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KINETICS OF ELECTRODE PROCESSES

by

A. N. Frumkin, V. S. Bagotskiy, et al.

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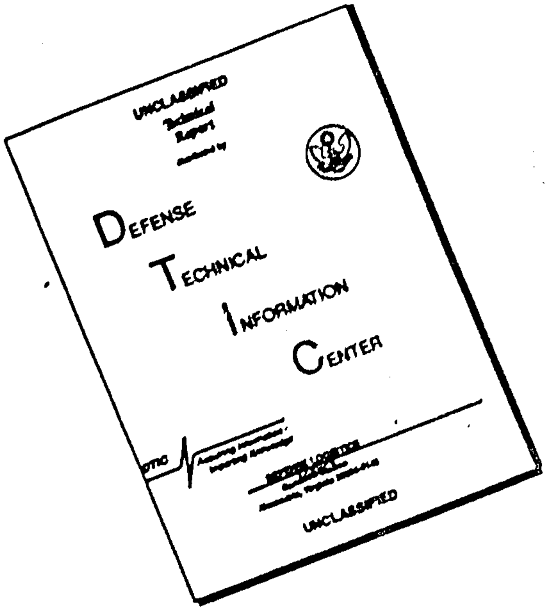

FTD-HT- 67-153

UNEDITED ROUGH DRAFT TRANSLATION

KINETICS OF ELECTRODE PROCESSES

By: A. N. Frumkin, V. S. Bagotskiy, et al.

English pages: 547

Translated under: Contract AF33(657)-16408

TT7000987

	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

FTD-HT - 67-153 Date 7 Aug 19 67

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A. N. Frumkin, V. S. Bagotskiy, Z. A. Iofa,
B. N. Kobanov

KINETIKA ELEKTRODNYKH PROTSESSOV

Dopushcheno Ministerstvom
vysshego obrazovaniya SSSR
v kachestve uchebnogo posobiya
dlya gosudarstvennykh universitetov

Izdatel'stvo
Moskovskogo Universiteta

1952

319 pages

FTD-HT-67-153

ITIS INDEX CONTROL FORM

01 Acc Nr	**68 Translation Nr**	**65 X Ref Acc Nr**	**76 Reel/Frame Nr**
TT7000987	HT6700153		1654 0941

97 Header Clas	**63 Clas**	**64 Control Markings**	**94 Expansion**	**40 Ctry Info**
UNCL	UNCL, 0	0		UR

02 Ctry	**03 Ref**	**04 Yr**	**05 Vol**	**06 Iss**	**07 B. Pg.**	**45 E. Pg.**	**10 Date**
UR	0000	52	000	000	0001	0319	NONE

Transliterated Title
SEE SOURCE

09 English Title
KINETICS OF ELECTRODE PROCESSES

43 Source
KINETIKA ELEKTRODNYKH PROTSESSOV (RUSSIAN)

42 Author FRUMKIN, A. N.	**98 Document Location**
16 Co-Author BAGOTSKIY, V. S.	**47 Subject Codes** 20, 07
16 Co-Author IOFA, Z. A.	**39 Topic Tags:** electrode polarization, electric current, kinetic energy, polargraphy, electrochemical analysis, electrolysis, STEEL CORROSION, ACID CORROSION
16 Co-Author KABANOV, B. N.	
16 Co-Author NONE	

ABSTRACT: An acquaintance with the theory of electrode processes is indispensable for the understanding of the phenomena which occur in technical electrolysis, the operation of chemical current sources, the electrodeposition of metals, corrosion and protection of metals, etc., and can help to introduce new production methods, to improve existing methods and to resolve numerous problems occurring in practice more speedily.

The purpose of this book is the presentation of this theory in a form which is accessible to a large circle of readers. It is based on a course of lectures given by academician A.N. Frumkin at the M.V. Lomonosov State University at Moscow. During the process of preparation of the material for the press it has been considerably enlarged and modified. It has not been possible however within the narrow framework of this book to give a full account of the branches of electrochemical science touched upon and particularly of its practical applications. We considered the elucidation of the physical basis of the processes under consideration to be its principal task. Hence the number of examples from the experimental material and from engineering, given to illustrate theoretical principles is not large and we have limited ourselves to an examination of the simplest of them.

An understanding of the mechanism of the electrode processes is impossible without a profound study of the metal solution interface in which they take place. Thus we thought it essential to preface the present work with a short introduction containing a summary of the most important results obtained in this field.

Several basic concepts of modern electrochemical kinetics have developed historically from the study of the phenomena which accompany the electrolytic separation of hydrogen. Hence we have dwelt on this reaction in much greater detail than on the other electrochemical processes.

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TT7000987 HT6700153

It must be emphasized that many problems of theoretical electrochemistry are still controversial today, and a single point of view with regard to them does not exist among the Soviet electrochemists. We have striven to present primarily the theoretical concepts which appear to us to be best substantiated by the experimental data, recognizing, however, that a final decision on the controversial questions requires further experimental work as well as discussion of the results thus obtained.

The introduction and the chapters 5, 6 and 7 were written by A.N. Frumkin and B.N. Kabanov. The other chapters were written by A.N. Frumkin, V.S. Bagotskiy and Z.A. Iofa.

We express our gratitude to the collective of workers of the chair of electrochemistry of the M.V. Lomonosov State University, Moscow, and the electrochemistry department of the Institute of Physical Chemistry of the Academy of Sciences of the USSR, who participated in the discussion of this book.

English translations: 545 pages.

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FOREWORD

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INTRODUCTION

BASIC PROPERTIES OF THE SURFACE LAYER AT THE INTERFACE BETWEEN METALS AND ELECTROLYTE SOLUTIONS

§1. ORIGIN OF THE ELECTRICAL DOUBLE LAYER DURING CONTACT BETWEEN A METAL AND A SOLUTION

The electrochemical processes, i.e., the processes in which metals or other conductors of the first kind either donate electrons* to the reacting particles (molecules or ions) or accept them from the latter, take place within a thin surface layer at the interface between electrode and solution. In order to understand the mechanism of the electrochemical processes it is essential to have an idea of the structure of this surface layer. The introduction to the present book will be devoted to this question.

A double electric layer exists at the interface between electrode and solution, formed by electrical charges present in the metal and by ions of the opposite sign present in the solution at the metal surface.

The double electric layer is formed upon contact of a metal with a solution when the solute ions yield their charges to the metal or if the metal sends ions into the solution. Thus, for example, when silver comes into contact with a solution of silver nitrate, the Ag^+ ions, depending on the concentration of the solution, can migrate to the metallic silver, imparting their positive charge to it, or, conversely, they can be formed at the expense of the metal which then becomes negatively charged.

In the case of contact between hydrochloric acid solution and iron hydrogen ions may be discharged on its surface, imparting their positive charge to the iron, and Fe^{++} ions may appear. Because the latter carry a positive charge, the metal is charged negatively during their formation. The appearance of charges can also take place through ionization of gases adsorbed on the surface of a metal, as, for example, in the case of platinum in a hydrogen atmosphere.

Let us assume that when a metal comes into contact with a solution, the predominating process is that the metal receives charges from positive ions, for example, silver ions are precipitated on silver. As will be shown in the following, the positive surface charge thus formed retards the reaction which proceeds in the above-indicated direction and, conversely, accelerates the reactions which result in the loss of positive charge by the surface. In consequence of this the increase in the positive surface charge is slowed down in time and, finally, a certain stationary condition is established at the metal solution interface with a certain density of the electrical charge on the surface.

The surface charges attract from the solution ions of the opposite sign and repel the ions with like charge. Thus, an excess of ions with a charge with a sign opposite to the sign of the charge of the metal surface appears in the layer of solution adjacent to the electrode. This layer forms the double electric layer at the metal solution interface together with the charged metal surface. Because of the presence of free charges in the double layer the value of the electrostatic potential within it is not constant but varies from point to point. Thus, the appearance of this layer results in the establishment of a certain potential difference between metal and solution. In this chapter we shall not examine the question concerning the connection between the value of this potential difference, the composition of the original solution and the nature of the reactions which take place, to which we shall revert later. We shall merely point out that in the case of reversible electrodes when an equilibrium is established between electrode and solution (as is the case, for example, when various metals such as silver, mercury, cadmium, etc., are immersed in solutions containing their ions) a relationship between the potential difference and the composition of the solution can be established on the basis of thermodynamic concepts. In this simplest case the magnitude of the potential difference φ between metal and solution is determined by the relation

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln a_{\mathrm{Me}^{n+}}, \qquad (1)$$

where n and $a_{\mathrm{Me}^{n+}}$ are the valency and activity of the metal ions Me^{n+} in the solution, φ^0 is the normal electrode potential, i.e., the value of φ at $a_{\mathrm{Me}^{n+}}$, equal to unity, R is the gas constant, T the absolute temperature and F the Faraday number.* Similar relations can be derived for other cases of equilibrium between a metal and a solution; they are given in physical chemistry manuals.** In the following we shall assume them as known.***

We have briefly examined how the double layer arises at the metal solution interface if electrochemical reactions can take place at this interface. The latter is not always the case, however. Thus, for example, electrochemical reactions do not take place on a fresh mercury surface in a solution of potassium chloride from which oxygen and other oxidants have been carefully eliminated. It would appear that one of the following two reactions should be possible in this case: a migration of mercury ions into the solution $2\mathrm{Hg} \rightarrow \mathrm{Hg}_2^{++} + 2e$ (in this case the metal would be charged negatively) or a transformation of potassium ions into potassium atoms which dissolve in the mercury in the form of potassium amalgam $\mathrm{K}^+ + e \rightarrow \mathrm{K}_{am}$ (with the appearance of a positive charge at the surface).

In actual fact, however, ionization of a relatively noble metal such as mercury can take place at a measurable rate only when the surface is strongly positively charged while discharge of the potassium ion is possible only in presence of a strong negative charge. Thus, these reactions cannot proceed on the uncharged mercury surface spontaneously (i.e., without a supply of charges from without) to an extent which would result in the formation of a measurable charge density; for this reason, when mercury is in contact with potassium chloride solution, which is free of oxygen, a double layer is not formed.

On the other hand, owing to the absence of a migration of ions from one phase into the other, any charge density can be easily realized on such a mercury surface within wide limits and, consequently, any potential difference, if a charge from an external current source is supplied to the mercury surface. Such electrodes are often termed ideally polarized. The potential of an ideally polarized electrode changes constantly during the passage of electricity, and such an electrode can obviously not be used as a current source, but the possibility of varying within wide limits the charge density on the surface makes the ideally polarized electrode particularly suitable for the study of the structure of surface layers. It must be remembered, however, that if the charge density and potential difference with a given solution composition pass certain limits, the properties of the ideal polarizability are lost, and diverse electrochemical reactions can take place at the electrode; thus, if the positive potential is sufficiently high, ionization of the mercury takes place at the mercury electrode in potassium chloride solution and, if it is sufficiently negative, potassium or hydrogen ions are discharged.*

§2. DENSE AND DIFFUSE DOUBLE LAYER [1]

In the simplest case when only the electrostatic forces acting between the charged surface and the ions of the solution are taken into account, one can imagine that the surface of the metal attracts from the solution a number of ions with charges whose sign is opposite to that of the surface charge and equivalent in number to the number of charges. These ions are situated at the surface very close to it; the double layer thus formed may be compared with a flat capacitor in which the distance between the plates is determined by the radius d of the ions. The potential distribution in such a double layer is represented in Fig. 1.

This simplified picture of the double layer as proposed by Helmholtz is correct only in individual cases, for example, when the concentration of the electrolyte solutions and the charge density are very high. In reality the double layer in most cases has a more complex structure. Under the influence of the disordered molecular movement the ions tend to be distributed uniformly in the solution. As a result of the molecular motion on the one hand and the electrostatic interaction of the ions with the charged metal surface on the other, the ion covering of the double layer assumes a diffusion structure, i.e., an ion distribution results in which the concentration of some ions (with a sign of the charge on the metal) increases in proportion to decreasing distance from the surface, while the concentration of the ions of the other sign decreases (Fig. 2). The average thickness of such a diffusion envelope of the double layer can be relatively great in dilute solutions, attaining a micron in completely clean water (i.e., in water containing only H^+ and OH^- ions formed by dissociation of their molecules). In more concentrated solutions this thickness is considerably less and is measured in tens and even units of angstrom.

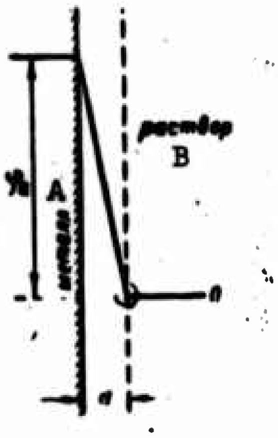


Fig. 1. Potential distribution in a dense double layer with positive charge of the metal surface; *d* is the thickness of the double layer; φ_a is the potential difference between metal and solution. A) Metal; B) solution.

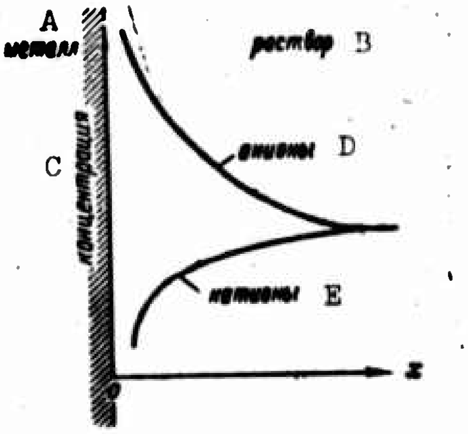


Fig. 2. Cation and anion concentration as a function if the distance in the case of a positive charge on the electrode surface. A) Metal; B) solution; C) concentration; D) anions; E) cations.

Generally the ion covering of the double layer can be conventionally divided into two parts. The first part is formed by the ions which are practically attracted closely to the metal surface ("close" or "Helmholtz" layer). The second part, the diffusion layer, is formed by ions which are at a given moment at distances from the surface comparable in magnitude to the radius of the ion or exceeding it.

We should point out that the charges in the different parts of the double layer are not fixed in place and that the magnitude of the effective charge in a given part of the double layer, determined by the excess charges of the positive ions over the charges of the negative ions, is of a statistical nature.

Specific adsorption of ions, atoms and molecules (i.e., adsorption caused by the action of chemical forces and superposed on the purely electrostatic attraction or repulsion (see §7)), can make the structure of the double layer even more complex.

Let us first stop to consider in greater detail the properties of the dense layer. As pointed out earlier, it can be likened to a flat capacitor, one plate of which is the metal surface and the other the layer of ions which are attracted to the surface by the electrical charges of the metal in such a way that the centers of these ions at a given moment are at a distance from the metal surface corresponding to the effective ionic radius (Fig. 3). In addition to the electrostatic forces, specific adsorption forces can attract ions to the electrode surface; in other cases the latter, conversely, repel the ions from the surface (negative adsorption), i.e., they weaken the action of the electrostatic forces.

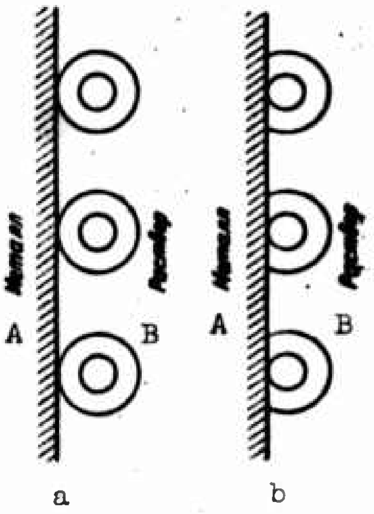


Fig. 3. Arrangement of the solvated ions at the charged electrode surface; a) ions with undeformed solvation envelope; b) approach of the ions to the surface, involving a deformation of the solvation envelope. A) Metal; B) solution.

The equation connecting the charge of a flat capacitor with the potential difference between its plates can be applied to the dense double layer:

$$C=\frac{\varepsilon}{\varphi_a}=\frac{D}{4\pi d}, \qquad (2)$$

where C is the capacitance of the layer per 1 cm^2 of surface, ε is the charge density at the metal surface; φ_a is the potential difference between metal and solution* which we shall consider as positive, if the metal has a positive charge; D is the dielectric constant of the medium between the plates of the capacitor and d the distance between the plates, i.e., between the metal surface and the ion centers. When Eq. (2) is used in practice one has to remember that the magnitude of C is normally expressed not in electrostatic units, but in microfarads (μF) per 1 cm^2. Because a microfarad is equal to $9 \cdot 10^5$ electrostatic units, the right part of the equation (2) must be divided by $9 \cdot 10^5$ in order to obtain C in μF per cm^2 if d is expressed in cm:

$$C = \frac{1}{9 \cdot 10^5} \frac{D}{4\pi d} \ \mu F/cm^2. \qquad (2a)$$

As will be shown later, the magnitude of C can be found experimentally. For the mercury electrode with negative surface charge, i.e., in the case when the ion envelope is formed by cations, C is 18 $\mu F/cm^2$. If the surface is positively charged, i.e., in presence of anions in the double layer, the minimum value of C is approximately twice as large. Thus there is an important difference between the behavior of cations and anions close to the surface.

This difference can be explained in the following manner. The cations as well as the anions in the solution are solvated, i.e., bound to solvent molecules, in particular, in aqueous solutions, to water molecules (hydrate envelope). If the hydrate envelope were not deformed when the ions come close to the electrode surface, the minimum distance between the center of the ion and the electrode surface would be equal to the sum of the radii of the unhydrated ion and the thickness of the hydrate envelope (Fig. 3a). However, a comparison of the behavior of cations and anions, a comparison of the capacitances of the double layer, obtained in different solvents* and a number of other concepts leads us to the conclusion that close to the electrode surface a considerable deformation of the hydrate envelope takes place so that the real picture of the structure of the double layer corresponds much more to Fig. 3b than to Fig. 3a [7]. The deformation of the hydrate envelope is obviously more pronounced in the case of the anions for which (at least for univalent anions) the hydration energy is less than for the cations. The closer approach of the anions to the electrode surface is also facilitated by the circumstance that, as will be seen from the following, specific adsorption forces which are not observed in the case of cations exist between the anions and the electrode surface in many cases. The interaction between the anion and the electrode surface leads also to a charge displacement within the ion itself, to its polarization, which is particularly strong when the surface is positively charged. As a result of this the effective thickness of the double layer becomes less than the ionic radius. Correspondingly, the capacitance of the double layer, considered as a capacitor, is strongly increased. At very large negative charges of the surface this increase in capacitance, although to a lesser degree, is also observed in the case of a cation layer.

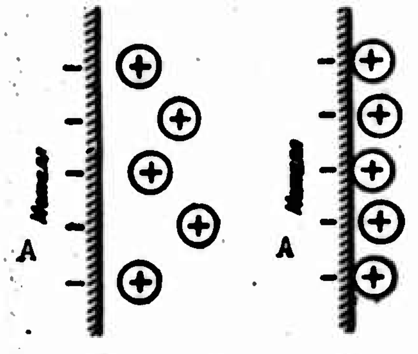
If a certain assumption concerning the magnitude d has been made, the value of the dielectric constant D can be calculated from Eq. (2). The radius, for example, of the unhydrated K^+ ion is $1.33 \cdot 10^{-8}$ cm; thus the value of d is probably close to $1.5 \cdot 10^{-8}$ cm. If we substitute this value in Eq. (2), one can find from the experimental quantity $C = 18$ $\mu F/cm^2$ that the dielectric constant of the dense part of the double layer is approximately 3 units. This small value is explained by the orienting effect of the electrical field of the ions in the double layer on the dipole water molecules which are in close proximity (we remember that the normal value of the dielectric constant for water outside of the double layer is 81 at a temperature of 18°C). The calculation of the dielectric constant within the double layer from the values of the capacitance C requires certain assumptions concerning the magnitude of d, which are not very reliable, so that in electrochemical calculations, based on the theory of the double layer, one must use not the value of D but the experimentally determined capacitance.

The structure of the double layer, represented in Fig. 3, is an extreme case. In reality, as has been pointed out above, not all ions of the double layer are in the direct vicinity of the metal surface. To a certain degree the ions in the ion envelope of the double layer are distributed diffusely. If the charge density is not very high, as in the case of dilute solutions, practically the entire ion envelope of the double layer is diffuse (see Fig. 4a). Conversely, at higher concentrations a considerable proportion of the ions of the double layer is very close to the surface, and the structure of the double layer comes near to that described in the foregoing (Fig. 4b).

It is highly probable that when a fluid moves relative to a solid body, the ions, which are directly in contact with its surface, remain continuously bound to it, while diffusely distributed ions are to some extent entrained by the fluid. The degree of diffusiveness of the double layer thus is of great significance for the so-called electrokinetic phenomena. Electrokinetic motion phenomena are termed those which arise at the solid/solution interface when an electric field is applied, for example, the motion of solid particles in a solution (cataphoresis) or the motion of a solution relative to the walls of solids (electroosmosis). These phenomena were discovered and first described in 1807 by F.F. Reyss in Moscow. It is shown in the elementary theory of the electrokinetic phenomena which is explained in most textbooks of colloid and physical chemistry [3] that it is possible to calculate the potential difference in the diffusion layer which is usually designated by the letter ζ (electrokinetic or zeta-potential) from the velocity of motion v of the particle in the electrical field:

$$\zeta = \frac{4\pi\eta v}{DE}. \qquad (3)$$

where η is the viscosity of the fluid, and E the electric field intensity.



a b

Fig. 4. Distribution of excess cations at the negatively charged surface of a metal at low (a) and higher (b) concentrations of the solution. A) Metal.

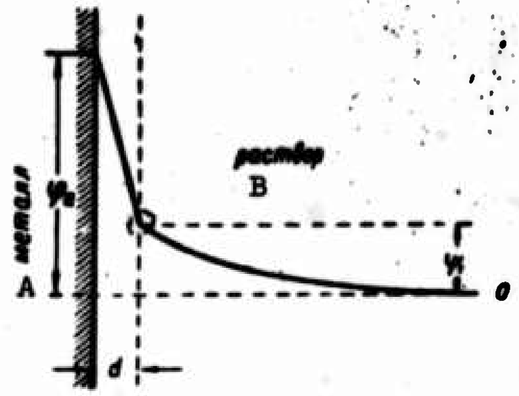


Fig. 5. Potential distribution in the dense and diffuse parts of the double layer; φ_a is the potential difference between metal and solution; ψ_1 is the mean value of the potential at a distance of one ionic radius from the metal surface. A) Metal; B) solution.

As will be evident from the following, the magnitude of the potential drop in the diffuse layer is also of great importance for the mechanism of the electrochemical processes. We designate it by ψ_1, thus defining ψ_1 as the mean potential in the solution at the distance of one ionic radius from the metal surface d (Fig. 5). Taking into account that this distance is evidently different for cations and anions, one could have correspondingly introduced two values of ψ_1. We shall not do so, however, as this would complicate the picture enormously.

It can be inferred from Eq. (3) that ζ represents the potential at the distance from the electrode surface at which the motion of the fluid relative to the solid begins. In fairly dilute solutions, in which the potential within the diffusion layer varies slowly with increase in the distance from the surface, the quantity of ψ_1 is probably identical with ζ. At higher concentrations, when the accumulation of ions near to the surface is considerable and the potential varies rapidly with distance, this identification would be incorrect. The conditions of motion of the fluid at molecular distance from the surface are unknown; in particular, it is not clear what value should be ascribed to the viscosity. The latter, as the works of B.V. Deryagin [4] have shown, can differ greatly close to the interface from the usual viscosity within the volume. Hence the physical meaning of the quantity ζ calculated by means of formula (3) is somewhat indeterminate in this case, and it is better to introduce a different criterion (ψ_1) for the potential drop in the diffusion layer which interests us.

In the following section we shall briefly examine the quantitative theory of the double layer taking its diffusion structure into account.

§3. EQUATIONS OF THE DOUBLE LAYER

The first quantitative expression for the charge density as a function of the ion concentration c in the solution and the electrode potential in presence of a diffusion structure of the double layer has been given by Gouy [5]. Later on, an analogous method of calculation has been used by Debye in the theory of the strong electrolytes. Shtern [5] pointed out that one cannot use the concept of point charges in the theory of the double layer but that it is necessary to take the ionic radii into account. Because the center of an ion cannot approach the electrode surface closer than within the distance of the radius,* there is in any case in the double layer close to the surface a region with the thickness d in which charges are absent; as follows from the laws of electrostatics, the potential varies in such a region linearly with distance, i.e., the gradient of the electrical potential is constant (Fig. 5). From the distance d onwards the solution contains charges.

The equation for the double layer, derived on these assumptions and taking into account the electrostatic interaction between the ions and the charged surface of the electrode and the thermal motion of the ions, can be represented in the following form:

$$\varepsilon = C(\varphi_a - \psi_1) = \pm \sqrt{\frac{DRT}{2\pi}} \sqrt{\sum_i \left(e^{-\frac{n_i F \psi_1}{RT}} - 1\right) c_i}. \qquad (4)$$

The quantities entering into this equation have the following meaning: ε is the charge density at the metal surface,* C is the capacitance of the capacitor, formed by the metal surface and a plane passing through at a distance d from it, calculated per 1 cm^2, φ_a is the potential directly at the electrode surface relative to the potential in the center of the solution, which is usually assumed to be zero. In order to determine φ_a from the potential φ of the electrode, measured relative to an arbitrary reference electrode, one has to deduct from φ the electrode potential φ_n at the charge density ε equal to zero, measured relative to the same reference electrode. Further, ψ_1 is the potential at the distance d (i.e., in the plane which passes through the centers of the ions of the first layer) relative to the potential in the center of the solution, n_i and c_i are the valency and concentration of the ions of the species i, D is the dielectric constant of the solution. In the case of a diffuse double layer, whose thickness considerably exceeds the molecular dimensions, we shall consider the value D in dilute solutions to be equal to the normal value of the dielectric constant of water, i.e., $D = 81$. The latter assumption is approximate.

The equation (4) has been derived on the assumption of the applicability of the laws of ideal solutions to the ions in the volume of the solution and in the double layer. We shall give in an abbreviated form the derivation of this equation for the simplest case of a univalent electrolyte.

The left part of Eq. (4) expresses the charge density ε of the metal plate of the double layer via the capacitance C of a flat capacitor (see Eq. (2) and the potential drop $\varphi_a - \psi_1$ in it). This expression is correct independently of whether all charges of the ion envelope of the double layer are in the plane in which the potential is ψ_1 or whether they are partially (or entirely) situated beyond this plane.*

The right part of Eq. (4) expresses the total charge density of the ionic part of the double layer.

Really, we designate by ψ the variable value of the potential in the diffusion ion layer which depends on the distance from the electrode. According to the Boltzmann law,** the cation concentration in this region is equal to

$$c_+ = c e^{-\frac{\psi F}{RT}}, \qquad (5)$$

and the anion concentration to:

$$c_- = c e^{\frac{\psi F}{RT}}, \qquad (5a)$$

where c is the electrolyte concentration in the solution, expressed in gram-ions per 1 cm^3. The volume charge density ρ is equal to:

$$\rho = F(c_+ - c_-) = Fc\left(e^{-\frac{\psi F}{RT}} - e^{\frac{\psi F}{RT}}\right). \qquad (6)$$

It follows from the laws of electrostatics that the following relation (Poisson equation) exists between the volume density of electricity and the potential ψ:

$$-\frac{4\pi\rho}{D} = \frac{\partial^2\psi}{\partial x^2}, \qquad (7)$$

where x is the distance from the electrode surface.***

If we integrate Eq. (7) between the limits d and ∞, we obtain: and, because at $x \to \infty$ $\psi = 0$ and $\partial\psi/\partial x = 0$ are valid and because the total charge $\int_d^\infty \rho \cdot dx$ in the solution is equal to the surface charge ε of the metal with opposite sign, we have

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=\infty} - \left(\frac{\partial\psi}{\partial x}\right)_{x=d} = -\frac{4\pi}{D}\int_d^\infty \rho\, dx, \qquad (8)$$

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=d} = -\frac{4\pi\varepsilon}{D}. \tag{8a}$$

By putting together (6) and (7), we obtain:

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi Fc}{D}\left(e^{-\frac{\psi F}{RT}} - e^{\frac{\psi F}{RT}}\right). \tag{9}$$

By integrating Eq. (9) within the limits from d to ∞ and taking into account that at $x = d$, $\psi = \psi_1$, we find:

$$\left(\frac{\partial\psi}{\partial x}\right)^2_{x=\infty} - \left(\frac{\partial\psi}{\partial x}\right)^2_{x=d} = +\frac{8\pi cRT}{D}\left| e^{-\frac{\psi F}{RT}} + e^{\frac{\psi F}{RT}} \right|_{x=d}^{x=\infty}$$

or

$$\left(\frac{\partial\psi}{\partial x}\right)^2_{x=d} = +\frac{8\pi cRT}{D}\left(e^{-\frac{\psi_1 F}{RT}} + e^{\frac{\psi_1 F}{RT}} - 2\right). \tag{9a}$$

It follows from (8a) and (9a) after extraction of the square root from the right and left parts of Eq. (9a):

$$\varepsilon = \sqrt{\frac{DRTc}{2\pi}}\left(e^{\frac{\psi_1 F}{2RT}} - e^{-\frac{\psi_1 F}{2RT}}\right). \tag{10}$$

The sign after the extraction of the square root must be chosen in accordance with the condition $\varepsilon > 0$ at $\psi_1 > 0$.

On the other hand, as has been shown in the foregoing, $\varepsilon = C(\varphi_a - \psi_1)$; hence follows:

$$\varepsilon = C(\varphi_a - \psi_1) = \sqrt{\frac{DRTc}{2\pi}}\left(e^{\frac{\psi_1 F}{2RT}} - e^{-\frac{\psi_1 F}{2RT}}\right). \tag{11}$$

The equation (11) is a partial case of Eq. (4) for the solution of a uni-univalent electrolyte.

The specific adsorption of the ions, i.e., not caused solely by electrostatic forces (see §7) has not been taken into account in the derivation of Eq. (4). Shtern [5] has made an attempt to take into account the specific ion adsorption. Because the forces which determine the specific adsorption decrease very repidly with distance, it can be assumed that these forces act only on ions in direct contact with the metal surface. The value of the adsorption potential which is independent of the electric field is introduces for these ions in Shtern's theory: Φ_+ for cations and Φ_- for anions. These quantities, Φ_+ and Φ_-, express the variation of the potential energy during the transfer of a mole of substance from the center of the solution to the surface at $\psi_1 = 0$.

The total variation of the potential energy during adsorption, taking also into account the effect of the electric field, is $\Phi_+ + \psi_1 nF$ for the cation and $\Phi_- - \psi_1 nF$ for the anion. By means of these quantities one can calculate the number of cations and anions adsorbed at the surface analogous to the derivation of the adsorption formula of Langmuir in the theory of gas adsorption, i.e., by assuming that there exists at the surface a number of places which are filled by the adsorbed cations and anions in correspondence with the aforementioned values of the variation of the potential energy during adsorption.

However, as the experimental determination of the surface charge shows, the filling of the surface by ions in the double layer is normally not very great in practice. For the case of partial occupancy the Shtern equation can be represented in the following simple form (for uni-univalent electrolyte):

$$\varepsilon = C(\varphi_0 - \psi_1) = -\varepsilon_1 - \varepsilon_2, \tag{12}$$

$$\varepsilon_1 = 2Fcd\left(e^{-\frac{\Phi_+ + \psi_1 F}{RT}} - e^{-\frac{\Phi_- - \psi_1 F}{RT}}\right), \tag{13}$$

$$\varepsilon_2 = +\sqrt{\frac{DRTc}{2\pi}}\left(e^{-\frac{\psi_1 F}{2RT}} - e^{\frac{\psi_1 F}{2RT}}\right), \tag{14}$$

where ε_1 is the charge of the adsorbed ions and ε_2 is the charge of the ions in the diffusion layer. The quantity ε_1, as is evident from Eq. (13), is equal to the difference of the charges of the adsorbed cations and anions. In fact, their volume concentrations in the surface layer according to the Boltzmann formula are, respectively:

$$c_+ = ce^{-\frac{\Phi_+ + \psi_1 F}{RT}} \;\&\; c_- = ce^{-\frac{\Phi_- - \psi_1 F}{RT}},$$

from which Eq. (13) is readily derived if we assume that the thickness of the adsorbed layer is $2d$. The charge of the diffusion layer is calculated in accordance with Eq. (10).

As Eq. (12) shows, the magnitude of the charge of the ion envelope, according to Shtern's theory, consists of two components, of which one expresses the charge of the adsorbed ions and the other the charge of the ions which are attracted only by electrostatic forces. This division is practical if considerable adsorption forces are present (large negative values of Φ_+ and Φ_-). However, in the absence of adsorption forces, i.e., at $\Phi_+ = \Phi_- = 0$, the expression for ε_1 does not vanish, although in this case the physical meaning of the separation of the charges of the ions which are in direct contact with the electrode surface into a separate component is not clear because the charges of all the ions have already been taken into account in the expression for ε_2; in this case the use of Eq. (11) instead of Eq. (12) is more logical.

The use of the Shtern equation in the presence of specific ion adsorption is made difficult by the circumstance that only one value of the capacitance of the dense layer is considered in this theory whereas, as has been pointed out earlier, its capacitance differs considerably in presence of cations and anions. Several attempts have been made to introduce improvements into the theory of the double layer to eliminate this deficiency, for example, by assuming that the centers of the anions can approach closer to the electrode surface than the centers of the cations [7].

Let us indicate certain consequences following from Eq. (11). For this purpose Eq. (11) is more conveniently written in this form:

$$\varphi_0 = \psi_1 + \frac{1}{C}\sqrt{\frac{DRTc}{2\pi}}\left(e^{\frac{\varphi_1 F}{2RT}} - e^{-\frac{\varphi_1 F}{2RT}}\right). \qquad (11a)$$

Let the quantity ψ_1 be small as compared with RT/F ($RT/F = 25$ mv at 18°), i.e., the work $\psi_1 F$ performed by the electrical forces in transporting a gram-ion from the solution into the double layer is small compared with the energy RT of the thermal motion. Then, expanding the exponential functions into a series and using only the first two terms of the expansion, the expression in brackets in the right part of Eq. (11a) can be replaced by $\psi_1 F/RT$, hence

$$\varphi_a = \psi_1 + \frac{1}{C}\sqrt{\frac{Dc}{2\pi RT}}\,\psi_1 F \qquad (15)$$

and

$$\varepsilon = \sqrt{\frac{Dc}{2\pi RT}}\,F\psi_1 = \frac{D}{4\pi}\sqrt{\frac{8\pi c}{RTD}}\,F\psi_1. \qquad (16)$$

If the quantity c is fairly small, the second term in the right part of Eq. (15) may be neglected compared with the first so that $\varphi_a \doteq \psi_1$ and

$$\varepsilon = \frac{D}{4\pi l}\,\varphi_a, \qquad (17)$$

where

$$l = \frac{1}{F}\sqrt{\frac{RTD}{8\pi c}}. \qquad (18)$$

As is evident from Eq. (17), the quantity l defines the thickness of a flat capacitor whose capacitance is equivalent to that of the diffuse double layer. This quantity is analogous to the so-called thickness of the ionic atmosphere known from the theory of the strong electrolytes. The thickness l of the diffusion layer varies in inverse proportion to the square root of the concentration Eq. (18). With increasing temperature and dielectric constant the diffuseness of the double layer increases.

If the electrolyte has not 1 – 1, but n – n valency (for example, $MgSO_4$), F must be replaced by nF; thus the thickness of the double layer is inversely proportional to the valency of the ions. The capacitance of the diffusion double layer in dilute solutions as calculated in accordance with Eq. (16) is considerably smaller than the capacitance of a dense layer. Thus, in 10^{-4} N solution of a uni-univalent electrolyte it is only 3 μF/cm^2.

If the quantity ψ_1 is positive and large compared with RT/F and the concentration c is not too small, the term containing $e^{\psi_1 F/2RT}$ assumes largest value in the right part of Eq. (11a) and the equation (11a) can be replaced by the approximate expression

$$\varphi_a \simeq \frac{1}{C}\sqrt{\frac{DRTc}{2\pi}}\,e^{\frac{\psi_1 F}{2RT}}, \tag{19}$$

$$\psi_1 \simeq \text{const} + \frac{2RT}{F}\ln\varphi_a - \frac{RT}{F}\ln c. \tag{20}$$

Under analogous conditions we obtain for a negative ψ_1

$$\psi_1 \simeq \text{const} - \frac{2RT}{F}\ln(-\varphi_a) + \frac{RT}{F}\ln c. \tag{20a}$$

At the same time it follows for small values of ψ_1 and c $\psi_1 \doteq \varphi_a$ from the equations (20) and (20a) that with increase in φ_a the further increase in ψ_1 takes place very slowly, in accordance with a logarithmic law. Thus, with increase of φ_a from 0.2 v to 1 v, i.e., by 0.8 v, ψ_1 increases, according to Eq. (20) by only 0.08 v. Hence for large values of φ_a and not too small c, the quantity ψ_1 becomes small compared with φ_a and the capacitance of the double layer approximates the value of C which is typical for the dense, nondiffuse layer. It follows from this that in dilute solutions a considerable increase in the capacitance of the double layer should take place in proportion to an increase in $|\varphi_a|$.

It can be seen from the equations (20) and (21) that with increasing concentration the absolute value of ψ_1 decreases in accordance with a law which is similar to the commonly used Nernst formula. Finally, it is easy to see that in the above case the quantity ψ_1 for an n-n-valent electrolyte, all other conditions being equal, is n times smaller than for a uni-univalent electrolyte. Calculation shows that in the case of an electrolyte with an asymmetrical structure the valency of the ion with a sign of the charge opposite to the sign of the surface charge plays the decisive part in the structure of the diffuse double layer.

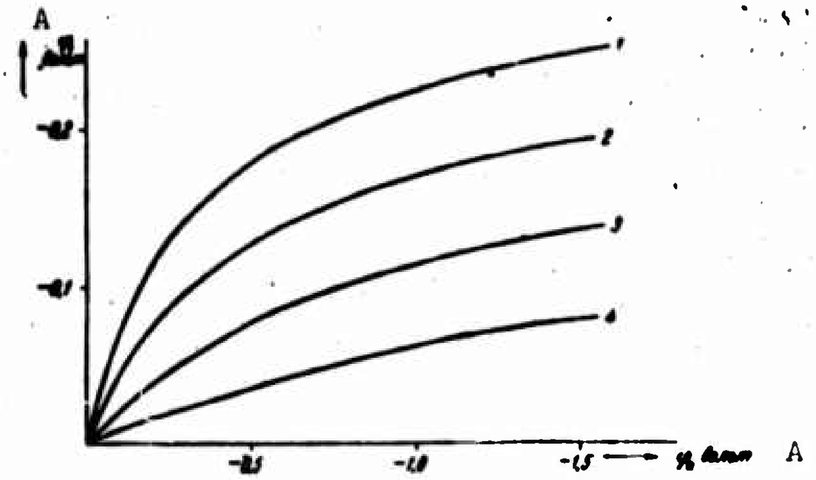


Fig. 6. ψ_1 as a function of φ_a in solutions of a uni-univalent electrolyte (at 20°C) at $C = 18$ μF/cm^2. Concentration in moles per liter: 1) 0.001; 2) 0.01; 3) 0.1; 4) 1.0. A) Volt.

It is clear from the above that with increasing electrolyte concentration, potential drop φ_a and valency of the ions, the structure of the double layer becomes less diffuse and comes close to the structure corresponding to an approach of the ions to the minimum possible distance to the electrode surface. By means of Eq. (11) and, in the general case, by means of Eq. (4) one can always find the value of ψ_1 and, consequently, also ε as a function of φ_a if the composition of the solution and the magnitude of C are known. The values for ψ_1 for a uni-univalent electrolyte of different concentration, calculated in this way, are given in Fig. 6.

In the following we shall consider the complications introduced into the structure of the double layer by the specific adsorption of ions.

§4. EXPERIMENTAL METHODS FOR THE STUDY OF THE DOUBLE LAYER

A number of methods has been developed within the last decades for the study of the double layer which have greatly enriched our knowledge of it [8]. Soviet scientists have played a prominent part in these investigations.

Measurement of the capacitance of an electrode with alternating current. The most accurate data on the structure of the double layer at the metal/solution interface were obtained by measurement of the electrode capacitance. The principle of this method consists in charging the metal surface and the solution with certain small quantities ΔQ and $-\Delta Q$ of electricity and measuring the potential variation $\Delta\varphi$ of the electrode.

In order that the quantity thus obtained, recalculated for the unit of electrode surface, should express the capacitance, it is essential that the imparted charge is not consumed in some electrochemical reaction, i.e., that the electrode has the properties of ideal polarizability. The measurements of this kind can be carried out by the same methods as those used for the measurement of the capacitance of a usual capacitor.

The basic conditions which must be fulfilled for the measurement of electrode capacitance with an alternating current have been first formulated in 1887 by A.P. Sokolov [9].

A.P. Sokolov proposed to use a high-frequency alternating current for capacitance measurement in order to compel the "voltameter to charge itself so rapidly that collateral processes (adsorption and convection) at the electrodes cannot take place to any great extent within this short period."

The principle of the use of an a.c. current consists in measuring the potential fluctuations during the passage of a current with a cer-

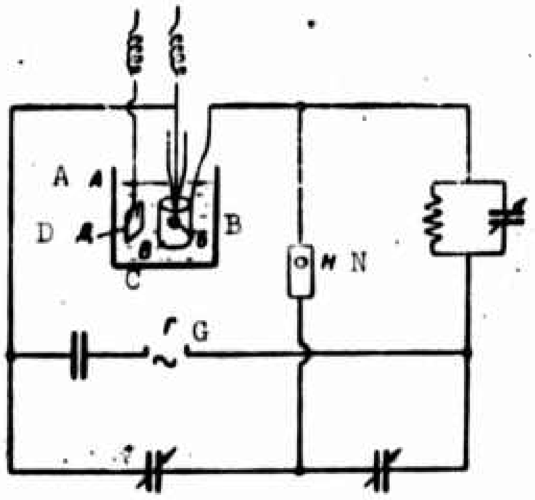


Fig. 7. Compensation circuit for the capacitance measurement on the double layer of an electrode with alternating current; A) Electrolytic cell; B) test electrode; C) auxiliary electrode with large surface for passing an a.c. current through the cell; D) auxiliary electrode for the polarization of electrode *B* with a d.c. current; G) a.c. current generator; N) null instrument for the a.c. current (oscillograph).

tain intensity or that one compares them with the potential fluctuations of a reference standard of known capacitance. One of the possible compensation circuits, suitable for the capacitance measurement of the double layer, is shown in Fig. 7. The letter *A* in the diagram indicates the cell into which the test electrode is immersed. The a.c. current is passed through the solution between the test electrode *B* and the auxiliary electrode *C*. The potential fluctuations of the small test electrode are large compared with the potential fluctuations of the large electrode. Hence capacitance measured by means of a compensation method can be considered, with a sufficient degree of accuracy, to be equal to the capacitance of the test electrode. The a.c. generator *G* serves as the current source.

Depending on the conditions, different current frequencies from 1 to 100,000 cycles per second are used for these measurements. A conventional sensitive cathode oscillograph, sometimes a telephone with amplifier and, at low frequencies, a galvanometer with short period serve usually as the null instrument N.

An ideally polarizable electrode is a limit case which can be achieved in practice only with a certain approximation. Normally the possibility of electrochemical reactions at the electrode surface cannot be excluded completely. A certain proportion of the electrical charge, imparted to the electrode in order to shift its potential, is actually lost not for charging the electrode but for an electrochemical reaction. The electrode behaves in this respect like a capacitor with a leakage, for example, a capacitor connected in parallel with a certain resistance R (Fig. 8). Hence to achieve compensation in accordance with the scheme of Fig. 7, a resistance must also be included in parallel with the standard capacitance. The presence of such a leakage during measurements with alternating current has the greater effect the lower the frequency of the alternating current. The inclusion of a resistance is also necessary to compensate the ohmic resistance of the electrolyte. When high-frequency currents are used the capacitance measurements can also be carried out in presence of relative large leakage currents, as pointed out long ago by A.P. Sokolov.

Let us consider the physical meaning of the capacitance determined experimentally by means of alternating current. The experimentally measured capacitance is evidently equal to $\Delta Q/\Delta\varphi$; recalculated to unit of electrode surface it is equal to $1/S\ \Delta Q/\Delta\varphi = \Delta\varepsilon/\Delta\varphi$ or, because φ and φ_a differ only by a constant amount, $\Delta\varepsilon/\Delta\varphi_a$. If the amplitude of the alternating current used for the measurement is fairly small (if it does not exceed 10-15 mv) we can assume approximately $\Delta\varepsilon/\Delta\varphi_a = \partial_3/\partial\varphi_a$. The quantity $\partial_\varepsilon/\partial\varphi_a$ is termed differential capacitance at the given value of the potential φ_a

$$C_d = \frac{\partial\varepsilon}{\partial\varphi_a}. \qquad (21)$$

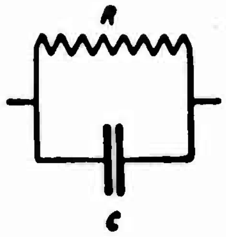


Fig. 8. Electrical circuit of a capacitor with capacitance *C* and leakage via the resistance *R*, which is equivalent to an electrode on which electrochemical reactions take place.

If the electrode had a constant capacitance, independent of its potential (i.e., if the charge were proportional to the potential $\varepsilon = C\varphi_a$), the measured differential capacitance would equal the capacitance of the electrode *C* (independently of the amplitude of the current used for the measurement).

Such a pattern will approximately occur in concentrated solutions in which, as has been shown in §3, the double layer is not very diffuse and comes close to the type of dense double layer with a constant distance between the plates and constant capacitance. In other cases, however, the double layer has a diffuse structure, the degree of diffusiveness and, consequently, also the capacitance depending on the electrode potential. The theoretical value of the differential capacitance C_d may be found in these cases by differentiation of the above expressions for ε with respect to φ_a.

Sometimes it is more convenient when studying the structure of the double layer to use the value of the integral capacitance

$$C_i = \frac{\varepsilon}{\varphi_a}. \qquad (21a)$$

The quantity C_i expresses the capacitance of a capacitor which, at a potential difference φ_a between the plates, carries a charge equal to the charge of the double layer and which can thus be considered as equivalent to the double layer at the given potential φ_a. Between C_i and C_d exists the obvious relationship

$$C_i = \frac{1}{\varphi_a}\int_0^{\varphi_a} C_d\, d\varphi, \qquad (22)$$

As will be evident from the following, the quantities C_i and C_d

can differ considerably in certain cases.

The capacitance measurement with alternating current can be used for verifying the double layer theory. Figure 9 gives curves showing the differential capacitance of a mercury electrode as a function of

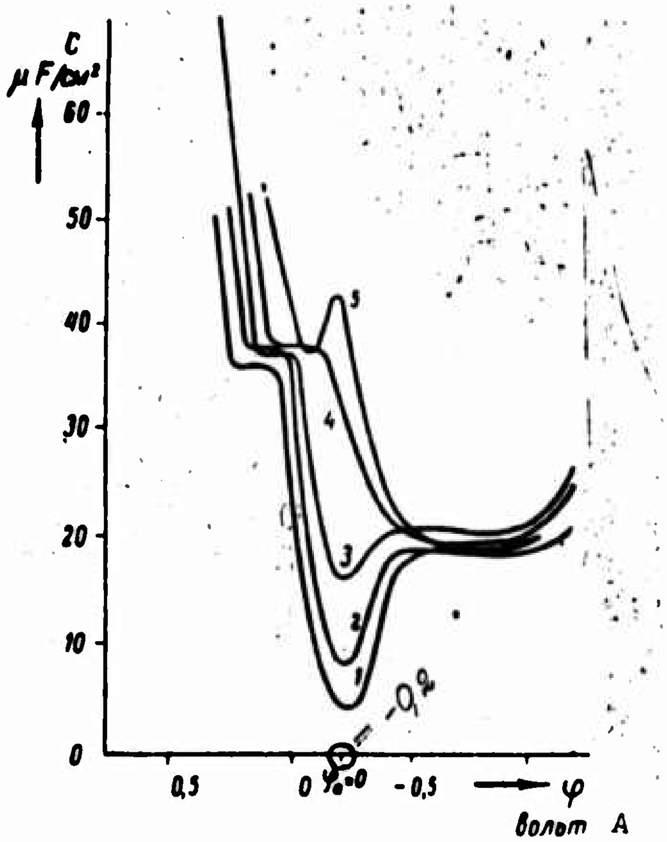


Fig. 9. Differential capacitance of a mercury electrode as a function of potential for KCl and HCl solutions with different concentration: 1) 0.0001 N, HCl; 2) 0.001 N KCl; 3) 0.01 N KCl; 4) 0.1 N KCl; 5) 1 N KCl. Potential measured against standard hydrogen electrode (n.v.e.). A) Volts.

the potential for different KCl and HCl solutions with different concentrations [10]. The potentials measured relative to a standard hydrogen electrode are plotted on the abscissa axis. In dilute solutions the potential of the "zero point" of mercury at which $\varepsilon = 0$ and $\varphi_a = 0$ is equal to $\varphi_n = -0.2$ v at this scale.

