coating to the area of the electrode.

V. THE INFLUENCE OF BULK-PHASE FORCES ON THE ELECTRODE

1. Inertial Oscillation of the Electrolyte on Passage of an Alternating Current

Suppose that an electrolyte solution is in a long open channel and that a current at a density $j = \Delta j \sin\omega t$, where t is the time and $\omega/2\pi$ the frequency, passes along the channel. Then at points remote from the walls of the channel the solvent coordination system is displaced relative to the laboratory coordinate system at the rate[7,32]

$$v_0 = (\Delta j/F\rho)\,\mathbf{M}\sin\omega t, \tag{28}$$

where F is the Faraday, ρ the density of the solution,

$$\mathbf{M} = \tau_a(m_a - \rho_0\psi_a) - \tau_c(m_c - \rho_0\psi_c) \tag{29}$$

the reduced mass, τ, m, and Ψ are respectively the transport number, the gram-ionic weight, and the apparent ionic volume of the anion (subscript a) and the cation (subscript c), ρ_0 is the solvent density, and Ψ_a and Ψ_c are the fractions of anions and cations in the volume displaced from the pure solvent on dissolution of one equivalent of the electrolyte; these values have been determined recently by several methods and are quoted in the literature[33,34].

2. The Viscous Force of the Electrolyte

The wall of the channel through which the sinusoidal current is flowing within the electrolyte is acted upon by a viscous force[32]

$$\mathfrak{g} = \sqrt{\omega\chi}\,(\mathbf{M}\Delta j/F)\cos\left(\omega t + \frac{3}{4}\pi\right), \tag{30}$$

where χ is the kinematic viscosity of the solution; the force $\mathfrak{g}$ is referred to unit area of the wall. It is manifested independently of the electrophoretic force.

Under the conditions of estance measurements, the alternating current flows only at right angles to the surface of the electrode, which does not therefore experience a tangential force. However, it is possible to devise a special experiment where conditions are created such that the alternating current in the electrolyte flows only parallel to the electrode surface. Then the surface is acted upon by the force $\mathfrak{g}$.

3. Generation of Ultrasound at the Electrode

Suppose that the electrode is absolutely rigid and consists of a plane bounding half the space of the electrolyte (this condition holds, for example, for a metallic membrane both sides of which are active to an equal extent). Then the pressure on the electrode caused by the displacement of the centre of gravity[7] in the volume of electrolyte adjoining the electrode on passage of the alternating current is $p_0 = -\Delta p_0 \sin\omega t$ with the amplitude

$$\Delta p_0 = u\mathbf{M}\Delta j/F, \tag{31}$$

where u is the velocity of sound in the solution.

The electrode processes also contribute to the pressure. For example, the passage of one equivalent of cations from the bulk of the electrolyte to the surface of the electrode leads to an increase of the overall volume of the layer near the electrode by $V_{ce} - V_{cs}$, where V_{ce} and V_{cs} are the partial equivalent volumes of the cation in the double layer and in the electrolyte respectively. The heat evolved at the electrode on passage of one equivalent of electricity, which increases the volume near the electrode by a certain amount (by $V_\Pi = \Pi F\mathfrak{b}/\zeta\rho$ for a thin membrane, where $\mathfrak{b}$ is the coefficient of cubic expansion of the solution, ζ the specific heat of the solution, and Π the effective Peltier coefficient). Thus the overall pressure amplitude in the given case is

$$\Delta p = u(\Delta j/F)[\mathbf{M} + \rho(V_{ce} - V_{cs} + V_\Pi)]. \tag{32}$$

On electrodeposition, V_{ce} is replaced by the equivalent volume of the metal. The quantity ρV_Π is of the order of 0.1 g equiv.$^{-1}$ for non-polarisable electrodes and is virtually zero for polarisable electrodes.

4. Diffusion Waves at the Electrode

Suppose that an electrically neutral substance present in the bulk of the electrolyte and supplied to the electrode via diffusion undergoes periodic adsorption and desorption at the electrode–electrolyte interface. If m is the molecular weight of the test substance, V_{ns} its partial molar volume in the solution, D its diffusion coefficient, and $c(x,t)$ its concentration at a distance x from the electrode at time t, then mass transport as a result of the diffusion of the substance in the layer near the electrode leads to a variable pressure:

$$p_v = D(m - \rho V_{ns})\,\partial c/\partial t\,(0,t)\ . \tag{33}$$

It is remarkable that the pressure p is completely independent of the distribution of the substance in the electrolyte and is determined solely by the rate of change of its concentration at the surface of the electrode.