It can be seen that, in agreement with the conclusions of the preceding section, a minimum is observed in the differential capacitance curve at this potential, which is the more pronounced, the lower the concentration of the solution, at the point of zero charge the double layer has the most diffuse structure.

It is also evident from Fig. 9 that the capacitance of a double layer with a positive charge of the surface (to the left of the zero point) is considerably larger than with negative charge, and that it increases very strongly in presence of a high positive surface charge (deformation of anions). For comparison purposes Fig. 10 gives curves showing the differential capacitance as a function of potential, calculated for solutions of the same concentration on the basis of the equations of the theory of the double layer. In this calculation the capacitance of the dense layer for a positively charged surface was taken as 36 μF/cm^2 (see page 10) and for a negatively charged one as 18 μF/cm^2. It can be seen that the agreement between theory and experiment is generally quite satisfactory so that one may conclude that the above-presented theory of the double layer is built on a correct foundation. We ought to point out that the observed minimum capacitances are slightly larger than the theoretical ones.

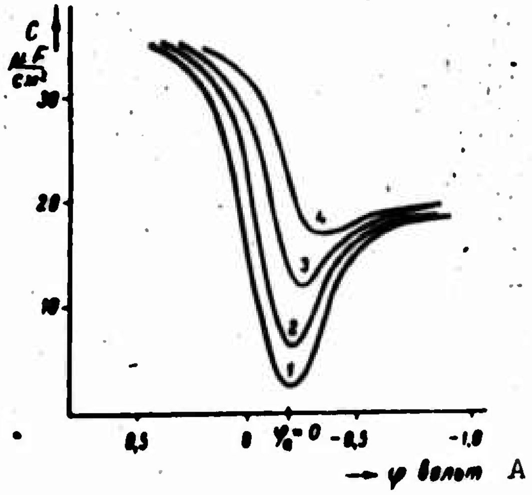


Fig. 10. Differential capacitance, calculated by means of the double layer equation for solutions of a uni-univalent electrolyte with different concentrations: 1) 0.0001 N; 2) 0.001 N; 3) 0.01 N; 4) 0.1 N. A) Volts; B) cm^2.

Figure 11 gives differential capacitance curves for the mercury electrode in normal solutions of several electrolytes [7].

Because the capacitance of the double layer is enormously sensitive to the adsorption of surface-active substances, the presence of traces of high-molecular organic compounds in the solution, which often contaminate "chemically pure" reagents, distorts the measurement results, usually reducing the capacitance. Hence, special measures should be taken in the measurement of the capacitance of the double layer to purify the reagents and the metal surface. Nonobservation of these precautions has for a long time had the result that many researchers have obtained too low capacitance values which could not be accounted for from the point of view of the theory of the double layer. Correct capacitance values were first obtained by M.A. Proskurnin [11].

<u>Measurement of surface charge by means of the charging current</u>. The most convenient method for the direct determination of the surface charge is the measurement of the quantity of electricity which must be supplied to the metal/solution interface during its formation, in order to create a certain potential difference in it. As in the preceding instance, it is assumed here that the entire quantity of electricity is used to charge the surface, or, in other words, that the electrode practically has the property of ideal polarizability. For a liquid metal, for example, mercury, this method is most easily carried out by means of a drop electrode. If the mercury flows into the solution in the form of individual drops at constant potential φ and if the surface of the drops, formed in unit time, is equal to S, εS coulombs per second should pass through the system. Thus, the mean intensity of the "charging current" I_z which is easily measured with a galvanometer, is

$$I_z = \varepsilon S. \qquad (23)$$

Knowing S, ε is readily found from the value of $\bar{I}_z$.

In Chapter 2 we shall consider in greater detail the charging currents in connection with the phenomena observed when the current of an electrochemical reaction is superposed on the charging current.

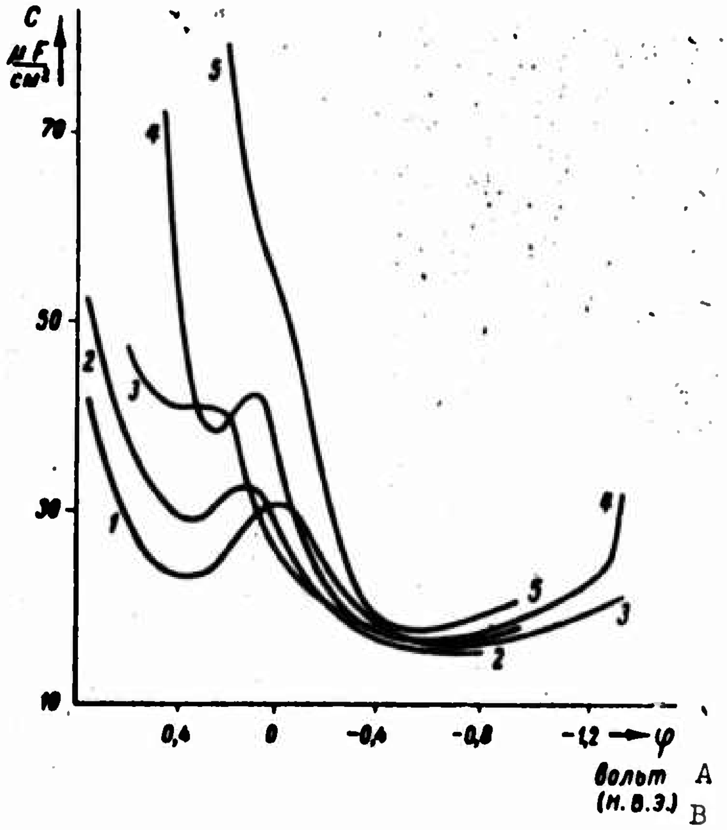


Fig. 11. Differential capacitance curves for the mercury electrode in 1 N solutions of $NaNO_3$ (1), H_2SO_4 (2), Na_2SO_4 (3), NaCl (4), NaI (5). A) Volts; B) n.v.e.

Variation of the electrode potential during the passage of a direct current. Polarization measurements consisting in the measurement of the intensity of a current flowing through the electrode at different potentials are very common in electrochemistry. When such polarization curves are recorded (expressing the rate of a certain electrochemical process as a function of the electrode potential) one tries to keep the electrode surface in an unchanged condition. A different picture is observed when the current is passed through an electrode under conditions in which a long duration of the electrochemical process at constant potential is impossible. In this case the electrode potential varies continuously depending on the quantity of electricity which has passed through it or, with polarization by a current with constant intensity, on time. The Kazan' professor R.A. Kolli [12] was the first to use the measurement of the potential shift of the electrode during the passage of a current for a certain length of time for the determination of capacitance and found a value of 150 μF/cm^2 for the capacitance of a platinum electrode.

The curves which show the potential as a function of the quantity of electricity imparted to the electrode are termed charging curves. The charging curve for mercury in HCl solution [2] is represented in Fig. 12. By means of the charging curves one can find the differential and, if the position of the zero point is known, also the integral capacitance of the electrode (Eq. (22)).

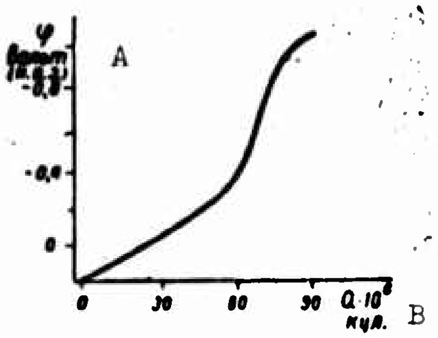


Fig. 12. Charging curve for mercury in 1 N HCl solution. A) Volt (n.v.e.); B) coul.

The method of capacitance measurement with a direct current can also be used as a method for determining the true surface area of the electrode, for example, the surface of the active material of the negative plate of a lead battery. As we know that the capacitance of a smooth negatively charged surface is 17 μF/cm^2, we obtain the true surface of the plate by dividing the capacitance of the real negative battery plate, measured by the method of charging curves, by this value [13].

In the practical application of the method of charging curves one has to take into account primarily the difficulty of a complete exclusion of electrochemical side reactions during the recording of the curve. For example, the solution always contains small quantities of oxygen or other oxidants, which are reduced during the cathodic polarization of the electrode. In order that the results should not be distorted, it is indispensable to reduce the influence of these reactions to a minimum, i.e., to create conditions such that the intensity of the charging current is great compared with the intensity of the current of these collateral electrochemical processes.

This problem can be solved by different methods. One of these consists in carrying out the recording of the charging curve within a minimum interval of time, i.e., with a large current density, with oscillographic recording of the potential. This method, which many British authors have used (for example, Raydil, Bowden, Butler), has an important deficiency which consists in the following. As will be evident from the following, while the charging of the double layer takes place very rapidly, other changes of the state of the metal surface often proceed slowly. When the potential varies quickly, they lag behind compared with the variation of the charge of the double layer, and the electrode thus cannot reach the equilibrium state corresponding to the new value of the potential.

Methods of recording charging curves which are free of these deficiencies have been developed by the Soviet scientists A.I. Shlygin and B.V. Ershler [8]. The first of these methods [14] consists in the use of an electrode with very large true surface, such as, for example, a platinized platinum electrode. In this case even if the true density of the charging current is small, the total current intensity is fairly large, and side processes caused by diffusion of impurities from the volume of the solution to the electrode cannot distort the charging curve. Electrodes of platinized platinum and analogous electrodes with a developed surface of iridium, rhodium, lead, silver and other metals have been studied by this method.

In the second method [15] an advantageous relation between the surface and volume processes is achieved not by increasing the surface but by decreasing the volume of the solution. To this end the electrode in the form of a cylinder *A* is inserted into the tube *B* which is filled with electrolyte and which has almost the same length and internal diameter as the electrode (Fig. 13). The impurities in the small volume of solution between the electrode and the walls of the cell are so few that they cannot interfere with the recording of the charging curves.

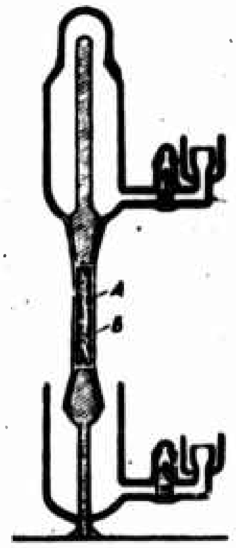


Fig. 13. Device for recording charging curves on electrodes with smooth surface.

Variation of the composition of the solution during the formation of the double layer. The formation of a double layer when a metal comes into contact with a solution causes a variation of the composition of the solution. Thus, for example, when silver comes into contact with a solution of silver nitrate, the silver ions donate their positive charges to the metal surface which attracts the NO_3^- ions. Thus, a certain quantity of silver nitrate disappears from the solution during the formation of the double layer. When platinized platinum, saturated with hydrogen under atmospheric pressure, comes into contact with a solution of potassium chloride, part of the adsorbed hydrogen is ionized and goes into solution, the surface is charged negatively and attracts potassium ions. As a result part of the potassium ions in the solution are replaced by hydrogen ions and the solution is acidified. At very low concentration of the adsorbed hydrogen the formation of the double layer is accompanied by a discharge of hydrogen ions at the surface of the plate which then becomes positive and attracts Cl^- anions. As a result a certain quantity of HCl disappears, and the initially neutral KCl solution becomes alkaline.

If the electrode surface is small, the variations in the composition of the solution are slight and escape detection. Indeed, for example, when the surface charge is $2 \cdot 10^{-5}$ coulombs per cm^2, only $2 \cdot 10^{-10}$ gram-equivalents of ions are consumed in the formation of the double layer. Hence in electrochemistry the equilibrium potential of the electrode is normally associated with the initial composition of the solution on the assumption that the latter does not undergo any changes upon contact with the electrode. However, if the true electrode surface is, for example, 10 m^2, the formation of a double layer already causes a variation of normally $2 \cdot 10^{-3}$ in 10 cm^3 of solution, which is easily observed.

A.N. Frumkin and A.D. Obrucheva were the first to point out the peculiarities of the adsorption effects which accompany the formation of the double layer. These adsorption phenomena are sometimes termed potential-determining adsorption, and in the case when the initial solution was neutral and free acids or alkali appeared in it as a result of the interaction with the electrode, as in the hydrolysis of salts, they were termed hydrolytic adsorption.

The variations of the composition of a solution can be utilized for the study of the structure of the double layer in the case of electrodes of platinum or carbon which have a highly disperse structure [16, 17], and also of mercury, which can be given a large surface by disintegrating a fast-moving jet into small droplets.

If the adsorption measurements are carried out at different electrode potentials it is possible to determine the charge of the double layer as a function of the potential. Figure 14 gives the adsorption of the Na^+ ion as a function of potential for the case of platinized platinum in a hydrogen atmosphere [14]. The potential of this electrode was varied by variation of the composition (pH) of the solution. Under conditions of "ideal polarizability" of the electrode the potential can be conveniently varied by supplying increasing quantities of charge to the electrode from without. Thus, the adsorption measurements can be combined with the recording of the charging curves and the data thus obtained can be compared. Further on we shall present some results of this comparison.

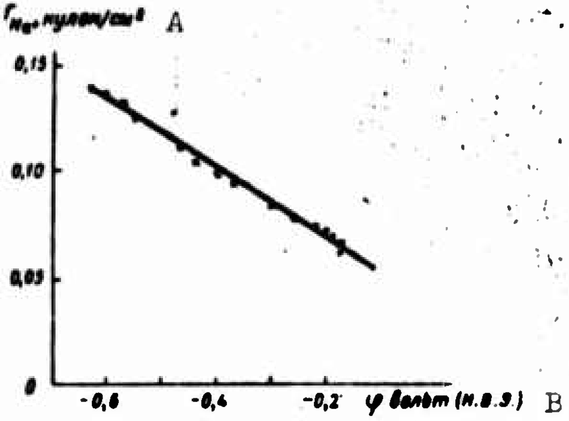


Fig. 14. Adsorption of sodium ions on platinized platinum in a hydrogen atmosphere from a NaCl solution as a function of potential at different pH values. A) g_{Na^+} coulomb/cm^2; B) φ volt (n.v.e.).

Motion of solid particles under the influence of an electric field. As has been pointed out in §2, the measurement of the velocity of motion of solid particles in a solution when an external field is applied, makes it possible to determine the electrokinetic potential, whose value for the case of dilute solutions is close to that which we have termed the ψ_1 potential. Thus the electrokinetic phenomena, such as, for example, the cataphoresis of metal salts or the deflection of metal wire, immersed in an electrolyte and attached at one end, in an electric field can also provide information on the structure of the double layer and the sign of the surface charge. The correctness of the results obtained by the method of charging curves and adsorption measurements has thus been confirmed [1, 41].

§5. ELECTROCAPILLARITY PHENOMENA

The first information on the structure of the double layer on mercury and other liquid or molten metals in different media has been obtained by the study of the interface surface tension at the metal/solution interface as a function of the potential.* This relationship can be found experimentally by determining the interface tension at different potentials by means of a capillary electrometer or other analogous methods.

In the capillary electrometer of Gouy (Fig. 15) normally used for this purpose one measures the pressure of a column of mercury required at a given potential of the mercury, measured relative to a constant auxiliary electrode, for causing the mercury meniscus at the conical capillary (a) to be at a certain distance from its end. It is assumed that the solution wets the walls of the capillary completely. According to the theory of capillarity the height of the mercury column under these conditions is proportional to the interface tension σ at the interface. The potential difference φ between the surface of the mercury or other liquid metal, which we shall consider as ideally polarizable, and the auxiliary electrode *c* is varied by means of the potentiometer *d*.

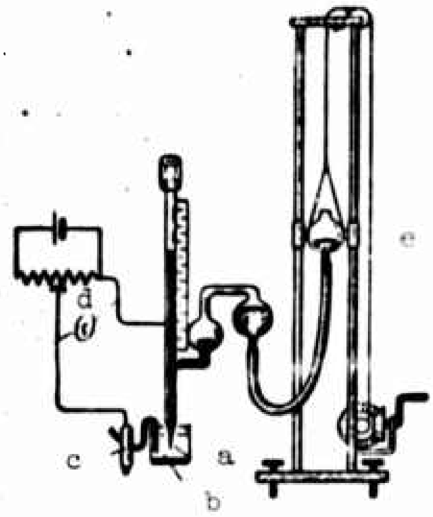


Fig. 15. Circuit of the capillary electrometer. a) Capillary; b) solution; c) auxiliary electrode; d) potentiometer (battery and resistance box) for applying the potential to the mercury meniscus in the capillary; e) lifting device for the mercury vessel for varying the mercury pressure in the capillary.

The graphic representation of σ as a function of φ is termed electrocapillary curve (Fig. 16, curve a). The differential equation of the electrocapillary curve which can be obtained by a thermodynamic method

(Lippman equation) has the following form:

$$\frac{\partial\sigma}{\partial\varphi} = -\varepsilon. \qquad (24)$$

Equation (24) enables the charge of the double layer to be determined from the slope of the electrocapillary curve. If σ is expressed in dynes per centimeter, and φ in volts, the numerical value of $-\frac{\partial\sigma}{\partial\varphi}$ must be multiplied by 10^{-7} in order to obtain the magnitude of ε in coulombs per cm^2. The Lippman equation can be verified by comparison of the quantity ε, calculated from the slope of the electrocapillary curve (curve b in Fig. 16) with the values found experimentally, for example, from the charging currents.

By differentiating Eq. (24) with respect to φ we obtain

$$\frac{\partial\varepsilon}{\partial\varphi} = -\frac{\partial^2\sigma}{\partial\varphi^2}. \qquad (25)$$

Thus the second derivative of the interface tension with respect to the potential taken with the opposite sign expresses the differential capacitance of the electrode which can be measured directly with great accuracy. This also makes an experimental verification of Eq.

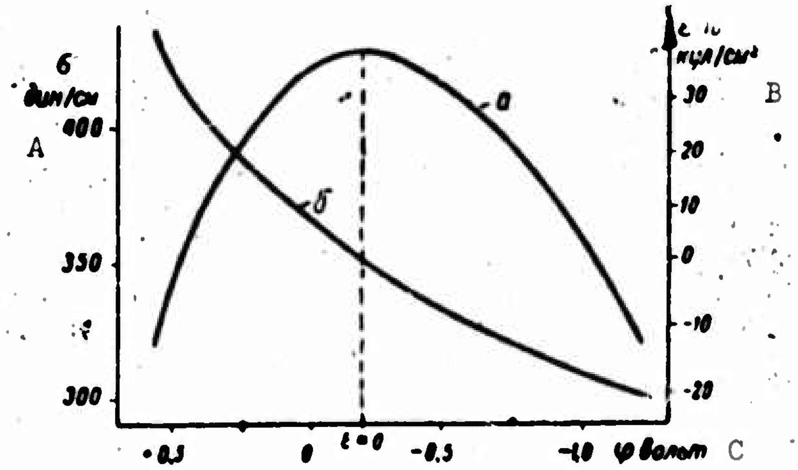


Fig. 16. Interphase tension σ (curve a) and charge ε of the mercury surface (curve b) as a function of potential. A) Dyne/cm; B) coulomb/cm^2; C) volt.

(24) possible. Different methods of verification confirmed the correctness of this equation.

It follows from Eq. (24) that the charge ε is zero at the potential corresponding to the maximum of the electrocapillary curve, positive at more positive potentials and negative at more negative potentials.

The literature contains a large number of derivations of Eq. (24). We present here a derivation which is based on the adsorption formula of Gibbs and which is discussed in most manuals on physical and colloid chemistry:

$$d\sigma = -\sum \Gamma_i \, d\mu_i. \qquad (26)$$

In this equation, μ_i expresses the chemical potential of the ith component of a solution. In dilute solutions, as we know,

$$\mu_i = \text{const} + RT \ln c_i \qquad (27)$$

The quantity Γ_i, the surface density of the ith component, can be determined by different methods. The following determination method will be convenient for our purposes. We increase the interface area by 1 cm^2. During the formation of fresh interfacial area the composition of the solution changes. If we desire that after the increase in the interfacial area the composition of the solution and the surface layer remain unchanged, Γ_i moles of each solution component must be added to the system. We carry out the summation in Eq. (26) for all components except for the solvent itself. In the case of the common adsorption processes the quantities Γ_i obviously express the number of moles of the ith component, adsorbed on 1 cm^2 of surface. In order to change over from the Gibbs equation to the Lippman equation, we isolate from all the components of the system the ions which can pass through the metal/solution interface, i.e., in the case of mercury, the Hg_2^{++} ions.

If during the formation of one square centimeter of fresh mercury/solution interface area the charge density is to be kept constant, $\varepsilon/2F$ moles of Hg_2^{++} ions must pass from the solution to the metal according to the Faraday law. Thus,

$$\Gamma_{Hg_2^{++}} = \frac{\varepsilon}{2F} \tag{28}$$

and, consequently,

$$d\sigma = -\Gamma_{Hg_2^{++}}\, d\mu_{Hg_2^{++}} - \sum \Gamma_i\, d\mu_i = -\frac{\varepsilon}{2F}\, d\mu_{Hg_2^{++}} - \sum \Gamma_i\, d\mu_i, \tag{29}$$

where the summation is now confined to the remaining dissolved substances.

Between the quantity $\mu_{Hg_2^{++}}$ and the potential difference φ exists the thermodynamic relation

$$\varphi = \text{const} + \frac{1}{2F}\mu_{Hg_2^{++}}, \tag{30}$$

which, according to Eq. (27), for dilute solutions assumes the form of the usual Nernst formula.

It follows from Eqs. (29) and (30) that

$$d\sigma = -\varepsilon\, d\varphi - \sum \Gamma_i\, d\mu_i. \tag{31}$$

Equation (31) is the general thermodynamic basis of the theory of the electrocapillarity phenomena.

For dilute solutions, expressing in accordance with Eq. (27) μ_i through c_i, we can write

$$d\sigma = -\varepsilon\, d\varphi - \sum RT\Gamma_i\, d\ln c_i. \tag{32}$$

In the particular case, when φ at the metal/solution interface varies, $d\mu_i = 0$ is valid in a solution of constant composition, and Eq. (31) is transformed into the Lippman equation.

If we determine σ as a function of c_i experimentally at constant φ, we can, according to Eq. (32) find the values of Γ_i, i.e., the adsorption on the mercury surface for different components of the solution. This problem will be investigated in greater detail in §7.

A comparison of the dependence of σ on φ with the dependence of σ on the concentration of the dissolved electrolyte enables us to predict how the shape of the electrocapillarity curve should vary with varia-

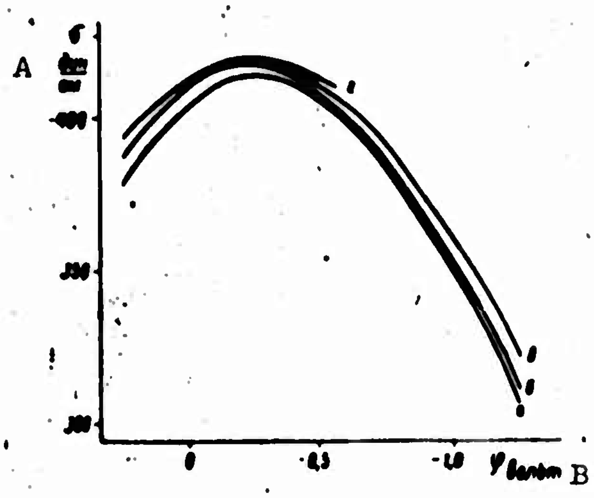


Fig. 17. Shape of the electrocapillarity curves as a function of the concentration of KNO_3 solutions: 1) 1 N; b) 0.1 N; c) 0.01 N; d) 0.001 N. A) Dyne/cm; B) volt.

tion of the concentration. For the sake of simplicity, we shall consider the case in which the adsorption of ions in the double layer is caused only by electrical forces and in which only one electrolyte with a concentration c is present in the solution. Then, according to Eq. (32)

$$d\sigma = -\varepsilon\, d\varphi - RT(\Gamma_K + \Gamma_A)\, d\ln c, \qquad (33)$$

where Γ_K and Γ_A, respectively, are the adsorbed quantities of cation and anion. The charge of the ion envelope of the double layer is obviously $(n_K\Gamma_K - n_A\Gamma_A)F$, where n_K and n_A are the valencies of the cation and anion, from which follows

$$\varepsilon = -(n_K\Gamma_K - n_A\Gamma_A)F. \qquad (34)$$

Let us assume that the metal surface carries a fairly strong negative charge and that specific adsorption phenomena are absent. Then we can use the approximation

$$\varepsilon \approx -n_K\Gamma_K F \qquad (35)$$

and, according to Eq. (33),

$$d\sigma = n_K\Gamma_K F\left(d\varphi - \frac{RT}{n_K F}\, d\ln c\right). \qquad (36)$$

It follows from Eq. (36) that $d\sigma = 0$ if

$$d\varphi - \frac{RT}{n_K F}\, d \ln c = 0,$$

or, in other words, when the concentration varies by the amount dc, the negative branch of the electrocapillarity curve is displaced parallel to itself by the distance $(RT/n_K F) d \ln c$.

When the solution is diluted this displacement occurs in the direction of the more negative potentials. Analogously, the displacement of the positive branch, as is easily shown, takes place in the opposite direction by the amount $(RT/n_A F) d \ln c$. As a result, the electrocapillary curves become flatter when the solution is diluted (Fig. 17). The above derived relations can also be obtained from the theory of the double layer which enables the quantity ψ_1 and, consequently, also ε, to be determined as a function of the concentration of the solution by means of the equations (20) and (20a).

§6. ZERO CHARGE POTENTIALS

The electrode potential at which $\varepsilon = 0$ (measured relative to some auxiliary electrode, for example, the normal hydrogen or normal calomel electrode) is termed zero charge potential or zero point of the metal φ_n. When the electrode potential passes through this point the sign of the surface charge changes which, as will be evident from the following, can be of great importance for the kinetics of the electrode processes. Further on it will also be shown that at potentials close to the zero charge potential, the electrode has the maximum capacity for adsorbing dissolved organic substances and is less well wetted by the solvent. These two circumstances are also of significance for the course of the electrochemical processes. Hence the determination of the zero charge potential is of interest for electrochemical kinetics [1, 25, 28].

In the absence of a surface charge at the metal/solution interface processes of adsorption of ions and molecules, which we have termed specific and which modify the potential difference between the metal and the solution, can also take place. In this section we shall examine the zero charge potentials in the absence of specific adsorption.

The above-described methods of measuring the surface charge and capacitance and also other methods such as the measurement of the interfacial tension, wettability, etc., are used for the determination of the zero charge potential.

The first data on the zero charge potential were obtained by means of measurement of the interfacial tension as a function of potential on the basis of Eq. (24) and also by means of a determination of the potential of the disconnected drop electrode.* The first method (electrocapillary measurements) has lately been frequently used for the determination of the zero points of liquid metals: gallium, thallium amalgam, molten tin, cadmium, lead, zinc, etc. The determination of the zero charge potentials in melts, carried out in several studies of S.V. Karpachev [18] is also of great interest for the electrochemistry of aqueous solutions because, as experiments have shown, the difference in the position of the zero points varies little upon transition from the solid metals in aqueous solutions at room temperature to molten metals at temperatures of 400-500°C.

The interface tension at the solid metal/solution interface cannot be measured directly, but P.A. Rebinder succeeded in observing a phenomenon which enables the variation of the surface energy of a solid during variation of the potential to be observed [19]. According to the theory of the disintegration of solids of P.A. Rebinder every influence which results in a decrease in the surface tension in the internal microcracks formed during the process of mechanical rupture, causes a decrease in the hardness of the solid and its capacity to withstand brittle or plastic deformation. Thus a possibility is opened up for determining the electrocapillarity curves of solids on the basis of their hardness change with potential variation.

Figure 18 gives the curve (a) representing the hardness of thallium as a function of the potential in 1 N Na_2SO_4 [10] and the curve (b) of the surface tension of saturated thallium amalgam in the same solution [20]. The two curves are entirely analogous and the potentials corresponding to the curve maxima are very close; this indicates that the hardness measurement can be used as a method for determining the zero points.

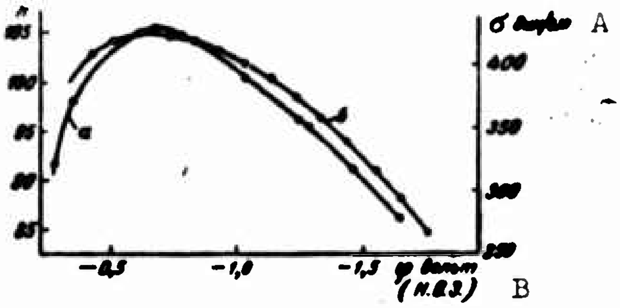
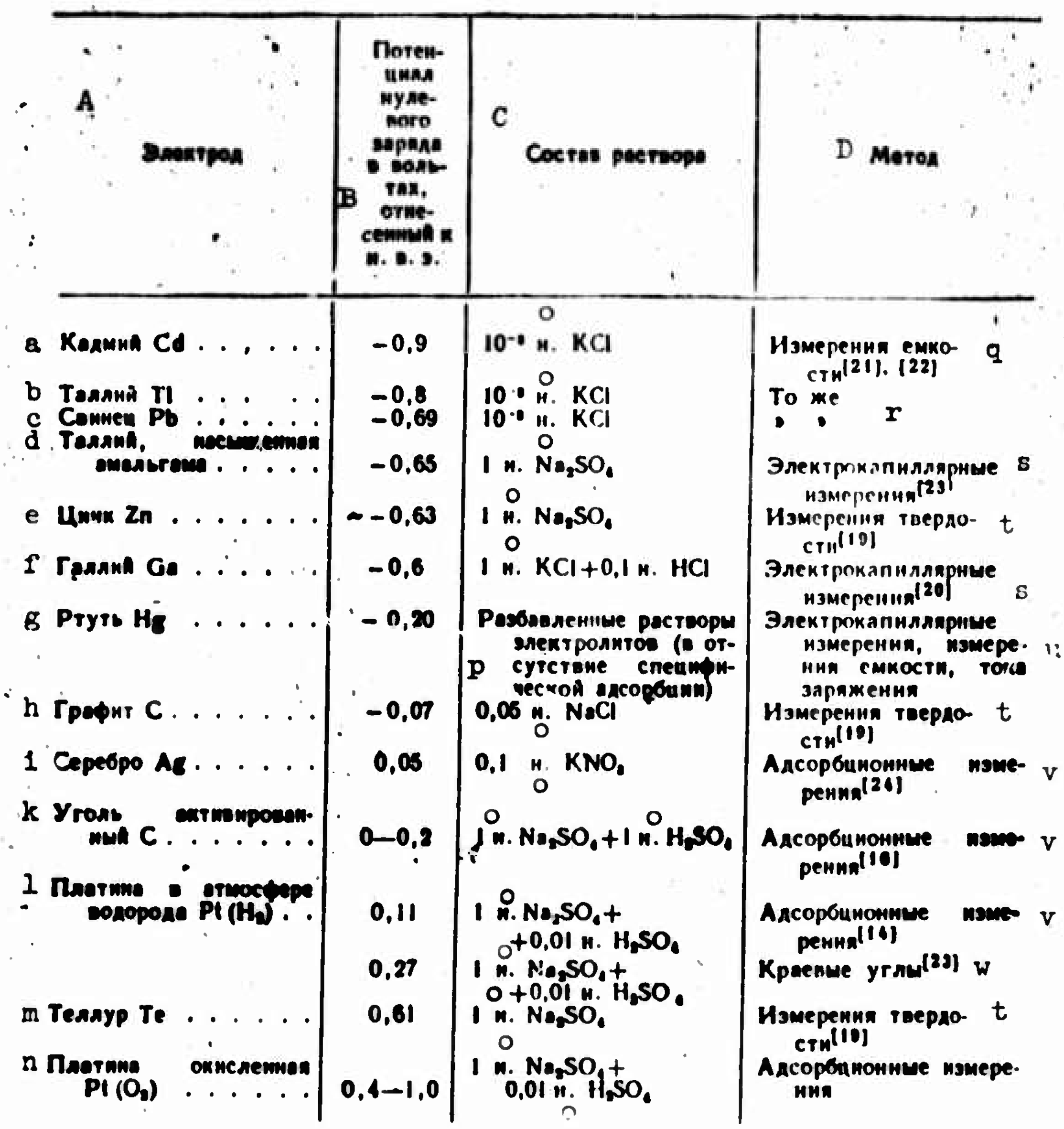


Fig. 18. Curve showing the hardness of thallium (a) and the surface tension of saturated thallium amalgam (b) in 1 N Na_2SO_4 as a function of the potential. A) Dyne/cm; B) volt (n.v.e.).

Another widely used method for the determination of the zero charge potential is the measurement of the capacitance of the double layer in dilute solution. As we have shown (page) it follows from the theory of the double layer that near the zero point the degree of diffuseness of the double layer is at a maximum and, consequently, its capacitance is a minimum. Thus the zero charge potential can be found from the position of the minimum on the curve which represents the differential capacitance as a function of the potential. For example, the

TABLE 1

Zero Charge Potentials φ_n in Aqueous Solutions at Room Temperature



A Электрод	B Потенциал нулевого заряда в вольтах, отнесенный к н. в. э.	C Состав раствора	D Метод
a Кадмий Cd	−0,9	10^{-3} н. KCl	Измерения емкости[21], [22] q
b Таллий Tl	−0,8	10^{-3} н. KCl	То же
c Свинец Pb	−0,69	10^{-3} н. KCl	» » r
d Таллий, насыщенная амальгама	−0,65	1 н. Na_2SO_4	Электрокапиллярные измерения[23] s
e Цинк Zn	∼−0,63	1 н. Na_2SO_4	Измерения твердости[19] t
f Галлий Ga	−0,6	1 н. KCl+0,1 н. HCl	Электрокапиллярные измерения[20] s
g Ртуть Hg	−0,20	p Разбавленные растворы электролитов (в отсутствие специфической адсорбции)	Электрокапиллярные измерения, измерения емкости, тока заряжения u
h Графит C	−0,07	0,05 н. NaCl	Измерения твердости[19] t
i Серебро Ag	0,05	0,1 н. KNO_3	Адсорбционные измерения[24] v
k Уголь активированный C	0—0,2	1 н. Na_2SO_4+1 н. H_2SO_4	Адсорбционные измерения[18] v
l Платина в атмосфере водорода Pt (H_2) . .	0,11	1 н. Na_2SO_4+ +0,01 н. H_2SO_4	Адсорбционные измерения[14] v
	0,27	1 н. Na_2SO_4+ +0,01 н. H_2SO_4	Краевые углы[23] w
m Теллур Te	0,61	1 н. Na_2SO_4	Измерения твердости[19] t
n Платина окисленная Pt (O_2)	0,4—1,0	1 н. Na_2SO_4+ 0,01 н. H_2SO_4	Адсорбционные измерения

A) Electrode; B) zero charge potential in volts, relative to n.v.e.; C) composition of solution; D) method; a) cadmium; b) thallium; c) lead; d) thallium, saturated amalgam; e) zinc; f) gallium; g) mercury; h) graphite; i) silver; k) activated charcoal; l) platinum in hydrogen atmosphere; m) tellurium; n) platinum oxidized; o) N; p) dilute electrolyte solutions (in absence of specific adsorption); q) capacitance measurements; r) the same; s) electrocapillarity measurements; t) hardness measurements; u) electrocapillarity, capacitance, and charging current measurements; v) adsorption measurements; w) contact angles.

zero points of solid lead, thallium and zinc [21, 22] have been determined by this method.

In the case of solids from which electrodes with a highly developed surface can be easily made, such as platinum or carbon, the potential of the zero point at which the adsorption of cations as well as anions ceases, can be found from measurements of electrolyte adsorption [16].

It will be shown in Chapter 5 that measurements of the contact angles at the three-phase interface metal/solution/gas can also be used for the determination of the position of the zero point of the electrodes. In the absence of a charge the wetting of the metal by the solution is a minimum and the above-mentioned contact angle is a maximum. The zero charge potentials of mercury, thallium amalgam, platinum and several other metals have been determined by this method [23].

Table 1 gives the zero charge potentials φ_n measured by different methods relative to the potential of the normal hydrogen electrode (n.v.e.) on several metals.

It can be seen from Table 1 that the zero point potentials of different electrodes differ considerably. From this follows an important conclusion which we shall explain by means of a concrete example. We construct a circuit of a thallium electrode, an electrolyte solution and a platinum electrode saturated with hydrogen. We choose the conditions at the interface between the thallium and the solution and also between the platinum and the solution in such a way that neither of the two interfaces carries a charge, i.e., that each electrode is at its zero point. Finally, we connect the electrodes by means, for example, of copper wires with some device for the potential measurement. Then, according to Table 1, we detect a potential difference of 0.91 v between the ends of the chain although there are no ionic double layers in this circuit.

This potential difference is composed of the potential differences which may be localized at the surface layers of the metals at the interface with the solution but which do not involve a process of ion migration and can also be present at the interfaces between metals. The presence of a solvent, water, is not essential for the appearance of such a potential difference.

In fact it is known that in presence of a conducting contact between two metals in a vacuum a potential drop is also established in the space between them which is usually referred to as contact potential difference. The existence of contact potential differences exerts an important influence on the processes of electron emission and is of great importance for radio engineering.* The zero charge potential differences of different metals may be regarded as quantities analogous to the contact potential differences, but measured not in vacuo but in a liquid medium, water.

The measurements of S.V. Karpachev [18] who showed that the zero point potential differences in many cases are similar to the contact potential differences measured in vacuo, are in complete agreement with this conclusion.

Thus the investigation of the structure of the double layer leads us to the conclusion that the potential difference at the ends of a galvanic circuit, equal to its electromotoric force, consists of two components: one of these is composed of the potential differences in the ionic double layers and the other is analogous to the contact potential difference between metals in vacuo.

The problem of the relationship between the e.d.s. of a galvanic circuit and the contact potential difference has always interested the electrochemists (the so-called Volta problem) [25].

F. Engels in his "Dialectic of Nature" has given great attention to it. The German electrochemical school following W. Nernst, has connected for a long time the appearance of a potential difference at the ends of a galvanic circuit exclusively with the formation of ionic double layers without taking into account the contact potentials. An opposite point of view was upheld, for example, by Langmuir [26] who identified the total e.d.s. of the circuit with the contact potential difference between metals. As follows from the above both these points of view are erroneous; a correct solution of the Volta problem became possible only after A.N. Frumkin and co-workers elucidated the meaning of the zero points of metals, gave methods for the determination of their positions and established their connection with the contact potential difference.

The existence of potential differences in the surface layer of a metal in vacuo according to Ya.I. Frenkel' [27] is due to the fact that the electron gas in the metal extends slightly beyond the limits of the positive ions of the metal lattice. This distribution of the electron cloud is connected with the so-called "zero" (i.e., retained at absolute zero) kinetic energy of the electron gas; these questions are discussed in the electronic theory of metals. The potential differences in the surface layer of a metal exist independently of whether the metal is in a vacuum or in contact with a solvent, but their magnitude may vary slightly during contact with a liquid medium. In consequence of this a certain parallelism should be observed between the contact potentials in vacuo and the difference of the position of the zero points but not necessarily an accurate quantitative coincidence.

When the metal comes into contact with a solvent the potential variation in the ionic double layer which we have already discussed is superposed on the electronic potential difference in the surface layer of the metal and, as we shall see in §7, the potential differences, caused by the adsorption of ions and molecules of the solvent and solutes. Thus the total potential difference at the metal/solution interface is composed of a number of hetergeneous components. At the present time there are not direct experimental methods for the determination of the magnitude of a single potential difference.* If we had an accurate picture of the electron distribution in the surface layer of the metal and liquid, we could calculate this value but the level of development of the theory does not enable such calculations to be carried out at present with a sufficient degree of accuracy. Hence the problem of the determination of the values of the individual potential differences or conditions at which they vanish (the so-called "absolute zero of the potentials") which has often been examined by the electrochemists, remains as yet unsolved.

However, a knowledge of the individual potential differences is not essential for the solution of concrete electrochemical problems so that the problem of the "absolute zero potentials" is not of great importance for the development of electrochemistry. On the contrary, we often have to deal with that part of the potential difference which lies in the ionic double layer and whose magnitude is determined by the position of the zero charge point of the metal.

§7. ADSORPTION OF IONS AND MOLECULES

At the metal/solution interface, as at any other interface, various adsorption phenomena take place in addition to those which are directly connected with the migration of ions from one phase into the other and the charge of the surface. In order to distinguish them from adsorption, which can be determined from the electric forces on the basis of the equations (5) and (5a), these phenomena are often termed specific. The existence of specific adsorption phenomena indicates that even in absence of an electric field there is a certain work of adsorption, which is gained during the transfer of a mole of substance from the interior of the solution to the interface. For the case of the adsorption of ions the positive work of adsorption at an uncharged surface is equal to the values which we have designated in §3 by Φ_+ and Φ_- with opposite sign. As has been indicated during the description of the theory of the double layer, the presence of an electric field modifies the magnitude of this work so that the specific and electrical adsorption phenomena are generally closely interrelated.

Our knowledge concerning the specific adsorption of ions and molecules at the metal/solution interface is primarily based on the data obtained in the study of the electrocapillarity phenomena on mercury and amalgams in solutions of different composition. A comparison of the specific adsorption on the uncharged mercury/solution interface with adsorption phenomena on other interfaces, for example, at the interface solution/air, shows that in spite of several characteristic features, connected with the presence of a metallic phase, these adsorption phenomena obey the same laws in many respects. Hence the experimental material relating to adsorption at the solution/gas interface [29] can also be used for the interpretation of the specific adsorption phenomena.

At the mercury/solution interface, as Gouy [30] showed, the specific adsorption of anions is particularly clearly manifested. The anions Br^-, SNS^-, I^- and SH^- lower the interfacial tension at an uncharged (or positively charged) mercury surface considerably and, consequently, according to Eq. (32) are strongly adsorbed on it (Fig. 19). In contrast to these ions, the anions CO_3^{--}, SO_4^{--}, HPO_4^{--}, OH^- and others do not lower the interfacial tension at the uncharged mercury/

solution interface, but in sufficiently concentrated solutions even slightly increase it, which indicates their negative adsorption. The first group of anions is usually termed surface-active, the second one, surface-inactive.

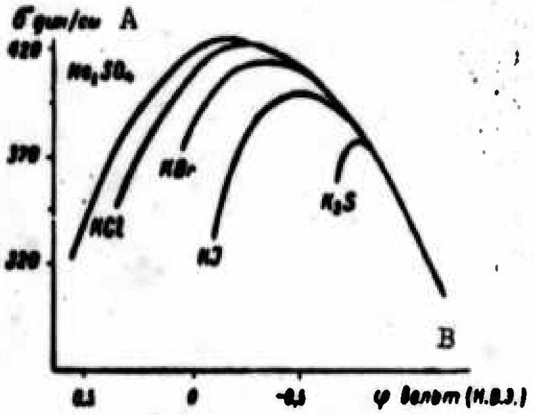


Fig. 19. Effect of the adsorption of the ions Cl^-, Br^-, I^- and SH^- on the shape of the electrocapillarity curve. A) Dyne/cm; B) volts (n.v.e.).

The lowering of the maximum of the electrocapillarity curve upon adsorption of anions, as can be seen in Fig. 19, corresponds to a displacement of it to more negative potentials.

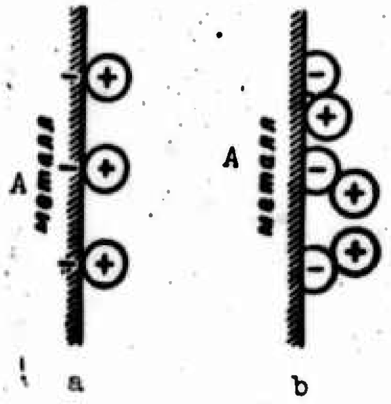


Fig. 20. Structure of the double layer in a solution of Na_2SO_4 (a) and KI (b) at the potential of the maximum of the electrocapillarity curve in a solution of KI. A) Metal.

Let us compare the state of the metal/solution interface in Na_2SO_4 and KI solutions at the same potential $\varphi = (\varphi_n)_{KI}$ corresponding to the maximum of the electrocapillarity curve in KI solution (Fig. 20a and 20b). In the case of the solution of the inactive electrolyte Na_2SO_4 the metal surface at this potential does carry a negative charge (Fig. 20a). In the KI solution at the same potential $\varepsilon = 0$ is valid, and the presence of a negative potential difference between metal and solution is determined by the presence of a layer of adsorbed anions at the metal surface which attracts the cations electrostatically (Fig. 20b). As follows from Eqs. (4) or (12), at $\varepsilon = 0$ $\varphi_a = \psi_1$, i.e., the total potential variation in the double layer is localized at distances from the metal surface which exceed the effective radius of the first ion layer. Let us point out that in the case of a strong specific adsorption the magnitude of ψ_1 may be considerable without the double layer having to extend far into the solution and does not decrease but increases with increasing concentration of the solution. The relation between the position of the maximum of the electrocapillarity curve in the solution of a surface-active electrolyte and the magnitude of ψ_1 is illustrated in Fig. 21.

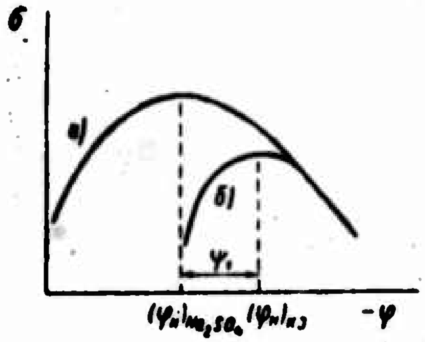


Fig. 21. Relation between the potential of the maximum of the electrocapillarity curve in an inactive ($a = Na_2SO_4$) and in an active ($b = KI$) electrolyte and the magnitude of the ψ_1 potential in the latter.

Let us dwell a little longer on the state of the metal surface in Na_2SO_4 and KI solutions in the potential range between the values $\varphi = (\varphi_n)_{Na_2SO_4}$ and $\varphi = (\varphi_n)_{KI}$. In this range (Fig. 21) the potential difference between a point on the mercury surface and a point on the interior of the solution is negative in both cases but the sign of the quantity ε is different: in the Na_2SO_4 solution $\varepsilon < 0$, and in the KI solution $\varepsilon > 0$. The existence of a negative potential difference between the surface and the interior of the solution with a positive sign

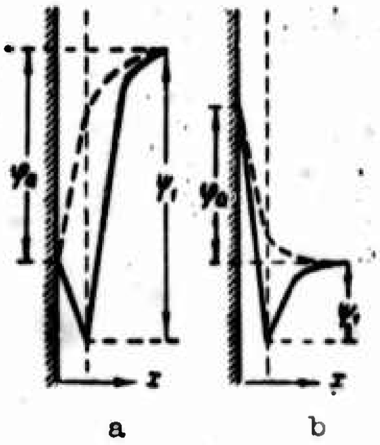


Fig. 22. Potential distribution at the metal/solution interface in presence of specific adsorption of anions (thick curves) and in the absence of such adsorption (dashed lines); a) the potential difference φ_a is negative; b) the potential difference φ_a is positive.

of the charge is possible only if the ψ_1 potential varies within the double layer with the distance x in such a way as indicated by the thick line in Fig. 22a. Going from the interface to the plane in which the centers of the adsorbed ions are situated, the potential drops; with further increase in the distance x, i.e., in the region which contains excess cations, it increases again. In this case it would have been more correct to speak of a triple and not a double electrical layer.

At potentials which are more positive than the zero charge potential, the quantity ψ_1 in a solution of an inactive electrolyte is positive. However, in presence of considerable specific adsorption the charge of the anions close to the interface exceeds in absolute magnitude the surface charge of the metal, in consequence of which, in accordance with Eq. (34), the quantity Γ_K should be positive. Thus, in presence of specific adsorption of anions the adsorption of cations is positive not only with a negative but also a positive surface charge. Because the cations in this case form the diffuse part of the double layer, the ψ_1 potential should increase with increase in x beyond the limits of the plane in which the centers of the anions are situated, as in Fig. 22a. On the whole the potential distribution in this case corresponds to the thick line in Fig. 22b. As this graph shows, in spite of the positive value of ε, the quantity ψ_1 in this case is negative. This phenomenon is normally termed surface charge reversal.

The magnitude of the anion adsorption, as follows, in particular, from Fig. 19, depends on the surface charge. At fairly high negative charges the electrostatic repulsion predominates over the specific adsorption forces, and the adsorption of anions ceases (the electrocapillarity curves flow together); in presence of a positive surface charge the action of the electrostatic and specific adsorption forces is additive and a strong adsorption effect is observed.

We have given here in an elementary form a picture of the phenomena, which occur in the adsorption of anions, based directly on experimental data. These conclusions can be refined on the basis of the double layer theory. To obtain correct results, however, it is necessary to take into account not merely the existence of the specific work of adsorption of the anions but also the difference in the distances of the "closest approach" of the cation and anion to the electrode surface. The problem of the dependence of the numerical value of ψ_1 on electrolyte concentration has been examined in the works of O.A. Yesin [31], B.V. Ershler [6] and others.

The adsorption of anions is a widespread phenomenon, which is frequently encountered in the consideration of the mechanism of electrode processes. It is observed at the metal/solution interface in the case of many metals, although possibly it is not always so clearly apparent as in the case of mercury. There exists a certain analogy between the specific adsorption of anions at the metal/solution interface and the formation of complexes of the type HgI_4^{--} or $PtCl_6^{--}$ in which the metal cation is surrounded by anions.

In contrast to the inorganic ions, the inorganic cations, as a rule, do not show a marked specific adsorption on the uncharged mercury/solution interface (the thallium ion Tl^+ forms an exception). More accurately, for the univalent cations there is even a certain negative work of adsorption, which can be detected by means of electrocapillarity measurements in concentrated solutions [32]. However, the measurement of the capacitance of the double layer, which is a more sensitive test method than the measurement of interfacial tension, shows that polyvalent cations such as La^{+++}, Th^{++++}, etc., are adsorbed on mercury in presence of a weak negative surface charge in quantities which represent an excess relative to the surface charge. In other words, like the surface-active anions, the polyvalent cations cause a charge reversal of the surface but with opposite sign of the effect [10]. Many organic cations, such as, for example, tetrasubstituted ammonium derivatives (Fig. 23) show a marked specific adsorption on the metal/solution interface. One can easily imagine that $\varepsilon = 0$ $\psi_1 > 0$ so that the specific adsorption should result in a shift of zero charge potential to more positive values of φ, as is actually observed in the experiment.

Numerous organic compounds are also adsorbed at the metal/solution interface with formation of monomolecular* orientated layers.

Figure 24 shows as a typical example the electrocapillarity curves of normal NaCl solutions containing tertiary amyl alcohol in different concentrations (in the measurement of the electrocapillarity curves of solutions of organic nonelectrolytes a surface-inactive electrolyte is always added to the latter which makes the solution sufficiently conductive).

As in the case of adsorption on the free surface of solutions, the adsorption at the metal/solution interface increases with increase in the length of the hydrocarbon chain. Many active-surface substances such as, for instance, the aliphatic alcohols, behave similarly on all interfaces, i.e., their adsorption is about the same in both cases.

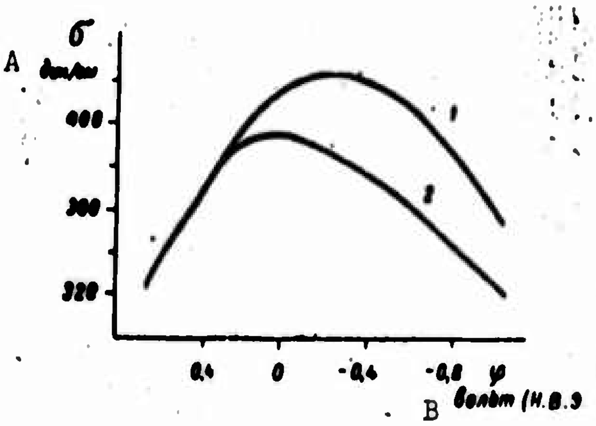


Fig. 23. Electrocapillarity curves of 1 N Na_2SO_4 (1) and 1 N Na_2SO_4 with addition of tetrabutyl ammonium sulfate (2). A) Dyne/cm; B) volt (n.v.e.).

In some respects, however, the adsorption at the metal surface has certain typical features compared with the adsorption at the solution/gas interface. Thus, the introduction of several hydroxyl and other oxygen-containing groups, although it reduces the adsorption at the metal interface, it does so to a much lesser extent than in adsorption at the gas interface so that compounds such as saccharose, which are entirely inactive in the last-mentioned case, are markedly adsorbed at the mercury surface. A characteristic feature of the adsorption at the metal interface is also the large adsorption of compounds containing sulfur, bromine, iodine atoms and also many aromatic compounds.

Figure 25 shows the electrocapillarity curves of solutions of thiourea with different concentration in presence of 1 N H_2SO_4. Thiourea is an example of a substance which is strongly adsorbed on metal surfaces and is inactive at the solution/gas interface.

A study of the electrocapillarity curves of solutions, containing organic substances, leads to several important conclusions regarding the properties of the adsorbed layers at the mercury/solution interface. Let us point out first of all that the adsorption of organic molecules usually shifts the maximum of the electrocapillarity curve. In the case of the adsorption of aliphatic compounds containing oxygen or nitrogen, the shift takes place in the direction of more positive potentials (Fig. 24). Compounds containing atoms of sulfur, halogens, and many aromatic derivatives displace the maximum in the direction of more negative potentials (Fig. 25) like the surface-active anions. Because at the maximum of the electrocapillarity curve $\varepsilon = 0$ and an ionic double layer at the interface is thus absent, the shift of the zero charge potential can be accounted for only by the fact that the adsorbed molecules, which are dipoles, are orientated in a certain way (Fig. 26). In presence of a layer of orientated dipoles between metal and solution there should be a potential difference whose sign coincides with the sign of the charge of the atoms situated close to the metal.*

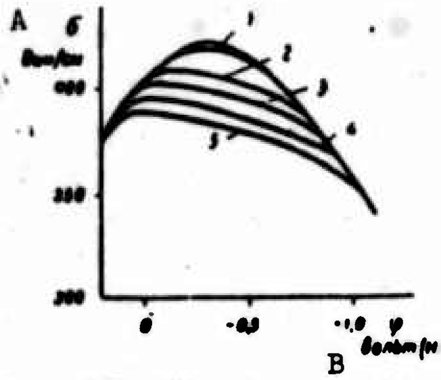


Fig. 24. Electrocapillarity curves of solutions of 1 N NaCl containing tertiary amyl alcohol. Concentration of the alcohol in moles per liter: 1) 0.01; 2) 0.05; 3) 0.1; 4) 0.2; 5) 0.4. Upper curve: 1 N NaCl without addition. A) dyne/cm; B) volt (n.v.e.).

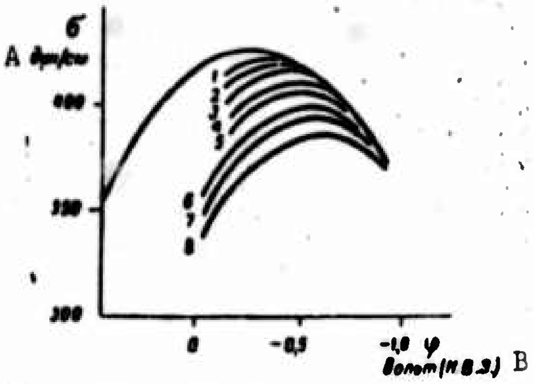


Fig. 25. Electrocapillarity curves of solutions of 1 N H_2SO_4 containing thiourea. Concentration of the thiourea: 1) 0.008; 2) 0.016; 3) 0.031; 4) 0.062; 5) 0.125; 6) 0.25; 7) 0.5; 8) 1 mole/liter. Upper curve: 1 N H_2SO_4 without addition. A) Dyne/cm; B) volt (n.v.e.).

Typical for the adsorption processes at the metal/solution interface is the marked dependence of the adsorption on the potential. The lowering of the surface tension caused by the adsorption of organic molecules is observed only within a certain potential range, situated on both sides of the zero charge potential of the electrode in the initial solution of the inorganic electrolyte (Fig. 24). With sufficient distance from the zero point on either side the lowering of the surface tension and, consequently, also the adsorption, disappear. Figure 27 shows the adsorbed quantity Γ of normal butyl alcohol as a function of the potential φ at constant concentrations of the butyl alcohol [33]. The quantity Γ has been calculated by means of Eq. (32) from the surface tension values measured at constant potential in solutions of 3 N KCl, containing different concentrations of butyl alcohol. It is evident from Fig. 27 that the quantity Γ attains its maximum in the potential region close to the zero charge potential* and converges to zero in presence of large surface charges.

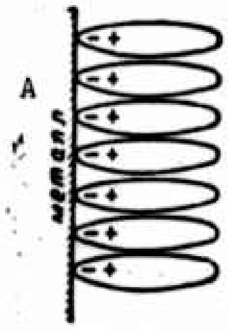


Fig. 26. Scheme of the arrangement of the adsorbed dipole molecules. A) Metal.

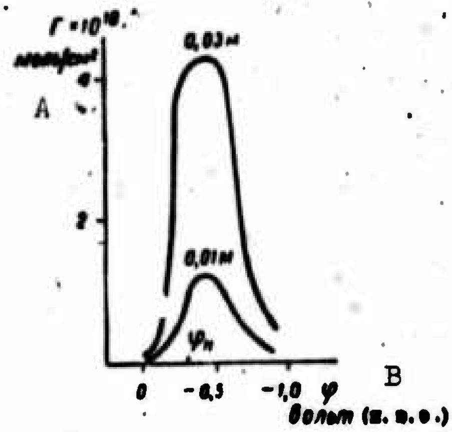


Fig. 27. Adsorbed quantity Γ of butyl alcohol as a function of the potential φ of the mercury electrode. Composition of the solutions: 3 N KCl + n-butyl alcohol (the concentration of the latter is indicated in the diagram). A) Mole/ cm^2; B) volt (n.v.e.).

This dependence of the adsorption of uncharged molecules on potential appears surprising at first glance. It can be explained, however, if attention is given to the variation of the capacitance of the double layer caused by the adsorption of the organic molecules [34]. Indeed, calculation of the capacitance by means of Eq. (25) shows that at potential values at which adsorption of organic substances occurs, the capacitance is considerably lower as follows directly from the very flat shape of the electrocapillarity curve in presence of organic substances. The capacitance of the electrode in presence of adsorbed substance can also be measured directly (see §4).

Figure 28 gives the differential capacitance as a function of potential for an Na_2SO_4 solution containing octyl alcohol and for comparison purposes the same dependence for Na_2SO_4 solution in the absence of the alcohol [35]. It can be seen that in the middle part of the curve, which corresponds to the region of adsorption of the alcohol, the capacitance is greatly reduced compared with the values in the initial solution. The differential capacitance curve in Fig. 28 has two sharp maxima at the ends of the adsorption range which will be discussed further on.

The lowering of the capacitance caused by the adsorption of organic molecules indicates that these molecules are introduced between the metal surface and the ions of the double layer. Between the plates of the double layer appears a layer of organic substance with a lower dielectric constant compared with water thus lowering the capacitance. At the same time the distance between the centers of the ions of the first layer and the metal surface is probably also reduced.

If one introduces into the space between the plates of a charged capacitor a body whose dielectric constant is less than the dielectric constant of the uniform medium, which fills this space, then, as we

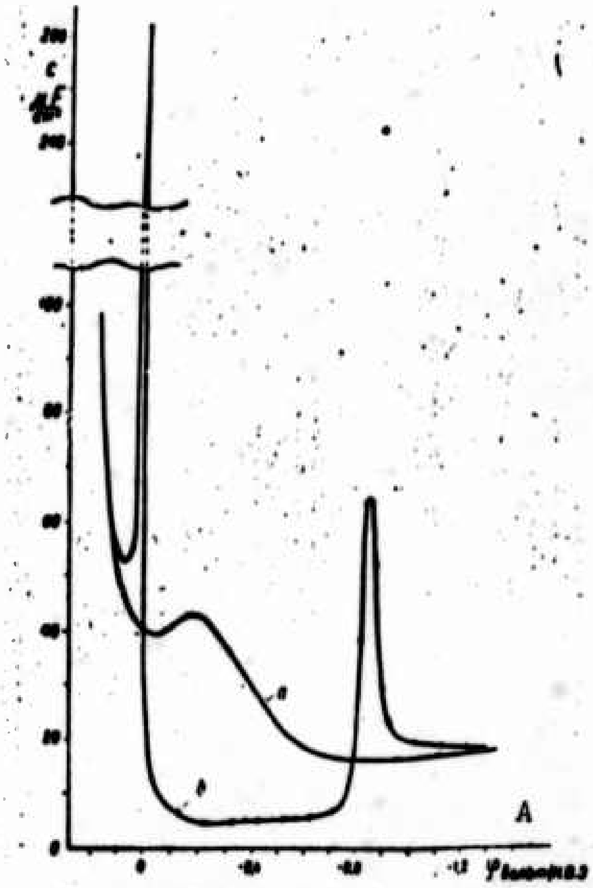


Fig. 28. Effect of surface-active substances on the differential capacitance *C* of the mercury electrode: a) 1 N Na_2SO_4; b) the same solution with addition of octyl alcohol. A) Volt (n.v.e.).

know from electrostatics, the electric field of the capacitor opposes this introduction. In the same way the electric field of the ionic double layer opposes the appearance of organic molecules, which lower the capacitance of the double layer, at the metal surface, and if the charge density is sufficiently high, the adsorption process is completely arrested.

This phenomenon is also reminiscent in many respects of the salting-out of organic substances from aqueous solutions when large quantities of electrolytes are added to them. To the lowering of the solubility of a substance with a lower dielectric constant, caused by the electric fields of ions, corresponds the lowering of the adsorption in the case which interests us here.

A quantitative treatment of this phenomenon can e given easily on the basis of Eq. (32) [34].

Let us assume that the variables in our system are the potential difference φ and the concentration c of the adsorbed substance. Then Eq. (32) is reduced to the following form:

$$d\sigma = -\varepsilon d\varphi - RT\Gamma d \ln c. \qquad (37)$$

Because the right part of the equation is a total differential,

$$\left(\frac{\partial\varepsilon}{\partial \ln c}\right)_{\varphi} = RT\left(\frac{\partial\Gamma}{\partial\varphi}\right)_{c}. \qquad (38)$$

Taking into account that

$$\left(\frac{\partial\varepsilon}{\partial \ln c}\right)_{\varphi} = \left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_{\varphi}\left(\frac{\partial\Gamma}{\partial \ln c}\right)_{\varphi}$$

and

$$\left(\frac{\partial\Gamma}{\partial\varphi}\right)_{c}\left(\frac{\partial \ln c}{\partial\Gamma}\right)_{\varphi} = -\left(\frac{\partial \ln c}{\partial\varphi}\right)_{\Gamma},$$

we find from Eq. (38)

$$\left(\frac{\partial\varepsilon}{\partial\Gamma}\right)_{\varphi} = RT\left(\frac{\partial\Gamma}{\partial\varphi}\right)_{c}\left(\frac{\partial \ln c}{\partial\Gamma}\right)_{\varphi} = -RT\left(\frac{\partial \ln c}{\partial\varphi}\right)_{\Gamma}. \qquad (39)$$

Equation (39) enables us to determine, if we make the simplest assumptions concerning the dependence of the charge on the adsorbed quantity Γ, how the concentration c corresponding to the constant adsorbed quantity Γ, varies with variation of φ, i.e., how the adsorption of the substance varies with potential. In this manner we can derive the following relation:

$$\ln\frac{c_{\varphi_a}}{c_0} = \left[\frac{1}{2}C\varphi_a^2 - \frac{1}{2}C'\varphi_a(\varphi_a - 2\varphi_b)\right]\frac{S}{RT} \qquad (40)$$

The quantities c_0 and $c\varphi_a$ here indicate the concentrations corresponding to the same adsorption at the zero charge potential and at a potential which differs from the latter by the amount φ_a; C is the capacitance of the double layer in the original electrolyte solution which is considered constant, C' is the capacitance of the double layer when the surface is filled with adsorbed molecules, φ_b the shift of the zero potential when the surface is filled, and S is the area covered by one mole of adsorbed substance under conditions of complete coverage.

By means of Eq. (40) it is possible to determine with satisfactory agreement with experiment the shape of the electrocapillarity curves obtained with solutions containing adsorbed substances. Because according to the above, $C > C'$, the sign of the right part of Eq. (40) is always positive at sufficiently large values of $|\varphi_a|$; in other words at sufficiently great distance from the zero point the concentration of the adsorbed substance corresponding to a certain adsorption value, increases with further increase in this distance. It follows from this that at constant concentration the adsorption decreases with increase in $|\varphi_a|$ as is actually observed in the experiment.*

A more detailed analysis of these relations leads to the conclusion that the variation of the adsorbed quantity with potential at the limits of the adsorption range should be very marked as is evident from Fig. 27. Such a variation of adsorption with potential should lead to the appearance of maxima on the curve representing the differential capacitance as a function of potential. In fact we designate the proportion of the surface occupied by the organic molecules by θ ($\theta = \Gamma \cdot S$). and we assume for the sake of simplicity that the adsorption of the organic molecules does not shift the zero point. The surface charge can be approximately expressed as the sum of the charges of the part of the surface $1 - \theta$, which is free of adsorbed molecules and the part θ of the surface occupied by them:

$$\varepsilon = C\varphi_a(1-\theta) + C'\varphi_a\theta. \qquad (41)$$

From Eq. (41) we obtain for the differential capacitance the expression

$$C_d = \frac{\partial \varepsilon}{\partial \varphi} = C(1-\theta) + C'\theta - \frac{\partial \theta}{\partial \varphi}(C - C')\varphi_a. \qquad (42)$$

The first two terms of the right part of Eq. (42) give the capacitance values situated between the capacitances at $\theta = 0$ and $\theta = 1$, i.e., C and C'. The third term connects the differential capacitance with the dependence of the adsorption Γ on the potential. It is easily seen that it always has a positive value at the limits of the adsorption range. Indeed, let us consider, for example, the left limit of the adsorption range in Fig. 27. In this case θ increases with decreasing φ_a so that $-(\partial\theta/\partial\varphi) > 0$; further, $\varphi_a = \varphi - \varphi_n > 0$ and, consequently,

$$-\frac{\partial \theta}{\partial \varphi}(C - C')\varphi_a > 0.$$

At the limits of the adsorption range, owing to the marked variation of the adsorption with the potential, the absolute value of $\partial\theta/\partial\varphi$ increases rapidly in consequence of which sharp maxima appear on the curve giving $\partial\varepsilon/\partial\varphi$ as a function of φ.

Whilst the measurement of the electrocapillarity curves is possible only in the case of liquid metals, the method of capacitance measurement has a larger field of application. Measurements of the differential capacitance C of different solid metals, for example lead, cadmium and tin in solutions, containing adsorbed impurities, have shown that in these cases adsorption takes place only within a certain potential interval near the zero point of the given metal [36]. Within this interval the differential capacitance values are low and pass through their maxima at the limit of this range.

§8. ADSORPTION OF HYDROGEN ATOMS

In addition to the adsorption of ions and molecules, the electrochemical properties of metal surfaces are strongly affected by the adsorption of hydrogen and oxygen atoms and in some cases of other elements as well.

As we know, many metals, particularly the platinum group metals, and under certain conditions also nickel, possess the capacity for adsorbing hydrogen to a high degree. The physical adsorption of hydrogen (i.e., adsorption by virtue of intermolecular forces) at normal temperatures is vanishingly small. Chemically the hydrogen molecule is completely saturated and marked adsorption of hydrogen thus indicates a decomposition of the hydrogen molecule during the adsorption process into chemically unsaturated free atoms. The existence of such a decomposition also follows from the parallelism existing between the phenomena of hydrogen adsorption and its solution in metals. As follows from experiment, the quantity of hydrogen in the metal at low hydrogen concentrations in the solution is proportional to square root of its concentration in the gas phase. It follows from this that hydrogen is dissolved in a metal not in the form of molecules but in the form of atoms. This inference can also be applied to the case of hydrogen adsorption.

Because the heat of dissociation of the hydrogen molecule is 102 kcal per mole, a positive heat of adsorption of hydrogen is possible only if the heat of adsorption of atomic hydrogen on the metal exceeds half this value, i.e., 51 kcal per gram-atom. Thus a marked adsorption of hydrogen can be observed only on metals which have a strong affinity for the hydrogen atom.

The ability of metals to adsorb hydrogen is retained in the presence of electrolyte solutions. In this case, as the work of A.N. Frumkin, A.I. Shlygin and B.V. Ershler showed, the method of charging curves can be used with success for the investigation of the properties of hydrogen adsorbed on the surface of a metal electrode [8, 14, 15].

According to §4, it is essential for the use of this method to exclude the possibility of electrochemical reactions with substances contained in the volume of the solution. If a positive charge is supplied to a platinum electrode which is in equilibrium with a solution saturated with hydrogen under atmospheric pressure, the dissolved molecular hydrogen is ionized, and a current passes through the electrode. Under these conditions it is impossible to record the charging curve. However, it is not difficult to create conditions under which the quantity of dissolved hydrogen is small compared with the quantity of adsorbed hydrogen. In addition to an increase in the electrode surface and a decrease in the volume of the solution (see §4) this can be achieved by lowering the concentration of the hydrogen dissolved in the electrolyte. As will be shown further on, the quantity of hydrogen adsorbed at the electrode decreases when its concentration in the volume is reduced much more slowly than the quantity of hydrogen in the solution with which the electrode is in equilibrium. Hence prior to recording the charging curve it is preferable to eliminate a large part of the hydrogen dissolved in the electrolyte, for example, by passing nitrogen through it. This removes only a small proportion of the adsorbed hydrogen from the electrode. By imparting then increasing quantities Q of electricity to the electrode, we obtain the charging curve of the platinum electrode without distortion by any collateral processes. Such a curve is shown in Fig. 29.

The slope of the charging curve obviously gives the value $\partial\varphi/\partial Q$ equal to $1/SC_d$, where S is the electrode surface area, and C_d its differential capacitance. In the case of smooth platinum the true surface exceeds the visible surface only slightly, and the capacitance per unit of surface can thus be estimated from the charging curve.

As Fig. 29 shows, the capacitance of a platinum electrode is quite different at different potentials. The charging curve consists of three

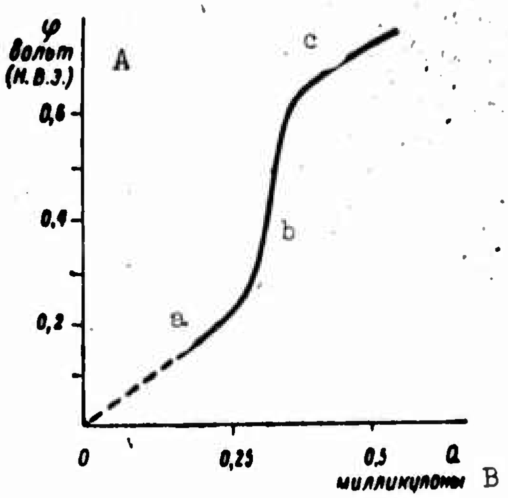


Fig. 29. Charging curve of the platinum electrode in 1 N HCl. A) Volt (n.v.e.); B) millicoulombs.

clearly delimited sections *a*, *b*, and *c*. The capacitance of the platinum electrode in the middle section of the curve is 20-50 μF/cm^2, i.e., it is similar to the capacitance of the mercury electrode. In the section *a* the electrode has a much greater capacity, up to 2000 μF/cm^2. Because in the measurement of the potential as a function of the transmitted quantity of electricity we start out with a state of the electrode in which adsorbed hydrogen is present on its surface it is logical to connect the observed capacitance increase with the removal of adsorbed hydrogen from the platinum surface. Indeed, if in the initial point of the charging curve the quantity of hydrogen adsorbed on the unit surface, were equal to A_0, $(A_0 - A)SF$ coulombs, which are used for the transformation of the adsorbed hydrogen into ions which pass into the solution, in accordance with the reaction

$$H_{\text{адс}} \rightarrow H^{\cdot} + e.$$

would have to be imparted to the electrode, to achieve a state in which the adsorbed quantity is equal to A.

This quantity of electricity is added to that used for the charging of the double layer and which is evidently $(\varepsilon - \varepsilon_0)S$, where the charge densities ε_0 and ε refer to the initial and final state of the electrode. Thus, between the quantity Q of electricity, supplied to the electrode, the variation of the adsorbed quantity of hydrogen and the surface charge there should exist the relation

$$Q = (A_0 - A)SF + (\varepsilon - \varepsilon_0)S \qquad (43)$$

or, in the differentiated form

$$\Delta Q = -\Delta A \cdot SF + \Delta\varepsilon \cdot S. \tag{43a}$$

Because in the section *b* of the charging curve the capacitance of the electrode, as we have pointed out earlier, has a value close to the normal capacitance of the double layer, the adsorption of hydrogen in this region is obviously slight and the first term of the right part of Eq. (43a) does not greatly affect the magnitude of ΔQ (double layer region of the charging curve*).

The situation is different in the section *a* of the charging curve. It follows from the very high capacitance that in this case $-\Delta A \cdot F$ is large compared with $\Delta\varepsilon$. By way of a first approximation it can also be assumed that practically all the electricity supplied to the electrode is consumed in the removal of the adsorbed hydrogen and thus it is possible to determine the quantity $A_0 - A$ from Q.

Because the value of A vanishes or becomes very small at the end of the section *a*, the value of A can also be determined for any point of this section of the charging curve. This determination can be made more accurate by estimating the magnitude of $\varepsilon - \varepsilon_0$ by means of the slope of the charging curve in the double layer region or by determining it in some other way (for example, from the dependence of the adsorption of the ions involved in the formation of the outer plate of the double layer on the potential, as has been explained in §4).

The process of removal of the adsorbed hydrogen is reversible. Indeed, if at any point of the section *a* or *b* of the charging curve (Fig. 29) the direction of the current is reversed, the charging curve can be traced in the opposite direction. Experiment shows that the "cathode" charging curve obtained under these conditions coincides almost completely with the "anode" curve during the recording of which the potentials changed from more negative to more positive. It follows from the reverse charging curve that the states during which the electrode passes during the recording of the charging curve may, with a sufficient degree of approximation, be considered as equilibrium states. In this way one can establish the equilibrium relationship between the electrode potential φ and the quantity A of adsorbed hydrogen.

It follows from the approximate linearity of the charging curve that this relationship is also linear:

$$A = p - q\varphi, \qquad (44)$$

where p and q are constants (A decreases with increasing φ).

The adsorption isotherm of hydrogen on the electrode surface is readily obtained from Eq. (44). Indeed, the value of φ can be expressed by the Nernst formula via the partial pressure p_{H_2} of the molecular hydrogen, which is in equilibrium with the electrode:

$$\varphi = \varphi^0 - \frac{RT}{2F} \ln p_{H_2}$$

where φ^0 is the value of φ in the given solution at $p_{H_2} = 1$ atm. Substituting this expression for φ in Eq. (44), we obtain

$$A = a' + b' \ln p_{H_2}, \qquad (44a)$$

where a' and b' are constants. Examination of the charging curve shows that the logarithmic relation applies over a wide range of variation of p_{H_2}.

The existence of such a relationship calls for an explanation. During the adsorption of a diatomic gas, involving dissociation into atoms, on a uniform surface in the absence of any forces of interaction between the adsorbed atoms the adsorption isotherm is determined by the following relation (Langmuir equation):

$$A = A_\infty \frac{\omega \sqrt{p_{H_2}}}{1 + \omega \sqrt{p_{H_2}}}, \qquad (45)$$

where A_∞ is the limit adsorption with complete filling of the surface, and ω is a constant. With a slight degree of filling this relation expresses the proportionality between A and the square root of p_{H_2}.

The experimentally observed logarithmic isotherm differs considerably from the isotherm derived on the basis of the aforementioned simple assumptions; it gives a much slower increase in the value of A with p_{H_2}. This slow increase shows that the differential work of adsorption decreases in proportion to the filling of the surface. The variation of the work of adsorption may be caused, for example, by nonuniformity of the surface. On a nonuniform surface and with low pressures of the adsorbed gas the more active sites of the surface are filled, and at large pressures the less active sites. In consequence of this the work of adsorption gradually decreases with increase in the degree of filling.

These problems have been examined in detail by the Soviet physical chemists S.Z. Roginskiy [37] and, particularly with application to electrochemistry, by M.I. Temkin [38]. Another cause of the decrease in the work of adsorption may be the existence of forces of repulsion between the adsorbed atoms [39]. Both these concepts give a logarithmic adsorption isotherm under certain assumptions. We ought to mention that an analogous logarithmic relationship between the quantity of adsorbed hydrogen and its pressure is observed in the dissolution of hydrogen in certain metals which dissolve hydrogen readily, for example, in palladium, provided that the concentration of the dissolved hydrogen in the metal is fairly large (the so-called β phase region in the system Pd-H). This leads us to the conclusion that the process of hydrogen adsorption under the above-considered conditions can be regarded as a dissolution of hydrogen limited to the surface layer of the metal [8].

The measurement of the charging curves also enables some other interesting properties of adsorbed hydrogen to be observed, in particular, the dependence of the metal/hydrogen bond energy on the nature of the electrolyte. As Fig. 30, which gives the charging curves of a platinized platinum electrode in solutions of KOH, H_2SO_4, HCl and HBr, shows the adsorbed hydrogen is removed from the surface at much less positive potentials in HBr than, for example, in H_2SO_4 and particularly in KOH. A more detailed examination of these relationships results in the conclusion that the presence of anions near the metal surface always causes a lowering of the Pt-H bond energy, and the presence of cations an increase. This can be explained by assuming that the metal and hydrogen atoms which are bound together form dipoles with the negative end turned outwards.

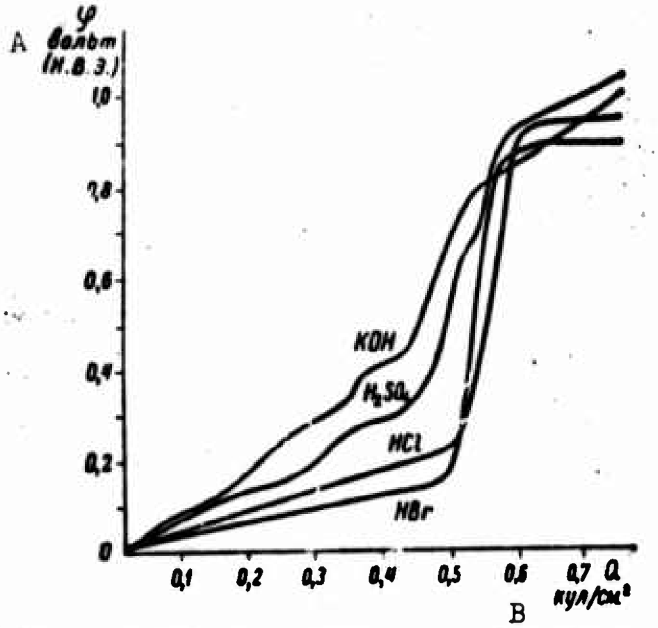


Fig. 30. Shape of the charging curve as a function of electrolyte composition: charging curves in 1 N KOH, 1 N HBr and 1 N H_2SO_4. A) Volt (n.v.e.); B) coulomb/cm^2.

By the method of charging curves it is possible to detect the presence of layers of adsorbed hydrogen in presence of electrolyte solutions on metals of the platinum group (platinum, iridium, rhodium) and also on nickel and silver in alkaline solutions.

On the surface of mercury, lead, zinc, thallium and cadmium adsorbed hydrogen could not be detected by these and other analogous electrochemical methods, and it may be assumed that adsorption of hydrogen in presence of electrolyte solutions on the surface of these metals does not take place in measurable quantities. The practically complete absence of adsorbed hydrogen at the solution/mercury interface has been particularly carefully confirmed.

As pointed out previously, the adsorption of hydrogen involves a decomposition of the H_2 molecule into atoms. However, the properties of the adsorbed hydrogen, owing to the large Me-H bond energy, differ considerably from the properties of free atomic hydrogen. This becomes particularly clear if the concentration of free atomic hydrogen in the gas phase in equilibrium with the adsorbed hydrogen is determined.

Because the standard free energy of the dissociation reaction of the hydrogen molecule, which can be determined from spectroscopic data, amounts to 96.7 kilogram calories, the potential of the hydrogen electrode in equilibrium not with molecular hydrogen but with atomic hydrogen at a partial pressure of the latter in the gas phase equal to atmospheric, should be $-(96{,}700/2\cdot 23{,}060) = -2.096$ v.

The partial pressure of atomic hydrogen in equilibrium with molecular hydrogen at atmospheric pressure, and, consequently, also with the adsorbed hydrogen at the potential of the standard hydrogen electrode, is thus $10^{-2.1/0.058} = 10^{-35.5}$ atm.

This pressure and the concentration corresponding to it are immeasurably small, while the concentration of the adsorbed hydrogen, for example, in the case of the platinum electrode at the potential of the normal hydrogen electrode is quite considerable as follows from the charging curves.

In Chapter 3 we shall return to the problem of the dependence of the adsorption energy on the nature of the metal.

§9. ADSORPTION OF OXYGEN AND OXIDE LAYERS

As will be shown in Chapter 7, oxygen atoms on the surface of metals exert a particularly strong effect on the electrochemical properties of metals. M. Faraday explained the transformation of metals to the passive state (in which the ability of metals to send their own ions into solution is reduced or disappears completely) by the appearance of oxygen on their surface. The investigations of Academician V.A. Kistyakovskiy [40] dealing with oxide layers were of great importance for substantiating this oxygen theory of passivation.

As in the case of hydrogen adsorption, the method of charging curves can be successfully employed for the study of the properties of adsorbed oxygen and oxide layers.

It is evident from Figs. 29 and 30 that during anodic polarization of a platinum electrode after passing the section of the charging curve in which the electrode capacitance is lowered to values corresponding to the capacitance of the double layer, the slope of the charging curve again decreases, i.e., the capacitance of the electrode increases. This capacitance increase is connected with the deposition of oxygen atoms* on the surface, which arise through discharge of water molecules or hydroxyl ions according to the reactions

$$H_2O \rightarrow O_{\text{адс}} + 2H^{\cdot} + 2e,$$
$$2OH^- \rightarrow O_{\text{адс}} + H_2O + 2e.$$

In the case of the platinum electrode in solutions of H_2SO_4 and HCl the oxygen and hydrogen sections of the charging curve are rigidly separated by the "double layer" region. In alkaline solutions, however, the removal of hydrogen is much more difficult so that at the potentials at which the deposition of oxygen begins, not all the hydrogen has been removed from the surface (Fig. 30); the hydrogen and oxygen regions of the potentials thus fuse continuously into each other.

If in the oxygen part of the charging curve the current direction is reversed, the complete cathodic charging curve can be recorded; the electrode then passes through the oxygen, double layer and hydrogen regions in the reverse sequence compared with the anodic charging curve. In this case, however, the direct and reverse charging curves do not coincide but form a hysteresis loop.

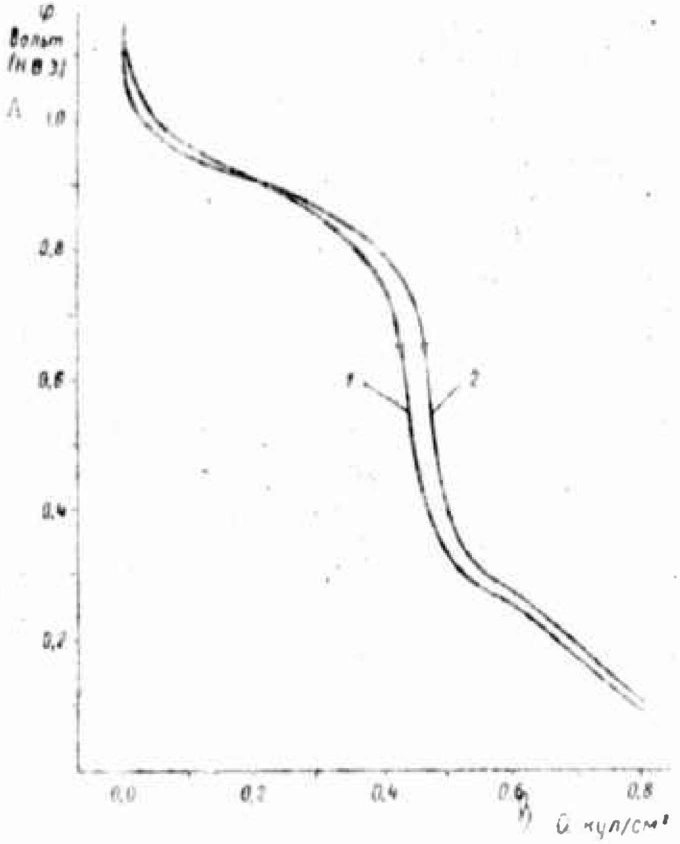


Fig. 31. Cathodic charging curves of platinized platinum in 1 N H_2SO_4: 1) Cathodic polarization after oxidation in moist oxygen at 18° for 24 hours; 2) cathodic polarization after oxidation under the same conditions for 60 days. A) Volt (n.v.e.); B) coulomb/cm^2.

The quantity of oxygen present on the electrode surface at the initial point can obviously be determined from the length of the oxygen part on the cathodic charging curve. If the electrode is brought in contact with oxygen prior to the recording of the charging curve, then it assumes the potential corresponding to the oxygen part of the charging curve immediately when it is immersed into the solution. By imparting negative charges to the electrode we can remove the oxygen adsorbed on the surface in this case and determine it quantitatively (Fig. 31 [58]).*

The anodic charging curve of a platinum electrode in the oxygen range has the same straight shape as in the hydrogen region. In other respects, however, an important difference is seen between the behavior of adsorbed hydrogen and oxygen. Whilst the processes of decomposition and removal of hydrogen atoms, as shown above, are reversible (at least if they are not carried out too quickly), the analogous processes in the case of the deposition and removal of oxygen are clearly not reversible, and the states through which the electrode passes in the oxygen part of the charging curve cannot be considered as equilibrium states. This irreversibility is expressed, in particular, in a different shape of the anodic and cationic charging curves in the oxygen region. On the cathode curve, as is evident from Fig. 31, there is a characteristic delay in the oxygen region corresponding to the removal of a large part of the adsorbed oxygen while in the anodic curves the deposition of oxygen merely causes a decrease in the slope of the charging curve without the appearance of such a delay (H_2SO_4 and KOH curves, Fig. 30).

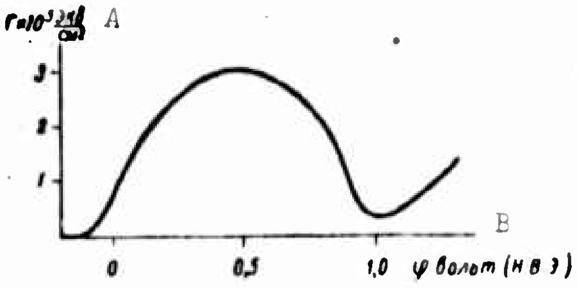


Fig. 32. Adsorption of sulfuric acid by platinized platinum as a function of potential. A) ekv.; B) volt (n.v.e.).

The bond between the metal and the oxygen is of a polar nature and the appearance of the layer of adsorbed oxygen atoms causes great changes in the distribution of the electric charges on the electrode surface. This can be verified by investigating the adsorption of ions on platinized platinum as a function of the electrode potential.

Let us consider the case of adsorption from a dilute solution of H_2SO_4 (Fig. 32). At potentials close to the potential of the reversible hydrogen electrode, the platinum surface is negatively charged. The ion covering of the double layer thus consists of H^+ ions formed through ionization of adsorbed hydrogen and does not contain SO_4^{--} anions, hence the acid concentration is not altered during the formation of the double layer. When the potential is shifted to the positive side, the electrode passes through the zero point, its surface acquires a positive charge and begins to attract anions. In this section of the charging curve the formation of the double layer is thus accompanied by adsorption of the acid from the solution. If the potential is raised further, the acid adsorption should continuously increase in proportion to the increase in the surface charge. Actually, however, as can be seen from Fig. 32, it attains a maximum after which it decreases markedly, nearly coming close to zero. In neutral solutions adsorption of acid goes over in this section of the charging curve into adsorption of alkali, in other words, the cations of the solution are consumed in the formation of the ion covering of the double layer. Thus, in spite of the increase in the positive potential difference between electrode and solution, the positive surface charge of the electrode decreases or can even change its sign to negative.

This charge reversal of the electrode is observed precisely in the potential region in which the layer of adsorbed oxygen atoms appears on the electrode surface. If it is considered that the bond between metal and oxygen is of a dipole nature, and if it is assumed that the adsorbed oxygen atom is the negative end of a dipole, the charge reversal of the platinum electrode can be explained in the same manner as the charge reversal of the mercury surface during the specific adsorption of anions (see §7).

Indeed the adsorbed layer of oxygen atoms with the dipole nature of the platinum-oxygen bond creates a positive potential difference between the metal and the solution. Owing to the considerable degree of filling of the surface with oxygen this potential difference is fairly great and can exceed the total electrode-solution potential difference, measured relative to the initial zero charge potential. Under these conditions, part of the potential difference caused by the ionic double layer should have a sign opposite to the sign of the total potential difference (Fig. 33).

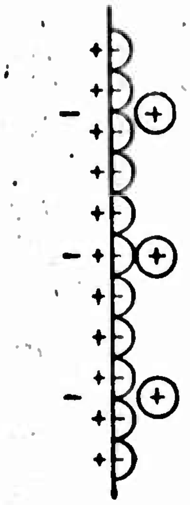


Fig. 33. Schematic representation of the structure of the double layer in presence of adsorbed oxygen.

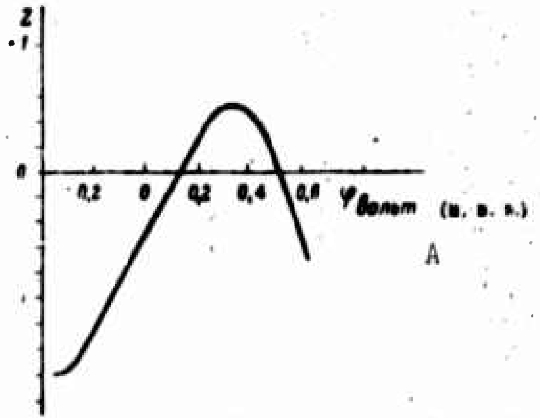


Fig. 34. Deflection Z of a platinum sire in $2 \cdot 10^{-5}$ N solution of H_2SO_4 under the influence of an external electric field. The sign of the deviation corresponds to the sign of the charge on the wire. A) Volt (n.v.e.).

An increase in the quantity of adsorbed oxygen is accompanied by an increase in the potential difference in the adsorbed layer only up to a certain limit as is evident from Fig. 32. When the potential is shifted to values above 1 v, the adsorption of acid, and, consequently, also the positive surface charge again begin to increase, i.e., the disturbance of the normal trend of the charge as a function of potential, caused by the appearance of the oxygen layer, vanishes.

The above-described trend of the variation of the charge on the platinum with variation of its potential can also be detected by observations of electrokinetic phenomena. A platinum sol obtained by atomizing the metal in the electric arc in a hydrogen atmosphere, is charged negatively which is easily verified by observing the motion of the particles under the influence of an external electric field. As N.A. Bakh and N.A. Balashova [41] have shown, when such a sol is carefully oxidized with oxygen, which shifts the potential of the platinum to the positive side, the sign of the charge becomes positive and the direction of motion is reversed. With further oxidation the mobility of the positive sol attains a maximum, begins to decrease and passes again through zero. When the oxidation is complete we obtain a charge-reversed negative platinum sol, which can also be prepared directly, by carrying out the atomization of the metal in presence of oxygen.

The dependence of the electrokinetic potential of platinum on the metal/solution potential difference can also be observed by following the deflection of a platinum wire immersed in the electrolyte under the influence of an external electric field, which is proportional to the potential. As Fig. 34 shows, when the potential difference between the platinum and the solution increases, the surface charge of the metal changes from negative to positive values; however, with further increase in the potential, the surface charge, as a result of the appearance of the oxygen layer, again becomes negative.

By examining the charging curves one can verify that the adsorbed oxygen undergoes slow changes in time which result in a strengthening of the bond between the oxygen and the metal. Figure 31 gives two cathodic charging curves (1 and 2) taken after the deposition of oxygen on platinum. In the case of curve 1 the oxidation of the platinum with oxygen was carried out for 24 hours, in the case of curve 2, for 60 days. As Fig. 31 shows, in spite of a certain increase in the total quantity of oxygen on the platinum surface in the second case, the initial part of curve 2 is lower than 1; in other words, after this treatment a more negative potential must be given the electrode for the removal of the oxygen adsorbed on its surface which indicates a strengthening of the bond between oxygen and metal.

Measurements of the contact potential differences in vacuo permit important conclusions to be drawn with regard to the nature of the bond between the oxygen and the metal. Because the problem of the properties of the metal/vacuum interface exceeds the framework of the present course, we shall merely indicate the main results which can be obtained with this method in the study of the adsorption of oxygen on metals from the gas phase. The contact potential difference between the unoxidized and oxidized metal is equal to the variation of the potential difference at the metal/vacuum interface, caused by the appearance of a layer of adsorbed oxygen. The measurement of the contact potential difference shows that when oxygen is deposited on the surface of tungsten and platinum, the oxygen atoms form the negative ends of dipoles which extend from the metal to the vacuum, in accordance with the conclusion at which we arrived during the examination of the influence of the adsorbed oxygen on the surface charge of the platinum in electrolyte solutions. Such a layer inhibits the escape of electrons from the metal, i.e., it increases the work function of the electron [42].

An analogous result is obtained in the adsorption of oxygen on the surface of iron at low temperature (-120°). However, if oxygen is deposited on iron not at low temperature, but, for example, at 100°C, the variation of the potential difference in the surface layer of the metal has the opposite sign and the work function of the electron is not increased [43]. The most probable assumption which can account for this phenomenon consists in assuming that at higher temperature the oxygen atoms penetrate more deeply into the metal lattice, i.e., that they sort of creep under the external layer of iron atoms, and the direction of the dipole potential difference is reversed. P.I. Lukirskiy and S. Ryzhanov [44] were the first to indicate the possibility of such a "creeping" of impurity atoms for the case of the adsorption of hydrogen on the surface of potassium and also S.Z. Roginskiy [45] and P.D. Dankov [46] for the case of oxygen adsorption.

With further increase in the temperature, at which adsorption of oxygen on iron takes place, the quantity of adsorbed oxygen increases and the work function again increases. It may be assumed that the oxygen atoms which are newly adsorbed occupy the external places vacated as consequence of the penetration of the oxygen into the lattice.

Whilst in the case of hydrogen chemical adsorption obviously always involves a decomposition of the H_2 molecule into atoms, in the case of oxygen (as shown, in particular, by the investigations of adsorption phenomena on the carbon electrode) one of the valency bonds between the atoms forming the O_2 molecule, may be retained during the first adsorption stage. Groups of a peroxide nature thus form at the surface. These peroxide groups, however, are not long-lived and decompose easily with formation of adsorbed atoms [47].

The alterations to which the adsorbed oxygen layers are subject are not limited to the decomposition of the adsorbed O_2 molecules into atoms and the creeping of these atoms under the external layer of metal atoms. By means of the method of charging curves it is possible to observe that during the increase in the quantity of adsorbed oxygen or after some time an alteration of a different kind takes place connected with an interaction between adjacent Me-O groups. During this alteration the adsorbed layer assumes properties similar to those of a new phase. In order to understand the phenomena which are observed in these situations, let us first examine the relationship between the potential and the quantity of electricity passed through in presence of a phase layer of a compound on the metal surface. If an oxide or hydroxide is present on the metal immersed in the electrolyte, which forms a phase, for example, HgO, then with a certain composition of the solution and under equilibrium conditions the electrode potential should have a constant value. This potential is independent of the quantity of oxidized compound because it is determined by the free energy of the reaction of formation of the solid phase from another phase, the metal, in a solution of constant composition, for example, in our case the free energy of the reaction

$$Hg + 2OH^- \rightarrow HgO + H_2O + 2e.$$

Hence the appearance or disappearance of a new compound, forming a phase, should be accompanied by the appearance of a horizontal section on the charging curve whose length is determined by the quantity of reacting substance.