Another component of the pressure, due to the change in the volume of the layer near the electrode caused by adsorption, is taken into account in the same way as in the electroadsorption of cations discussed above.

5. The Mass Attached to the Electrode

For an electrode with identical current densities on both sides (a vertically immersed plate, a foil strip), the pressures experienced by these two sides fully cancel out and have no influence on the results of estance measurements. The pressure applied to a narrow suprameniscus electrode, only one side of which is operative, differs from that which was defined above relative to an absolutely rigid electrode infinite in extent.

Like the deformation of a solid electrode occurring when the surface tension changes, the linear velocity of the electrode vibrations is so small that viscous forces may be neglected and the electrode may be assumed to move in a non-viscous liquid. Since the suprameniscus electrode can be in contact with its electrolyte, the electrolyte oscillating at a frequency v_0 acts on the electrode with a force $G_0 = -m_0(dv_0/dt)$, where m_0 is the mass attached to the electrode. On the other hand, the inertial force due to the transverse vibrations of the electrode itself when the surface tension is altered amounts to $G_e = -m_e(dv_e/dt)$, where v_e is the velocity of the electrode and m_e its mass. The acceleration dv_0/dt is smaller by two orders of magnitude than dv_e/dt. Furthermore, usually $m_0 \ll m$. As a result of this, the pressure hardly distorts the estance measurements with the aid of the suprameniscus electrode. Electrodes of special shape, for which the influence of the transverse surface tension is compensated, are used to record the pressure.

6. Diffusion of the Electrolyte and Thermal Vibrations of the Electrode

Heating of the electrolyte by the sinusoidal current leads to thermal vibrations of the electrode at twice the current frequency. The electrode is acted upon at the same frequency by the second harmonic of the surface tension[35]. For each of these two effects, there is a special form of the alternating current (other than sinusoidal) for which the influence of the second effect is fully ruled out. In particular, thermal vibrations of the electrode can be distinguished.

Only a thin layer of electrolyte is involved in the transfer of heat from the electrolyte to the electrode. Its thickness $b = \sqrt{2/D_T/\omega}$ decreases at a frequency $\omega/2\pi$; D_T is the thermal diffusivity of the liquid electrolyte. Suppose that the electrolyte consists of two components at concentrations c_1 and c_2 (in equivalents) and with the equivalent conductances Λ_1 and Λ_2, which are independent of concentration in dilute solutions. The steady-state values of c_1 and c_2, which are equal to those in the bulk of the solution, are designated by c_{10} and c_{20}. We introduce the parameter $v = c_{20}\,c_2/c_{10}\,c_1$. When the concentration near the electrode c_1 changes abruptly from c_{10} to 0, the thickness of the diffusion layer is defined by the expression $d = \sqrt{\pi D_C t}$, where t is the time elapsed from the instant of the concentration jump and D_C the effective diffusion coefficient taking into account the migration in the electric field. We introduce the notation

$$\lambda = \frac{d}{b} = \sqrt{\frac{\pi}{2}\frac{D_c}{D_\tau}\omega t}; \qquad (34)$$

$\mathfrak{P}$ is the ratio of the amplitudes of the thermal vibrations of the electrode before and after the concentration jump for the same alternating heating current.

Suppose that $\lambda \gg 1$ and $\lambda v \ll 1$; the thickness of the diffusion layer is then large compared with that of the thermal layer, but the c_1 concentration drop in the thermal layer continues to be greater than the background concentration c_{20}. Then

$$\mathfrak{P} = \sqrt{2}\lambda(1+v)e^{\lambda v}\sqrt{[\mathfrak{C} + \ln(\sqrt{2}\lambda v) - \lambda v]^2 + \left(\frac{\pi}{4} - \lambda v\right)^2}, \qquad (35)$$

where $\mathfrak{C} = 0.5772$ is the Euler constant.

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Institute of Electrochemistry,
USSR Academy of Sciences