The above discussion strictly applies only in the case when the formation or reduction of the oxide takes place under equilibrium conditions. This condition is frequently not fulfilled which causes certain modifications of the charging curve which we shall discuss in Chapter 7. Here we shall merely indicate that in presence of an oxide phase, which covers the entire electrode surface, the beginning of the reduction process, which takes place most readily at the interface between the filled and unfilled parts of the surface, may be retarded. Hence when negative charges are imparted to the electrode the potential initially goes to the negative side beyond the values corresponding to the establishment of the reduction process and after the inception of this process return to more positive values. A typical jump is then obtained on the charging curve. These peculiarities are also apparent on the charging curves given in Figs. 35 [59] and 36.

As previously pointed out, typical delays occur on the cathodic charging curves (Fig. 31) obtained after oxidation of platinized platinum in an atmosphere of moist oxygen. Within the limits of these delays the slope of the charging curve is small, particularly in curve 2, and its trend tends to horizontal. Figure 35 gives the cathodic charging curves of a smooth platinum electrode, measured after anodic oxidation. Curve 1 was obtained after relatively mild oxidation; its shape is similar to that of the curves in Fig. 31. Curve 2 corresponds to a greater current density and higher anodic potential with preliminary anode treatment. In this case the quantity of oxygen on the surface is much greater (tens of monatomic layers) and most of it is strongly bound to the surface. Curve 2 contains two delays. Within the limits of the second delay the charging curve is almost horizontal which indicates a transition to the formation of oxides with the properties of a new phase. Before the second delay there is a jump on the curve beyond the value of the potential corresponding to the horizontal part. The same and even more pronounced jump is seen on the charging curve 2 of Fig. 36 obtained during cathodic reduction of the oxidized electrode surface covered with rhodium black. Of interest is the fact that in this case the phase properties of the oxide layer appear in presence of a quanti-

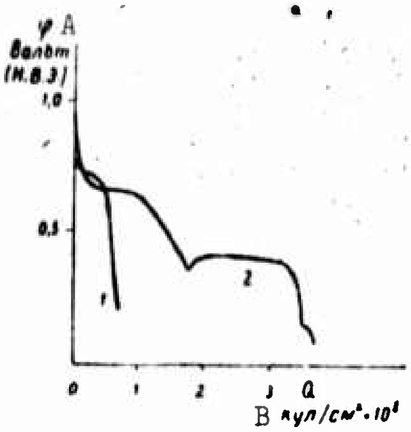


Fig. 35. Cathodic charging curves of a smooth platinum electrode in 1 N H_2SO_4: 1) Cathodic polarization after anodic oxidation with a current density of 10^{-3} a/cm^2; 2) cathodic polarization after anodic oxidation with a current density of 10^{-1} a/cm^2. A) Volt (n.v.e.); B) coulomb/cm^2.

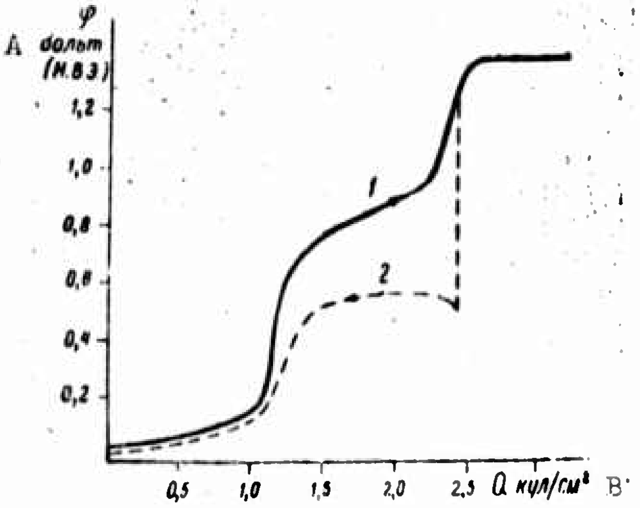


Fig. 36. Anodic (1) and cathodic (2) charging curves of an electrode, covered with rhodium black, in 1 N HCl. A) Volt (n.v.e.); B) coulo
cm^2.

ty of oxygen which is not sufficient to fill a monatomic layer.

We have examined the properties of adsorbed monatomic oxygen layers and thicker layers which represent an intermediate stage in the formation of a new phase. In the investigation of the electrochemical properties of metals one often has to deal with relatively thick layers which have full phase properties. Such layers can cover the metal surface partly or wholly, and for the covered part of the surface we must consider in this case instead of the metal/electrolyte interface two interfaces: the metal/oxide (or hydroxide) layer and the oxide layer/electrolyte interface. Such layers can also be formed by sparingly soluble salts, for example, lead sulfate or silver chloride.

In order that a phase layer can exist at the metal/solution interface it is obviously necessary that the potential of the metal electrode is sufficiently positive thus excluding the possibility of a reduction of the layer of this substance. Thus, for example, the reversible potential of the lead electrode in 8 N H_2SO_4 solution, saturated with $PbSO_4$, is -0.35 v; hence the $PbSO_4$ layer on the surface of the lead in this solution can exist in equilibrium only at potentials which are more positive than -0.35 v; at more negative potentials the $PbSO_4$ layer should be reduced with formation of metallic lead as is actually the case when the negative plate of a lead battery is negatively charged. The reversible potential of a nickel electrode in 1 N NaOH, saturated with $Ni(OH)_2$, is +0.17 v against the hydrogen electrode in the same solution. At more negative potentials, for example, at the reversible hydrogen potential, a phase layer of $Ni(OH)_2$ can no longer exist on a nickel surface. As a rule, the potential interval within which such phase layers can exist is not accurately defined; for kinetic reasons a delay takes place during the removal of previously formed layers (which causes an enlargement of this interval) as well as during the formation and growth of a layer of new phase.

Very important is the circumstance that at potentials which metals acquire in contact with atmospheric oxygen, the oxides or hydroxides of the metals (including those of platinum) are already thermodynamically stable at normal temperatures. Hence the adsorbed oxygen layers which we have discussed are in a certain sense intermediate formations on the way to the appearance of new chemical compounds which is reflected in a number of their above-described properties. In this respect there exists an important difference between the adsorbed oxygen and hydrogen layers because the formation of the latter, at least in the case of metals such as platinum, leads to the establishment of an equilibrium between the metal and the hydrogen.*

The adsorbed layers of oxygen obtained by interaction of metals with gaseous oxygen at different temperatures and pressures are in many cases also only an intermediate stage in the formation of an oxide. However, the growth of an oxide film, if it forms a compact layer, which adheres tightly to the metal surface, is often strongly retarded until it attains a certain, sometimes extremely small, thickness.

We shall not dwell here in greater detail on the laws of the growth of phase films arising during the interaction of metals with gases or electrolyte solutions and shall return to this problem in Chapter 7; let us merely indicate the great theoretical and applied importance of this problem, to which numerous scientific studies have been devoted.

The existence of phase layers or layers which are intermediate in properties between adsorbed layers and phase formations has a great influence on the electrochemical behavior of metals. In the case of adsorbed layers we are dealing with variations of the electrochemical properties of the metal/solution interface; thicker layers can simply shield the metal surface by inhibiting the access of electrolyte which in this case takes place only through the pores in the layer.

A number of methods is at present available for investigating the structure and properties of different types of layers on metal surfaces. Considerable successes in this direction have been attained by Soviet researchers. A beginning in this direction was made in our country by the classical works of Academician V.A. Kistyakovskiy [56]. Here we can only briefly enumerate the most important directions of research in this field.

The presence of layers which adhere firmly to a metal surface, if they are sufficiently thin, does not alter the external appearance of the metal and remains unnoticed when the metal surface is examined with the unaided eye. Thus, for example, the bright surface of metals such as iron is always covered with an oxide film under the usual conditions. The following simple experiment demonstrates clearly the formation of the oxide film upon contact or iron or steel with air. As we know, a normal iron surface is not wetted by mercury. However, if iron, immersed in mercury, is ruptured so that it does not come into contact with the air, the fresh fracture is immediately wetted.

In some cases, as Evans [48] has shown, an oxide film can be separated and made visible if the underlying metal is dissolved by means of reagents which do not affect the oxide film. However, more sensitive optical methods enable an oxide film to be detected and its thickness measured without removing it from the metal surface which is of particularly great importance in the case of very thin films. One of these methods is the measurement of the elliptical polarization of reflected light. This method has been applied to the study of films formed during the oxidation of metals by gaseous by the Norwegian scientist Tronstadt et al. [49]. T.N. Krylova [49] measured the rate of oxidation of several metals at different temperatures by means of this method. The method of determining the thickness of thin layers by means of elliptical polarization has recently been brought to a high degree of perfection by B.V. Deryagin [50] and can find wide application also in the study of layers at the interface between metals and electrolytes at thicknesses which do not greatly exceed the molecular dimensions (from a few A to several hundred A).

Thicker layers, whose thickness is comparable with the wavelength of light, from several hundred to several thousand A, are made visible on the metal surface by the interference phenomena produced by them (temper colors). If the index of refraction of the substance of the film is known its thickness can be determined on the basis of the temper color.

If the substance of the film is an insulator or poor conductor, its presence results in a strong decrease in the electrode capacitance. The electrons in the metal and the ions in the solution can freely approach only to the metal/solution interface with the insulating layer, and when we measure the capacitance, for example, by means of an alternating current, we no longer measure the capacitance of the double layer, but the capacitance of the capacitor in which the distance between the plates is defined by the thickness of the insulating layer. At a thickness of the layer of 20 A and a dielectric constant of 5, the electrode capacitance is only 2 μF/cm^2 instead of the 18-20 μF/cm^2, observed in the case of a normal double layer. Oxide films which do not yet form a new phase and even adsorbed monatomic oxygen layers already cause a marked decrease in the capacitance.

According to Eq. (2) the capacitance measurement can be used for the determination of the thickness of an oxide film. It is essential, though, to keep in mind that the presence of pores leading to the electrode surface in the film, must cause a considerable increase in the capacitance according to Eq. (2) even if the cross-section area of these pores is only a small part of the electrode surface. The method of capacitance measurement has been used for the study of oxide layers in several works [51].

The presence of oxide films on a metal surface exerts an important influence on the electrical resistance during contact between two metal surfaces in vacuo or in any gaseous atmosphere. The measurement of this resistance and also of the breakdown voltage of the oxide films on metal surfaces is carried out by means of the method of measuring the intensity of a direct current flowing when a gradually increasing voltage is applied between the electrode and a layer of mercury applied to the dry electrode surface [47]. Such measurements make it possible to follow the process of formation of the oxide film.

The investigation of oxide layers by means of the above-described optical and electrical methods gives a certain average value for the parameters. Such average values cannot completely characterize the films because in reality the films are not completely homogeneous. This can be verified, in particular, by examining an isolated film under the electron microscope; the microphotographs obtained by this method show clearly numerous pores in the film whose diameter can be very small, for example, in films on aluminum they are of the order of 50-100 A.* The presence of pores in films facilitates chemical and electrochemical reactions with participation of the base metal which makes it possible to detect individual pores by the localization of the products resulting from such reactions. Methods of studying the structure of films on iron and aluminum based on this principle have been worked out by G.V. Akimov and co-workers [52]

The appearance of oxide films on a metal in an electrolyte solution can result in an increase in the sensitivity of the electrode to the action of light compared with an electrode whose surface is free of an oxide film, because the absorption of light energy takes place over the entire thickness of the oxide film. Owing to the semiconductor properties of many oxides the absorbed energy may be transferred to the particles at the oxide film/solution interface at which the electrochemical reaction takes place. The determination of photoelectrochemical processes, for example, the variation of the electrode potential or variation of the current density, flowing through the electrode at a certain potential, during the action of light, in combination with other electrochemical measurements, as V.I. Veselovskiy [53] showed, can be used as a sensitive method of studying oxide films. With this method it is possible, for example, to detect the formation of an electrochemically active oxide on the Pt electrode at a potential of 1.5 v.

The method of electron diffraction has assumed great importance for the study of the structure of oxide and other layers on metal surfaces. In contrast to x-rays, the electron beam penetrates the substance to a relatively slight depth. Because of this the method of electron scattering is particularly suitable for the investigation of the structure of thin layers and surface films. Experience has shown that electron diffraction in oxide and other layers in some cases causes the appearance of sharply outlined rings on a photographic plate placed in the path of the electron beam, i.e., the electron scattering takes place under completely determined angles. This indicates a crystalline structure of the thin layers, whose nature can be determined on the basis of the electron diffraction patterns. In the case of layers which are on the surface of a metal, the lines of the metal itself naturally also appear on the electron diffraction pattern together with the oxide lines.

The electron diffraction method makes it possible to observe crystal structures in very thin layers (for example, with a thickness of only 20A) consisting merely of a few unit cells. It is found in this case, as the works of P.D. Dankov [54], in particular, showed, that between the lattices of the surface film and the metal on which it has formed, a certain correspondence is often observed so that the oxide lattice may be regarded as a continuation of the metal lattice. The oxide lattice can be obtained in these cases by a limited expansion of the metal lattice which makes it possible to introduce impurity atoms into it, for example, oxygen. Such a "crystal chemical correspondence" (a term, proposed by P.D. Dankov) ensures a tight adhesion of the film to the base metal. The orientating effect of the base has the consequence that in some cases (for example, ZnO on Zn) the thin layers have a crystal structure which differs from the structure of the same oxide in its normal voluminous form. The application of the electron diffraction method has shown that the oxide layers normally have a crystalline structure but in some cases, for example, low-temperature oxidation of aluminum, only diffuse rings can be observed on the electron diffraction patterns, indicating that the oxide layer has a disordered structure.*

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[Footnotes]

3 In the following instead of saying "the metal gives off electrons" we shall also say "the metal acquires a positive charge."

5* Here as in the following, when we speak of a potential difference between two phases, if not specially stipulated otherwise, we shall mean the potential difference measured by means of some auxiliary, for example, calomel or hydrogen electrode. The quantitative determination of the absolute potential difference between metal and solution, which is of considerable theoretical interest, cannot be finally achieved at the present time, primarily because of our insufficient knowledge concerning the potential distribution in the surface layer of the metal itself. See also §6.

5** See, for example, A.I. Brodskiy, Fizicheskaya khimiya [Physical Chemistry], GNTI [Gosudarstvennoye nauchno-tekhnicheskoye izdatel'stvo = State Scientific Technical Publishing House] of chemical literature, 1948.

5*** In dilute solutions the activity in Eq. (1) can be replaced by the concentration. In this case Eq. (1) is normally termed the Nernst formula. An analogous relation has been independently derived by V. Tyurin for amalgam circuits.

6 Concerning the origin of the double layer see also [1, 2].

9 This quantity will be more accurately defined in the following section.

10 The capacitance of the double layer varies when the water is replaced by other solvents but its variation is considerably less than the variation of the dielectric constant.

14 It is assumed here that an ion can be regarded as a charged sphere and that its charge is considered as equivalent to a point charge placed at the center of this sphere.

15 On condition of electrical neutrality the surface charge of the metal is equal in absolute magnitude to the charge of the ion part of the double layer and opposite in sign.

16* The latter follows directly from the relationship between the charge density ε on the surface of a metallic conductor and the potential gradient ψ close to the surface of the metal, known from electrostatics:

$$\varepsilon = -\frac{D}{4\pi}\left(\frac{\partial\psi}{\partial x}\right)_{x=0}.$$

Because within the dense part of the double layer the relation between ψ and x is linear, we have

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=0} = \frac{\psi_1 - \varphi_0}{d},$$

and, consequently

$$\varepsilon = \frac{D}{4\pi d}(\varphi - \psi_1) = C(\varphi_0 - \psi_1).$$

16** See, for example, A.I. Brodskiy. Fizicheskaya khimiya, GNTI of chemical literature, Vol. 1, 1948, page 455.

16*** See, for example, I.Ye. Tamm, Osnovy teorii elektrichestva [Fundamentals of the Theory of Electricity], 1949, page 56.

When applying the Poisson equation we assume that ψ depends only on x, i.e., that by neglecting the discontinuous arrangement of the charges in the double layer, we can average the value of the potential in a plane parallel to the electrode surface. Up to now it has not yet been possible to build a quantitative theory of the double layer taking the discrete structure of its ion envelope into account [6].

35 In the following we shall use the term "interface" tension for the case of a boundary between two phases, reserving the term "surface tension" for the free surface of liquids.

42 If charges are not supplied from without to the mercury electrode whose surface increases continuously in consequence of the disintegration of the stream into droplets, the charge density ε evidently becomes zero.

46 The contact potential difference V_{AB} between the metals A and B is equal to the difference of the work functions λ_A and λ_B of the electrons in these metals:

$$V_{AD}=\lambda_A-\lambda_B.$$

A metal which has a smaller electron work function is charged positively upon contact with a metal having a larger value of λ. Every alteration of the state of the surface which affects λ, for example, the formation of an adsorbed layer, causes a corresponding alteration of the contact potential.

48 It can also be shown that the values of the individual potential differences at the interface of two phases cannot be found from the experimental data by a thermodynamic method [28].

54 At concentrations close to saturation the thickness of the adsorbed layer can exceed that of a single molecule.

56 This result compels us to assume that even in the absence of impurity molecules an orientated layer of water molecules can also cause the appearance of a potential difference between metal and solution, which does not vanish at the zero charge potential.

57 The maximum adsorption, however, does not completely coincide with the zero charge point [34]. In the case of substances which like butyl alcohol shift the zero charge point in the direction of more positive potentials, the adsorption maximum is at weakly negative values of φ_n.

61 High-molecular organic cations, as, for example, the ion $N(C_4H_8)^+$ behave partly as ions and partly as molecules; although they are also adsorbed preferentially on a negatively charged surface; at very large values of negative charge desorption again takes place.

66 More detailed examination shows, however, that certain, al-

though relatively not large quantities of adsorbed gases remain on the electrode surface even in the double layer region.

71 In solutions containing Cl^- and Br^- ions, some dissolution of the platinum also takes place at the same time.

73 During the anodic oxidation of smooth platinum by a current with high density or by prolonged action of oxygen on it considerable quantities of oxygen are built into the metal lattice. The oxygen dissolved in the metal is partly reduced during the recording of the cathodic charging curves, which sometimes makes the accurate determination of the potential as a function of the quantity of electricity passed through more difficult. These phenomena are not observed when electrodes of platinized platinum are used.

83 This remark obviously refers only to metals which do not form stable hydrides under normal conditions of temperature and pressure, such as, for example, Cd.

86 However, the pores in films normally do not penetrate to the surface of the pure metal but only to a thinner, already compact film which covers the metal.

88 On the oxidation of metals, see also the book by V.I. Arkharov [55].

Manuscript Pages No.	[Transliterated Symbols]
5	ам = am = amal'gama = amalgam
15	н = n = nulevoy = zero
24	Г = G = generator = generator
25	Н = N = nul' = null
27	н.в.э. = n.v.e. = normal'nyy vodorodnyy elektrod=standard hydrogen electrode
29	з = z = zarayazheniye = charging
40	К = K = kation = cation
47	э.д.с. = e.d.з. = elektrodvizhushchaya sila = = electromotive force
65	адс = ads = adsorbirovannyy = adsorbed
73	экв = ekv = ekvivalentnyy = equivalent

Chapter 1

DIFFUSION KINETICS

§1. CONCENTRATION CHANGES NEAR THE ELECTRODE DURING PASSAGE OF CURRENT

We shall begin the study of the kinetics of electrochemical reactions with the question of how the supply of the reacting substances to the electrode takes place. The processes of diffusion of dissolved substances are of fundamental importance in this; hence this section of kinetics is often termed diffusion kinetics. Let us point out that the mechanism of the removal of the reaction products from the electrode surface is reminiscent in many respects of the mechanism by which the reacting substance is supplied; the study of these two processes is thus closely related. In many cases the processes which supply the reacting substances and remove the reaction products determine the overall rate of the electrochemical reactions. Under these conditions the latter reactions proceed in accordance with the laws of general diffusion kinetics of heterogeneous reactions in solutions, the fundamentals of which have been described in 1896 [1] by A.N. Shchukarev.

Let us consider a galvanic circuit through which a current is flowing. Initially, before the switching on of the current, the concentration of the dissolved substances (electrolytes and nonelectrolytes) had the same value at all points of the solution; certain equilibrium potential differences were observed at the electrode surface. After switching on of the current composition changes occur at the electrode surface: ions or dissolved molecules of one species enter into reaction, and ions or molecules of another species are formed as a result of the reactions. The concentration of the dissolved ions or molecules near the electrode changes and the initial distribution is altered. Diffusion processes then occur in the solution which tend to equalize the concentration differences which have arisen and which ensure a supply of reacting substances to the surface or the removal of reaction products from the electrode surface. The potentials of the individual electrodes assume new values (differing from the equilibrium values) which depend on the intensity of the current passing through the galvanic circuit.

In order to analyze the process of motion of the particles in the solution it is useful to make first the simplified assumption that the electrochemical properties of the electrode under consideration are not altered under the influence of the flowing current, i.e., that the electrode potential is determined by the ion concentration near the electrode in exactly the same manner as it would be under equilibrium conditions. The only correction which is introduced according to this assumption into the formula for the equilibrium potential is that the initial concentration of the substance which determines the electrode potential is replaced by a new modified concentration, namely the value established near the electrode during the passage of the current.

The assumption made in the foregoing is a certain approximation which is not always equally justified. Cases can be mentioned (for example, the formation of the amalgams of many metals) in which it applies and it is consequently easier to analyze the phenomena connected with the motion of the ions in the solution. In other cases additional changes are superposed on these phenomena which complicates the discussion of the over-all kinetics of the electrochemical processes.

The concept of the concentrations of the potential-determining ions near the electrode surface which we have used requires a more accurate definition. Let us visualize a metallic electrode, for example, a silver electrode, immersed in a solution of its salt. At the electrode surface, as has been explained in the Introduction, there is a double electrical layer in which the uniform distribution of charges (ions), existing in the volume of the solution, is upset. The concentration of the silver ions within the double layer even under equilibrium conditions differs from the volume concentration of these ions; if the electrode surface is positively charged, this concentration is less than in the volume of the solution, and, if it is negatively charged, greater.

The problem arises what value of the concentration should be substituted in the expression for the equilibrium potential

$$\varphi = \varphi^0 + \frac{RT}{F} \ln c_{Ag}. \tag{46}$$

Obviously, it would have been incorrect to introduce into this formula the concentration present at a point within the double layer. In this case it would have been necessary to take into account the electrostatic field of the double layer and the variation of the chemical potential at each point of the double layer, caused by the action of this field. If we use Eq. (46) in its general form, the concentration of the potential-determining silver ions at a distance from the electrode surface at which the action of the forces of the double electrical layer can be neglected, would have to be substituted in it.

In the case of a polarized system, however, i.e., a system through which an electric current flows, the concentration of the ions in the layer of the solution near the electrode, as we have pointed out above, changes with distance from the electrode, and the concentration of the potential-determining ions close to the electrode must be substituted in the expression for the potential of the polarized electrode. A certain contradiction results due to the fact that the term "close to the electrode surface" has a different meaning in the two cases.

The disturbance of the charge distribution at the electrode surface, caused by the electric field of the double layer, extends for only a short distance into the depth of the solution, equal to the thickness of the diffuse double layer. This distance, as has been explained previously, depends on the total electrolyte concentration in the solution and for not very low concentrations is of the order of 10^{-7}-10^{-6} cm. In the solution zone adjacent to the double layer the ion concentration is everywhere the same under equilibrium conditions; under non-equilibrium conditions; however, it varies in accordance with a certain law. Under the usual mixing conditions this concentration variation extends to a distance of not less than 10^{-3}-10^{-2} cm; the layer in which this concentration change, caused by the electrochemical reaction at the electrode surface, is termed, for reasons which will be clear from the following, diffusion boundary layer (not to be confused with the diffuse double layer). Compared with the thickness of the diffusion layer the thickness of the double layer is small. In other words, points can be selected which would simultaneously satisfy the following two conditions: firstly, that they lie outside the double layer, i.e., that the effect of the electric field of the double layer should not be observed in them and, secondly, that they should nonetheless be so close to the electrode surface that from the point of view of the concentration variation in the diffusion layer one could speak of an ion concentration at the actual electrode surface (point *A* in Fig. 37).

The combination of these requirements, however, cannot always be fulfilled. In the extreme case of a very low total concentration of the solution at the electrode surface the thickness of the diffuse part of the double layer increases and approximates the thickness of the dif-

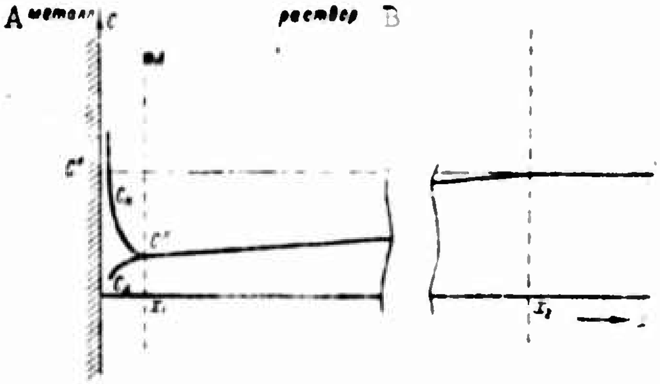

Fig. 37. Distribution of the electrolyte concentration c^s, the concentrations of the anions (c_A) and cations (c_K) in the diffuse part of the double layer and in the diffuse layer of the negatively charged electrode; x_1 is the boundary of the diffuse part of the double layer; x_2 is the boundary of the diffusion layer; c^0 is the initial electrolyte concentration at a distance from the electrode. A) Metal; B) solution.

fusion layer; under these conditions, the elementary relations which will be presented further on are not applicable. Although such phenomena can sometimes occur, they are nevertheless not of any great practical importance for the usual electrolysis conditions, and the assumption made in the foregoing is completely justified in most cases. Thus, if the concept of concentrations near the electrode surface is used in the following, this concept must be understood in a macroscopic and not a microscopic sense of the term. To avoid ambiguities we shall speak of concentrations "near the electrode surface" or "in the space around the electrode," reserving the term "surface concentration" for designating the concentration of the particles at molecular distances from the phase boundary.

As A.G. Samartsev [2] showed, the variation of the ion concentration near the electrode surface during the passage of the current can be directly observed optically by the variation of the index of refraction of the solution. The use of a sensitive interferometer in combination with a polarization microscope enables the concentration gradient in different parts of the diffusion layer and also the total concentration difference between points in the volume of the solution and near the electrode surface to be determined.

Let us now examine the conditions of variation of the concentration during the passage of an electric current in the simplest case. Assuming we have a metallic electrode, for example, silver, in a capillary and occupying its entire cross section. The capillary is filled with a dilute silver nitrate solution and at the second, open end, it is connected with a large vessel, containing the same solution (Fig. 38). Because the volume of the solution in the large vessel is large

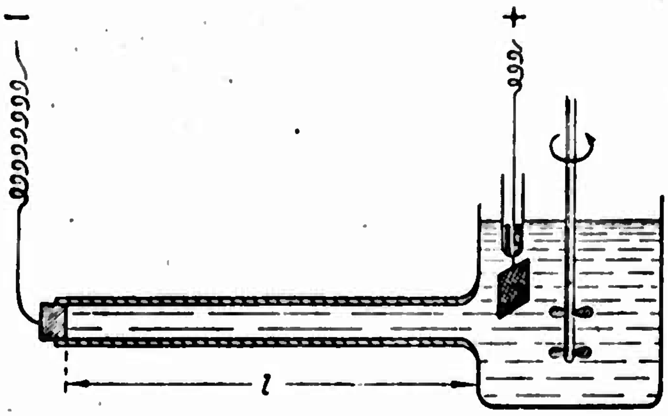

Fig. 38.

compared with the volume of the solution in the glass capillary, the electrolyte concentration in this vessel during the passage of current varies only slightly and can be neglected. In other words, it can be assumed that the ion concentration at the open end does not change and remains always equal to the initial ion concentration in the solution.

Let us first consider the case, which, as will be evident from the following, is the simplest. Namely this: we assume that in addition to the ions which determine the electrode potential and which can be discharged at the metal surface (i.e., in our example, in addition to the ions of the silver salt) a foreign electrolyte which does not participate in the electrolysis process, for example, an excess of potassium nitrate, is present in excess.

Let us consider the conditions of the supply of silver ions to the electrode surface during electrolysis. At the first moment after the switching on of the current, the silver ions begin to be discharged and their concentration near the electrode surface will decrease. A certain concentration gradient will appear in the solution in the capillary resulting in a diffusion of the discharged ions from the more remote parts to the electrode surface. The diffusion rate of the ions will be proportional to the concentration gradient.

In addition to the diffusion, a movement of charged ions under the influence of the electrostatic field in the solution takes place. This movement is often termed ion migration in the electrochemical literature. The electrostatic field in the solution causes a migration of all the ions, those discharged at the electrode surface as well as those which are not discharged, i.e., in the above case the Ag^+ ions as well as the K^+ and NO_3^- ions. According to the above assumption, the concentration of the silver ions is low compared with the concentration of the other ions; hence only a small part of the current in the solution is due to the migration of silver ions. This assumption thus permits us to neglect the migration of the silver ions in the general process of the transport of these ions to the electrode surface.

Thirdly, an enormously important factor on which the transport of substance to the electrode depends, is the movement of the liquid itself, which arises spontaneously or due to stirring of the solution. In order to exclude this influence, the motion of the ions in a capillary is considered in the selected example, i.e., under conditions which exclude any convection movement and mixing of the liquid (Fig. 38).

The effect of the ion migration and the convection of the liquid on the process of transport of the reactants to the electrode surface will be examined in the following sections.

In proportion to the passage of current the solution at the electrode surface is progressively impoverished in silver ions which in turn causes an increase in the concentration gradient and at the same time an intensification of the transport of these ions via diffusion. After a certain time conditions are established under which the number of ions disappearing because of the discharge reaction becomes equal to the number brought to the electrode surface by diffusion. A certain stationary state, i.e., one which does not change with time, is established; this state is of course not an equilibrium state because it is maintained by the passage of current through the solution and is immediately upset when the current ceases.

§2. DIFFUSION EQUATIONS

In order to determine the regularities connected with the passage of current through a solution under stationary conditions one has to solve the simplest problem of diffusion kinetics.

According to the laws of diffusion, the quantity m of substance diffusing within the time Δt through a certain cross section perpendicular to the axis x which is in the direction of increasing concentrations, is proportional to the concentration gradient $\partial c/\partial x$, the magnitude of the cross section S and also the time interval Δt:

$$m = DS\frac{\partial c}{\partial x}\Delta t. \tag{47}$$

The proportionality factor D, the diffusion coefficient, has the dimension of the square of the length, divided by time; it is normally expressed in units of $\mathrm{cm}^2/\mathrm{sec}$ or $\mathrm{cm}^2/\mathrm{day}$. Diffusion in the direction of decreasing concentrations we shall consider as the positive diffusion direction.

If the concentration of the diffusing substance at every point of the solution is not constant but varies with time, we can find the connection between its rate of change and the quantity which characterizes the concentration distribution along the diffusion path. For this purpose we make two identical parallel cross sections $S_1 = S_2$ at a distance dx from each other (Fig. 39). If the concentration gradient at the first cross section is designated by $(\partial c/\partial x)_1$, then near the second cross section it will differ by an infinitely small value, i.e., it will be equal to $\left(\frac{\partial c}{\partial x}\right)_2 = \left(\frac{\partial c}{\partial x}\right)_1 + \frac{\partial^2 c}{\partial x^2}dx$.

The quantity of substance diffusing through the first cross section is equal to $m_1 = DS\left(\frac{\partial c}{\partial x}\right)_1 \cdot \Delta t$, and the quantity of substance diffusing through the second cross section to $m_2 = DS\left\{\left(\frac{\partial c}{\partial x}\right)_1 + \frac{\partial^2 c}{\partial x^2}dx\right\}\Delta t$. The rate of change of the concentration in the volume $dv = Sdx$, included between the two cross sections, is equal to the ratio of the difference of the quantities of substance coming in and going out in unit time to the volume dv, i.e.,

$$\frac{\partial c}{\partial t} = \frac{m_2 - m_1}{Sdx \cdot \Delta t} \qquad (48)$$

Substituting the values for m_1 and m_2, we obtain the following differential equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (49)$$

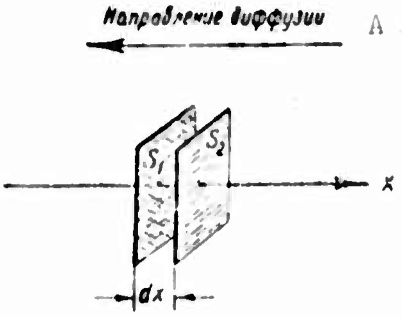

Fig. 39. A) Diffusion direction.

In the above-considered case of diffusion in a capillary, a stationary state is established some time after the beginning of the passage of the current, i.e., the concentration at any point in the capillary in time is constant and $\partial c/\partial t = 0$. It follows from Eq. (49) that in this case $\partial c/\partial x = \mathrm{const}$, i.e., the concentration gradient at all points of the capillary has the same val ue, which is evidently equal to $\partial c/\partial x = (c^0 - c^s)/l$, where l is the length of the capillary, c^s is the concentration of the ions established near the electrode surface during passage of the current and c^0 is the concentration at the open end of the capillary which is identical with the initial ion concentration in the solution prior to the passage of current.

The number of ions diffusing in unit time to one square centimeter of electrode surface is equal to

$$\frac{m}{S \cdot \Delta t} = D\left(\frac{\partial c}{\partial x}\right)_{x=0} \qquad (50)$$

(in the description of diffusion processes this quantity is often termed the diffusion flow). From this formula one can readily compute the density of the electric current (i.e., the intensity of the current, related to unit of electrode surface), passing through the system. Indeed, under stationary conditions the current is determined by the number of diffusing ions and, in order to calculate the current density, one has to multiply the ion diffusion flow with the charge of the ion. If the concentration is expressed in gram-moles per cubic centimeter, the diffusion flow must be multiplied with nF, where n is the valency of the ions,* and F the Faraday number:

$$i = nFD\left(\frac{\partial c}{3x}\right)_{x=0} \qquad (51)$$

In the case of stationary diffusion the current density is

$$i = nFD\frac{c^0 - c^s}{l}. \qquad (52)$$

Formula (2) expresses the relation between the density of the current flowing through the system and the stationary concentration c^s of the metal ions at the electrode surface. Let us consider in greater detail the nature of the expression thus obtained. If the current density is increased, the ion concentration at the electrode surface should decrease. The quantity c^s may vary, beginning from the initial concentration c^0 at a current density close to zero and with increase in i it may decrease to zero. In the latter case the current density attains a certain limit value which we shall designate by i_d. This limit current density is often termed "limit diffusion current." It is equal to

$$i_d = \frac{nFDc^0}{l}. \tag{53}$$

i.e., the limit current density is proportional to the initial concentration of the silver ions in the solution and inversely proportional to the length of the capillary. As long as the assumption made by us, according to which only silver ions are discharged at the cathode, holds, we must not pass a current through the system under consideration whose density exceeds the above limit value.

Because the diffusion coefficient increases with temperature, the limit diffusion flow for this system should also increase with temperature, according to the relation

$$\frac{\partial i_d}{\partial T} = \frac{nFc^0}{l}\frac{\partial D}{\partial t} = \frac{i_d}{D}\cdot\frac{\partial D}{\partial t} \tag{54}$$

§3. EQUATIONS OF THE CONCENTRATION POLARIZATION

Using the expression for the limit diffusion current we can write Formula (52) in the form:

$$i = i_d\left(1 - \frac{c^s}{c^0}\right). \tag{55}$$

It follows from this that the concentration of silver ions at the electrode surface, expressed by the current density, is equal to

$$c^s = c^0\left(1 - \frac{i}{i_d}\right). \tag{56}$$

Knowing the connection between current density and ion concentration at the electrode surface, we can solve our problem concerning the depending of the electrode potential on the diffusion flow, if it is assumed, as we did in the foregoing, that the electrode potential is determined in accordance with the usual thermodynamic formula

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln c^s, \qquad (46a)$$

in which c^s is the concentration of the potential-determining ions near the electrode surface.

Substituting in this formula the expression for c^s from (56), we obtain

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln c^0 + \frac{RT}{nF} \ln\left(1 - \frac{i}{i_d}\right). \qquad (57)$$

Frequently we are not interested in the potential itself but in its variation compared with the value which the potential had under equilibrium conditions, i.e., prior to the passage of the current. The magnitude of this shift which we designate by $\Delta\varphi$, is normally termed the polarization of the electrode

$$\Delta\varphi = \frac{RT}{nF} \ln \frac{c^s}{c^0} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_d}\right). \qquad (58)$$

Equation (58) which connects the potential variation with the current density on the assumption that the passage of current affects the electrode potential only by the variation of the ion concentration, is termed the concentration polarization equation.

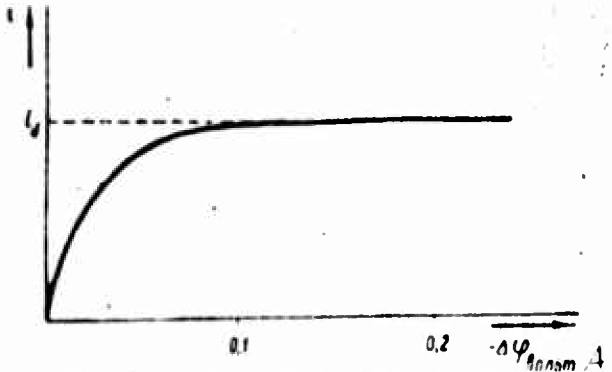

Fig. 40. Current density as a function of the electrode potential presence of concentration polarization. A) Volt.

It is evident from Eq. (58) that at a current density close to zero the polarization is also close to zero, i.e., in agreement with the above statements, a polarization of the electrodes is not observed in absence of a current. When the current density increases, the electrode potential, in consequence of the decrease in the surface concentration of the potential-determining ions, shifts to the negative side, i.e., $\Delta\varphi$ assumes a negative value.

At small values of i/i_d Eq. (58) can be replaced by the following simpler expression:

$$-\Delta\varphi = \frac{RT}{nF}\frac{i}{i_d} \qquad (58a)$$

According to Eq. (58a) the electrode polarization, although it is small compared with RT/nF, is proportional to the current density i and inversely proportional to the limit diffusion current i_d.

When the current density tends to its limit value i_d, the absolute value of the polarization becomes infinite. Such an infinite increase in the polarization naturally is devoid of any physical meaning. However, there is nothing surprising in this deduction, because it follows from the assumption of the possibility of a single electrochemical reaction, which has been made in the foregoing. When the ion concentration at the electrode surface c^s is exactly zero, then according to the thermodynamic formula (46a), the electrode potential assumes the value $-\infty$. In reality, however, when the polarization increases, new electrochemical processes at the electrode surface become possible (discharge of other ions or molecules) which require part of the current, owing to which the further potential variation is delayed.

Figure 40 shows the curve representing the current density as a function of electrode potential for the case of concentration polarization according to Eq. (58). Attention should be given to the fact that different methods of representing polarization curves are encountered in the electrochemical literature, such as, for example, in the form of a dependence of the intensity or density of the current on the polarization (Fig. 40), in the form of the dependence of the potential on the logarithm of the current intensity or density (Fig. 41) or in other forms.

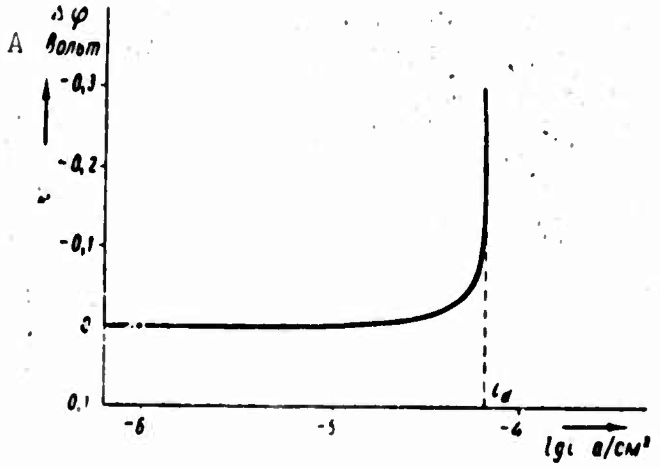

Fig. 41. Potential as a function of the logarithm of the current density in the case of concentration polarization. A) Volt.

The above-derived equations are applicable only to non-concentrated solutions. In the case of concentrated solutions difficulties arise, connected with the fact that not the concentration of the potential-determining ions near the electrode but their activity must be substituted in the formula for the electrode potential (46a).

The picture is even more complicated by the circumstance that the diffusion coefficient in concentrated solutions is no longer constant but depends on the concentration. In consequence of this, concentration polarization in concentrated solutions cannot be described accurately by means of the simple equation (58).

§4. CONCENTRATION POLARIZATION DURING FORMATION OF AMALGAMS

Let us examine the diffusion processes and the phenomenon of concentration polarization during the discharge of metal ions, for example, of zinc ions, on a mercury cathode. In contrast to the earlier considered case, where the discharge of the silver ions merely resulted in the formation of a new silver layer on a silver electrode and did not alter its electrochemical nature, formation of zinc amalgam takes place when zinc ions are discharged at the mercury cathode. The concentration of the amalgam will be a maximum in the direct vicinity of the point of the electrochemical reaction, i.e., near the surface of the mercury electrode, which is in contact with the solution. Owing to the presence of a concentration gradient of zinc in mercury a process of diffusion of zinc atoms from the surface of the amalgam into the volume of the mercury phase takes place, which tends to equalize the zinc concentration in the amalgam. Under certain conditions a stationary state may be established in which the quantity of zinc discharged in unit time is equal to the quantity of zinc moving away from the surface of the amalgam in consequence of the diffusion.

The stationary state of diffusion in a solution and amalgam can be achieved by means of the device which is schematically represented in Fig. 42. The capillary tube communicates with two large reservoirs, of which one contains pure mercury and the other an electrolyte solution, for example, $ZnCl_2$ and an excess of impurity salt. In the capillary there is a mercury meniscus on which the electrochemical reaction of the discharge of zinc ions takes place during the passage of current. On the one hand, a diffusion of zinc ions towards the surface of the mercury meniscus takes place within the capillary and, on the other, a diffusion of zinc atoms from the meniscus to the mercury reservoir.

The potential of the amalgam electrode is determined not only by the concentration of the zinc ions at a point of the solution close to the electrode surface but also by the concentration of the zinc atoms in the amalgam at the point close to the amalgam-solution interface. If

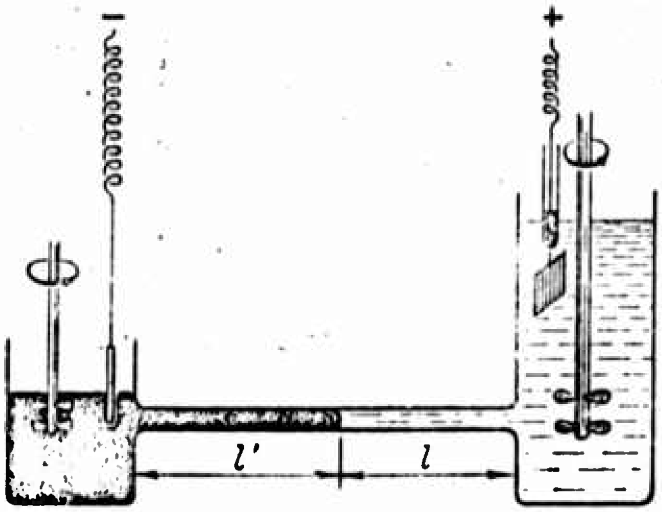

Fig. 42.

we designate the ion concentration in the solution by c_u^0, the concentration of the zinc amalgam by c_M^0 and the corresponding concentrations close to the electrode surface by c_u^s and c_M^s, then we have for the amalgam at the electrode

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{c_u^s}{c_M^s}. \qquad (59)$$

In order to derive an equation for the concentration polarization during the formation of amalgam, we must, as previously, connect the concentration near the surface with the density of the polarizing current.

The diffusion of the zinc ions in the solution proceeds in accordance with the same laws as in the first example considered in the foregoing; according to (53) and (56) the stationary ion concentration near the surface is connected with the current density by the relation

$$c_u^s = \frac{c_u^0}{i_d}(i_d - i) = \frac{l}{nFD}(i_d - i).$$

The diffusion flow of the zinc in the amalgam depends on the concentration gradient of the zinc in the amalgam. The concentration of the amalgam near the phase boundary with the solution is c_M^s; the amalgam concentration c_M^0 at the end of the capillary is zero because the end of the capillary is in contact with the reservoir of pure mercury. Hence the diffusion flow is simply proportional to the amalgam concentration near the electrode surface. As previously pointed out, under stationary conditions the diffusion flow expressed in electrical units is equal to the density of the discharge current; thus the simple relation

$$i = \frac{nFD'}{l'} c_M^s \qquad (60)$$

or

$$c_M^s = \frac{l'}{nFD'} i$$

exists between the current density and the stationary amalgam concentration near the surface, where D' is the diffusion coefficient of the zinc in the amalgam and l' the length of the capillary section filled with amalgam.

By substituting these expressions for the surface concentrations into the thermodynamic formula (59), we obtain an equation for the potential of the polarized electrode, expressed by the current density and the limit current

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{lD'}{l'D} + \frac{RT}{nF} \ln \frac{i_d - i}{i} = \text{const} + \frac{RT}{nF} \ln \frac{i_d - i}{i}. \qquad (61)$$

Equation (61) is the equation for the concentration polarization in presence of concentration variations in the solution as well as within the metallic phase.

Let us consider the physical meaning of the constant which enters into Eq. (61). It is easy to see that this constant is equal to the potential at which the polarizing current attains half its maximum, i.e., at which $i = \frac{1}{2} i_a$. This potential, for reasons which will be clear from the following, is often termed half-wave potential and is designated by $\varphi_{1/2}$; thus,

$$\varphi = \varphi_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i}. \qquad (61a)$$

It can be seen that the half-wave potential is independent of the initial concentration of the solution.

In order to carry out a graphic analysis of Eq. (61), it is conveniently rewritten in a slightly different form, solving it for the current density

$$i = \frac{i_d}{1 + e^{\frac{nF(\varphi - \varphi_{1/2})}{RT}}} \qquad (62)$$

Figure 43 shows the curve representing the density of the polarizing current as a function of the electrode potential, corresponding to Eq. (62). As follows from this equation, the current is small compared with i_d in the potential region, in which the difference $\varphi - \varphi_{1/2}$ considerably exceeds the magnitude of RT/nF (we remember that the numerical value of RT/F is 25 millivolts).

In the potential region in which the absolute value of the difference $\varphi - \varphi_{1/2}$ is small, a marked increase in the current takes place when the negative cathode potential is increased. With further increase in the cathode polarization the quantity $\varphi - \varphi_{1/2}$ assumes more negative values and the diffusion current tends to its maximum. Every curve of the current density as a function of potential has the shape of a wave; hence the term half-wave point for the point at which $i = \frac{1}{2}i_d$. We find

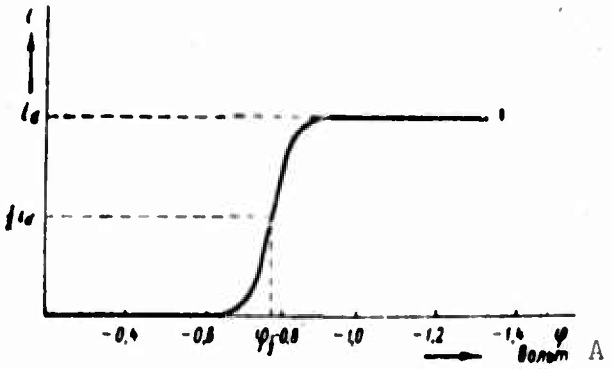

Fig. 43. Current density as a function of the potential in the case of concentration polarization during the formation of amalgam. A) Volt.

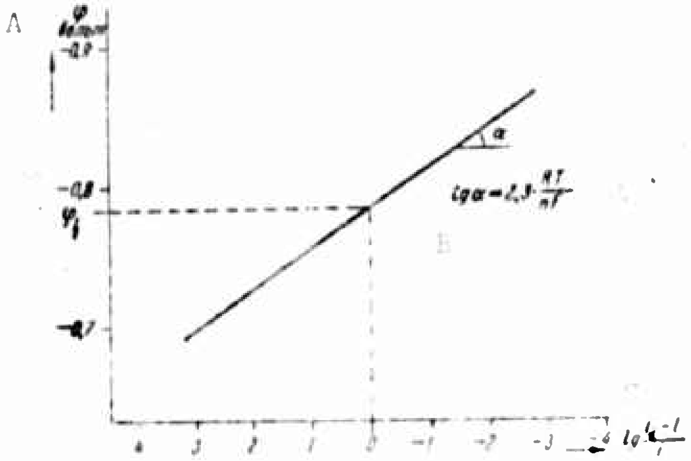

Fig. 44. Electrode potential as a function of log $[(i_d - i)/i]$ in amalgam formation. A) V[illegible]; B) tan...; C) log...

that the curve is completely symmetrical with respect to the half-wave point.

Another method of graphic representation of the curve corresponding to Eq. (61) is possible which is sometimes more convenient for practical purposes. If the potential of the amalgam electrode (or the difference $\varphi - \varphi_{1/2}$) is plotted on the ordinate axis and lg $(i_d - i)/i$ on the abscissa axis, a straight line is obtained with a slope coefficient of 2.3 × RT/nF (Fig. 44). By laying off the experimental points on this graph it is possible, in particular, to determine the valency of the metal which is discharged with formation of amalgam.

§5. EFFECT OF THE ELECTRIC FIELD ON THE LIMIT CURRENT

In the above-discussed examples of electrolysis with concentration polarization we have eliminated the effect of the electric field on the movement of the discharging ions by adding to the solution an excess of a foreign electrolyte. Let us now examine in what manner the conditions of supply of the substance are modified when in addition to the concentration gradient in the solution an electric field is also acting and how the limit current varies in this case.

Let the silver electrode to be studied, as in the first example, be in a thin capillary filled with silver nitrate solution, but this time not containing any potassium nitrate. After switching on of the current the concentration of silver ions near the cathode begins to decrease; the concentration of the NO_3^- ions which are carried out of the capillary by the current decreases at the same time. Because foreign cations are not present in the solution, the concentrations of Ag^+ and NO_3^- remain equal, i.e., at any point of the solution outside the double layer, by virtue of electrical neutrality, the concentrations of the positive and negative ions must be the same (in the case of ions with the same valency). Some time after the switching on of the current a stationary state is attained in which the ion concentration at any point of the solution no longer changes with time. Because the NO_3^- ions are not discharged at the surface of the silver cathode the constancy of their concentration means that they move neither to the cathode nor to the anode in the solution, i.e., that the sum of forces acting on these ions is zero.

Let us consider what forces act in the solution on the NO_3^- ions. The first force which causes the diffusion of the ions and which arise in presence of a concentration difference of the ions in the solution, is determined by the osmotic pressure gradient $\partial P/\partial x$; the average force acting on a single ion is

$$f_0 = \frac{1}{cN}\frac{\partial P}{\partial x}. \qquad (63)$$

where cN is the number of ions in unit volume (N is the Avogadro number). Under the action of this osmotic force the NO_3^- ions, like the Ag^+ ions, are directed towards the cathode surface.

The second force acting on the ion in solution and due to the electric field, is

$$f_e = \varepsilon E. \qquad (64)$$

where E is the intensity of the electric field in the solution and ε is the charge of the univalent ion.

The force of the electric field acting on the NO_3^- ions is directed towards the anode, i.e., oppositely to the direction of the osmotic force.

Because in the stationary state the osmotic and electrical forces acting on the ion are mutually compensating,

$$f_e = f_0. \qquad (65)$$

i.e.,

$$\frac{1}{cN}\frac{\partial P}{\partial x} = \varepsilon E. \qquad (65a)$$

On the basis of this relation it is easy to visualize how the movement of the cations takes place. The osmotic pressure gradient of the cations has the same value as in the case of the anions. The electrical force acting on the cations has the same value and the inverse direction as that acting on the anions. Hence in the case of the cat ions the osmotic and electrical forces do not cancel out but are super-

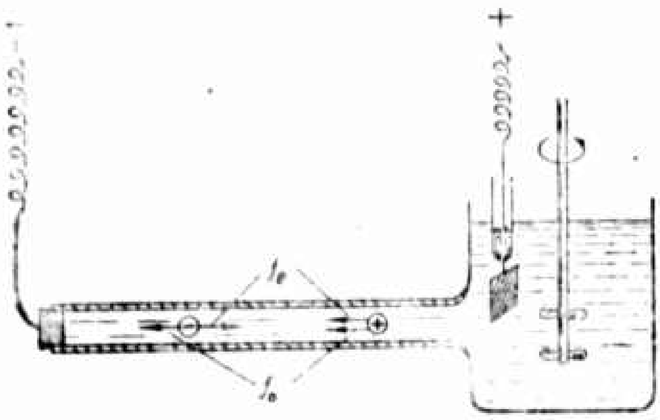

Fig. 45. Schematic of the action of the forces of osmotic pressure (f_0) and the electrostatic field (f_e) on the anions and cations.

posed (Fig. 45). By virtue of the relation (65) the total force acting on the cations is twice the osmotic pressure. Thus the velocity of the silver ions will be twice as great as the velocity which they would have if the osmotic force alone were acting. In other words, in the case under consideration here, owing to the effect of the electric field in the solution, the limit current is doubled as compared with the limit current, passing through the system in presence of an excess of foreign electrolytes in the solution as was shown by Eucken [3].

We must point out that the doubling of the limit current takes place only when the cations and anions have the same valency. In other cases other numerical relations are obtained but the physical nature of the observed phenomena is not altered.

We can arrive at the same result by another pathway, by considering, not the forces acting on the anions and cations separately, but the total velocity of the ions under the action of these forces. This treatment is more general and is used for the examination of these phenomena in more complex cases. Let us consider the motion of an anion, taking place under the influence of two factors: diffusion under the influence of osmotic forces and migration under the action of the electric field. The magnitude of the diffusion flow, i.e., the number of anions, diffusing in unit time through unit cross section, is $D_A(\partial c_A/\partial x)$, where D_A is the diffusion coefficient of the anions. The velocity of the anions under the influence of the electric field intensity E is $w_A = U_A^0 E$, where U_A^0 is the so-called absolute anion mobility, i.e., their speed acquired in an electric field whose intensity is 1 v/cm. The number of anions passing through unit cross section in unit time under the influence of the electrical force is obviously $c_A U_A^0 E$ (i.e., equal to the number of moles of ions contained in a cylinder with a cross section of 1 cm^2 and a length numerically equal to $U_A^0 E$).

Under stationary conditions the anion concentration at any point of our system does not change, i.e., the number of anions moving under the influence of the two factors to either side is mutually compensated. From this follows

$$D_A \frac{\partial c_A}{\partial x} - c_A U_A^0 E = 0. \qquad (66)$$

In the case of the cations the ion flow moving under the influence of the osmotic and electrical forces has the same direction. The total magnitude of this flow expressed in electrical units, i.e., the current density, passing through our system, is obviously

$$i = F\left(D_K \frac{\partial c_K}{\partial x} + c_K U_K^0 E\right). \qquad (67)$$

Let us examine the equations (66) and (67). In the case under investigation of an electrolyte with ions of equal valency the cation and anion concentration at any point in the solution are equal, i.e., $c_K = c_A$. In addition to the concentrations, the mobilities and diffusion coefficients of the anions and cations enter into these equations. The mobilities and diffusion coefficients should evidently be proportional because both quantities depend on the resistance which the solution offers to the motion of a given ion. The connection between these quantities is expressed by the following formula [4]*:

$$D_i = \frac{RT}{F} U_i^0. \qquad (68)$$

Substituting (68) in Eqs. (66) and (67) we find:

$$\frac{RT}{F} \frac{\partial c}{\partial x} - cE = 0, \qquad (69)$$

$$i = F U_K^0 \left(\frac{RT}{F} \frac{\partial c}{\partial x} + cE\right). \qquad (70)$$

where $c = c_A = c_K$.

From this we find the final expression for the current density:

$$i = 2 \frac{RT}{F} U_K^0 F \frac{\partial c}{\partial x} = 2FD_K \frac{\partial c}{\partial x}. \qquad (71)$$

i.e., we have arrived, as previously, at the conclusion that under the influence of the electric field the current is doubled compared with the diffusion current.

§6. OHMIC POTENTIAL DROP IN THE DIFFUSION LAYER

In the above-considered case of concentration polarization in the absence of an excess of an indifferent electrolyte in the solution during the passage of current a certain potential drop occurs. Let us attempt to derive the relations for the potential difference $\varphi_0 - \varphi_l$ at the ends of the layer of the solution, in which the alteration of the electrolyte concentration is concentrated; in our example, this layer will be the part of the solution between a point close to the electrode surface and the end of the capillary which is in contact with the solution in the larger cross section of the device.

To this end we divide both parts of Eq. (69) by c and integrate over the entire length of the capillary, i.e., from $x = 0$ to $x = l$

$$\int_0^l E\,dx = \frac{RT}{F}\int_0^l \frac{\partial \ln c}{\partial x}\,dx = \frac{RT}{F}\ln\frac{c^0}{c^0}. \qquad (72)$$

The left part, the integral of the electric field intensity over the path, is simply the potential difference $\varphi_l - \varphi_0$.

It follows from this that the sought-for potential difference $\Delta\varphi_{om}$ between a point near the electrode surface and the end of the capillary is

$$\varphi_l - \varphi_0 = \frac{i}{\varkappa}\,l = \frac{nFD(c^0 - c^0)}{\varkappa}. \qquad (72a)$$

The quantity $\Delta\varphi_{om}$ is evidently negative because the current flows from the solution to the electrode.

Equation (72a) can be obtained directly by applying to the anion of the electrolyte the Boltzmann formula. Because the anions are immobile; we have

$$c_A^s = c_A^0 \cdot e^{\frac{(\varphi_0 - \varphi_l)F}{RT}} \qquad (73)$$

(comp. Eq. (5a)). Because $c_A^s = c^s$ and $c_A^0 = c^0$ Eq. (72a) is obtained directly from Eq. (73).

The passage of current in an electrochemical system, due to concentration changes, thus causes not only a certain shift of the electrode potential, termed concentration polarization, but also a certain potential drop in the diffusion layer of the solution near the electrode which in the case of equal valency of the cation and anion is equal to the concentration polarization. This circumstance must be given special attention because the textbooks on electrochemistry normally do not take it into account, and in the literature it is often incorrectly described.

It would be of interest to return to the case of concentration polarization in presence of an excess of indifferent electrolyte in the solution and to calculate the ohmic potential drop for this case. The Ohm law is conveniently used for this calculation. The density of the diffusion current according to Formula (52) is equal to $i = nFD(c^0 - c^s)/l$. In order to find the potential drop at the ends of a capillary with length l we must divide the current density by the electrical conductivity of the solution and multiply by the length*

$$\Delta\varphi_{ом} = \varphi_0 - \varphi_l = \frac{RT}{F} \ln \frac{c^s}{c^0}. \qquad (74)$$

The specific electrical conductivity of a solution, as we know, can be expressed by the concentration, mobility and valency of the ions in the solution

$$\varkappa = F \sum_i n_i c_i U_i^0, \qquad (75)$$

where the summation is carried out for all ions. Substituting into Eq. (74) the value κ and replacing D by $RT/nF \cdot U^0$, we obtain:

$$\varphi_l - \varphi_0 = \frac{RT}{F} \cdot \frac{U^0 (c^0 - c^s)}{\sum_i n_i c_i U^0}. \tag{76}$$

As the numerator of this expression figures the absolute mobility and concentration of the discharging ion, and as denominator the absolute mobilities and concentrations of all ions in the solution. In presence of a large excess of foreign electrolyte the ohmic potential drop in the diffusion layer can consequently be reduced as much as desired. Thus, for example, with a tenfold excess of foreign electrolyte, in which the ion mobilities are close to the mobilities of the discharging electrolyte, the ohmic potential drop is of the order of millivolts. If the concentration of the foreign electrolyte is small compared with the concentration of the basic electrolyte, the variation of the electrical conductivity because of the decrease in the total ion concentration near the electrode surface must be taken into account when calculating the quantity $\varphi_l - \varphi_0$ by the above method. In absence of a foreign electrolyte an accurate calculation of the ion concentration and electrical conductivity variation of the solution leads to a formula which is identical with Formula (73) derived earlier on the basis of other considerations, if the potential drop caused by the difference in ion mobility is also taken into account (see footnote, page 122).

17. THE ROLE OF MIXING IN DIFFUSION PROCESSES

As has been evident from the preceding sections, the intensity of the electric current which can be passed through a quiescent solution, does not exceed a certain limit value. The latter is relatively small because in absence of any motion of the liquid the charge transfer is brought about only by the diffusion and ion migration processes, whose rate is low.

In practical electrolysis one often tries to use greater current intensities, and for this purpose the electrolysis is carried out not in a quiescent solution but with intense stirring. Strictly speaking, without special precautions it is impossible to carry out electrolysis in a completely quiescent liquid, because even in the absence of artificial mixing there is always some movement of the liquid during the passage of current due to unequal heating, concentration changes and, consequently, a different density of the solution at different points and also gas evolution at the electrodes and other causes. Such natural mixing greatly increases the possible values of the limit current intensity. By means of artificial mixing (for example, a special stirrer) the rate at which the reactants are supplied to the electrode surface can be considerably increased and thus the intensity of the current flowing through the system.

In this connection arises the problem of establishing the diffusion laws in a moving liquid, i.e., the laws of convection diffusion. To solve this problem, equations of motion must be written which take into account the transfer of the dissolved substance by the moving liquid as well as the movement of the dissolved substance relative to the liquid. However, if the problem is stated in such a general form, a complex system of mathematical relations is obtained which does not immediately yield tangible results. For this reason the interesting and practically very important problem of convective diffusion has for a long time been solved only in a coarsely approximate fashion. Only in recent years has it been possible to achieve some successes on the way to its exact solution.

When solving any problem on convective diffusion it is essential first to investigate the nature of the motion of the liquid relative to the solid electrode on which the electrochemical reaction of discharge or ionization takes place and to establish the law of the velocity distribution of the liquid at different distances from the electrode surface.

It is known from physics that a layer of liquid directly adjacent to the surface of a solid does not move relative to this body. This conclusion, which is by no means self-evident, follows, for example, from the fact that the determination of the viscosity of liquids by means of the capillary viscosimeter gives values which are independent of the nature of the capillary walls. If the fluid were sliding relative to the capillary walls, different velocities would be found depending on the material used for the capillary and, consequently, different values for the viscosity coefficient.*

It follows that a solid, present in a fluid flow, exerts an important influence on the nature of movement of the fluid and causes a variation of its velocity. The braking effect of the solid, however, extends only to a limited distance from the surface into the depth of the moving fluid; beyond the limits of this distance the solid does not affect the velocity distribution in the fluid. Between the surface of a solid close to which the relative velocity of the fluid is zero and a point at a great distance from it the velocity of the moving fluid varies in accordance with a certain general law. This braking effect is determined only by the geometrical configuration and macroscopic state of the surface but does not depend on the nature of the solid.

The problem concerning the effect of mixing on the diffusion current has been investigated by Nernst [5]. According to the theory developed by him, diffusion takes place in a certain layer at the electrode surface whose thickness is designated by δ. Within this diffusion layer diffusion takes place as if liquid motion were entirely absent. At the boundary of this diffusion layer, owing to the mixing, the initial concentration of the reactants is permanently maintained. This corresponds to the simplest pattern of velocity distribution: inside the diffusion layer the velocity of the liquid is zero and at its boundary it increases suddenly to some large value (Fig. 46). The diffusion rate of the substance reacting at the electrode surface under these assumptions is determined by the laws of diffusion in a quiescent liquid; in other words, the current density, according to the Nernst theory, is

$$i = \frac{nFD\,(c^0 - c^s)}{\delta}. \qquad (77)$$

The Nernst theory has the advantage of great simplicity and clearness but it has the great deficiency that it operates with the diffusion layer thickness δ which cannot be calculated theoretically and whose physical meaning is not clear.

Fig. 46. Velocity (*u*) and concentration (*c*) distribution of a discharging substance in the diffusion layer according to the Nernst theory.

Nernst and his co-workers and also other authors have carried out a number of investigations on the basis of which conclusions concerning the magnitude of δ were obtained. In particular, they have shown that this quantity cannot be regarded as a constant, but that for an electrode of given shape it varies with variation of the velocity of motion of the liquid. It was found [6] that for an electrode in the form of a rotating disc the thickness of the diffusion layer is connected with the angular velocity of rotation ω by the following relation:

$$\delta = \frac{\text{const}}{\omega^n}, \qquad (78)$$

where $n \approx 0.6$.

Nernst assumed that the thickness δ depends only on the rate of mixing and that other factors do not affect it. In particular, he assumed that under given conditions of motion δ is a constant quantity, which is independent of the nature of the diffusing substance.

Knowing the magnitude of the limit current and the concentration of the discharging substance, it is possible, on the basis of Eq. (77) to compute the thickness of the diffusion layer. This calculation shows that depending on the rate of mixing this thickness is of the order of 10^{-2}-10^{-3} cm. A thickness of 10^{-3} cm corresponds to tens of thousands of molecular layers. A layer of such thickness cannot be maintained by molecular forces on the electrode surface in an immobile condition, i.e., the liquid in the diffusion layer cannot remain immobile. This is the physical deficiency of the Nernst theory.

An attempt to circumvent the difficulties, connected with the concept of a quiescent diffusion layer, has been made by Eucken [7], who pointed out the necessity of considering the conditions of liquid motion in the diffusion zone of the dissolved substance. However, the theory of Eucken is too general and has been worked out only for certain partial cases. In addition, it contains certain mathematical errors and incorrect assumptions [8].

§8. THEORY OF CONVECTIVE DIFFUSION

Comparatively recently V.G. Levich worked out a theory of diffusion and concentration polarization in a moving liquid [8, 9], which takes the conditions of motion of the liquid in the diffusion layer into account in a fairly rigorous mathematical form; this theory is undoubtedly the first physically and mathematically acceptable solution of the above-formulated problem.

In order to explain the basic concepts of the theory of Levich let us consider as an example an electrode in the form of a plate along which a flow of liquid takes place. As pointed out in the foregoing, close to the surface of the plate the velocity of the liquid is zero; at a certain distance from the plate the liquid moves with the initial velocity of the flow which we shall designate by u_0. As the hydrodynamic theory, developed by Prandtl [10] shows, a gradual increase in the velocity takes place within a certain layer from zero at the surface of the solid to the velocity u_0 at a large distance. The velocity distribution of the liquid flow as a function of distance is shown in Fig. 47 by arrows. The layer within which the uniform motion of the flow is upset is termed in hydrodynamics the Prandtl boundary layer; its thickness we shall designate in the following by δ_{gr}.

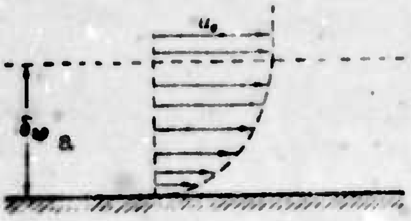

Fig. 47. Velocity distribution of the liquid flow near a solid surface. a) gr.

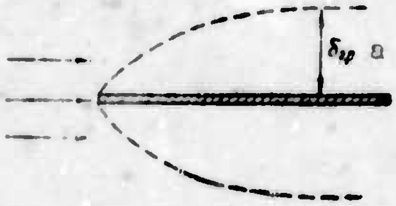

Fig. 48. Distribution of the boundary layer thickness along the surface of a plate immersed in a liquid flow. a) gr.

Hydrodynamic theory shows that the thickness of the boundary layer δ_{gr} depends on the speed u_0 of motion of the flow relative to the solid and on the kinematic viscosity ν of the liquid (the kinematic viscosity is equal to the ratio of the viscosity of the liquid to its density). Moreover, for the above-given example of a flat electrode, placed in a liquid flow, the thickness of the boundary layer is not constant for all points of the electrode surface but depends on the distance of the point concerned from the point of impact of the flow (Fig. 48). In proportion to the increase in this distance x the thickness of the boundary layer increases. The theory gives the relation

$$\delta_{\text{гр}} \approx \sqrt{\frac{\nu x}{u_0}}. \tag{79}$$

It must be emphasized that the hydrodynamic boundary layer is formed under conditions of an external flow around the body at Reynolds numbers which are large compared to unity. The Reynolds number Re is the dimensionless ratio $u_0 l/\nu$, where l is the characteristic dimension of the body, for example, the length of a flat electrode in a liquid flow. In flow inside a tube the boundary layer forms at the orifice and increases in accordance with the law (79) until it fills the entire tube. At very large Reynolds numbers (for example on a plate with $Re >$ $> 10^4$) so-called turbulent flow occurs, i.e., markedly nonstationary vertical flow of the liquid with typical irregular pulsating velocity variations in space and time. Under conditions of turbulent flow the above-given simple theory can be subject to important modifications.

To solve the diffusion problem we should take an interest not only in the velocity distribution of the liquid near the solid plate but also in the distribution of the concentrations of the substance which is discharged at the electrode surface, because knowing this distribution, we can derive conclusions concerning the laws of the diffusion process.

It would seem that we can equate the Prandtl boundary layer with the Nernst diffusion layer and assume that the initial concentration of the diffusing substance is maintained at the boundary of this layer while within the layer the concentration gradually decreases to zero concentration at the electrode surface (in presence of limit current). This concept is incorrect, however. As the theory, developed by Levich, shows, the thickness of the layer in which the variation of the concentration of the diffusing substance takes place is considerably less than the thickness of the layer, in which the velocity of the liquid motion varies, although there is also a certain analogy between these layers. The coincidence or noncoincidence of the thicknesses of these two layers depends on the ratio between the quantities which characterize the corresponding process of the momentum transfer and the diffusion process, i.e., the transfer of matter.

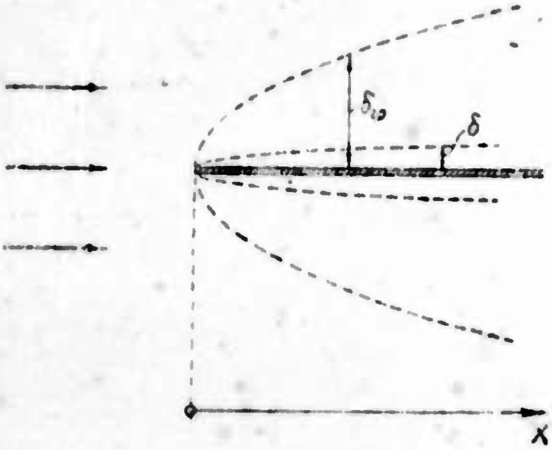

Fig. 49. Thickness (δ_{gr}) of the boundary layer and thickness (δ) of the diffusion layer.

The momentum transfer between liquid layers, moving with different velocities, depends on the force of the internal friction and is determined by the kinematic viscosity of the liquid. Analogously, the process of transfer of substance between layers of a solution with different concentration depends on the diffusion coefficient of the solute. In aqueous solutions the diffusion coefficient of dissolved molecules or ions is of the order of 10^{-5} $cm^2 \cdot sec^{-1}$; the kinematic viscosity which is expressed in the same units assumes values of the order of 10^{-2} $cm^2 \cdot sec^{-1}$, i.e., there is a great numerical difference between these quantities. This signifies that a much larger gradient, i.e., a much more marked variation of concentration as a function of distance is required for the transfer of matter via diffusion, than for the momentum transfer in presence of a velocity gradient. In consequence of this the concentration disturbances are propagated in a much thinner layer than the disturbances of the velocity of motion in a liquid flow. The layer in which an impoverishment of the solution takes place is thus thinner than the Prandtl boundary layer (Fig. 49).

Mathematical calculation shows that the following relation exists between the thickness δ of the diffusion layer and the thickness δ_{gr} of the boundary layer:

$$\frac{\delta}{\delta_{\text{гр}}} \approx \left(\frac{D}{\nu}\right)^{1/3}. \tag{80}$$

For aqueous solutions, in which, as previously pointed out, D and ν are of the order of 10^{-5} and 10^{-2} $\text{cm}^2 \cdot \text{sec}^{-1}$, the thickness of the diffusion layer is approximately one-tenth the thickness of the boundary layer.

By comparing Eqs. (79) and (80) we find for the thickness of the diffusion layer

$$\delta \sim D^{1/3} \nu^{1/6} x^{1/2} u_0^{-1/2}. \tag{81}$$

Knowing the thickness of the diffusion layer, we can calculate the current density down to the electrode surface by means of the basic formulas of diffusion kinetics:

$$i = \frac{nFD\,(c^0 - c^s)}{\delta}, \tag{82}$$

and

$$i_d = \frac{nFDc^0}{\delta}. \tag{82a}$$

In the above-considered theory, Formula (82), however, differs in its significance considerably from the corresponding formula in the theory of Nernst (77) because the thickness δ which figures in the denominator of the right part of Eq. (82) is not the thickness of the immobile layer; on the contrary, a gradual increase in the velocity of the liquid flow takes place in this layer.*

The second important difference compared with the Nernst theory consists in the fact the quantity δ depends not only on the velocity of motion (stirring) of the liquid, but also on the diffusion coefficient of the discharging substance. It follows that under identical geometrical and hydrodynamic conditions, the quantity δ is not constant but depends on the nature of the particles reacting at the electrode surface. A substance which has a larger diffusion coefficient can diffuse to the electrode surface from a greater depth, i.e., the thickness of its diffusion layer is greater than for a substance with a smaller diffusion coefficient. From this follows the interesting consequence that the density of the diffusion current is not linearly proportional to the diffusion coefficient as this was the case in the earlier considered cases of diffusion in a quiescent liquid and as Nernst also assumed for diffusion in a moving liquid, but is proportional to the 2/3 power of the diffusion coefficient:

$$i \sim nFD^{2/3} u_0^{1/2} \nu^{-1/6} x^{-1/2} (c^0 - c^s). \qquad (83)$$

True, the difference in the diffusion current as a function of the diffusion coefficient (according to the Nernst theory $i \sim D$, according to the theory of levich $i \sim D^{2/3}$) is not of great practical importance, because the diffusion coefficients of different substances vary within fairly narrow limits. However, this difference is nonetheless important in principle because it shows that we are dealing with two different diffusion patterns. Whilst the Nernst theory assumed that the quantity δ is given by the velocity distribution in the liquid, this quantity is determined in the modern theory by the diffusion process itself. This difference becomes even clearer when we consider more complex cases of convective diffusion but we cannot dwell on this here.

The most important difference between the two theories consists in the fact that the quantity δ in the theory of Levich is not introduced as an arbitrary constant as this was the case in the Nernst theory, but assumes a defined physical meaning.

§9. ROTATING DISC ELECTRODE

We have discussed in greater detail the case of an electrode in the form of a thin plate immersed in a liquid flow, primarily because the nature of the liquid motion can be clearly observed on it. In the following we shall consider the case of an electrode in the form of a rotating disc. An electrode with this shape is frequently used in electrolysis.

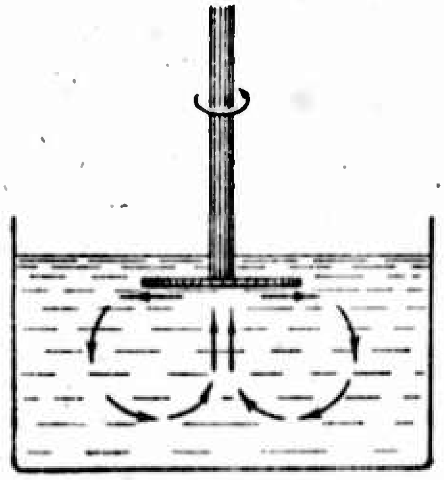

Fig. 50. Motion of the liquid near a rotating disc electrode.

When the disc electrode rotates rapidly around an axis attached perpendicularly to the plane of the disc at its center, the liquid in contact with the central parts of the disc is thrown off towards its edges by centrifugal force. In consequence of this, a negative pressure is created around the center of the disc and the liquid flow is directed from the volume of the solution towards the center of the disc. The lines of movement of the liquid flow have the form shown in Fig. 50. If it is considered that the flow of the solution from the volume impinges on the center of the disc, the thickness of the boundary layer must increase in proportion to the distance towards the edges of the disc. On the other hand, in proportion to the approach to the disc edges the linear velocity of motion of a point on the disc increases, in consequence of which this thickness should decrease. It is readily seen from the relation (79) that these two influences are mutually compensating. In reality the increase in the thickness δ_{gr} takes place in proportion to the square root of the distance from the point of impact, i.e., in this case the square root of the radius. The linear velocity of the motion of a point on the disc is proportional to the radius, and the thickness δ_{gr} is inversely proportional to the root of the linear velocity. The net result is that the thickness of the Prandtl boundary layer is the same for all points on the surface of the rotating disc. For this reason the hydrodynamic problem is simplified and the diffusion problem can be finally resolved for this case.

The first conclusion which can be made is that the diffusion layer, like the boundary layer, has the same thickness for all points on the surface of the rotating disc. In consequence of this the current density is also the same at all points. If some metal, for example, copper, is deposited on a rotating disc electrode, it covers the entire surface of the disc with a uniform layer whose thickness is the same at the edges and the center.

Calculation gives for the thickness of the diffusion layer on a rotating disc electrode:

$$\delta = 1{,}62\, D^{1/3} \nu^{1/6} \omega^{-1/2}, \qquad (84)$$

where ω is the angular velocity of rotation (i.e., the number of revolutions per second, multiplied by 2π). Using this expression, we find for the current density

$$i = 0{,}62\, nFD^{2/3} \omega^{1/2} \nu^{-1/6} (c^0 - c^s). \qquad (85)$$

As previously pointed out, it has long ago [7] been found experimentally that the diffusion current of the rotating disc electrode is approximately proportional to $\omega^{0.6}$. The slight deviation between the exponent 0.6, found experimentally, and the exponent 0.5, required by theory, is due to the fact that the precautions were not taken in the experiments to exclude the formation of vortices. If such precautionary measures are taken, an exponent 0.5 is indeed found in the experiment. The complete quantitative applicability of Formula (85) has been shown by experimental investigations [11]. In Fig. 51 the thick line indicates the limit diffusion current as a function of the rate of rotation of a disc electrode, calculated in accordance with Eq. (85) for the case of the reduction of oxygen dissolved in 0.05 N HCl; the points represent the experimental values of the limit current. As follows from these tests, the above-described theory of convective diffusion can be considered to have been proved correct with complete confidence. The exact expression for the current on the rotating disc electrode can be used in analytical practice for the determination of the concentrations of a reacting substance by measurement of the limit current.

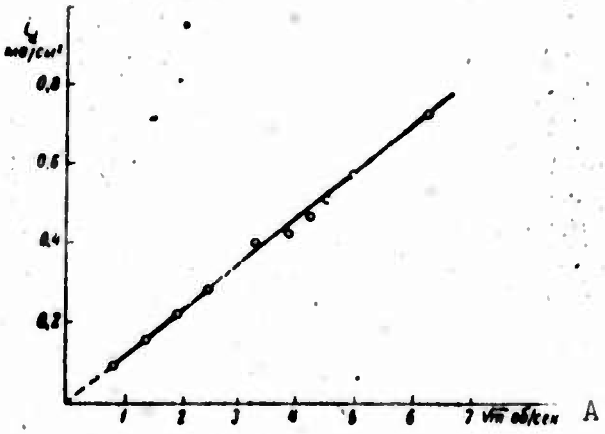

Fig. 51. Limit diffusion current of the reduction of oxygen as a function of the rate of rotation of the disc electrode (*m* is the number of revolutions of the disc electrode per second). A) Rotations per second.

For electrodes of other shapes than the rotating disc electrode, the solution of the problem cannot be taken to the calculation of the numerical coefficients. This is due to the fact that in these cases the hydrodynamic aspect of the phenomenon is unduly complicated. With the above-explained theory it is possible, however, to reduce in all cases the electrochemical problem to a hydrodynamic problem and thus to expose its physical meaning fully.

The relations derived in §3 of this chapter for the magnitude of the concentration polarization also applies to the case of electrolysis in a stirred liquid; it is merely necessary to substitute in it the correct expressions for the limit current. For the case of the rotating disc electrode the limit current is found from Eq. (85). Likewise the relations derived in §6 for the ohmic potential drop in the diffusion layer retain their validity. The ohmic potential drop outside the limits of the diffusion layer, where the composition of the solution does not change during electrolysis, can be found in the case of an electrode of simple geometrical shape from the current intensity and the electrolyte resistance.

In the derivation of the equations in §7-9 we have assumed that convective diffusion is not complicated by ion migration. In the case where the electric field in the solution affects the motion of the reacting charged particles (for example, in absence of a foreign electrolyte), the corresponding corrections must be introduced into the expressions for the limit current, as described in §5. However, in the case of a stirred liquid the quantitative calculation of the ion migration differs somewhat from the case of a quiescent liquid. Thus, when univalent cations are discharged in a stirred liquid, the migration does not cause doubling of the limit current (see Eq. (71)) but a smaller increase.

§10. NONSTATIONARY DIFFUSION EQUATION FOR THE FLAT ELECTRODE

In the preceding sections we have examined the phenomena which take place in stationary diffusion, i.e., in diffusion processes whose rate has already been established and does not change in time subsequently. Of interest is also an examination of the diffusion processes whose nature has not yet been established and whose rate varies with time. The study of these phenomena is of importance for two reasons. Firstly, in some cases we encounter in practice precisely such nonstationary processes. One very important case, the diffusion at the mercury drop electrode, will be discussed in greater detail later on. Secondly, when considering stationary diffusion processes, the assumption is made that a stationary state can be attained; this assumption requires proofs which we have omitted in the preceding discussions. Hence, without an examination of the nonstationary states, it is, generally speaking, not possible to obtain complete certainty of the correctness of the treatment of the stationary processes.

We ought to mention that the first approximate solution of the problem of nonstationary diffusion as applied to the electrochemical problem has been obtained by A.P. Sokolov (1890) [12].

Let us begin the examination of nonstationary diffusion with the simplest case of a flat electrode, immersed in a large volume of solution, which is not agitated, for example, a silver electrode in silver nitrate solution in presence of an excess of an indifferent electrolyte. This solution has the same composition at all points, i.e., the same concentration of the discharging ions. At a certain moment of time which we designate as $t = 0$, a considerable cathodic polarization is superposed on the electrode (by means of any auxiliary electrode immersed in the solution). If the polarization of the silver electrode is sufficiently large, the concentration of the silver ions at its surface drops instantly practically to zero in consequence of the process of cathodic discharge of the silver ions. At the same time begins the process of diffusion of the silver ions from the volume of the solution towards the electrode surface. The task is reduced to finding the distribution of the ion concentration in the solution at any moment of time. Knowing this concentration distribution, we can readily compute the diffusion current.

This diffusion problem has an analogy in a large number of other phenomena in physics, in particular, in the phenomena of thermal conductivity. The diffusion phenomenon in the case under consideration here corresponds entirely to the phenomenon of thermal conductivity in an infinitely large body in which the temperature initially was the same at all points and which then begins to cool by virtue of the fact that a plane boundary of the body assumes a lower temperature. The temperature distribution in this body at any moment of time and the heat flux in it are completely analogous to the concentration distribution and the diffusion flow in the solution near the flat electrode.

It is clear that the above diffusion problem leads to a nonstationary diffusion process. The initial ion concentration was the same at all points; after the switching on of the current this uniform distribution is upset. The concentration change is first limited to a region of the solution close to the electrode and then spreads to ever greater distances from this surface into the depth of the solution. At different moments of time after this disturbance has occurred, the concentration distribution will be different.

In order to give a quantitative solution of this problem one has to solve the diffusion equation corresponding to the above conditions.

If we designate the distance from the electrode surface in a direction perpendicular to the surface by x, then, as we have seen in §2, the differential diffusion equation has the form

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{86}$$

where t is the time elapsed since the initial moment of the process, and $c = c(x, t)$ is the concentration of the silver ions which is a function not only of the distance x but, in contrast to the cases of stationary diffusion, also of the time t. In this we make the assumption that the concentration distribution does not vary if we move along the surface, i.e., that the concentration at any moment of time is the same at all points which are at the same distance from the surface. We are justified in making this assumption if we limit consideration to an area of the electrode surface which is sufficiently far from the edges of the electrode. Mathematically this requirement is expressed by the condition that the distance x is small compared with the electrode dimensions; this condition is often formulated as a condition of an infinite electrode dimension.

According to the conditions of the problem it is required to find an expression for the ion concentration as a function of distance and time which would satisfy the diffusion equation (86). Moreover, the desired solution should satisfy the following boundary conditions, which follow from the nature of the problem itself. At the moment of time $t = 0$ the concentration at all points has the same, initial value, i.e.,

$$\text{for } t=0 \qquad c=c^0. \tag{87}$$

The second condition states that at any moment after the polarization current has been switched on, the ion concentration at actual electrode surface is zero, i.e.,

$$\text{for } x=0 \text{ and } t>0 \quad c=0. \tag{88}$$

The above differential equation with the boundary conditions (87) and (88) is well known in mathematic physics [13]. The solution of this equation has the form

$$c(x,t)=c^0\frac{2}{\sqrt{\pi}}\int\limits_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2}dy. \tag{89}$$

The solution thus obtained contains the definite integral $\int\limits_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2}dy$. The variable y in the integrand is an auxiliary mathematical quantity. Because a definite integral depends only on the magnitude of the lower and upper limits, this variable vanishes in the final solution. The numerical values of this integral for different values of the upper limit are given in special tables. If the upper limit becomes infinite, then, as we know, the integral assumes the value

$$\int_0^\infty e^{-y^2}dy = \frac{\sqrt{\pi}}{2}. \qquad (90)$$

Figure 52 represents the magnitude of this integral as a function of the value of the upper limit u; it is evident from this diagram that it varies from zero to $\sqrt{\pi}/2$.

By simple differentiation and substitution of the derivatives into the initial differential equation it is readily seen that the solution thus obtained really satisfies the problem set above and its boundary conditions.

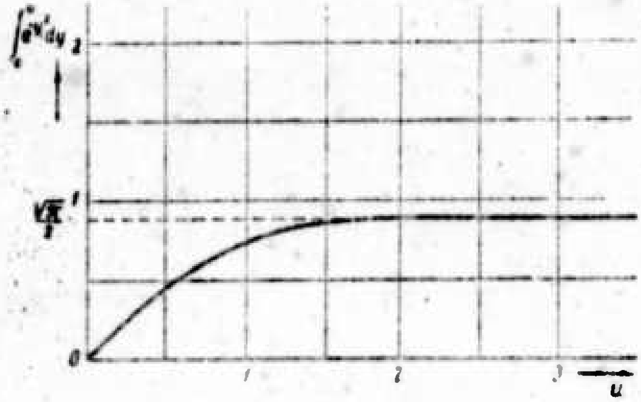

Fig. 52. Graphic representation of the function $f(u) = \int_0^u e^{-y^2}dy$

At the initial moment of time $t = 0$, and also at great distances from the electrode, i.e., at $x \to \infty$, the upper limit tends to infinity, i.e., the integral assumes the value $\sqrt{\pi}/2$ and the concentration of the initial value c^0 which also corresponds to the physical reasoning.

For the values $x = 0$ and $t > 0$ of the variables the upper limit of the integral vanishes and together with it naturally also the value of the integral itself; thus the concentration is zero. This corresponds to the boundary condition (88).

If we subject the expression (89) which we have obtained to an analysis, we find that it is proportional to the initial concentration c^0. It is easy to visualize that this ought to be so since all the quantities entering into the differential equation are linear with respect to the concentration; it follows that if we vary the initial concentration in any proportion, the concentrations at any other moment of time will vary in the same proportion.

The solution thus obtained has a typical peculiarity consisting in the fact that the variables which interest us, the distance x and the time t, enter into it not independently but only in the form of the relation $x/\sqrt{t}$, i.e., at the same value of this relation the concentration has the same value, independently of the values of x and t taken separately. Thus for two points in the solution, at a distance of x_1 and x_2 from the electrode surface, the concentration will be the same for any two intervals of time t_1 (at the point x_1) and t_2 (at the point x_2) which satisfy the condition $x_1 : x_2 = \sqrt{t_1} : \sqrt{t_2}$. The diffusion front thus advances within the solution a distance which is proportional not to time, but to the square root of the time. This is the case because in proportion to the impoverishment of the solution and the advance of the

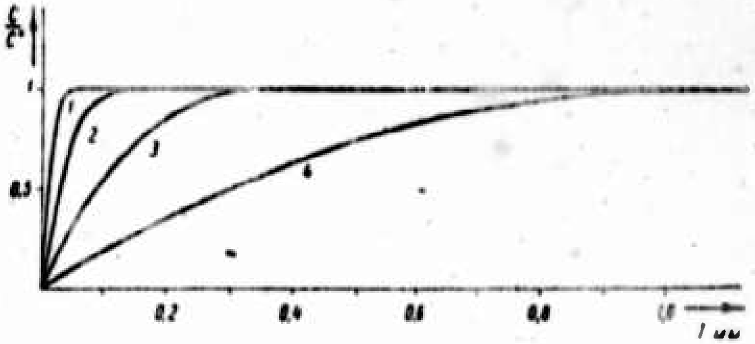

Fig. 53. Distribution of the concentration of the reacting substance near the surface of a flat electrode at different moments of time after the switching on of the current: 1) After 0.1 sec; 2) after 1 sec; 3) after 10 sec; 4) after 100 sec.

diffusion front into the depth of the solution the concentration gradient decreases and the diffusion is progressively slowed down.

Figure 53 gives the distribution pattern of the concentration as a function of the distance from the electrode surface at different moments of time after the switching on of the current. The concentrations are plotted on the ordinate axis in fractions of the initial concentration, i.e., the ratio c/c^0. The diffusion coefficient D is conventiontionally taken as being $1 \cdot 10^{-5}$ $cm^2 \cdot sec^{-1}$.

The distribution of the concentrations near the electrode at different moments of time after the switching on of the current can be found very conveniently experimentally by means of the interferometric method mentioned in §1, developed by A.G. Samartsev [2].

In order to calculate the diffusion flow, one must know the concentration gradient, i.e., the value $\partial c/\partial x$. Because we are interested in the number of ions arriving from the solution at the electrode surface, we must use the value of the derivative $\partial c/\partial x$ at $x = 0$.

The first derivative of the concentration with respect to distance is

$$\frac{\partial c}{\partial x} = \frac{c^0}{\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}} \qquad (91)$$

Hence

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c^0}{\sqrt{\pi D t}} \qquad (92)$$

and for the diffusion current expressed in electrical units, we find

$$i_d = \frac{nF\sqrt{D}c^0}{\sqrt{\pi t}}. \qquad (93)$$

As is evident from Eq. (93), the diffusion current is inversely proportional to the square root of the time. If the electrolysis process is continued for a long time, the current intensity can be brought down to as small values as desired; it follows that in this case a stationary state of the concentration polarization is not established.

At the initial moment of time at $t = 0$ the current density, according to Eq. (93), is infinitely large. Such a result of course has not physical meaning. It is obtained because of the simplification which we introduced when we considered that at the moment of switching on of the current the ion concentration at the actual electrode surface drops instantly from the initial value c^0 to zero. With this simplified assumption we obtain at the moment of time $t = 0$ a finite concentration difference at an infinitely small distance, i.e., an infinite gradient. In actual fact, however, the concentration at the electrode surface drops to zero not instantly, but within a certain, admittedly very short interval of time so that the impoverishment can extend to a certain distance into the depth of the solution.

The relation expressed by Eq. (93) has been experimentally confirmed in several works. Ye.M. Skobets and N.S. Kavetskiy [14] measured the variation of the density of the diffusion current on a solid electrode with time. In all cases they observed an abrupt current surge upon closing of the circuit, followed by a relatively slow current drop, which obeys the law

$$i \sim \frac{1}{\sqrt{t}}.$$

In the derivation of the above equations it was assumed that the ion concentration at the actual electrode surface is zero, i.e., that the limit value of the diffusion current is attained. In order to extend this solution to a case where the ion concentration at the surface is not zero but has a certain constant value (differing from the initial concentration), it is sufficient to replace everywhere in these solutions the initial concentration c^0 by the difference between the initial concentration and the concentration near the surface $c^0 - c^s$. The formula for the diffusion current, for example, is rewritten in the form

$$\text{for } t = 0 \quad c = c^0 \qquad (94)$$

i.e., the values of the current are modified compared with the limit values by a factor of $(c^0 - c^s)/c^0$.

§11. EQUATION OF NONSTATIONARY DIFFUSION TOWARDS A SPHERICAL ELECTRODE

The case which will be considered in the present section is very similar to the preceding one and differs from it only by the geometrical conditions, namely: instead of diffusion towards a flat electrode we shall examine diffusion towards an electrode with a spherical shape, immersed in an infinitely large volume of solution.

We designate the radius of the spherical electrode by r_0. Otherwise we retain all the assumptions made during the examination of the previous problem. At the moment of time $t = 0$ the ion concentration at all points of the solution is equal to the initial concentration; immediately after the switching on of the current the ion concentration near the electrode surface begins to decrease and retains its initial value only at a great distance from it.

In the study of processes taking place near a spherical surface and depending only on the distance from the center of the sphere and not on the choice of the direction in space, it is convenient to use a spherical coordinate system. It is obvious that in the problem formulated by us such spherical symmetry is present and that the concentrations and the concentration gradient is the same for all points of the solution at the same distance from the center of the spherical electrode (Fig. 54).

For this reason we can regard the concentration at any point of the solution and at any moment of time as a function of two variables:

the time t and the length of the radius vector r (i.e., the distance from the center of the sphere). The first boundary condition has the same form as in the preceding problem, i.e.,

$$i = \frac{nF\sqrt{D}}{\sqrt{\pi t}}(c^0 - c^s). \qquad (95)$$

The second boundary condition assumes a slightly different form because the electrode surface is no longer described in the Cartesian coordinate $x = 0$ but in the spherical coordinate $r = r_0$; hence

$$\text{for } r = r_0 \text{ and for } t > 0 \quad c = 0. \qquad (96)$$

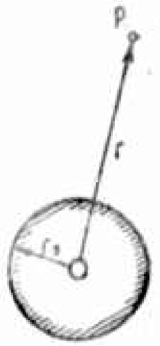

Fig. 54. r_0 is the radius of the spherical electrode; r the distance of a point P in the solution from the center of the spherical electrode.

When going over to a spherical coordinate system, a transformation of the original diffusion equation is necessary, which assumes the form

$$\frac{\partial c}{\partial t} = D\left[\frac{2}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right]. \qquad (97)$$

Equation (97) can be obtained from Eq. (86) by transformation of the coordinates from Cartesian to spherical; one can also derive Eq. (97) directly if we regard the diffusion process towards a spherical surface as analogous to that in the derivation of Eq. (86).*

The solution of the differential equation (97) at the above-mentioned boundary conditions has the form

$$c(r, t) = c^0 \frac{r_0}{r} \frac{2}{\sqrt{\pi}} \int_0^{\frac{r - r_0}{2\sqrt{Dt}}} e^{-y^2} dy + c^0\left(1 - \frac{r_0}{r}\right). \qquad (98)$$

This solution consists of two components of which the first is entirely analogous to the solution of the previous problem (Eq. (89)) with the only difference that the distance not from the plane surface but from the spherical surface figures in the upper boundary and that the coefficient in front of the integral contains an additional factor. The meaning of the second term of Eq. (98) will be clear from the following.

If we analyze the solution thus obtained it is at once apparent that for values of r tending to r_0, it is transformed into the solution of the previous problem for diffusion towards a flat electrode. Physically this means that at very close distances to the spherical surface it may be regarded as a flat electrode. In this the concept of close distance to the spherical surface naturally means a distance which is small compared with the radius of curvature. At distances which are not very small compared with the dimensions of the sphere, the diffusion phenomena will differ markedly from the pattern which is established at the flat electrode. The difference between the solution for the flat electrode and the spherical electrode is particularly clear cut if the corresponding values of the diffusion current are compared. By differentiating Eq. (98) with respect to r, we find

$$\frac{\partial c}{\partial r} = -\frac{2r_0c^0}{r\sqrt{\pi}} \cdot \int_0^{\frac{r-r_0}{2\sqrt{Dt}}} e^{-y^2}dy + \frac{2r_0c^0}{r\sqrt{\pi}} \cdot \frac{1}{2\sqrt{Dt}} e^{-\frac{(r-r_0)^2}{4Dt}} + \frac{cr_0}{r^2}. \quad (99)$$

At $r = r_0$ this derivative assumes the value

$$\left(\frac{\partial c}{\partial r}\right)_{r=r_0} = \frac{c^0}{\sqrt{\pi Dt}} + \frac{c^0}{r}. \quad (99a)$$

Hence the diffusion current (in electrical units) is equal to

$$i = nFDc^0\left\{\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r_0}\right\}. \quad (100)$$

This expression also consists of two addends, the first addend corresponding exactly to the expression for the diffusion current towards a flat surface (see Eq. (93)). This addend decreases in inverse proportion to the square root of the time. The second addend for the current is a constant and is independent of time.

The relation between the two addends of Eq. (100) depends on the value of the time t. At the initial moments of time when t is small, the first addend considerably exceeds the second one and the diffusion to the surface of the drop takes place in accordance with the same laws as those pertaining to diffusion towards a flat surface. When the values of t increase the first term decreases and the relative proportion of the current, due to the second term, increases. With further increase in the time the current does not tend to zero as in the case of diffusion towards a flat surface but to the constant value $i = nFDc^0/r_0$, i.e., the diffusion goes over from the nonstationary to the stationary state.

It can be shown that the establishment of a stationary diffusion state with a diffusion current different from zero is not connected with the spherical shape of the electrode with with its finite linear dimensions. Had we not assumed an infinite plane but a disc in the preceding section or in general any body with certain dimensions, which is placed into an infinite uniform medium, we would also have observed a gradual transition from nonstationary diffusion to the stationary state. The magnitude of the stationary current under these conditions depends on the linear dimensions of the surface under consideration.

It would be of interest to calculate for a spherical electrode with certain dimensions the time interval after which the diffusion approximates the stationary state. At the moment of time $t_k = r_0^2/\pi D$ the values of the stationary and nonstationary diffusion currents (the first and second addends of Eq. (100)) are equal; this moment can thus serve as a certain characteristic for the transition to the stationary diffusion state. The impoverishment of the solution up to the moment t is considerable at distances r for which $(r - r_0)/2\sqrt{Dt}$ is not yet large.* It follows that within the time t_k the diffusion front has penetrated into the depth of the solution to a distance of the order of the radius of the sphere. For a spherical electrode with radius 1 mm and with normal values of the diffusion coefficient the time t_k is about 300 sec. Thus, during the first few tens of seconds after the switching on of the current the thickness of the diffusion layer is still small compared with the radius of the sphere, and the laws applying to diffusion toward a plane electrode can be applied to the diffusion towards a sphere. We shall make use of this consequence in the following.

The establishment of the regularities observed with an electrode of spherical shape permit us to pass on to the examination of an important and widely occurring object, the mercury drop electrode, which is widely used for various analytical and electrochemical measurements (see Chapter 2).

§12. OTHER CASES OF NONSTATIONARY DIFFUSION. POLARIZATION OF AN ELECTRODE BY AN ALTERNATING CURRENT

In the preceding sections we have considered one of the cases of nonstationary diffusion in which a constant concentration of the potential-determining ions is established at the electrode surface (in particular, zero concentration) and in which, owing to the advance of the diffusion front into the depth of the solution the current intensity decreases gradually.

Other cases of nonstationary concentration polarization are also possible in which by means of suitable external devices different conditions are maintained at the electrode surface. For example, one can polarize the electrode with an absolutely constant current intensity. The electrode potential in this case will not remain constant: in proportion to the advance of the diffusion front into the depth of the solution the concentration of the reacting ions at the electrode surface should decrease in order to retain a constant concentration gradient near the electrode. It is easily imagined that the passage of a current with a certain intensity under these conditions is possible only for a certain time interval, namely until the concentration of the discharging ions at the electrode surface has dropped to zero* [15].

The case of the polarization of an electrode with an alternating current deserves attention. Periodic current pulses in opposite directions cause a periodic decrease and increase in the concentration of the potential-determining ions and at the same time a periodic variation of the electrode potential. As will be evident from the following, when an electrode is polarized with an alternating current, the potential shift caused by the variation of the ion concentration is considerably less than with prolonged polarization with a direct current; this circumstance is used to advantage for the study of electrochemical phenomena in which it is desirable to exclude the concentration polarization or to reduce it as far as possible [16].

Let us consider the derivation of the equations for nonstationary diffusion with a.c. polarization of the electrode using two simplifying assumptions. Firstly, we assume that the intensity of the alternating current is not very great so that the maximum fluctuations of the electrode potential are small compared with the quantity RT/nF. Secondly, we assume at first that the quantity of electricity consumed for charging the double layer at the electrode surface is small compared with the quantity consumed for the alteration of the ion concentration, i.e., for the electrical process taking place at the electrode surface. The last assumption is exactly the reverse of that made in the discussion of the conditions for carrying out capacitance measurements on the double layer with an alternating current (see §4 of the Introduction).

The differential diffusion equation derived in §2

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (49)$$

also remains in force in the above-considered case of the polarization of a flat electrode with an alternating current. At a large distance from the electrode the concentration of the potential-determining ions is invariant, being equal to the initial concentration,

$$\text{for} \quad x \to \infty \quad c = c^0. \qquad (104)$$

If the electrode is polarized with an alternating current, the boundary condition at the electrode surface is altered.

According to the second of our assumptions, the total magnitude of the charges arriving at the electrode at any given moment of time is equal to the number of charges which participate in the electrochemical reaction, i.e., the diffusion current is equal to the density of the electric current passing through the electrode.

For a sinusoidal alternating current, i.e., a current varying in time in accordance with the law

$$i = i_0 \sin \omega t$$

(i_0 is the amplitude of the current density of the a.c. current; ω is the frequency of the alternating current), we can write

$$i_0 \sin \omega t = nFD\left(\frac{\partial c}{\partial x}\right)_{x=0}. \qquad (105)$$

From this we find that the concentration gradient at the electrode surface

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{i_0}{nFD}\sin \omega t \qquad (105a)$$

varies periodically in accordance with the same law as the current density.

The solution of the differential equation (49) for the boundary conditions (104) and (105a) has the form:

$$c = c^0 - \frac{i_0}{nF\sqrt{\omega D}}\, e^{-\frac{x}{\sqrt{2D/\omega}}} \cos\left[\omega t - \frac{x}{\sqrt{2D/\omega}} + \frac{\pi}{4}\right]. \qquad (106)$$

According to Eq. (106), when an alternating current passes through the solution, periodic concentration fluctuations occur in it with the same frequency, which advance from the electrode surface into the depth of the solution with an amplitude which decreases in proportion to the quantity $e^{x/(\sqrt{2D/\omega})}$, i.e., the more rapidly, the greater the frequency of the alternating current.

The variation of the electrode potential is connected with the variation of the concentration of the potential-determining ions near the electrode surface (i.e., at the point $x = 0$) by the basic equation of concentration polarization

$$\Delta\varphi = \frac{RT}{nF}\ln\frac{c}{c^0} = \frac{RT}{nF}\ln\left(1 + \frac{c - c^0}{c^0}\right). \qquad (107)$$

If the electrode is not strongly polarized, when $\Delta\varphi < RT/nF$ (first assumption) and $(c - c^0)/c^0$ is small compared with unity, $\ln(1 + (c - c^0)/c^0)$ can be replaced with sufficient approximation by $(c - c^0)/c^0$:

$$\Delta\varphi = \frac{RT}{nF}\,\frac{c - c^0}{c^0}. \qquad (107a)$$

Substituting the value of c at $x = 0$ from Eq. (106) we find finally

$$\Delta\varphi = i_0\,\frac{RT}{n^2F^2c^0\sqrt{D\omega}}\sin\left(\omega t - \frac{\pi}{4}\right) \qquad (108)$$

It can be seen from Eqs. (106) and (108) that during the passage of a sinusoidal alternating through the electrode, a phase shift is observed between the current, on the one hand, and the concentration and potential, on the other, namely the potential lags 45° behind the current.

The passage of an alternating current through an electrode corresponding to concentration polarization thus can be compared with the passage of an alternating current through an electrical circuit consisting of series or parallel connected resistances and capacitances; in this case, as we know, a phase shift between current and potential is also observed, varying from 0° for the case of resistance only to 90! in the case of capacitance only. The equation (108) was worked out by Krueger [17].

It is interesting to compare the amplitude of the variable concentration polarization $\Delta\varphi_{\sim} = i_0 \frac{RT}{n^2F^2c^0\sqrt{D\omega}}$ arising at a density of the alternating current i_0, with the concentration polarization $\Delta\varphi_{=}$ in presence of a direct current of the same density. Under stationary conditions

$$\Delta\varphi_{=} = -\frac{RT}{nF}\frac{i_0}{i_d} \qquad \text{(see Eq. (58a))},$$

from which we find, using (82a),

$$\left|\frac{\Delta\varphi_{\sim}}{\Delta\varphi_{=}}\right| = \frac{i_d}{nFc^0\sqrt{D\omega}} = \frac{\sqrt{D}}{\delta\sqrt{\omega}}. \tag{109}$$

Assuming $D = 10^{-5}$ cm$^2\cdot$sec^{-1} and $\delta = 0.003$, we find that at a frequency $\omega = 10{,}000$ c $\frac{\Delta\varphi_{\sim}}{\Delta\varphi_{=}} \approx 0{,}01$, i.e., the polarization caused by the alternating current.is approximately one hundred times less than the polarization with direct current. Such a marked decrease in the magnitude of the potential shift through the use of alternating current is explained by the fact that if the current direction is periodically reversed, the diffusion front cannot move away from the electrode surface to a great distance. This means that a state is all the time maintained at the electrode surface which is analogous to the state at the first moment after the switching on of the direct current, when the concentration polarization is as yet slight.

As mentioned previously, during the derivation of Eq. (108) we did not take into account that the electrode has a certain double layer capacitance C and that part of the passing current is consumed for the variation of the charge density in the double layer. If the converse assumption is made that no electrochemical reaction takes place at the electrode surface (i.e., that the electrode possesses ideal polarizability and behaves like a capacitor without leakage), the passage of a sinusoidal alternating current causes a potential fluctuation, which, as we know from the physics course, is expressed by the equation

$$\Delta\varphi = -\frac{i_0}{\omega C}\cos\omega t. \qquad (110)$$

It is not difficult to derive relations for the case in which during the passage of alternating current both processes take place simultaneously: the charging of the double layer and the variation of the concentration of the potential-determining ions as a result of the electrode reaction. The corresponding equations are fairly cumbersome, and we shall not present them here. However, it is easy to arrive at a conclusion concerning the relative importance of the two effects with regard to their order of magnitude by comparing the equations (108) and (110). Indeed, the ratio of the amplitudes of the alternating current which give equal amplitudes Δφ, respectively, for the case of an electrode which behaves like a capacitor with the capacitance $C(i_0)_{\text{emk}}$ and for an electrode at the surface of which the concentration variation $(i_0)_{\text{konts}}$ takes place during the passage of an alternating current, is equal to

$$(i_0)_{\text{емк.}} : (i_0)_{\text{конц.}} = \omega C : \frac{n^2F^2c^0\sqrt{D\omega}}{RT} = \frac{RT}{n^2F^2\sqrt{D}} \cdot \frac{\sqrt{\omega}C}{c^0}. \qquad (111)$$

It can be seen that this ratio increases in proportion to the increase in ω and the decrease in c^0. Thus the behavior of the electrode in the alternating current approximates the behavior of the double layer capacitor the more, the higher the frequency of the oscillations and the lower the concentration of the potential-determining ions, and, conversely, the double layer capacitance can be neglected with more justification, the lower the frequency of the oscillations and the larger the value of the concentration c^0.

These results can also be formulated in the following way. An electrode at the surface of which variations of the concentration of the potential-determining ions take place during the passage of a current behaves during measurements with alternating current as if it had a certain capacitance in excess of that due to the double layer and a certain conductivity, which are the greater, the higher the concentration of the potential-determining ions. The magnitude of this additional capacitance decreases, however, with increase in the frequency of the oscillations, being inversely proportional to $\sqrt{\omega}$.

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107	In the general case when the electrochemical process does not consist in a discharge of metal ions, the quantity n designates the number of electrons per molecule of reactant, disappearing (or liberated) during tne electrode process.
120	In the case of an n-valent ion the quantity F in Eq. (68) must be replaced by nF.

122 This calculation is incomplete because it does not take account of the fact that in consequence of a difference in the ion mobilities a potential difference exists in a liquid column with a concentration gradient even without the passage of current. In this case, however, we are interested only in the order of magnitude of the quantity $\varphi_l - \varphi_0$.

125 The precise position of the immobile liquid layer (from the point of view of molecular dimensions) which we have analyzed in §2 of the Introduction is normally of no significance when the motion of a mechanically stirred liquid relative to a solid is considered.

131 In this connection the question may arise as to the validity of using Eq. (82) which has been derived for the case of a quiescent boundary layer. However, as calculation shows, the concentration distribution in a moving fluid near the electrode surface is almost linear which allows us to use Eq. (82) with a sufficient degree of approximation.

145 Indeed, the difference between the diffusion currents which penetrate a spherical layer bounded by the radii r and $r + dr$ and which emerge from it, is

$$\frac{\partial}{\partial r}\left(4\pi r^2 D \frac{\partial c}{\partial r}\right) dr,$$

and the volume of this layer is $4\pi r^2 dr$, hence

$$\frac{\partial c}{\partial t} = \frac{1}{4\pi r^2}\frac{\partial}{\partial r}\left(4\pi r^2 D \frac{\partial c}{\partial r}\right) = D\left[\frac{2}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right].$$

147 Indeed, as follows from Eq. (98), for large values of $(r - r_0)/2\sqrt{Dt}$ the magnitude of $c(r, t)$ coincides with c^0, i.e., the composition of the solution remains unchanged.

149 The above-discussed boundary condition (88) must be replaced in this case by the following:

$$\text{for } x = 0 \text{ и } t > 0 \quad D\frac{\partial c}{\partial x} = \frac{i}{nF}, \qquad (101)$$

where i is the constant density of the applied current. Under these boundary conditions the concentration as a function of x and t is expressed by the relation

$$c(x, t) = c^0 - \frac{2i}{nF}\sqrt{\frac{t}{\pi D}}\, e^{-\frac{x^2}{4Dt}} + \frac{2ix}{nDF\sqrt{\pi}} \int\limits_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-y^2}\, dy. \qquad (102)$$

It follows that at $x = 0$, i.e., at the electrode surface,

$$c = c^0 - \frac{2i}{nF}\sqrt{\frac{t}{\pi D}}. \qquad (102a)$$

The time t_C, after the expiry of which the concentration c at the electrode surface vanishes and a further passage of a current with the density i is consequently impossible, as follows from the above-presented expression for c, is

$$t_0 = \frac{\pi D c_0^2 n^2 F^2}{4 i^2}. \qquad (103)$$

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[Transliterated Symbols]

121 ом = om = omicheskiy = ohmic

128 гр = gr = granichnyy [sloy] = boundary [layer]

153 емк = emk = emkost' = capacitance

конц = konts = kontsentratsiya = concentration

Chapter 2

POLAROGRAPHY

§1. PRINCIPLE OF THE POLAROGRAPHIC METHOD

The phenomena of concentration polarization described in the previous chapter are encountered in various cases of electrolysis or the operation of chemical current sources and leave their imprint on the current-voltage curves which are obtained. A descriptive example of the application of the above concepts to a practically important case of electrolysis is the polarographic method of chemical analysis, whose theory is based to a large degree on the laws of diffusion kinetics.

The polarographic method of analysis which has been proposed by the Czech scientist Heyrovsky [1] is based on the electrolysis of test solutions in an electrolytic cell whose cathode is a mercury drop electrode. The current intensity versus applied voltage curves thus obtained make it possible to determine the nature as well as concentration of the substances which are reduced at the cathode, in the solution. Solutions containing substances capable of electrical oxidation can also be investigated by polarography; in this case the mercury drop electrode serves as the anode.

The mercury drop electrode device (Fig. 55) consists of a glass capillary from which mercury flows out slowly under the pressure of the mercury column. Mercury drops are formed at the tip of the capillary which break away from the capillary at equal time intervals of several seconds and drop to the bottom of the vessel. Up to the moment of breakaway, the growing mercury drop hanging on the end of the capillary serves as the electrode.

By means of the external current source *B* and the voltage divider *P* one can impose any voltage on the galvanic circuits, consisting of the drop electrode *K* and the auxiliary electrode *A*. A certain current then flows through the system which is measured by means of the sensitive galvanometer *G*.

The application of an external voltage *E* on the galvanic cell generally causes a variation of the potentials of both electrodes and, as a result of the application of the current, the appearance of an ohmic voltage drop in the solution. The connection between these quantities is expressed by the relation

$$E = \varphi_A - \varphi_K + IR,$$

where the anode and cathode potentials φ_A and φ_K are a function of the current density. As a rule, either a nonpolarizable calomel electrode or a mercury electrode with large surface on the bottom of the vessel which is only slightly polarized by the passage of a current with relatively low current density is used as auxiliary electrode in polarographic measurements. Hence, provided that the solution contains a sufficient excess of an indifferent electrolyte, the quantity *IR* and the

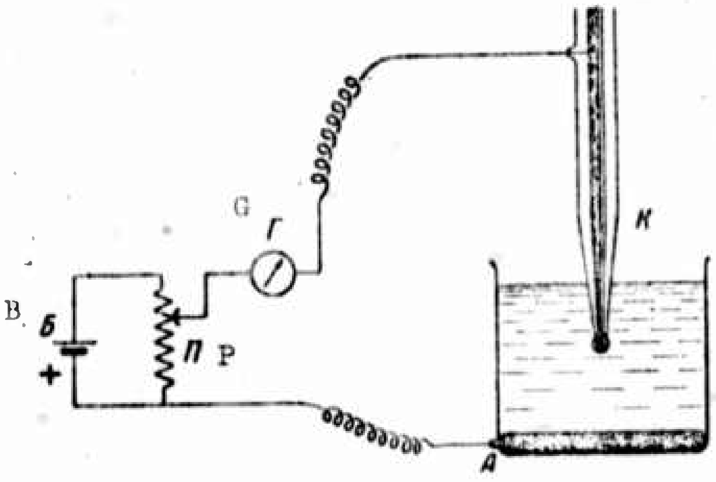


Fig. 55. Scheme of the polarographic apparatus: *K*) Capillary with hanging mercury drop; *A*) auxiliary electrode; *B*) current source; *P*) potentiometer; *G*) mirror galvanometer.

variation of φ_A can be neglected, i.e., it may be assumed that practically the entire applied voltage is used for the variation of the potential $\Delta E = -\Delta\varphi_K$ of the drop electrode. If the last condition is not fulfilled, the ohmic potential drop in the solution must also be taken into account.

By means of a special device, the polarograph, an automatic continuous increase in the applied voltage with simultaneous photographic recording of the current-voltage curves is possible. These automatically recorded curves are termed polarograms.

§2. MAGNITUDE OF THE DIFFUSION CURRENT AT THE DROP ELECTRODE

Certain electrode reactions take place at the surface during the polarization of the drop electrode. If, for example, the solution contains zinc ions in low concentration, then at a certain shift of the potential of the drop electrode in the direction of negative values the zinc ions begin to be discharged with formation of zinc amalgam at the surface of the mercury drop. The more negative the potential is made, the concentration of the zinc ions near the surface begins to decrease, and the phenomenon of concentration polarization sets in. With further increase of cathodic polarization the concentration of the zinc ions near the electrode surface drops practically to zero, and the current attains its limit value.

In order to calculate the limit diffusion current we must analyze the phenomena of diffusion towards the drop electrode. The diffusion pattern in this case is considerably more complex than for the immobile spherical electrode, discussed in §11 of the preceding chapter because the mercury drop grows continually as long as it does not break away from the capillary and is replaced by a new drop. Here and further on in this chapter we shall limit consideration to the case in which the solution contains an excess of an impurity electrolyte which does not participate in the reaction* (the so-called background), i.e., we shall take into account only the diffusion proper and not the ion migration under the influence of the electric current.

We shall also refrain here from explaining completely the theory of diffusion towards a sphere with continuously increasing radius but shall limit consideration to a simplified, not entirely rigorous development of the consequences of the theory. For this purpose we assume that the diffusion towards the growing drop takes place in accordance with the same law as diffusion towards a quiescent sphere, with only the difference that the total electrode surface increases with time. In other words, we do not take into account the fact that during the growth of the drop its surface does not only increase but also sort of moves towards the diffusion current directed towards it, thus continuously enlarging the diffusion layer.

The maximum size of the mercury drops during polarographic measurement (the size at the moment of breakaway of the drop) is of the order of one millimeter; the period of dropping, i.e., the "life" time of an individual drop varies, as a rule, between 2 to 6 sec. As follows from the calculation given in §11 of Chapter 1, the diffusion towards the spherical electrode is not yet stationary under these conditions. In other words, the impoverishment of the solution around the growing drop during the observation cannot extend to distances commensurable with the drop dimension; the observation time on an individual drop in turn is limited by the fact that the drop periodically breaks away and that the whole pattern of growth of the drop and diffusion starts all over again with every new drop.

The thickness of the diffusion layer, generally speaking, can be estimated by independent optical methods because the variation of the concentration of one of the components of the solution causes a variation of its index of refraction. The best known method is the so-called schlieren method by means of which the layer of the solution with a slightly modified refractive index is made visible on a photograph in analogy to photographing, for example, currents of warm or cold air. Such photographs show that around the drop electrode there is a film of impoverished solution, whose thickness is really small compared with the radius of the drop. It follows from this that during the lifetime of an individual drop the diffusion cannot go over from the nonstationary to a stationary regime.

The density of the diffusion current moving towards the drop under these conditions, thus, according to Formula (93) is

$$i = \frac{nFc^0\sqrt{D}}{\sqrt{\pi t}},$$

where t is the time elapsed from the initial moment of formation of the drop (i.e., from the moment of breakaway of the preceding drop).

The current intensity at the moment of time t is

$$I = 4\pi r_0^2 i = 4\pi r_0^2 \frac{nFc^0\sqrt{D}}{\sqrt{\pi t}}, \qquad (112)$$

where r_0 is the drop radius, depending on the time t.

The dependence of r_0 on time is determined by the law of growth of the drop. As a rule, the mercury drop electrode is designed in such a way that the mercury flows through a long, narrow capillary. The rate of flow of the mercury depends in this case mainly on the height of the mercury column and the internal friction of the mercury in the capillary; by way of first approximation it will be constant and independent of time and the polarization of the drop.* It follows from this that the volume of the drop is proportional to the time, elapsed since the initial moment of its formation.

If we designate the rate of flow of the mercury (in grams per second) by m, the weight of a single drop at the time t is

$$Q_t = \frac{4\pi}{3} r_0^3 d = mt, \tag{113}$$

where d is the density of mercury (d = 13.55 g/cm^3) at room temperature). From this follows the expression for the drop radius

$$r_0 = \left(\frac{3mt}{4\pi d}\right)^{1/3}. \tag{114}$$

By substituting the expression for the drop radius thus obtained in Formula (112), we obtain for the current density

$$I = 4\sqrt{\pi}\left(\frac{3}{4\pi d}\right)^{2/3} nFc^0 D^{1/2} m^{2/3} t^{1/6}. \tag{115}$$

As pointed out previously, the derivation of Formula (115) is not rigorous because the movement of the surface of the mercury drop in proportion to its growth is not taken into account in its derivation. Accurate diffusion theory [2] results in an analogous formula which differs from the above one only by the numerical factor $\sqrt{7/3}$, i.e., taking into account the movement of the surface of the growing mercury drop leads to an increase of the diffusion current of $\sqrt{7/3}$ = 1.53 times:

$$I = 4\sqrt{\frac{7\pi}{3}}\left(\frac{3}{4\pi d}\right)^{2/3} nFc^0 D^{1/2} m^{2/3} t^{1/6} \tag{116}$$

or, combining all the numerical coefficients (including also the density of mercury)

$$I = 0{,}732\, nFc^0 D^{1/2} m^{2/3} t^{1/6}. \tag{116a}$$

It follows from Formula (116) that the current intensity increases with the growth of the drop proportionally to the 6*th* root of the time. This slightly unusual dependence of the current intensity increases with the growth of the drop proportionally to the 6*th* root of the time. This slightly unusual dependence of the current intensity on time is a consequence of the superposition of two effects: on the one hand, the current increases because of the surface increase which is proportional to $t^{2/3}$ and on the other hand, the current density is inversely proportional to the square root of the time because the diffusion is nonstationary. As a result of the combination of the action of these two factors the proportionality $I \sim t^{1/6}$ results.

This relationship can be verified by recording by means of a measurement device, which responds quickly to variations of current intensity (for example, by means of a short-period galvanometer or oscillograph) the current intensities at different moments of the lifetime and growth of the drop. The functional relationship $I \sim t^{1/6}$ corresponds to a very steep parabola as shown in Fig. 56. The current intensity increases suddenly during the initial moments of the lifetime of the drop and then the increase in the current intensity slows down markedly. The experiment actually confirms this relationship.

When the mercury drop electrode is used in practice it is not convenient to use the formula for the diffusion current in the above form

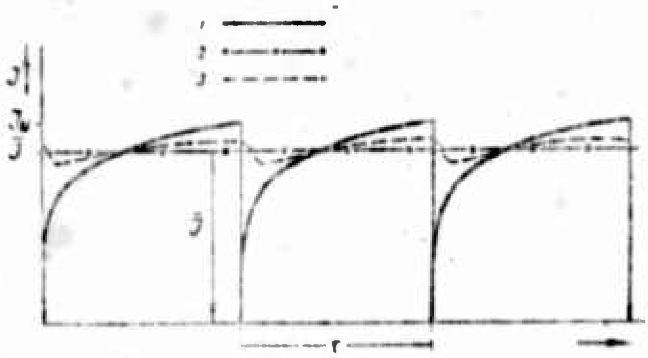


Fig. 56. Variation of the diffusion current of the drop electrode with the time t: 1) True current (I_m = maximum value); 2) mean current $\bar{I}$; 3) current recorded by the galvanometer.

(Eq. 116a) because in this case it would be necessary to follow all the variations with fast-reacting measurement devices which are relatively difficult to handle. On the contrary, galvanometers with a fairly large period of natural oscillation are normally used which follows variations of the current intensity only slowly and thus indicate only a certain average current intensity during the lifetime of the drop.

If we designate the life time of an individual drop by τ, the mean current $\bar{I}_d$ can be calculated in the following manner:

$$\bar{I}_d = \frac{1}{\tau}\int_0^{\tau} I_d\,dt = \frac{6}{7}\cdot 4\sqrt{\frac{7\pi}{3}}\left(\frac{3}{4\pi d}\right)^{2/3} nFc^0D^{1/2}m^{2/3}\tau^{1/6} = \qquad (117)$$
$$= 0{,}627\,nFc^0D^{1/2}m^{2/3}\tau^{1/6}$$

It follows from Formula (117) that the mean current during the lifetime of the drop is 6/7 of the current flowing through the drop at the moment of breakaway.

In reality, as a rule, the averaging is not complete; thus, when the galvanometer readings are recorded photographically (during work with an automatic polarograph), certain fluctuations of the current around the average are observed. It is essential that the magnitude of these fluctuations is small compared with the total current intensity because otherwise the results of the recording cannot be used for the determination of the current intensity. The current recorded by the galvanometer in Fig. 56 is shown by a dotted line.

The equations (116) and (117) are termed Ilkovic-Rideal-McGillavry equations [2]* in the polarographic literature.

It follows from Eq. (117) that the mean maximum diffusion current is proportional to the volume concentration of the reacting substance $\bar{I}_d \sim c^0$. The proportionality coefficient $\kappa = 0.627\ n\ FD^{1/2}m^{2/3}\tau^{1/6}$ depends on several quantities which characterize the nature of the reacting particle (n and D) and the measurement device used (m and τ). The latter quantities depend on the shape, length and diameter of the capillary and also on the height of the mercury column. As follows the above presented theory and is also confirmed by the experimental data, the ratio $\kappa/m^{2/3}\tau^{1/6}$ for a given substance should be constant and independent of the characteristics of the capillary which is used.

A specific feature of the mercury drop electrode is a certain dependence of the limit diffusion current on it on the electrode potential. This relationship is due to the inconstancy of the dripping period τ. The lifetime of an individual mercury drop is proportional in first approximation to the interfacial tension of the mercury. In fact, the breakaway of the mercury drop takes place at the moment when the weight of the hanging drop ($Q = m\tau$) becomes equal to the holding power. The latter is equal in first approximation to $F_\sigma = \sigma \cdot 2\pi r$ (where r is the internal diameter of the capillary at the point where the hanging drop is attached to it).* From this follows for the dropping period

$$\tau = \frac{2\pi r\sigma}{m} \tag{118}$$

During variation of the drop electrode potential the dropping period should vary in accordance with a curve analogous to the electrocapillarity curve of mercury (see §5 of the introduction). The limit diffusion current also varies in analogy with this curve; however, because the current $\bar{I}_d$ is proportional to $\tau^{1/6}$, the variation of the limit diffusion current with potential is much less than the variation of τ with potential. Whereas, for example, in the region of the zero charge point (i.e., in the usual solutions at a potential of −0.5 v according to the n.k.e.) the dropping period is 5 seconds, it is about 3 seconds at a potential of −1.7 v. Correspondingly the limit diffusion current at −1.7 v is approximately $(3/5)^{1/6}$ or 0.92 of the limit diffusion current at a potential of −0.5 v; thus, as a result of a potential shift by 1.2 v, the limit diffusion current is reduced by 8%. In some cases when considering the limit current in narrower potential ranges one can neglect this slight dependence of $\bar{I}_d$ on the potential.

Equation (117) can be applied with success to the determination of the diffusion coefficient of the reacting substance from the limit current, obtained in a solution of accurately known concentration. This method is not very precise but is characterized by simplicity. In particular, the dependence of the diffusion coefficient of the reacting substance on the concentration of the foreign electrolyte in the solution can be readily determined by means of it [4].

§3. SHAPE OF THE POLAROGRAPHIC CURVES

All expressions for the diffusion current towards the drop electrode, derived in the preceding section, referred to the case of the limit current when the concentration of the reacting substances at the electrode surface is zero. If the concentration at the electrode surface has the value c^{ε} which differs from zero, the current, as in the earlier discussed cases, varies by a factor of $(c^0 - c^{\varepsilon})/c^0$. The expression for the mean diffusion current towards the drop electrode assumes the following form:

$$\bar{I} = \varkappa (c^0 - c^s) = 0{,}627 nF (c^0 - c^s) D^{1/2} m^{2/3} \tau^{1/6}. \qquad (119)$$

If the relation between electrode potential and the concentration of the reacting substances and those obtained as a result of the electrochemical reaction is known, an equation can be derived by means of (119) which gives the relation between the electrode potential and the intensity of the polarizing current, i.e., an analytical expression for the polarographic curve.

If metal ions are present in the solution, an amalgam forms after their discharge at the surface of the drop electrode (of course, only on condition that this metal is soluble in mercury). In this case the concentration polarization phenomena at the drop electrode do not differ in any way from the pattern described in §4 of Chapter 1 for the amalgam electrode. The potential of the amalgam electrode is expressed by the formula

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{c_{\text{и}}^{s}}{c_{\text{м}}^{s}}. \qquad (120)$$

The concentration of the reacting ions near the surface is connected with their volume concentration by the relation

$$c_{\text{и}}^{s} = c_{\text{и}}^{0}\left(1 - \frac{\bar{I}}{\bar{I}_d}\right) = \frac{1}{\varkappa_{\text{и}}}(\bar{I}_d - \bar{I}), \qquad (121)$$

where the limit diffusion current is determined by Eq. (117).

The diffusion current within the mercury phase which results in a transfer of the dissolved metal from the surface into the volume of the mercury drop is proportional to the concentration of the metal at the amalgam surface. If we apply the same arguments to the process of diffusion of the metal within the mercury drop as to the diffusion of the ions towards the surface of the drop, it can be shown that the intensity of this diffusion current is defined by an equation which is identical with Eq. (117):

$$\bar{I} = 0{,}627 nF D_{\text{м}}^{1/2} m^{2/3} \tau^{1/6} c_{\text{м}}^{s} = \varkappa_{\text{м}} c_{\text{м}}^{s}, \qquad (122)$$

except that the values of D_M and c_M relate to the atoms of the metal dissolved in the mercury.

By substituting (121) and (122) into the equation for the potential (120) we obtain the previously derived equation for the curve of the concentration polarization at the mercury drop electrode

$$\varphi = \varphi_{1/2} + \frac{RT}{nF} \ln \frac{\bar{I}_d - \bar{I}}{\bar{I}}, \qquad (123)$$

or

$$\bar{I} = \frac{I_d}{1 + e^{\frac{nF}{RT}(\varphi - \varphi_{1/2})}}, \qquad (123a)$$

where

$$\varphi_{1/2} = \varphi^0 + \frac{RT}{nF} \ln \frac{\varkappa_{\text{м}}}{\varkappa_{\text{и}}} = \varphi^0 + \frac{RT}{nF} \ln \frac{D_{\text{м}}^{1/2}}{D_{\text{и}}^{1/2}}. \qquad (124)$$

As has been shown earlier, Eq. (123a) corresponds to a curve with a characteristic hump which is often termed polarographic wave.

For small values of the current intensity (i.e., when $\overline{I} \ll \overline{I}_d$) at relatively positive values of the potential, the one in the denominator of the expression (123a) can be neglected:

$$\overline{I} = \text{const} \cdot e^{-\frac{nF\varphi}{RT}}, \qquad (125)$$

i.e., the current intensity increases exponentially if the potential is shifted to the negative side. With further intensification of the cathodic polarization the polarographic curve deviates increasingly from exponential and approaches the limit current intensity asymptotically.

If not metal ions, forming an amalgam, but other substances, capable of being reduced at the mercury cathode, are present in the solution, the shape of the polarization curves in many cases coincides nonetheless with the shape of the curve which corresponds to the discharge of metal ions. As an example let us consider one more case in which the initial substances as well as the reaction products are dissolved in the electrolyte (redox reactions of dissolved substances). To these reactions belong, for example, the reactions of reduction of univalent metal ions to ions of lower valency (for example, $Cr^{+++} + e \rightarrow Cr^{++}$) and, the reactions of reduction of a number of organic substances (for example, of quinone to hydroquinone $C_6H_4O_2 + 2H^+ + 2e \rightarrow C_6H_4(OH)_2$), etc.

If the redox reaction is reversible, i.e., if forms of polarization other than the concentration polarization are not observed, and the electrode remains in equilibrium with regard to the composition of the layer of solution at the electrode, the electrode potential at any moment is expressed by a thermodynamic equation, which, for example, for the reaction of the reduction of quinone (kh) to hydroquinone (gkh) assumes the form

$$\varphi = \varphi^0 + \frac{RT}{2F} \ln \frac{c^s_{\text{х}} (c^s_{\text{H}^+})^2}{c^s_{\text{гх}}}. \qquad (126)$$

In the general case, if the electrochemical reaction takes place with participation of hydrogen ions the concentration of the latter around the electrode differs from their volume concentration in the same way as that of the other reacting substances. Frequently, however, when reactions with organic substances are studied, the measurements are carried out in buffer solutions with a fairly large excess of buffer components compared with the concentration of the reacting substances. In these cases the concentration of the hydrogen ions near the surface varies hardly at all during the passage of current and can with sufficient accuracy be equated with the volume concentration $c^{s}_{H^+} \approx c^{0}_{H^+}$. This simplifies considerably the form of the equation for the polarographic curve and facilitates the interpretation of the measurement results.

The concentration of the initial substances of the reaction at the electrode surface obey Eq. (121). The concentration of the reaction products at the surface is not reduced in consequence of the passage of current, but increased. Because the diffusion current of the products from the surface into the volume of the solution is proportional to the concentration difference at the surface and in the volume

$$\bar{I} = \varkappa\,(c^{s}_{\text{гх}} - c^{0}_{\text{гх}}), \qquad (127)$$

the concentration near the surface is expressed by the relation

$$c^{s}_{\text{гх}} = c^{0}_{\text{гх}} + \frac{\bar{I}}{\varkappa_{\text{гх}}} = \frac{1}{\varkappa_{\text{гх}}}\,(\varkappa_{\text{гх}}\, c^{0}_{\text{гх}} + \bar{I}). \qquad (127a)$$

The first term in brackets is equal to the limit current of hydroquinone *towards the electrode*, i.e., to the limit current which would be observed during the *anodic reaction* of oxidation of hydroquinone. This limit current we designate by $-I_{d_{\text{gkh}}}$ (the sign indicates that during the anodic reaction the current flows through the cell in the reverse direction compared with the current during the cathodic reaction, whose direction we have conventionally taken as positive).

Hence

$$c^{s}_{rx} = \frac{1}{\varkappa_{rx}}(-\bar{I}_{d_{rx}} + \bar{I}). \qquad (127b)$$

Substituting (121) and (127b) into Eq. (126), we find the following equation for the polarographic curve

$$\varphi = \varphi_{1/2} + \frac{RT}{2F}\ln\frac{\bar{I}_{d_x} - \bar{I}}{-\bar{I}_{d_{rx}} + \bar{I}}, \qquad (128)$$

where

$$\varphi_{1/2} = \varphi^0 + \frac{RT}{F}\ln c_{H^+} + \frac{RT}{2F}\ln\frac{\varkappa_{rx}}{\varkappa_x}. \qquad (128a)$$

In the particular case of $I_{d_{gkh}} = 0$ (i.e., in solutions which do not contain earlier added hydroquinone, $c_{gkh} = 0$), Eq. (128) assumes a form which coincides exactly with that of Eq. (123). In the particular case of $I_{d_{kh}} = 0$ (or $c_{kh} = 0$, i.e., in the absence of quinone), Eq. (128) is transformed into the equation for the anodic wave of the oxidation of hydroquinone

$$\varphi = \varphi_{1/2} - \frac{RT}{2F}\ln\frac{(-\bar{I}_{d_{rx}}) - (-\bar{I})}{(-\bar{I})}. \qquad (129)$$

In its general form Eq. (128) encompasses both the process of reduction of quinone and the process of oxidation of hydroquinone. Curve 1 in Fig. 57 represents such a mixed anodic-cathodic polarographic wave, recorded in a buffer solution at pH = 7. Curve 2 corresponds to the cathodic wave in the absence of hydroquinone, and curve 3 to the anodic wave in the absence of quinone.

As follows from the above equations, and also from Fig. 57, the halfwave potentials of the anodic, cathodic and mixed waves coincide. This general half-wave potential thus characterizes the redox system quinone/hydroquinone. Because for this system $\varphi^0 = +0.700$ v (n.v.e.), and the ratio $\varkappa_{gkh}/\varkappa_{kh}$ is fairly close to unity, the halfwave potential at pH = 7, according to Eq. (128a), should be $\varphi_{1/2} = 0.700 - 0.059 \cdot 7 =$

= 0.287, which is found to be in good agreement with the experimentally measured value of 0.280 v.

In a number of cases the shape of the polarographic curve and the halfwave potential for the oxidation or reduction reactions does not conform to the above-derived equations. This indicates that our assumption concerning the reversibility of the reactions is not observed and that other forms of polarization are superposed on the concentration polarization. Several examples of nonreversible redox reactions will be considered in greater detail in Chapter 4.

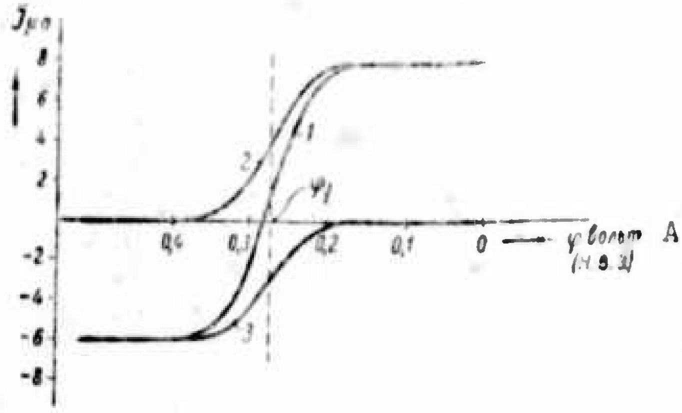


Fig. 57. Polarographic curves for quinone and hydroquinone in phosphate buffer solution at pH = 7: 1) Mixed anodic and cathodic curve; 2) cathode curve of quinone reduction; 3) anode curve of hydroquinone oxidation. A) Volt (n.v.e.).

The theoretical interpretation of the shape of the polarographic curve for various other types of reactions (for example, for the reactions of the discharge of metal ions from solutions of complex salts, etc.) is given in the special literature on polarographic analysis.

§4. PRACTICAL APPLICATIONS OF THE POLAROGRAPHIC METHOD

It was clear from the preceding section that during the reduction of an ion or neutral molecule at the mercury drop electrode the concentration polarization curve has the shape of a wave and is characterized by two quantities: the height of the wave, which indicates the intensity of the limit diffusion current, and the half-wave potential.

As is evident from Eq. (124), the half-wave potential during the discharge of metals with the formation of amalgam depends on the normal potential of the corresponding amalgam electrode and also on the quantities which characterize the diffusion of the metal ions in the solution and the metal atoms in the amalgam. The half-wave potential is entirely specific for a given reaction; of particular significance is the circumstance that the half-wave potential is independent of the initial concentration that the half-wave potential is independent of the initial concentration of the reacting substance. This makes it possible to gage the nature of the reaction taking place at the electrode surface on the basis of the measured value of this potential, i.e., the nature of the reducing substance present in the solution.

The independence of the half-wave potential on the concentration of the reacting components (except the hydrogen ions) is observed not only in the case of metal discharge reactions, but also, as has been shown in §3, for other reactions taking place at the mercury drop electrode, for example, for the redox reactions of dissolved substances.

Table 2 gives the half-wave potentials for several inorganic ions. More complete tables of half-wave potentials are given in special textbooks and manuals on polarography [5]. By means of such tables it is possible in many cases to determine the composition of a solution qualitatively on the basis of the experimental half-wave potentials.

The height of the polarographic wave, i.e., the limit current, is proportional to the concentration of the reduced substance and can thus serve for the quantitative determination of this concentration. If the diffusion coefficient of the reduced substance is known, the proportionality coefficient can be found from the Ilkovic equation (117). An

TABLE 2

Half-Wave Potentials of Various Inorganic Substances (in relation to the standard calomel electrode)

A Вещество	B Состав раствора («фона»)	$\varphi_{1/2}$
a Медь $Cu^{\cdot\cdot}$	0,1 н.^{v} KNO_3	−0,02
b Сурьма $Sb^{\cdot\cdot\cdot}$	1,0 н. KCl	−0,19
c Серебро $Ag^{\cdot}$	$KCN + KNO_3$	−0,34
d Олово $Sn^{\cdot\cdot}$	2 н. $HClO_4$ + 0,5 н. HCl	−0,39
d Олово $Sn^{\cdot\cdot\cdot\cdot}$	2 н. $HClO_4$ + 0,5 н. HCl	−0,51
e Свинец $Pb^{\cdot\cdot}$	1,0 н. KCl	−0,47
f Таллий $Tl^{\cdot}$	1,0 н. KCl	−0,52
g Индий $In^{\cdot\cdot\cdot}$	1,0 н. KCl	−0,63
h Кадмий $Cd^{\cdot\cdot}$	1,0 н. KCl	−0,68
i. Хром $Cr^{\cdot\cdot\cdot} \to Cr^{\cdot\cdot}$	0,1 н. KCl	−0,92
k. Цинк $Zn^{\cdot\cdot}$	1,0 н. KCl	−1,06
l. Никель $Ni^{\cdot\cdot}$	1,0 н. KCl	−1,14
m. Кобальт $Co^{\cdot\cdot}$	0,1 н. KCl	−1,24
n. Железо $Fe^{\cdot\cdot}$	0,1 н. KCl	−1,34
o Марганец $Mn^{\cdot\cdot}$	1,0 н. KCl	−1,55
p Алюминий $Al^{\cdot\cdot\cdot}$	0,05 н. KCl	−1,75
q Барий $Ba^{\cdot\cdot}$	0,1 н. LiCl	−1,84
r Натрий $Na^{\cdot}$	0,1 н. $N(CH_3)_4Cl$	−2,15
s Калий $K^{\cdot}$	0,1 н. $N(CH_3)_4Cl$	−2,17
t Кальций $Ca^{\cdot\cdot}$	0,1 н. $N(CH_3)_4Cl$	−2,25
u Магний $Mg^{\cdot\cdot}$	0,1 н. $N(CH_3)_4Cl$	−2,25

A) Substance; B) composition of solution ("background"); a) copper: b) antimony; c) silver; d) tin; e) lead; f) thallium; g) indium; h) cadmium; i) chromium; k) zinc; l) nickel; m) cobalt; no) iron; o) manganese; p) aluminum; q) barium; r) sodium; s) potassium; t) calcium; u) magnesium; v) normal.

empirical method is often used, however, in which the limit current for several known concentrations of the reduced substance is determined for a given apparatus; the calibration curve thus obtained can serve for subsequent quantitative determinations. The accuracy of quantitative determinations by means of the polarographic method is within the limits of 2-5%.

The diffusion coefficients of different simple ions (with the exception of hydrogen and hydroxyl ions) do not differ greatly. Hence in a first, very rough approximation it can be assumed that the limit current for different ions at the same equivalent concentration is about the same. This makes it possible to estimate the concentration of different ions, using the calibration curve for a single ion.

If several substances are present in the solution, capable of being reduced at the mercury drop electrode or if the electrode reaction can take place in several consecutive stages, a concentration polarization curve is obtained, consisting of several wavelike humps (Fig. 58). If the voltage applied to the polarographic cell is gradually increased

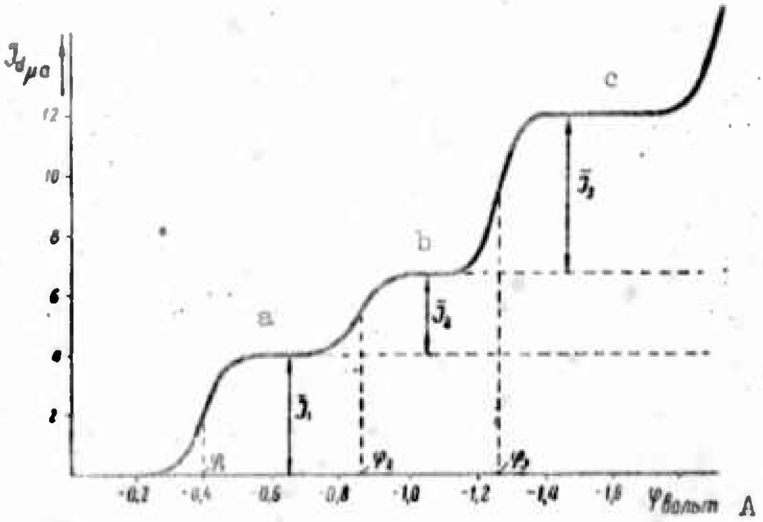


Fig. 58. Polarographic curve in the simultaneous presence of three reducible substances in the solution. A) Volt.

(i.e., if the potential of the drop electrode is gradually shifted to the negative side), the deposition of the ion whose halfwave potential has the most positive value begins first. During the deposition of this ion the current consumed for the discharging of the other ions is as yet small and can be neglected. Hence the conditions of discharge of the first ion within a certain potential range are the same as if the other ions, also capable of being discharged, were entirely absent. The height of the step *a* (Fig. 58) corresponds to the limit current of the first ion.

With further shift of the potential of the drop electrode to the negative side and its approach to the halfwave potential of another electrode reaction (for example, the reaction of reduction of the second cation) the rate of this second reaction increases and is superposed on the first reaction. A new wave and a new limit current appear on the polarographic curve: it is obvious that the total limit current of the second step *b* is equal to the sum of the limit currents due to the reduction of the first and second ion.

If the half-wave potentials differ sufficiently one can decipher the process of deposition of each ion independently of the simultaneous deposition of the other ions. In practice up to 4-6 such waves can be obtained on a single polarogram without any superposition. If the half-wave potentials of two or several substances are too close to each other (for example, they are at a distance of less than 0.2 v), the individual waves cannot be considered as separate from each other and their separation will not be very accurate.

It follows from the foregoing that the polarographic method makes possible the qualitative and quantitative analysis of a solution containing one or several substances capable of being reduced at the cathode (or oxidized at the anode) of the mercury drop electrode. The complete analysis of the solution is carried out by the recording of the concentration polarization curve which takes 2 to 15 minutes and requires only a very small volume of solution (from 10 to 0.1 ml). The polarographic method is particularly suitable for the analysis of solutions, containing the test components in low concentrations, for example, from 10^{-4} to 10^{-2} equivalents/liter. The polarographic study of 1 ml of a 10^{-4} N solution does not offer any difficulty although only 10^{-7} equivalents of the test component (for example, for zinc -0.003 mg) is contained in this quantity of solution. If necessary, the sensitivity of the polarographic method can be increased by one or two more orders of magnitude.

The practical applicability of the polarographic method is very diverse and broad. By means of it one can determine nearly all metal cations and several oxygen-containing and oxygen-free anions under the corresponding conditions. This method is widely used for the determination of small quantities of impurities in metals or ores. Thus, for example, it is possible to determine from a single sample the content of copper, lead, cadmium and zinc in aluminum, while the normal chemical determination of such impurities involves considerable difficulties.

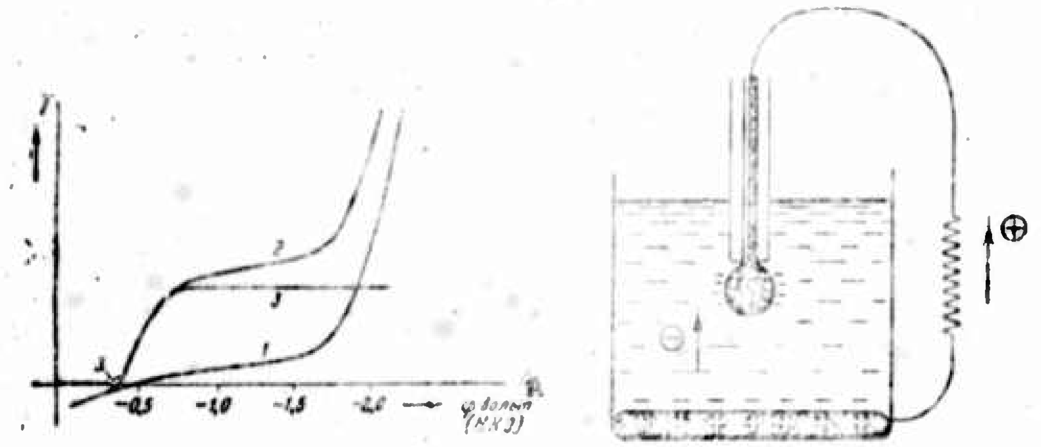
Of great importance is the polarographic investigation of organic substances. A number of organic substances which are difficult to determine when they are present simultaneously by the usual analytical methods can be analyzed by the polarographic method. In addition to analytical purposes, the polarographic measurements can be used for the determination of the mechanism of organic reactions and, in individual cases, also for the elucidation of certain peculiarities of the structure of organic compounds.

The polarographic method has also found widespread application in biology and medicine. It is most often used for the determination of different organic and inorganic components of various biological materials and preparations (blood, etc.). By means of it one can trace the variations in the composition of such preparations in pathological processes. Thus, for example, the question of the feasibility of early cancer diagnosis by means of polarographic analysis of blood serum has often been discussed in the literature.

Not being in a position to dwell in greater detail on the numerous practical applications of polarography here, we refer those interested to the special literature on these problems [6].

§5. CHARGING CURRENT

In the practical utilization of the mercury drop electrode we encounter various peculiar phenomena connected with the specific features of this electrode. We shall discuss in somewhat greater detail two of these phenomena, the charging current of the drop electrode and the so-called polarographic maxima.



a b

Fig. 59. a) Influence of the charging current on the shape of the polarographic curve; 1) charging current; 2) polarographic curve; 3) polarographic curve from which the charging current has been deducted; b) charging current of the mercury drop electrode with positive charging of the mercury surface. A) Volt (n.k.e.).

It follows from the discussions in the preceding sections that in the absence of reducible substances in the solution, the current, passing through the drop electrode cell, should be zero. If, however, measurements are carried out in such a solution, for example, in a solution of potassium chloride, from which the dissolved oxygen has been carefully removed, then even in the range, in which a discharge of the potassium ion does not yet take place, a certain small current is seen to pass through the cell. When the applied voltage is less than 0.5 v relative to the normal calomel electrode, the current passing through the cell is negative, i.e., reversed in direction relative to the reducing current. At larger voltages it changes sign. In first approximation the current varies linearly with the electrode potential (see Fig. 59a, curve 1).*

The existence of a current independent of the occurrence of electrode reactions at the electrode surface is connected with the growth of the drop and the presence of a double electric layer at the interface between drop and solution, as has been briefly explained in the introduction.

Let us assume that the mercury drop electrode is immersed in a solution of potassium chloride and that the mercury drop is at a more positive potential than the potential of the zero charge point (which is approximately –0.5 v relative to the normal calomel electrode in such a solution). At these potentials the mercury drop is charged positive and attracts an equivalent quantity of negative charges (ions) from the solution towards the surface. If the electrode surface increases as is the case during the operation of the drop electrode, and if the electrode potential is held constant during this, a certain additional number of positive charges must be imparted to the drop to preserve a certain charge density of the surface. Thus, the growth of the drop at constant potential, independent of any electrochemical reactions, involves the passage of a current which is conventionally termed charging current or non-Faraday current. The direction of flow of the charging current in the case of a positively charged mercury surface is indicated by arrows in Fig. 59b.

In polarographic measurements of reduction processes the cathode current is usually plotted on the ordinate axis; with this method of graphic representation the charging current for the positively charged mercury surface, whose direction is opposite to that of the cathode current, has a negative value.

We designate the surface charge density (i.e., the number of charges in the double layer per 1 cm^2 of surface) by ε and the radius of the growing drop by r_0. The charging current, flowing to the drop, is determined by the rate of growth of the total surface charge on the mercury, i.e.,

$$I_{з} = \frac{d}{dt}(\varepsilon \cdot 4\pi r_0^2) = \varepsilon \cdot 4\pi \frac{d}{dt}(r_0^2). \qquad (130)$$

Using the earlier derived relation (114) for the drop radius as a function of time, we obtain:

$$I_{з} = \underbrace{4\pi\left(\frac{3m}{4\pi d}\right)^{2/3}}_{k} \varepsilon \frac{d}{dt}(t^{2/3}) = \frac{2}{3} k\varepsilon t^{-1/3}. \qquad (131)$$

The mean charging current during the lifetime τ of a single drop, i.e., the quantity which is directly observed in the polarographic measurements, is

$$\bar{I}_{з} = \frac{1}{\tau}\int_0^\tau I_{з}\,dt = k\varepsilon\tau^{-1/3} = \frac{S_\tau \varepsilon}{\tau}, \qquad (132)$$

where $S_\tau = k\tau^{2/3}$ is the surface area of the drop at the moment of breakaway.

It is evident from Formula (131) that the charging current drops in proportion to the growth of the drop (with increase in the time t). At the initial moment of time ($t = 0$) the charging current is very large because at that moment the rate of growth of the surface is a maximum (mathematically the charging current assumes an infinite value, which of course does not have any physical meaning and results in consequence of simplified assumptions). As can be seen from Eq. (132), the charging current is proportional to the surface charge density ε. At the zero charge point it vanishes. At more negative potentials the surface charge ε assumes negative values and the charging current coincides in direction with the cathode current.

If an electrochemical reduction (or oxidation) reaction takes place on the surface of the drop electrode, the charging current is superposed on the discharge current. Figure 59a shows the charging current (curve 1) and the reduction current (curve 3) as functions of the potential. The total current (curve 2) measured by the galvanometer is the sum of the reduction and charging currents. At more positive potentials than the zero charge point its absolute value is slightly less than that of the reduction current, and at more negative potentials it is slightly higher.

The order of magnitude of the charging current is easily calculated. Assuming that the drop is formed within three seconds and that the drop diameter at the moment of breakaway is 1 mm. In this case the surface of the drop during breakaway is approximately 0.03 cm^2, i.e., the surface area increases on the average by 0.01 cm^2. As we know from the study of the structure of the double layer, at a potential of the mercury electrode which is more negative than the zero charge point by 1 v, the value of ε can be assumed to be $10 \cdot 10^{-6}$ coulombs/cm^2. It follows that the charging current for this potential is of the order of $2 \cdot 10^{-7}$ amp. The reduction current depends on the concentration of the reacting substance according to Eq. (117). For low concentrations (10^{-5} equiv./liter) the charging current is comparable with the current of the electrochemical reaction. For this reason, when carrying out quantitative determinations in the case of low concentrations of the reacting substances it is essential to take into account the charging current and to introduce a corresponding correction into the observed current. The existence of the charging current limits the application of the polarographic method of analysis at low concentrations of the test substance (under 10^{-5} equiv./liter).

§6. POLAROGRAPHIC MAXIMA

In the discussion of the diffusion phenomena at the drop electrode we have assumed that the growth of the drop does not cause mixing of the solution, i.e., that it takes place in the same way as, for example, the growth of an inflatable rubber balloon, whose surface elements are all moving in a strictly radial direction (see Fig. 60).

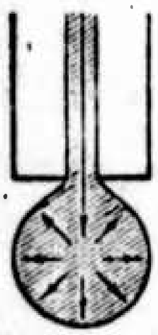


Fig. 60. Radial growth of the mercury drop.

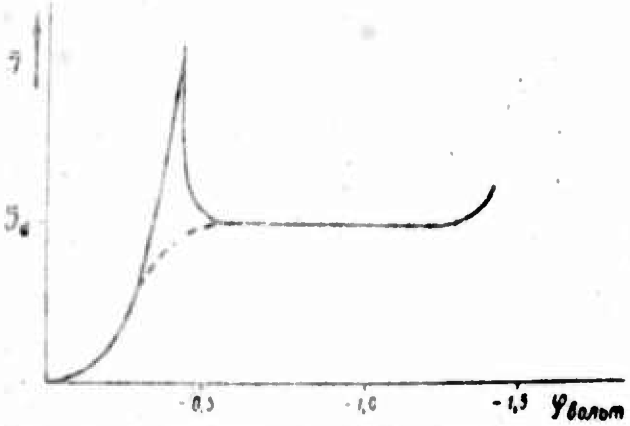


Fig. 61. Polarographic maximum of the 1st kind. A) Volt.

In actual fact tangential movements may occur at the surface of a mercury drop during its growth which result in an additional mixing of the electrolyte. If the measurements on the drop electrode are carried out under conditions in which these tangential movements are not completely inhibited, current intensities are observed in consequence of this agitation which many times exceed the values corresponding to diffusion with strictly radial growth of the drop. Such anomalously large currents are often observed within a certain limited, not very wide potential range; sections with sudden increase in current appear on the current-potential curves in these cases, which are termed polarographic maxima (see Fig. 61).

One of the possible causes of the appearance of tangential movements is connected with the unequal polarization of the surface of the mercury drop. The potential of every part of the electrode surface is a function of the current density established on it. During the passage of current through the circuit with the drop electrode the current is not distributed completely uniformly along its surface; the current density is greater in the lower parts of the drop, primarily because the upper part of the drop is to some degree shielded by the end of the capillary. For this reason the potential differs slightly at different parts of the surface, which in turn causes a nonuniform distribution of the surface tension at the drop. If the surface tension at different points of the drop surface is different, a movement of the mercury along the surface from the parts with lower surface tension (trying to expand) to the parts with higher surface tension (which try to contract) takes place.*

If the electrochemical reduction reaction takes place at potentials corresponding to the positive branch of the electrocapillarity curve, i.e., at potentials which are more positive than the zero charge potential, the surface movement is directed from the upper parts of the mercury drop towards its lower parts (so-called positive polarographic maxima). This is due to the fact that the lower parts of the drop, at which the current density is greater and which consequently have a more negative potential, have a greater surface tension in this case. The additional supply of discharged substance due to mixing takes place under these conditions mainly from above which reduces the concentration polarization, shifts the potential of the upper parts of the drop to the positive side and increase the potential difference and the surface tension difference between different parts of the drop even more, i.e., increase the tangential movement even more (Fig. 62a). Such an intensified mixing can cause a tenfold increase in current intensity. When the negative potential of the drop is increased and approaches the potential of the point of the electrocapillarity maximum the surface tension gradient along the drop surface disappears, the movement ceases and the current drops suddenly to the usual magnitude of the diffusion current.

At potentials corresponding to the negative branch of the electrocapillarity curve, the electrochemical reaction causes a movement in the opposite direction because a lower surface tension corresponds to the more negative potential of the lower part of the drop (negative polarographic maxima, Fig. 62b). In this case the supply of reducible substance takes place downwards and does not increase the potential

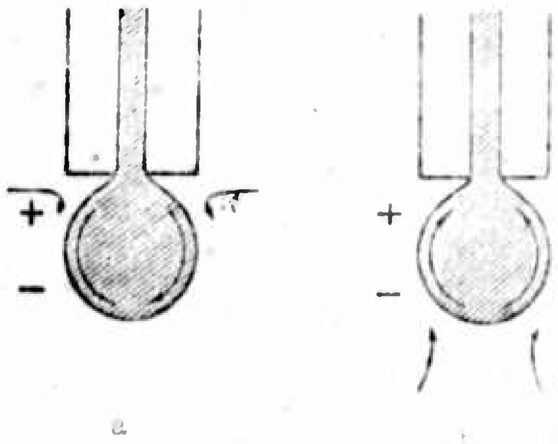


Fig. 62. Movement of the surface of the mercury drop, caused by nonuniform polarization: a) With positive surface charge on the mercury; b) with negative surface charge on the mercury.

difference between the upper and lower parts of the drop, but, on the contrary, reduces it so much under certain conditions that the surface movement ceases. In consequence of this the negative polarographic maxima are usually less pronounced than the positive maxima. A more detailed analysis of the origin of the movement [8] leads to the conclusion that even in the case of negative maxima an increase in the polarization beyond a certain limit results in a cessation of the tangential movements and a drop of the current intensity. Because the nonuniform

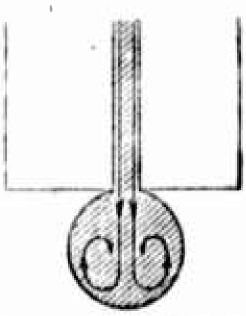


Fig. 63. Movement of the surface of the mercury drop caused by the flow of the mercury from the capillary.

polarization is connected with the difference in the ohmic potential drop along the path of the current towards different parts of the drop, the above-described polarographic maxima (the positive as well as the negative ones) are more pronounced if the solution has a high specific resistance and high current density, i.e., at a low background concentration and a relatively high concentration of the reducible substance.

Another possible cause of the appearance of tangential movements on the surface of the mercury drop, as T.A. Kryukova [9] has shown, is connected with the flow of the mercury from the capillary and the growth process of the drop itself. The mercury flows out from the capillary in the form of a thin jet which penetrates the hanging drop to its lower part. Because of the presence of surface tension this jet cannot leave the drop itself, hence it is bent and rises along the drop surface (Fig. 63). The real growth mechanism of the drop thus differs from the purely radial growth, shown in Fig. 60. The velocity of these surface movements depends on the rate of flow of the mercury from the capillary. In contrast to the above-discussed case, under otherwise equal conditions, it is greatest at the zero charge point of the mercury surface. If the potential is shifted to either side from the zero charge point, the velocity of the surface movement decreases because the charges appearing on the mercury surface inhibit the movement. The mechanism of this inhibition, which, as the quantitative theory shows, is proportional to the square of the surface density of the charge on the drop and inversely proportional to the specific electrical conductivity of the solution, will be elucidated further on. Thus the increase in the current in this case has the greatest effect at the zero charge point and decreases slowly with recession of the potential to either side of this point (Fig. 64). The maxima on the current-voltage curve caused by the flow of mercury we shall term polarographic maxima of the *2nd* kind in contrast to the above-described maxima of the *1st* kind. For reasons which will be explained further on, the maxima of the *2nd* kind are stronger if the background concentration is higher.

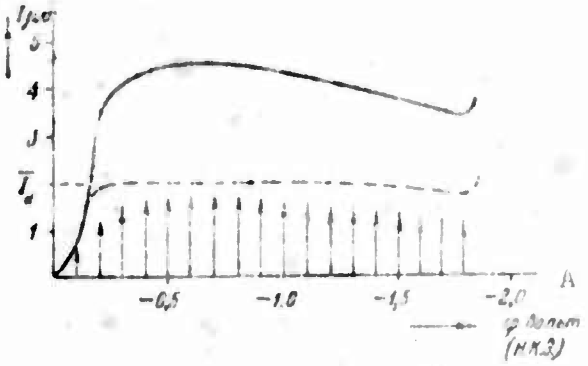


Fig. 64. Polarographic maximum of the second kind on the polarization curve in a solution of 3 N KCl + $3\cdot 10^{-4}$ N $HgCl_2$ (thick line). The dotted line indicates the current intensities which are not distorted by tangential surface movements. The arrows indicate the relative speeds of the surface movement at different potentials. A) Volt (n.k.e.).

It follows from the above-stated that a flow usually exists at the surface of the mercury drop which results in a mixing of the liquid. These flows can be made visible if a finely divided powder, for example, activated carbon, is suspended in the liquid. These effects (particularly the effect of the *2nd* kind) are inseparably linked with the operation of the drop electrode and thus it would seem that one cannot but take into account the intensification of diffusion due to the mixing of the liquid.

Nonetheless the diffusion current, determined in polarographic studies, agrees in many cases well with the values calculated by means of the above-presented formulae for diffusion towards a radially growing drop; in other words, the tangential surface movements do not affect these measurements. This can be explained only by the fact that conditions could be found under which these tangential movements of the mercury surface are practically completely inhibited, i.e., under which the surface does not possess the mobility which is normally typical for a liquid surface and behaves like the surface of an inflated rubber balloon. These conditions were first found experimentally and have only recently been interpreted theoretically.

The simplest, although not the only, method of suppressing the tangential movements which has long been used consists in the addition to the solution of small quantities of a substance capable of being adsorbed on the mercury surface. The mechanism of action of such a surface-active substance can be visualized in the following manner. When the mercury surface moves, for example, from the lower to the upper part of the drop, the surface concentration of the adsorbed molecules changes: in the lower part of the drop in which the surface is dilated, this concentration decreases; in the upper part, where the surface contracts, it increases. In the lower part of the drop, owing to the partial removal of the adsorbed molecules, the surface tension increases the increase in the concentration of adsorbed molecules in the upper part of the drop, by contrast, results in a lowering of surface tension. As a result forces appear acting along the surface from the upper part of the drop to the lower, i.e., in a direction opposite to the surface movement which tend to stop it. In the presence of adsorbed particles the surface thus has a certain elasticity. Under favorable conditions the braking effect due to adsorption is so great that the tangential movement of the mercury surface is completely arrested.

One would think that the charges of the double layer should exert a braking effect on the surface movement like that of the adsorbed molecules. Actually when the charged surface is extended, its surface tension increases and if it is compressed, it drops. Because the differences in the surface charge density in different parts of the drop can be equalized because of the volume electrical conductivity of the solution, the braking effect by the charges is strongest at low electrolyte concentrations which causes a narrowing of the potential range within which maxima of the *2nd* kind are observed, in proportion to the decrease in the background concentration.

The complete theory of these phenomena has been worked out relatively recently and a more detailed examination of it is impossible within the framework of the present book [10].

Every influence which impedes the tangential movement of the surface, such as, for example, the addition of surface-active substances to the solution, results in a depression of the maxima and the establishment of a current intensity, which agrees with the Ilkovic equation.

Current measurements in the presence of polarographic maxima can also be used in analytical chemistry because the decrease in the rate of motion of the surface of the mercury drop, as a result of which the maximum current decreases, is a measure of the content of surface-active substances in the solution. The polarographic maximum thus can serve for the determination of traces of organic surface-active substances which are not reduced at the mercury calomel cathode and which cannot be determined by the usual polarographic methods [11].

§7. OTHER FORMS OF POLAROGRAPHIC ANALYSIS

The drop electrode has two basic advantages which are responsible for its widespread introduction into the practice of electrochemical investigations: 1) owing to the constant renewal, the surface of the mercury drop is not contaminated and its properties are always easily reproducible; 2) if the dropping rate is constant, the limit diffusion current has a fully defined value which can be calculated in advance by means of Eq. (11). However, as is evident from §§ 5 and 6, the use of an electrode with a mobile surface which varies with time also involves a number of inconveniences. Other variants of the polarographic method have also been proposed recently in which these difficulties are circumvented. Thus, instead of a drop electrode one can use a rotating solid electrode, for example, a disc electrode; in this case the limit current is calculated by means of Eq. (85). If the voltage applied to the rotating electrode immersed in a solution of reducible substances is increased, then, as in the case of the drop electrode, a series of waves is obtained, whose height is proportional to the concentration of these substances. The rotating solid electrode, made, for example, of platinum, is free of the above-described deficiencies of the mercury drop electrode and can be used for the study of reactions taking place at more positive potentials, at which mercury is already subject to oxidation. However, its use requires a certain mechanical device for maintaining a constant rate of rotation. A certain inconvenience consists also in the fact that the surface of such an electrode varies when solid substances are deposited on it as a result of the electrochemical reaction.

An interesting form of current as a function of voltage is obtained in the case of application of a voltage which increases with time to an electrode immersed in a quiescent liquid. In this case the current intensity also increases with approximation to the potential at which a reduction of the dissolved substance is possible. With further increase in the voltage the current, however, does not go over into a constant diffusion current, as in the case of the rotating electrode, because with the passage of time the diffusion front is removed from the electrode surface (see §10 of Chapter 1) and the supply of substance to the electrode is slowed down. Instead of the wave which characterizes the reduction reaction in the usual polarogram, a curve with a maximum is obtained in this case. Because under the usual conditions a certain mixing of the liquid always takes place near the electrode surface, caused by the variation of the density of the solution during electrolysis, it is necessary, when using the last method, to carry out the potential variation within a short interval of time, during which the diffusion front cannot move away from the surface to distances at which the mixing of the liquid, caused by natural convection, already exerts an effect. In this case it must be remembered that if the potential is varied rapidly a considerable part of the current is expended for the charging of the electrode surface (see §4 of the introduction). If the time during which the potential variation takes place is short compared with the dropping period, then the drop electrode can also be used with this form of polarographic analysis and its advantages, connected with the possibility of renewing the surface, can be retained. The use of an oscillograph is essential for the recording of the current intensity variation with time during rapid potential variation [12].

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[Footnotes]

161 In polarography salts are normally used as "background" with cations which are difficult to discharge and anions which are not reduced, for example, the chlorides or sulfates of the alkali metals (potassium, sodium, lithium) and sometimes dilute acids. In cases where the process under investigation takes place only at very strongly negative potentials (see §4 of the present chapter), it is best to use salts of substituted ammonium as background, for example, tetramethylammonium chloride, whose cations are even more difficult to discharge on the mercury surface than the cations of the alkali metals.

162 In order to keep the rate of flow constant, the pressure on the mercury which flows out must be constant. The latter, however, varies slightly during the growth of the drop, namely: it decreases by the amount of the capillary pressure within the drop which is $2\sigma/r_0$.

165 Attempts have been made recently to improve Eq. (116) by taking into account the gradual change from nonstationary to stationary diffusion in proportion to the growth of the drop [3].

166 A more accurate discussion of the breakaway conditions will be given in Chapter 5.

179 The rise in the curve in the range of strongly negative potentials is connected with the discharge of potassium ions.

183 The potential gradients and, consequently, also the tangential movements along the mercury surface arise when the free mercury drop falls in an electrolyte solution in which a constant electrical field is maintained. In consequence of the reactive repulsion from the surrounding medium the tangential

movement of the surface causes a movement of the drop as a whole, which is easily observed. The relative simplicity of the geometrical conditions makes it possible in this case to give an accurate mathematical expression for the velocity v of motion of the drop in the direction of the electric field:

$$v=\frac{\varepsilon E r}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}}, \qquad (133)$$

where E is the field strength; ε is the charge density on the mercury surface; r is the drop radius; μ and μ' are the viscosities of the ambient solution and the mercury; $\varkappa$ is the specific electrical conductivity of the solution. This equation has been confirmed by measurements of the deflection of mercury drops falling in an electric field in a viscous glycerol solution [7].

Manuscript Page No.	[Transliterated Symbols]
170	rx = gkh = gidrokhinon = hydroquinone

Chapter 3

HYDROGEN OVERVOLTAGE

§1. ELECTROCHEMICAL POLARIZATION

Once a reacting particle has reached the electrode surface because of diffusion or migration, it enters the field of its molecular influence. If the reacting particle is an ion, it should enter the double layer; a neutral molecule can be adsorbed on the electrode surface. These stages precede the electrochemical reaction proper, during which the transfer of charges from the electrode to the reacting particle takes place.

The question arises whether the rate of these adsorption stages plays an important part in electrochemical kinetics. Up to now these phenomena have been relatively rarely considered in the study of electrochemical processes. On the basis of the existing experimental data it can be stated that most of these adsorptions take place fairly rapidly and hence should not affect the kinetics of the process as a whole. This is confirmed, for example, by measurements of the capacitance of the double layer of the mercury electrode with a.c. currents of different frequency, which were mentioned in the introduction. These measurements were carried out up to frequencies of the order of 100-200 thousand cycles, the capacitance proving to be independent of frequency. The latter indicates that the equilibrium in the double layer is established within a period which is short compared with such oscillation periods of the alternating current.*

On the other hand, it follows from experiment that the electrochemical reactions often proceed at a low rate. In order to increase this rate (in other words, in order to make possible the passage of a current with a certain density) the potential must be altered compared with the equilibrium potential. Such a shift of the potential during the passage of current cannot always be ascribed to concentration polarization because it is also observed when there can be no question of an insufficient quantity of reacting substance at the electrode surface. Thus, a polarization of a different kind appears in such cases, which is often referred to as electrochemical polarization. In proportion to the refinement of measurement technique, the number of electrochemical reactions in which such a polarization could be observed has greatly increased.

The potential shift of the electrode from its equilibrium value has been termed overvoltage in electrochemistry.

The phenomenon of polarization of the electrodes during the passage of an electric current through them has been known already during the first half of the 19th century. In earlier works this phenomenon has often been explained by the presence of a certain contact resistance between electrode and solution.

During the Forties of the previous century the professor of physics of Petersburg University, Academician E.Kh. Lents [1] and A.S. Savel'yev [2] pointed out the erroneous nature of this view and made a rigorous distinction between normal resistance and polarization. They pointed out that in contrast to the ohmic voltage drop which is a linear function of the current intensity, the magnitude of the polarization during the evolution of gases increases only slowly when the current intensity is increased. The works of Lents and Savel'yev provided a foundation for the quantitative study of the polarization phenomena.

The electrochemists have long given attention to the fact that the electrolytic separation of hydrogen from aqueous solutions on cathodes of different metals is accompanied by considerable polarization. Hence this relatively simple and at the same time one of the most important electrochemical reactions in technology have been most thoroughly studied from all aspects.

During the last two decades a number of investigations were carried out in the Soviet Union on the study of the process of the discharge of hydrogen ions and the separation of hydrogen in the gaseous state and also on the study of other electrochemical processes. In these works use was made of novel accurate methods of investigation which exclude a distortion of the results by extraneous factors to a considerable degree.

The results obtained in these studies will be primarily considered in the following sections. The relative great attention which has been given to the presentation of experimental data for the reaction of hydrogen separation and their theoretical discussion is due to the fact that using this reaction as an example it is easy to follow various laws of electrochemical kinetics which are general and can also be applied to other electrochemical reactions.

The experimental method worked out in the example of the separation of hydrogen and described in the following is also applicable to the study of the polarization phenomena in other electrode processes.

§2. EQUILIBRIUM HYDROGEN ELECTRODE AND HYDROGEN OVERVOLTAGE

When an electrode of platinized platinum is immersed in an electrolyte solution, saturated with gaseous hydrogen, an equilibrium is established on it, as we know, between the molecules, adsorbed atoms and hydrogen ions

$$H_2 \rightleftarrows 2H \rightleftarrows 2H^{\cdot} + 2e. \qquad (A)$$

The potential of the platinum electrode assumes a value which is determined by this equilibrium. The potential as a function of the activity a_{H^+} of the hydrogen ions in the solution and the partial pressure p_{H_2} of the gaseous hydrogen over the solution is given by the thermodynamic equation

$$\varphi_p = \varphi_p^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{p_{H_2}^{1/2}}. \qquad (134)$$

According to the generally accepted definition of the electrode potentials, the constant φ_p^0 for the equilibrium hydrogen electrode is conventionally taken as zero (standard hydrogen scale of the electrode potentials).

The value of the potential of the equilibrium hydrogen electrode, naturally, is independent of the electrode material. The use of platinized platinum is due to the fact that the equilibrium reactions for the reaction (A) are rapidly established at such an electrode and that other electrochemical reactions with participation of the electrode material do not take place on it.

When a current is passed through the electrode, the equilitrium (A) is upset and, depending on the direction of the current, an electrochemical reaction of the reduction of hydrogen ions with formation of molecular hydrogen takes place at the electrode surface (if the electrode serves as the cathode) or the reverse reaction of the ionization of hydrogen molecules (if it serves as the anode). The electrode potential is shifted from the equilibrium value in the first case to the negative side and in the second to the positive side (cathodic and anodic polarization of the electrode). The magnitude of the potential shift depends on the nature of the metallic electrode, on the current density, on the composition of the solution and on other factors. In the above-considered case of platinized platinum the polarization is very slight; in other cases it may attain several tenths of a volt and sometimes exceeds one volt.

Thus, for example, during the cathodic separation of hydrogen at the mercury electrode from 1 N hydrochloric acid solution at a current density of $i = 1 \cdot 10^{-4}$ amp/cm^2 the potential is shifted 0.94 v to the negative side compared with the equilibrium hydrogen potential. The limit diffusion current i_d of the hydrogen ions in this solution, depending on the mixing conditions, can attain values of the order of 0.1 or 1 amp/cm^2, i.e., it exceeds the above-mentioned current density several thousand times.

As follows from the laws of concentration polarization, explained in Chapter 1 (Eq. 58), the potential shift, causes by concentration changes near the electrode surface, under these conditions, is negligibly small and can practically be ignored. Hence the potential shift by 0.94 v cannot be due to concentration polarization but is a consequence of other causes which are obviously connected with the electrochemical reaction taking place at the electrode surface during the passage of current.

As has been pointed out in the preceding section, the potential shift of the electrode caused by electrochemical polarization is termed overvoltage. It is convenient to distinguish between the anodic and cathodic overvoltages η_A and η_K. If we designate the potential of the equilibrium hydrogen electrode by φ_p and the potential of the polarized electrode by φ, the overvoltage for the anodic reaction (for example, the reaction of ionization of the hydrogen molecules) is

$$\eta_A = \varphi - \varphi_p, \qquad (135)$$

and for the cathodic reaction during which the potential is shifted to the negative side, it is

$$\eta_K = \varphi_p - \varphi. \qquad (135a)$$

With this definition, the quantity η_A obviously has the positive sign in the case of anodic and the quantity η_K in the case of cathodic polarization.

If the electrochemical polarization is slight and particularly if the concentration of the reacting substances is low, so that the concentration polarization occurs already at low current densities, we must take into account at the same time the concentration and electrochemical polarization. In this case it is more correct, in order to determine η rationally, to relate in Eq. (135) the equilibrium potential φ_p to the values of the concentrations of the reacting substances and reaction products, which are established at the electrode surface during the reaction. In practice, however, this is not always possible because these values are often unknown, and Eq. (135) is often used in such a manner that φ_p is taken to be the equilibrium potential in a system whose composition is not affected by the passage of current. In the following we shall assume, unless otherwise indicated, that the electrochemical polarization is not complicated by concentration polarization, i.e., that the current densities used are considerably lower than the limit densities possible under these conditions.

The concept of overvoltage is connected with the excess voltage which must be applied to the electrolytic bath over and above its equilibrium electromotoric force to carry out the electrolysis. It must be kept in mind, however, that under the conditions of technical electrolysis this excess voltage is due not only to the electrochemical polarization of the two electrodes in the bath (i.e., the actual "overvoltage" at the electrodes), but also to the ohmic voltage drop in the solution.

The overvoltage phenomenon during the cathodic separation of hydrogen is of great technical importance due to the fact that this reaction, either as a main or side reaction, is part of many important electrochemical processes. In individual cases a large overvoltage promotes the desired process and is thus desirable; in other cases the appearance of an overvoltage is undesirable.

The most obvious example of the undesirability and economic disadvantage of overvoltage is the process of the electrolysis of water with the aim of electrolytic production of hydrogen. The overvoltage increases the required electrical voltage and causes an additional consumption of electrical energy. At an overvoltage of 0.3 v an additional consumption of 8300 kwh of electrical energy is required for every 1000 kg of hydrogen which is uselessly transformed into heat. An overconsumption of energy in consequence of the hydrogen overvoltage at the cathodes of the same order occurs in chlorine electrolysis and in other industrial electrochemical processes.

On the other hand, a large number of electrochemical processes of cathodic reduction takes place at electrode potentials which are more negative than the potential of the equilibrium hydrogen electrode. If the separation of hydrogen were not accompanied by a large overvoltage, the realization of these processes would be entirely impossible it would give very low current yields because most of the current would be used up for the, in this case undesirable, separation of hydrogen. To these processes belongs, for example, the process of producing sodium amalgam during chlorine electrolysis, which takes place at potentials which are approximately 1 v more negative than the potential of the equilibrium hydrogen electrode in this electrolyte. Hence this process is possible only because of the large overvoltage of the hydrogen on the mercury. In the same way the use of a lead storage battery would not be possible if the cathodic separation of hydrogen at the lead did not involve a large overvoltage. Traces of arsenic, platinum, and other substances in the electrolyte of a lead battery are exceptionally harmful precisely because these substances lower the hydrogen overvoltage on lead, and in their presence a large proportion of the chemical energy of the battery is lost for the useless evolution of hydrogen at the negative electrode (self-discharge of the battery).

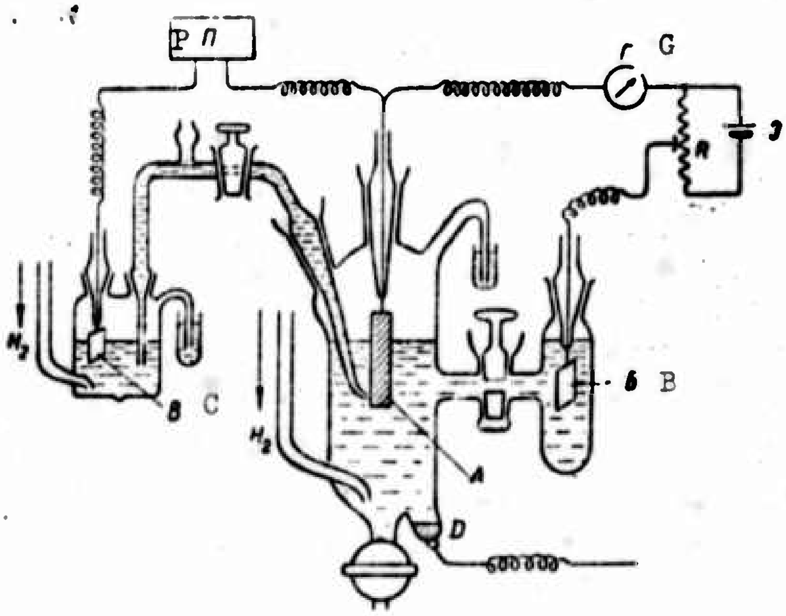

Fig. 65. Scheme of device for the measurement of hydrogen overvoltage: A) Test electrode; B) auxiliary electrode for polarization: C) hydrogen electrode for potential measurement; D) auxiliary electrode for purifying the solution; G) galvanometer; P) potentiometer; R) rheostat: Z) current source.

The above examples show that when solving practical problems it will frequently be useful to decrease or increase by some method or other the hydrogen overvoltage at different electrodes. This can be achieved by correct selection of the material and surface condition o the electrode, the composition of the solution and, finally, the electrolysis regime, the temperature, current density, etc. This problem can be solved only on the basis of a careful study of the separate influence of all these factors on the kinetics of the process of cathodic hydrogen separation.

The methods of overvoltage measurement consist in a measurement of the electrode potential during the passage of current through it. The measurements can be carried out, for example, using the circuit shown in Fig. 65.

The test electrode *A* is polarized by means of the auxiliary electrode *B*, i.e., through the circuit, consisting of these two electrodes, current from the external source *Z* is passed. When the process of the reduction of the hydrogen ions is investigated, the test electrode is made the cathode. The current intensity is regulated by means of the rheostat *R* and is read off from the ammeter or galvanometer *G*. The potential φ_A of the electrode *A* cannot be measured in relation to the auxiliary electrode *B* because the potential of this electrode is also shifted during the passage of current. For this reason the potential φ_A is determined by means of a second auxiliary electrode *C* through which the current does not pass and whose potential thus remains constant. The potential difference $\varphi_A - \varphi_C$ can be measured with the potentiometer *P* by means of a normal bridge circuit suitable for the measurement of equilibrium e.d.s.

In dilute solutions or at large values of the current intensity a considerable ohmic potential drop occurs in the solution between the electrodes *A* and *B*. To prevent this from affecting the results of the measurement of the potential difference $\varphi_A - \varphi_C$, it is essential that no current passes through the layer of solution between the electrodes *A* and *C*.

This is achieved leading to the surface of the electrode *A* a thin glass tube (siphon) ending in a tip which is connected with the part of the cell containing the electrode *C*. The closer the end of the siphon is to the electrode *A* the less is the ohmic potential drop between the surface of the electrode and the end. Within the siphon there is no ohmic potential drop because current does not pass through it during the measurement of the potential by the bridge method. This adaptation is termed the Luggin capillary in electrochemical literature, named after the Russian scientist who proposed it.

Any electrode with sufficient stable and reproducible potential, for example, a calomel electrode, can be used as the auxiliary electrode *C*. However when studying the kinetics of hydrogen evolution, it is more convenient to use the equilibrium hydrogen electrode of platinized platinum, immersed in a solution of the same composition, as electrode *A* and at the same temperature, as an auxiliary electrode. In this case the measured potential difference between the electrodes *A* and *C* according to definition will exactly equal the hydrogen overvoltage.

In some cases the electrode potential is not determined during the passage of current, but a very short time after the current has been switched off. By means of special devices (commutators) one can reduce the time interval between the switching off of the current and the measurement to 10^{-4}-10^{-5} seconds. This method of commutator measurement of overvoltage has the advantage that the measured potential shift does not contain the ohmic potential drop in the solution or in the thin surface films on the electrode. The use of this method, however, involves certain difficulties, which are due to the fact that after polarization with a current of high density, for example of several tens of amperes per square centimeter, the overvoltage decreases very quickly after the switching off of the current so that even 10^{-5} seconds later the electrode potential can markedly differ from the stationary value observed during the passage of the current. In these cases it is necessary to record the curve showing the electrode potential as a function of time elapsed since the switching off of the current and to extrapolate this curve for the moment at which the current had been turned off. This interpolation often involves considerable errors, as is evident from the example of the works of several contemporary British authors (Hickling and Salt) [3, 20].

Measurements of hydrogen overvoltage, as many other measurements in the kinetics of electrochemical processes, make great demands on the purity of the electrode surface and the purity of the solution. The slightest admixture of many organic or inorganic substances distorts the measurement results strongly and in an uncontrolled manner; this robs many of the experimental data published in the literature of their value. The purity of the solution is attained by double distillation of the water in apparatus without any rubber or cork connections and by repeated recrystallization, ignition or distillation of the reagents. Of great importance is also prolonged purification immediately before the measurement of the cathodic polarization solution by means of an auxiliary cathode, for example, one made of the same metal as the test cathode (*D* in Fig. 65), on which the traces of various impurities present in the solution are deposited or decomposed.

The most convenient material for electrodes in overvoltage studies in many respects is mercury which can be easily purified, gives an ideally smooth and easily renewed surface for contact with the solution and has a high overvoltage. Hence many experimental investigations on the kinetics of hydrogen separation or other electrochemical reactions are carried out with the mercury electrode. When using solid metal electrodes, the surface contamination and also the surface oxides which are formed must be removed prior to the measurement as far as possible.

Before the measurement it is essential to free the solution and measurement cell carefully of atmospheric oxygen because the oxygen is reduced at the cathode and distorts the measurement results if the current density is low. The removal of the oxygen is carried out, as a rule, by passing pure hydrogen through the measurement cell with the electrolyte for many hours and by prolonged cathodic polarization by means of an auxiliary electrode.

If measurements are carried out at high current densities or in dilute solutions, the influence of the concentration polarization must be taken into account. Some method or other of mixing [4] is used, for example, an electrode in the form of a rotating disc, whose theory has been given in Chapter 1, is used in order to increase the limit current densities and to achieve uniform conditions of convective diffusion.

§3. DEPENDENCE OF THE OVERVOLTAGE ON CURRENT DENSITY, ELECTRODE MATERIAL AND TEMPERATURE

The appearance of overvoltage is connected with the passage of current through the electrode and is different for different current intensities. Hence there is no sense in indicating overvoltages without giving the current intensities or densities* to which they refer. From this point of view the so-called minimum overvoltages during the evolution of gases, which are given in the older handbooks and textbooks and which refer to the beginning of visible separation of gas bubbles, are also of little use.

The dependence of the electrode potential or overvoltage on the density of the polarizing current is a polarization characteristic of a given electrode and is expressed by the polarization curve or by certain mathematical relations.

For convenience in the consideration of the experimental regularities during the polarization of the hydrogen electrode it is best to distinguish two current density ranges: on the one hand, the current density range in which the overvoltage on a given electrode is considerably greater than RT/F, i.e., more than 25 mv, and, on the other, the current density range in which the overvoltage is less than this quantity.

As follows from numerous experimental data, a linear relation is observed in the first case between the overvoltage of many electrodes and the logarithm of the current density

$$\eta = a + b \ln i \quad \text{for} \quad i = k \cdot e^{\frac{\eta}{b}}, \qquad (136)$$

where a, b and k are constants $(k = e^{-(a/b)})$.

This law is termed the Tafel formula.

The constant a in Eq. (136), i.e., the overvoltage at unit current density (i = 1 amp/cm^2) depends on the nature of the electrode metal on its surface condition, the composition of the solution and the temperature. This constant characterizes mainly the degree of irreversibility of the electrode process: the larger a, the higher is the overvoltage at a given current density, i.e., the greater is the deviation from the equilibrium state because the variation of b as a function of the nature of the electrode is usually relatively slight.

For a mercury cathode in 1 N sulfuric acid a for the process of hydrogen separation is 1.415 v, for the lead electrode, 1.56 v. This large value of a is typical for a certain group of metals. In addition to lead and mercury, it includes, for example, zinc, cadmium, tin and thallium. For other metals this quantity is considerably less. Thus, for nickel a = 0.6 v, i.e., approximately one volt less than for lead. The metals of the platinum group have an even smaller value of the constant a, for example, for platinum a = 0.1-0.3 v. It should be pointed out that the values of a in the case of these metals depends enormously greatly on the degree of purity of their surface. Such low values of a are found only on electrodes with an active surface and with thorough removal of impurities from the solution. The surface activation can be achieved, for example, by cathodic reduction after preliminary anodic

TABLE 3

Values of the Constants *a* and *b* for the Reactions of Cathodic Separation of Hydrogen on Different Metals at *t* = 20°

	A Металл	B Состав раствора	C *a* в польтах	C *b* в вольтах	D Автор
E	Свинец Pb . . .	1,0 F н. H_2SO_4	1,56	0,110	Я. М. Колотыркин[6] G
H	Таллий Tl . . .	1,7F н. H_2SO_4	1,55	0,140	То же I
K	Ртуть Hg	F 1,0 н. H_2SO_4	1,415	0,113	З. А. Иофа[7] L
K	Ртуть Hg	F 1,0 н. HCl	1,406	0,116	То же I
K	Ртуть Hg	F 1,0 н. KOH	1,51	0,105	О. Л. Капцан и З. А. Иофа[8] M
N	Кадмий Cd . . .	F 1,3 н. H_2SO_4	1,40	0,120	Я. М. Колотыркин[6] G
O	Цинк Zn	F 1,0 н. H_2SO_4	1,24	0,118	—
P	Олово Sn	F 1,0 н. HCl	1,24	0,116	Бокрис и Парсонс[9] Q
R	Медь Cu	F 1,0 н. H_2SO_4	0,80	0,115	Г. М. Майтак[10] S
T	Серебро Ag . .	F 1,0 н. HCl	0,95	0,116	Бокрис и Парсонс[9] Q
T	Серебро Ag . . .	F 5,0 н. H_2SO_4	0,95	0,13	Б. Н. Кабанов[4] U
V	Железо Fe . . .	F 1,0 н. HCl	0,70	0,125	В. А. Кузнецов и З. А. Иофа[11] W
V	Железо Fe . . .	F 2,0 н. NaOH	0,76*	0,112	С. А. Розенцвейг и Б. Н. Кабанов[12] X
Y	Никель Ni . . .	F 0,11 н. NaOH	0,64	0,100	П. Д. Лукoвцев и С. Д. Левина[13] T
a	Кобальт Co . . .	F 1,0 н. HCl	0,62	0,140	А. М. Муртазаев[14] b
c	Палладий Pd . .	F 1,1 н. KOH	0,53	0,130	Н. А. Аладжалова[15] d
e	Вольфрам W . .	F 1,0 н. HCl	0,23	0,040	Бокрис и Парсонс[9] Q
e	Вольфрам W . .	F 5,0 н. HCl	0,65	0,11	Бокрис и Аззам[16] f
g	Платина Pt гладкая	F 1,0 н. HCl	0,10**	0,13**	П. И. Долин и Б. В. Эршлер h
g	Платина Pt гладкая	F 1,0 н. NaOH+ +1,5F н. Na_2SO_4	0,31**	0,097**	То же I
g	Платина Pt гладкая	F 1,0 н. HCl	0,3***	0,14***	Бокрис и Аззам[16] f

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* Extrapolation from *i* = 10^{-5} amp/cm^2.
** Correlated for concentration polarization.
*** At *i* > 1 amp/cm^2.

A) Metal; B) composition of the solution; C) in volts; D) author: E) lead; F) normal; G) Ya.M. Kolotyrkin; H) thallium; I) the same: K) mercury; L) Z.A. Iofa; M) O.L. Kaptsan and Z.A. Iofa; N) cadmium: O) zinc: P) tin; Q) Bockris and Parsons; R) copper; S) G.M. Maytak; T) silver: U) B.N. Kabanov; V) iron; W) V.A. Kuznetsov and Z.A. Iofa; X) S.A. Rozentsveyg and B.N. Kabanov; Y) nickel; Z) P.D. Lukovtsev and S.D. Levina; a) cobalt; b) A.M. Murtazayev; c) palladium: d) N.A. Aladzhalova; e) tungsten; f) Bockris and Azzam; g) smooth platinum; h) P.I. Dolin and B.V. Ershler.

polarization. The dependence of the constant *a* for different metals on the composition of the solution will be considered in detail in §5.

The most reliable values of the constants *a* and *b* for the reaction of hydrogen evolution on various metals are presented in Table 3.*

Attempts have been made recently to establish quantitative relations between the constant *a*, which determines the overvoltage on a metal, and other quantities, which characterize the physical properties of the metal.

Thus, A.K. Lorents [17] established an interesting relation between the constant *a* in the overvoltage equation and the compressibility factor κ of the metal. Figure 66 gives a comparison of the values of *a* and the quantities $1/\sqrt{\kappa}$ for the most diverse metals (these metals are indicated in Fig. 66). On the basis of these data it may be inferred that the dependence of the constant *a* in the formula for the hydrogen overvoltage on the compressibility factor κ is expressed by the relation:

$$a = 2 - \frac{1}{\sqrt{\kappa \cdot 10^6}}.$$

N.Ye. Khomutov [18] compared the hydrogen overvoltage with the minimum interatomic distances in metals and found that the minimum overvoltage corresponds to a distance of about 2.7 A; for metals with greater or smaller interatomic distance the overvoltage is greater.**

The constant *b*, in contrast to the constant *a*, depends little on the nature of the metal or the composition of the solution. For many metals with a clean nonoxidized surface *b* assumes values close to $2RT/F$, i.e., at room temperature it is 50 mv if the logarithm of *i* is expressed in natural logarithms or 50 × 2.3 = 115 mv if decadic logarithms are used. (The values of *b*, given in Table 3, have been calculated for decadic logarithms. This means that within the range of applicability of Eq. (136) the overvoltage increases approximately by 0.116 v with tenfold increase in current density. On some metals with

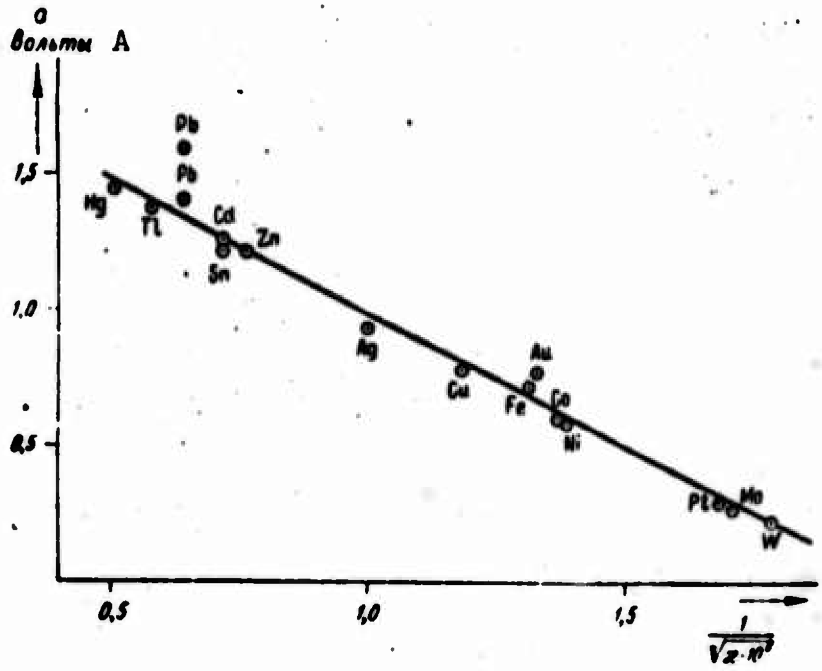

Fig. 66. Constant *a* as a function of the compressibility factor κ of a metal, expressed in cm^2/g. A) Volt.

not very large overvoltage the coefficient *b* is somewhat less, for example, on nickel. Lower values of *b* have also been observed by some investigators on platinum; the data for tungsten are contradictory. On metals with an oxidized surface, with which one normally has to deal, in particular, under the conditions of technical electrolysis, this coefficient often has a higher value, up to 0.2 v and over. For reasons which will become clear when the theory of hydrogen overvoltage is explained, it is important for elucidating the reaction mechanism to determine the ratio between the quantity *b* and the quantity *RT/F*. Hence the factor in front of the logarithm of the current density in the Tafel equation is often expressed by *RT/αF*, where α is a constant, defined by the relation

$$\alpha = \frac{RT}{bF}. \qquad (136a)$$

Thus,

$$\eta = a + \frac{RT}{\alpha F} \ln i. \qquad (136b)$$

As follows from the foregoing, for most metals α is close to 0.5.

When estimating the accuracy of the data given in Table 3 it must be remembered that the overvoltages found by different authors in earlier works, often differed by several tenths of a volt. At the present time the overvoltage on mercury has been determined with an accuracy of several millivolts. In the case of solid metals it must always be taken into account that the overvoltage depends on the method of surface preparation. If a certain method of surface preparation prior to the measurement on solid surface is adhered to, the overvoltage can be reproduced with an accuracy of two to three-hundredths of a volt.

The relation (136) naturally cannot be used in the case of very low current densities because in proportion to the decrease in current density to zero the overvoltage, according to definition, tends to zero and not towards $-\infty$, as follows from Eq. (136).

At low overvoltages a relation of a different nature is observed, namely that the overvoltage is directly proportional to the current density passing through the electrode:

$$\eta = wi. \qquad (137)$$

The coefficient w depends on the nature of the metal and on other factors; like the constant a, it characterizes the degree of irreversibility of the hydrogen electrode for the given metal.

The above-indicated relationship between overvoltage and current density is formally analogous to the Ohm law, the quantity w playing the part of the resistance per unit of electrode surface. Thus, for Pt in alkaline solution $w = 41$ ohm·cm^2. As long as the currents passing through the electrode are small, the potential shifts are such as if they were caused by a certain contact resistance. This similarity, however, as pointed out previously, is only external. In reality, the causes of the appearance of the potential shift in this case are different; this will be considered in greater detail in the following.

The laws (136) and (137) are valid for the cathodic process of discharge of hydrogen ions as well as for the anodic process of ionization of molecular hydrogen.

The range of low overvoltages within which a proportionality between overvoltage and current density is observed can be conveniently studied on the platinum electrode or on electrodes of other metals with low values of the constants *a* and *w*. Numerous measurements have shown that the constant *w* for the same electrode has a different value for the anodic and cathodic processes. The anodic and cathodic overvoltage curves for the platinum electrode thus can be expressed by a line passing through the coordinate origin and which does not have an inflection point (section *C-D* of the curve in Fig. 67). If the current density increases the polarization curves begin to bend towards the axis of the current density and gradually, in agreement with the law expressed by Eq. (136), assume a logarithmic form (sections *B-C* and *D-E*).

The polarization curves for the anodic process of ionization of hydrogen cannot be prolonged to high current densities because in consequence of the low solubility of gaseous hydrogen in aqueous solutions the hydrogen concentration polarization soon begins to exert its effect and the current tends to the limit value, determined by the rate of supply of dissolved hydrogen to the electrode (section *A-B* of the curve in Fig. 67). The measurement range of the anodic branch can be enlarged if, by increasing the hydrogen pressure, its solubility in the electrolyte is increased.

On other metals (with the exception of the metals of the platinum

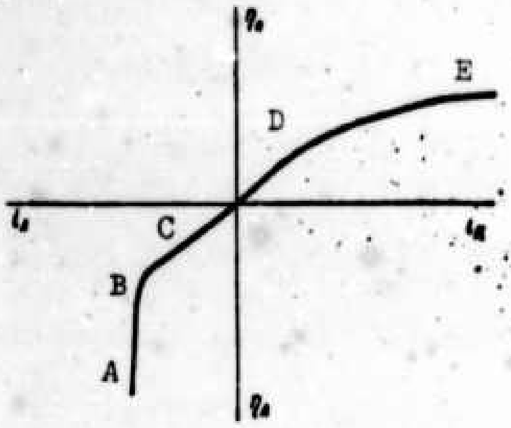

Fig. 67. Anodic and cathodic sections of the polarization curve of the hydrogen electrode.

group and in alkaline medium, of cobalt and nickel and, under certain conditions, silver) the process of hydrogen ionization can generally not be studied because with anodic polarization we get into a range of potentials at which the metal is strongly oxidized or dissolved. Hence, most experimental investigations of the polarization of the hydrogen electrode refer only to the cathode process of the reduction of hydrogen ions and not to the anodic process; for this reason we shall consider mainly the laws of the cathodic process in the following.

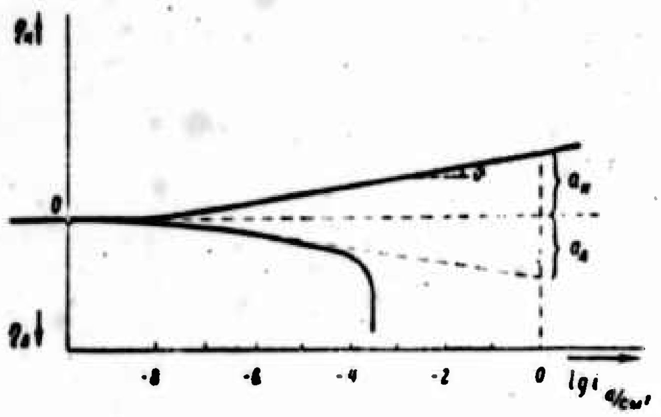

Fig. 68. Overvoltage during the cathodic and anodic processes as a function of the current density on the semilogarithmic scale: tan $\vartheta = b$.

For the graphic representation of the overvoltage curve at not too low current densities it is convenient to use the semilogarithmic system of coordinates, i.e., to plot along one of the coordinate axes not the current densities but their logarithms (see Fig. 68). The polarization curve then is expressed within the entire current density range, in which Eq. (136) applies, by a straight line. In the region of low overvoltages the curve bends towards the axis of the current density logarithm and approaches zero overvoltage asymptotically with increase in the negative value of the logarithm. With this method of representation we can compare on a single graph the overvoltages within a large range of variation of the current densities; this method, however, is not suitable at very low current densities.

The range of the "high" overvoltages of the reaction of cathodic separation of hydrogen can be observed and studied on nearly all metals. On metals of the platinum group the transition to the logarithmic relation (136) takes place only at high current densities; when measuring overvoltages in this range one must take the concentration polarization into account. On other metals the hydrogen overvoltage is fairly high so that the logarithmic relation can be observed even at relatively low current densities (for example, at $i = 10^{-6}$ amp/cm^2).

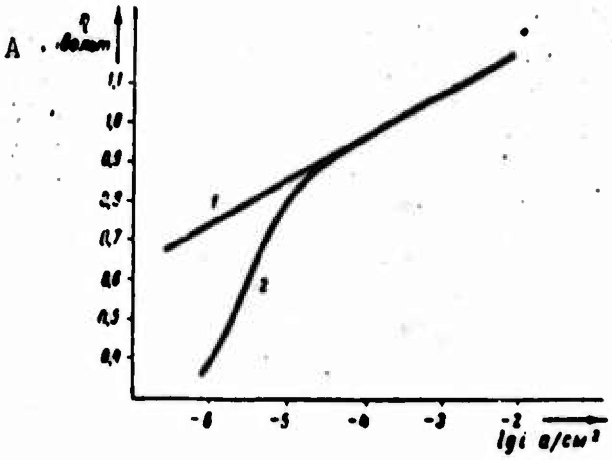

Fig. 69. Effect of traces of oxygen on polarization during hydrogen evolution; 1) normal relation between hydrogen overvoltage and current density; 2) polarization as a function of current density in presence of small quantities of oxygen. A) Volt.

One would have expected that even on these metals a further decrease in the current density would permit a transition to the range of low overvoltages with a proportional dependence on current density. The measurement at very low current densities, however, is greatly complicated by the circumstance that at least small traces of oxygen and other substances, which are reduced at the cathode together with the hydrogen ions, are always present in the solution. The occurrence of this additional reduction process increases the current density at the same potential, or, which is the same, lowers the overvoltage at the same current density (depolarization of the electrode). These subsidiary processes can be neglected as long as the hydrogen reduction current is large. If, however, the density of the polarizing current is small, the rates of the processes of hydrogen ion reduction of other oxidants may become comparable which causes a distortion of the polarization curve of the process of hydrogen ion reduction, expressed in a strong decrease in the measured overvoltage at low current densities (see Fig. 69).

Another peculiar source of difficulty in measurements with very low current densities is the existence of the charge of the double layer. Let us assume by way of an example that during the polarization measurement we have varied the current density from 10^{-10} to 10^{-9} amp/cm^2. Then the electrode potential should become 0.12 v more negative for which we must supply about 2 microcoulombs per cm^2 to it (if we consider the capacitance of the double layer to be 18 microfarad per cm^2). Even if the entire polarization current (10^{-9} amp/cm^2) were used only for charging the surface, we would need $2 \cdot 10^{-6}/10^{-9}$ sec, i.e., about 30 minutes to establish the new potential. Thus the large capacitance of the double layer capacitor complicates the polarization measurements at extremely low current densities (for example, 10^{-10} amp/cm^2). For the above reasons the study of the range of low overvoltages on metals with large values of the constant a involves great experimental difficulties.

The simple relation (136) established by Tafel on the basis of in-

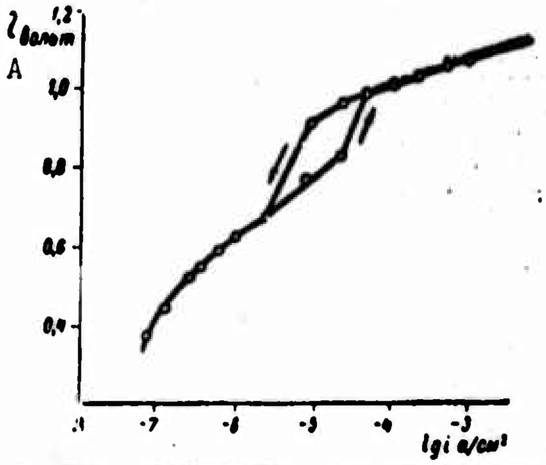

Fig. 70. Hydrogen overvoltage on the lead electrode as function of the current density. A) Volt.

sufficiently accurate experimental data has now been verified for several metals over a broad range of current densities. For example, it can be affirmed with assurance that for the mercury electrode it has been proved to be correct within the range of current densities from 10^{-7} to 1 amp/cm^2 with constant values of the coefficients a and b; with somewhat less confidence we can extend this range to current densities of 10^{-9} to 100 amp/cm^2 [4, 16]. Thus the current density or reaction rate can be varied a million or even billion times and the same quantitative relationship can be maintained. In chemical kinetics there is no other example in which the equation for the reaction rate is retained over such a large range of variation of the reaction rate. In such cases, depending on conditions, the reaction mechanism is usually altered and, consequently, the law is modified. In this respect Eq. (136) is remarkable for its simplicity and the wide range of reaction rates to which it is applicable.

However, there are electrodes for which a more complex relation holds within a certain current density range. For example, for the lead electrode, as Ya.M. Kolotyrkin has shown, the dependence of the overvoltage on ln i is represented by two curves intersecting at a certain relatively low current density. This current density differs somewhat for the transition from low current densities to higher ones and conversely, which causes the appearance of a hysteresis loop on the polarization curve [19] (see Fig. 70). Analogous phenomena are observed on cadmium and thallium electrodes [6]. For all these three metals the potential, at which the transition from one curve to the other takes place, lies near the potential of the zero charge point. In some cases this more complex polarization dependence can be connected with changes in the condition of the surface as a function of the electrode potential. Such changes of the condition are also caused by the frequently observed prolonged variations of the overvoltage when a constant current density is maintained.

Some researchers have expressed the opinion that if the current density is greatly increased the increase in the overvoltage slows down and that the overvoltage tends to its limit value or even decreases [20]. These works, however, have caused some objections and the reality of the described phenomena is doubted. Thus, to avoid the need for introducing corrections for the potential drop in the solution, these authors measured the potential drop after the switching off of the current and extrapolated the potentials to the moment of switching off. As pointed out previously, extrapolation can easily lead to errors at high current densities. It has been shown for the case of the mercury relation between potential and the time elapsed since the switching off of the current is correctly taken into account (see further on), the results obtained by means of the above-described method, confirm the applicability of the Tafel equation also for the range of high current densities.

In some cases anomalous overvoltage — current density relations are observed in the presence of impurities, which lower the overvoltage at the cathode, if the latter are adsorbed only in presence of strong cathodic polarization [21].

Several works have described how the current during hydrogen evolution tends to the limit value in proportion to an increase in cathodic polarization. The latter, however, is usually due to concentration and not to electrochemical polarization; the limit current in these cases can be increased by intensified mixing. The possibility that the hydrogen evolution current reaches the limit point is due to the slowness of the electrochemical and not the diffusion process has not yet been completely refuted for the case of the Ni electrode [16].

The hydrogen overvoltage depends greatly on temperature, the overvoltage decreasing, as a rule, with rise in the temperature. For metals with a large overvoltage, such as mercury, lead, etc., the temperature coefficient of the overvoltage at medium current densities is about 2-4 mv per degree. The slope of the curves which represent η as a function of log i, i.e., the constant b in Eq. (136) increases with increasing temperature in first approximation in proportion to the absolute temperature. In other words, the constant α in Eq. (146b) is practically independent of temperature. Hence we obtain for the temperature coefficient of the overvoltage the expression

$$\left(\frac{\partial\eta}{\partial t}\right)_i = \frac{da}{dt} + \frac{R}{\alpha F}\ln i. \qquad (138)$$

Because $da/dt < 0$, the absolute magnitude of the temperature coefficient of the overvoltage is greater at low current densities and smaller at large current densities as can be seen in Fig. 71 where the curves of the hydrogen overvoltage on a mercury electrode in a solution of 0.25 N H_2SO_4 at temperatures of 0.3°, 20°, 40°, 60° and 80°C are shown [22].

The lowering of the hydrogen overvoltage with increasing temperature indicates an acceleration of the reaction of discharge of the hydrogen ion. As we know, the activation energy of the reaction can be determined on the basis of the relation between reaction rate and temperature. The relation between the temperature coefficient of the reaction rate v and the activation energy W is expressed by the Arrhenius equation

$$\frac{d \ln v}{dT} = \frac{W}{RT^2}. \qquad (139)$$

The use of Eq. (138) for calculating the activation energy of the discharge of the hydrogen ion, however, involves certain difficulties [23]. The fact is that when v is differentiated with respect to T, all other variables on which the reaction rate depends, such as, for example, the concentrations of the reacting substances, should remain constant. In the case of an electrochemical reaction, however, the rate of the process depends not only on the composition of the solution but also on the electrode potential. Hence, when we apply Eq. (138) to an electrochemical process, we must keep not only the composition of the solution constant but also the electrode potential when we differentiate with respect to T. In other words, the magnitude of W should be found from the equation

$$\left(\frac{\partial \ln i}{\partial T}\right)_{\varphi} = \frac{W}{RT^2}. \qquad (139a)$$

In practice, however, we cannot fulfill the condition $\varphi = \text{const}$ during the comparison of current densities at different temperatures. This is due to the fact that the potentials of electrodes which are at different temperatures are not directly comparable because the presence of a temperature gradient in the electrolyte solution causes a potential difference to be formed in it which cannot be calculated or measured directly. Hence a slightly different relation is normally used as

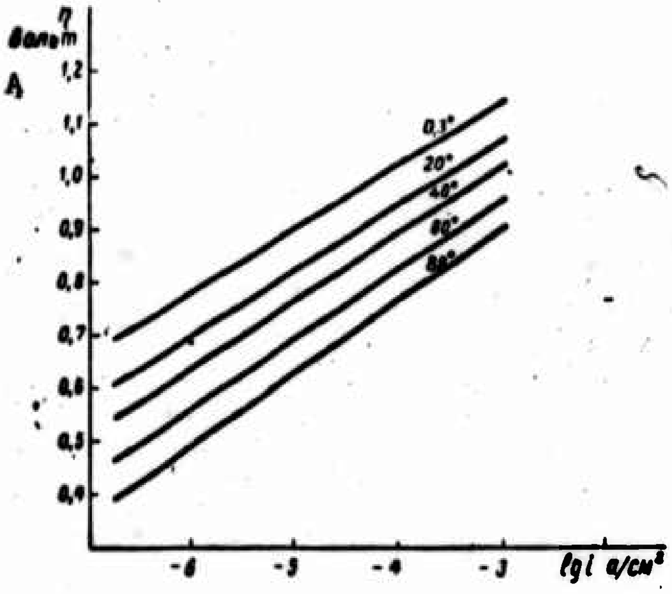

Fig. 71. Hydrogen overvoltage on the mercury electrode as a function of current density in 0.25 N H_2SO_4 solutions at different temperatures. A) Volt.

a basis for the determination of the activation energy of the discharge process, namely the differentiation of ln i with respect to T is carried out not at constant potential but at the constant overvoltage η in consequence of which one avoids the necessity of comparing the potentials of electrodes which have different temperatures. The activation energy thus found, in contrast to W, is designated by the letter A

$$\left(\frac{\partial \ln i}{\partial T}\right)_\eta = \frac{A}{RT^2}. \qquad (139b)$$

As Temkin [23] has shown, the following simple relation exists between W and A

$$W = A + \alpha q,$$

where q is the quantity of heat, absorbed during the formation of 1 gram-equivalent of hydrogen ions from gaseous molecular hydrogen at the equilibrium potential.

The quantity A (like W) depends on η. Indeed, as can be readily derived from Eq. (136b),

$$A = A_0' - \alpha F\eta, \qquad (140)$$

where A_0 is the quantity A at $\eta = 0$. According to the most accurate data for 0.1 N HCl, A_0 is 21,700 calories. The physical meaning of this quantity will be defined more accurately further on.

§4. THE EXCHANGE CURRENT

The existence of two different kinetic laws for the process of hydrogen evolution at high and low overvoltages should not be interpreted as the result of the existence of two different mechanisms of this process. On the contrary, it is easy to show that the appearance of a proportionality between overvoltage and current density at low overvoltages is the natural consequence of the logarithmic relation at high current densities. The following reasoning does not involve the assumption of the correctness of any reaction mechanism.

Up to now we have always understood the intensity (or density) of the anodic or cathodic current to mean the current flowing in the external circuit (for example, from the current source) and passing through the electrode under consideration. In the equilibrium state the measured external current is zero. However, as we know, from the point of view of molecular kinetics, the equilibrium state cannot be regarded as a state of quiescence. A constant exchange takes place between the molecular hydrogen and the hydrogen ions in the solution. A certain number of molecules goes over into the ionic state, yielding electrons to the electrode; at the same time an equivalent number of ions is discharged, absorbing excess electrons. By the magnitude of the exchange current i^0 is meant the quantity of electricity participating in unit time in this exchange reaction.

The existence of an exchange current at the equilibrium potential can be demonstrated by the method of labeled atoms. If, for example, the hydrogen electrode is immersed in a solution containing heavy water, but saturated with normal hydrogen, then even in absence of polarization of the electrode the presence of heavy hydrogen, deuterium, in the gas phase can be demonstrated. The exchange current can be even more clearly detected by means of the unstable hydrogen atoms with the atomic weight 3, tritium, which is radioactive. It should be pointed out, however, that when the exchange current is determined quantitatively by this method, the difference existing between the reactivity of the different isotopes must be taken into account. Thus, the exchange current between deuterium and the D^+ ion is slightly less than the exchange current between hydrogen and the H^+ ion.

If the electrode is polarized, the equilibrium is disturbed and the number of ions formed in unit time is no longer equal to the number of those which disappear. The quantity of electricity required in unit time per cm^2 of surface during the process of the discharge of the hydrogen ions we shall term the discharge current density and designate it by $\overrightarrow{i}$. The ionization current density $\overleftarrow{i}$ is defined analogously.

During cathodic polarization of the electrode the discharge current exceeds the ionization current by the amount of the polarizing cathodic current,

$$i_K = \overrightarrow{i} - \overleftarrow{i}. \tag{141}$$

In proportion to the increase in the cathodic polarization the quantity $\overrightarrow{i}$ increases; conversely, there is not reason for assuming an increase in $\overleftarrow{i}$; if the polarization is sufficiently great, one can thus neglect $\overleftarrow{i}$ compared with $\overrightarrow{i}$ and approximately assume that $i_K \approx \overrightarrow{i}$.

The external current of the anodic polarization is equal to the excess of the ionization current over the discharge current:

$$i_A = \overleftarrow{i} - \overrightarrow{i}. \tag{141a}$$

In a completely analogous manner we can approximately assume $i_A \approx \overleftarrow{i}$ if the anodic polarization is sufficiently high.

During equilibrium the measured external current is zero and the discharge current is equal to the ionization current

$$\overrightarrow{i}_p = \overleftarrow{i}_p = i^0,$$

where i^0, according to definition, is the exchange current.

The previously described experimental regularities which connect overvoltage and current density, related to the directly measured cathodic and anodic currents and not to the discharge or ionization currents. Because, however, the logarithmic relation is observed in the range of large polarizations, in which the cathodic and anodic currents can be approximately equated with the discharge and ionization currents, respectively, it can be inferred that the logarithmic relation is also typical for these currents.

The equation (136) for the cathodic polarization can thus be written in the form

$$\eta_K = a_K + b_K \ln \overrightarrow{i} \quad \text{or} \quad \overrightarrow{i} = k' e^{\frac{\eta_K}{b_K}}, \qquad (142)$$

(where $k' = e^{-(a_K/b_K)}$), and for the anodic polarization,

$$\eta_A = a_A + b_A \ln \overleftarrow{i} \quad \text{or} \quad \overleftarrow{i} = k'' e^{\frac{\eta_A}{b_A}}, \qquad (143)$$

(where $\kappa'' = e^{-(a_A/b_A)}$).

Let us make the only assumption that this logarithmic relation for the discharge and ionization currents which applies over a broad range of potentials, also holds in the range close to the equilibrium potential of the hydrogen electrode.

Then we can write for the cathodic current at low polarizations

$$i_K = \overrightarrow{i} - \overleftarrow{i} = k' e^{\frac{\eta_K}{b_K}} - k'' e^{\frac{\eta_A}{b_A}}. \qquad (144)$$

It follows from the equilibrium condition $i = 0$ at $\eta_K = \eta_A = 0$ that $k' = k'' = i^0$. Moreover, according to the definition of overvoltage, according to Eqs. (135) and (135a), $\eta_K = -\eta_A$. Equation (144) thus can be rewritten in the form

$$i_K = i^0\left(e^{\frac{\eta_K}{b_K}} - e^{-\frac{\eta_K}{b_A}}\right). \qquad (144a)$$

If the electrode polarization is small, and the overvoltage is low compared with b_K and b_A, the exponential terms of Eq. (144a) can be expanded into series and we can limit ourselves to the first two terms of the expansion

$$i_K = i^0\left[\left(1+\frac{\eta_K}{b_K}+\dots\right)-\left(1-\frac{\eta_K}{b_A}+\dots\right)\right] = i^0\left(\frac{1}{b_K}+\frac{1}{b_A}\right)\eta_K. \qquad (145)$$

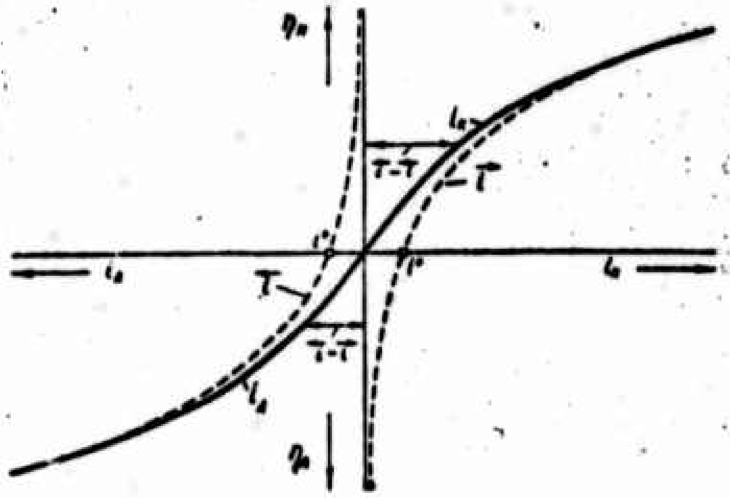

Fig. 72. Overvoltage as a function of the discharge and ionization currents and of the cathodic and anodic currents.

The same relation is obtained for i_A so that the index k at i and η in Eq. (145) can be omitted:

$$i = i^0\left(\frac{1}{b_K}+\frac{1}{b_A}\right)\eta. \qquad (145a)$$

It can be seen from the derivation of Eq. (145) that the proportionality between overvoltage and current density at low polarization arises naturally as a result of the superposition of two processes, the discharge process and the ionization process, each of which obeys a logarithmic law. Moreover from this equation follows the relation between the constants a, b and w of the experimental overvoltage equations (136) and (137)

$$w = \frac{\eta}{i} = \frac{1}{i^{\circ}\left(\frac{1}{b_K}+\frac{1}{b_A}\right)} = \frac{e^{\frac{\eta_K}{b_K}}}{\frac{1}{b_K}+\frac{1}{b_A}}. \qquad (146)$$

The foregoing is clearly illustrated by Fig. 72 in which the overvoltage is shown as a function of the discharge and ionization currents and also of the density of the external current. The points corresponding to the values $\vec{i}$, $\overleftarrow{i}$ and $i_K = \vec{i} - \overleftarrow{i}$ and in the same manner, those corresponding to the values $\vec{i}$, $\overleftarrow{i}$ and $i_A = \overleftarrow{i} - \vec{i}$ at a given η_A, lie on lines which are parallel to the abscissa at the corresponding values of η_K or η_A. It is evident from Fig. 72 that near the equilibrium potential ($\eta = 0$) the curve plotted on the basis of the absolute differences of the abscissae of the logarithmic curves is a straight line which passes through the origin of the coordinates; when the polarization is increased, the linearity is lost and the curve for the external current approximates increasingly a logarithmic curve. The points of intersection of curves for $\vec{i}$ and $\overleftarrow{i}$ with the abscissa axis (with the overvoltage value $\eta = 0$) give the exchange current. In the semilogarithmic presentation these curves assume the form shown in Fig. 73. With this method of representation the curves for the discharge current and the ioniza-

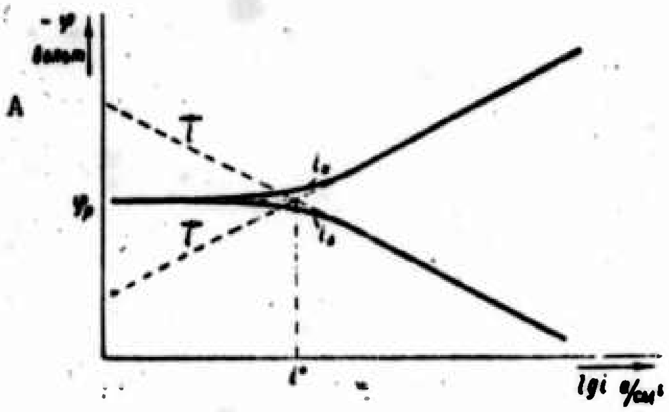

Fig. 73. Overvoltage as a function of the logarithm of the discharge and ionization current densities and the logarithm of the cathodic and anodic currents. A) Volt.

tion current are linear over the entire range of current densities.

We remember that from the polarization measurements we can determine directly only the overvoltage – external current curves. It follows from Fig. 73 that by an indirect method one can find the exchange current from the polarization measurements if we extrapolate the linear section of the overvoltage curve (in the semilogarithmic coordinate system) the the overvoltage value of zero.*

§5. EFFECT OF THE COMPOSITION OF THE SOLUTION ON THE HYDROGEN OVERVOLTAGE

Of great importance for the elucidation of the mechanism of the electrochemical reaction of cathodic hydrogen separation and for the determination of the causes of the overvoltage is the investigation of the effect of the composition of the solution on the overvoltage. This problem has been repeatedly examined in the foreign electrochemical literature but has not been solved correctly. In most older works, in review articles and textbooks the concept of the independence of the overvoltage of the composition of the solution and, in particular, of the hydrogen ion concentration or pH of the solution has taken a firm hold. Actually, however, as follows from the investigations of the Czech scientist Herasymenko [63] and, particularly, from the work of Soviet authors, the composition of the solution exerts a strong influence on the kinetics of hydrogen separation and on the overvoltage. Within the framework of this course it is not possible to present all the experimental data; let us consider merely a few important cases.

The hydrogen overvoltage in not very concentrated solutions of strong acids which do not contain foreign electrolytes (for example, neutral salts) is really independent of the concentration of the acid, i.e., of the pH of the solution. Thus, for example, the polarization curves of the process of hydrogen evolution at the mercury cathode from 0.1 N, 0.01 N and 0.001 N HCl solutions coincide almost completely

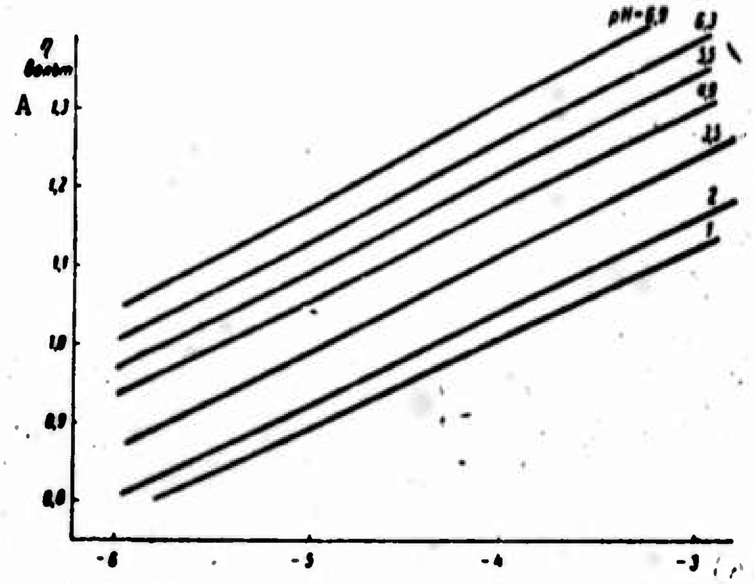

Fig. 74. Hydrogen overvoltage on the mercury electrode as a function of the current density in buffer solutions within the pH range of 1 to 7; A) Volt.

[24]. This coincidence was the cause of the widespread belief that the overvoltage is independent of the pH of the solution. However, as will be shown further on, this independence of the overvoltage of the pH in pure solutions of strong acids is the result of the opposite effect of two factors and should by no means be regarded as a typical feature of the process of hydrogen separation. On the contrary, in all other cases the overvoltage varies considerably as a function of the pH of the solution, on the total electrolyte concentration and on the presence of surface-active substances in the solution.

The most typical measurement results are those on the overvoltages in solutions with constant total electrolyte concentration in which the pH is varied by variation of the ratio of the individual components, for example, in buffer solutions or in acidified salt solutions [25]. Figure 74 shows the curves of the overvoltage during hydrogen separation at the mercury electrode as a function of the logarithm of the current density in solutions with a total electrolyte concentration of 0.3 eq/liters; the pH of these solutions was varied from 1 (0.1 N hydrochloric acid + 0.2 N KCl) to 7 (phosphate buffer solution). If comparing the overvoltages in these solutions at the same current density, for example, at $i = 10^{-4}$ amp/cm^2 (Fig. 75, left), it can be seen that the overvoltage increases by about 55-58 mv with unit increase of the pH.

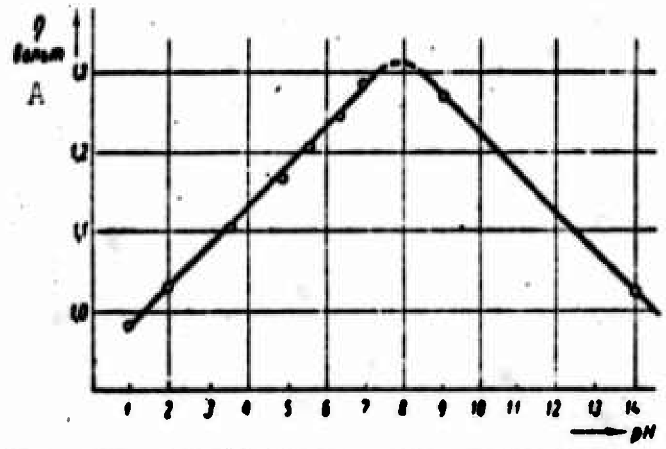

Fig. 75. Hydrogen overvoltage at the mercury electrode as a function of the pH of the solution at a current density of $1 \cdot 10^{-4}$ amp/cm^2; A) Volt.

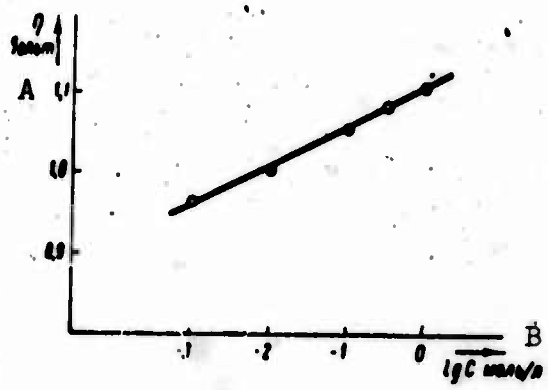

Fig. 76. Hydrogen overvoltage in 0.001 N solutions of HCl + xKCl as a function of total electrolyte concentration $c = 0.001 + x$ at a current density $i = 10^{-4}$ amp/cm^2; A) Volt; B) mole/liter.

Also of interest are the overvoltage measurements in solutions with constant pH, in which the total electrolyte concentration is increased by the addition of neutral indifferent salts. Figure 76 shows the measurement results on the mercury electrode in 0.001 N solutions of hydrochloric acid, containing different concentrations of potassium chloride, in which the overvoltages are compared at constant current density [26]. It follows from these data that when the total concentration of the uni-univalent electrolyte is increased ten times at constant pH, the overvoltage increases by about 55-56 mv. Neutral salts with polyvalent cations exert a particularly strong influence on the hydrogen overvoltage. Thus, for example, the addition of $1 \cdot 10^{-4}$ eq/liter of lanthanum chloride to 0.001 N HCl solution increases the overvoltage by 0.120 v, i.e., it has the same effect as the addition of 0.1 eq/liter of potassium chloride [24].

Analogous regularities are observed on other metals, for example, nickel, although they are often less clearly expressed than at the mercury electrode.

Relatively little experimental data are as yet available for alkaline solutions. The direct quantitative study of the process of hydrogen separation on the mercury electrode at a pH over 8 is difficult because the potential of hydrogen separation is so strongly shifted to the negative side that in addition to hydrogen separation the process of discharge of alkali metal ions with formation of amalgam begins. For this reason the rate of the hydrogen separation reaction at the mercury electrode in alkaline solution at a given overvoltage can be determined only by the volume of liberated hydrogen or indirectly from the data on the kinetics of the decomposition of the amalgams of the alkali metals [27, 8] (see Chapter 8). On other metals, on which the hydrogen overvoltage is less (for example, on nickel or platinum), direct measurements are possible [13].

The results obtained for the nickel and mercury electrode show that in alkaline solutions, in contrast to acid solutions, the hydrogen overvoltage does not increase, but, on the contrary, decreases by approximately 58 mv if the pH increases by unity, i.e., if the alkali concentration is increased tenfold. This regularity, however, is not observed in the case of the platinum electrode on which the overvoltage in alkaline solutions depends only slightly on concentration. In a normal alkaline solution the overvoltage at the nickel electrode has almost the same value as in normal acid; on mercury it is slightly greater in alkaline solution. The curves for the overvoltage as a function of pH for the mercury electrode in acid and alkaline solutions with constant total electrolyte concentration are given in Fig. 75.

The above-given simple regularities are observed in not too concentrated electrolyte solutions. In solutions with an electrolyte concentration of more than 0.5-1 eq/liter, deviations are observed which increase with increase in concentration.

The problem of the hydrogen overvoltage in concentrated solutions is of great practical importance because in engineering one often has to deal with concentrated solutions, for example, in electrometallurgical processes (electrolytic refining of copper and other metals), in industrial electrolysis, corrosion of metals, etc. A detailed study of overvoltage in concentrated solutions of acids, carried out by Z.A. Iofa, showed that the independence of the overvoltage on acid concentration observed in dilute solutions does not apply here and that the overvoltage decreases regularly with increase in the acid concentration. Figure 77 gives curves of the overvoltage as a function of the logarithm of the current density in hydrochloric acid solutions. The upper curve shows the overvoltages in 0.1 N solution. As pointed out previously, the overvoltage curves for more dilute solutions practically coincide with the curve for the 0.1 N solution. The overvoltage curves for more concentrated solutions are lower; these curves are no longer parallel. The decrease in the overvoltage at low current densities and moderate concentration is more pronounced than for high concentrations; in very low concentrations it is more pronounced than for high concentrations; in very concentrated solutions it attains several tenths of a volt. Thus, the effect of the drop of the overvoltage is quite considerable; it corresponds to an increase in current density, i.e., the reaction rate at the same overvoltage (line *A-A'*) of several thousand times [7].

When studying and comparing the kinetic regularities in solutions with different pH it is best to compare the potentials of the polarized electrode and not the overvoltages. The fact is that when the pH of the solution varies, the variation of the overvoltage is due not only to the shift of the potential of the polarized electrode but also to the potential shift of the equilibrium electrode. Hence the overvoltage variation upon transition to a solution with different pH cannot serve as a characteristic of the potential variation of the polarized electrode.

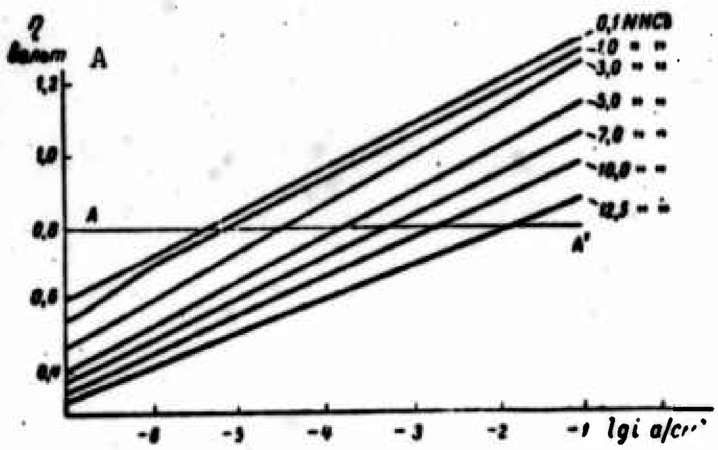

Fig. 77. Hydrogen overvoltage at the mercury electrode as a function of current density in concentrated solutions of hydrochloric acid. A) Volt.

It has been pointed out in the foregoing that in dilute solutions of pure strong acids the overvoltage is independent of the acid concentration. This means that the potential of the polarized cathode at a certain constant current density is shifted as a function of pH approximately in the same way as the potential of the equilibrium electrode, i.e., by 58 mv to the positive side if the hydrogen ion concentration is increased tenfold. The equation for the potential as a function of the hydrogen ion concentration and the current density is obtained by substituting the respective expressions for the overvoltages (see Eq. (136b))

$$\eta = a + \frac{2RT}{F} \ln i \qquad (147)$$

and for the potential of the equilibrium hydrogen electrode

$$\varphi_p = \text{const} + \frac{RT}{F} \ln [\mathrm{H}^{\cdot}] \qquad (134a)$$

into the equation $\eta = \varphi_p - \varphi$ (Eq. 135a):

$$\varphi = \text{const} + \frac{RT}{F} \ln [\mathrm{H}^{\cdot}] - \frac{2RT}{F} \ln i. \qquad (148)$$

In solutions containing in addition to acid a neutral salt with constant total electrolyte concentration, the overvoltage at i = const decreases by 55-58 mv when the pH decreases by unity, i.e., it obeys the law

$$\eta = a' - \frac{RT}{F} \ln [\mathrm{H}^{\cdot}] + \frac{2RT}{F} \ln i, \qquad (149)$$

where a' is a constant independent of the pH. The equilibrium potential is then shifted by the same amount to the positive side. This means that with tenfold increase in the hydrogen ion concentration the electrode potential at i = const becomes 2 × 0.058 = 0.116 v more positive:

$$\varphi = \text{const} + \frac{2RT}{F} \ln [\mathrm{H}^{\cdot}] - \frac{2RT}{F} \ln i. \qquad (150)$$

In the last equation the coefficients in front of the logarithm of the hydrogen ion concentration and the logarithm of the current density are equal in magnitude but differ in sign. This circumstance allows an important conclusion with regard to the order of the reaction of cathodic hydrogen separation; equation (150) can be rewritten in the form

$$i = k [\mathrm{H}^{\cdot}] e^{-\frac{\varphi F}{2RT}}, \qquad (151)$$

from which follows that a constant electrode potential the rate of the reaction (current density) is directly proportional to the hydrogen ion concentration in the solution, i.e., that the reaction of the discharge of hydrogen ions is a first-order reaction.

It is easy to see that the law (148) corresponds to a reaction order of one-half; it will be shown further on, however, that this fractional order of the reaction is merely apparent and that in this case the reaction is also a first-order reaction.

In alkaline solutions with constant electrolyte concentration the overvoltage at the mercury electrode decreases approximately by 58 mv when the pH increases by unity; the equilibrium potential is then shifted the same amount to the negative side. It follows from this that in alkaline solutions at constant current density the electrode potential remains constant and independent of the pH

$$\varphi = \text{const} - \frac{2RT}{F} \ln i. \qquad (152)$$

In this case the hydrogen ion concentration does not affect the rate of hydrogen separation and the reaction is of zeroth order with respect to the hydrogen ions.

Equation (150), which expresses the cathode potential as a function of the hydrogen ion concentration at constant total electrolyte concentration, enables us to derive the equation for the concentration polarization during the separation of hydrogen from solution of acids, containing an excess of an indifferent salt. The concentration polarization is caused by a decrease in the hydrogen ion concentration near the electrode surface during the passage of current. According to Eq. (56) the concentration at the surface* $[H^+]^s$ is connected with the volume concentration of the hydrogen ions $[H^+]^0$, the current density i and the limit current density i_d by the relation

$$[H^+]^s = [H^+]^0 \left(1 - \frac{i}{i_d}\right). \qquad (153)$$

By substituting (153) into Eq. (150) which, during concentration polarization, naturally contains the H^+ ion concentration at the surface and not in the volume, we obtain

$$\varphi = \text{const} + \frac{2RT}{F} \ln \frac{[H^+]^0}{i_d} + \frac{2RT}{F} \ln \frac{i_d - i}{i}. \qquad (154)$$

Because the limit current density i_d is proportional to the volume concentration H^+, the relation $[H^+]^0/i_d$ is a constant and Eq. (154) assumes the form

$$\varphi = \text{const} + \frac{2RT}{F} \ln \frac{i_d - i}{i}. \qquad (155)$$

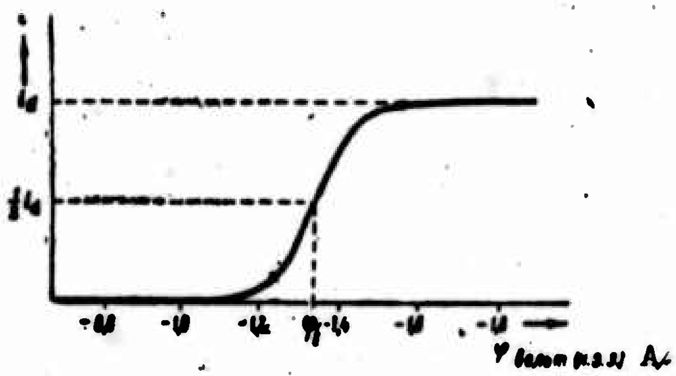

Fig. 78. Current density as a function of potential during concentration polarization for the case of discharge of the hydrogen ion. A) Volt (n.v.e.).

Equation (155) is formally reminiscent of the equation for the concentration polarization for the deposition of a metal with formation of amalgam (Eq. (61a) at $n = 1/2$. The current density i as a function of the potential φ is expressed by the waveshaped curve shown in Fig. 78, in consequence of which Eq. (155) is termed the equation of the hydrogen wave. As follows from Eq. (154), the half-wave potential during hydrogen separation at the mercury electrode from acid solutions in presence of an excess of indifferent electrolyte is independent of the hydrogen ion concentration in the solution. However, because the quantity $[H^+]^0/i_d$ enters into this equation, this potential is slightly dependent on the conditions of supply of the substance to the electrode. Under normal conditions of operation of the drop electrode it is −1.34

V.

In spite of the external similarity between the hydrogen wave equation and the concentration polarization equation during the formation of amalgam there is an important difference between them. For the reaction of amalgam formation, which is a reversible electrochemical process, involving only concentration polarization, the quantity n is an integral number which expresses the valency of the metal; in the case of the irreversible process of hydrogen separation this quantity is replaced by a certain fraction which characterizes the dependence of the rate of the electrode process on the potential.*

There are several substances whose addition to the solution alters the hydrogen overvoltage considerably, although these substances do not participate directly in the electrode reaction.

The simplest and most obvious case is that when the addition of a substance alters the composition or properties of the surface of the metallic electrode. If we use, for example, a lead electrode and add a certain quantity of platinum chloride to the electrolyte, the platinum is deposited on the lead; following this, the separation of hydrogen will take place predominantly on the crystals of the deposited platinum and, consequently, the overvoltage on this electrode will be considerably reduced.

Additions of organic acids or alcohols can cause a very marked increase in the overvoltage, attaining 0.1-0.2 v, which corresponds to a decrease in the rate of hydrogen separation (at constant overvoltage) by a factor of tens or hundreds [61]. With increase in the length of the carbon chain of the organic substances their effect increases at a given concentration. The increase in the overvoltage, however, is observed only within a fairly narrow potential range which is not very far from the zero charge potential in a given solution.

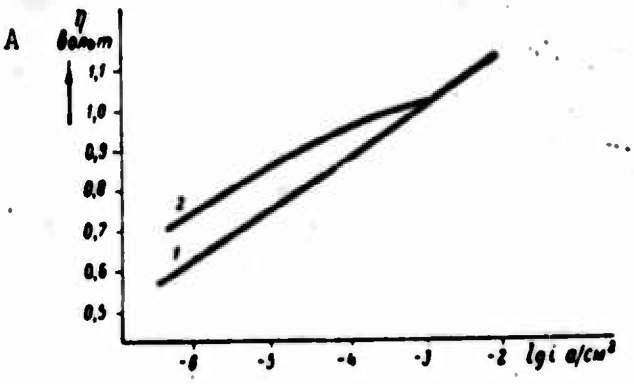

Fig. 79. Effect of organic surface-active molecules on the hydrogen overvoltage on the mercury electrode: 1) Overvoltage as a function of the current density in 2 N HCl; 2) overvoltage as a function of the current density in the same solution in presence of caproic acid. A) Volt.

Figure 79 gives the curve of the hydrogen overvoltage at the mercury electrode in a solution of pure 2 N hydrochloric acid and in the same solution, containing caproic acid [29]. As this diagram shows, the effect of the caproic acid on the reaction of hydrogen separation is apparent only at low current densities when the overvoltage is less than 1.020 v. As soon as this overvoltage is attained, the effect ceases; the current density, with the overvoltage almost constant, increases to the value typical for the pure solution of hydrochloric acid. At greater current densities the overvoltage curves for a solution of pure hydrochloric acid and for a solution containing caproic acid coincide completely.

It is natural to connect the cessation of the effect of the caproic acid on the reaction of hydrogen separation at more negative potentials than −1.00 v* with the desorption of the acid molecules from the electrode surface. This is also indicated by the data on the electrocapillarity measurements in these solutions and the measurements of the double layer capacitance, from which follows that the caproic acid is adsorbed on the surface of the mercury electrode within the potential

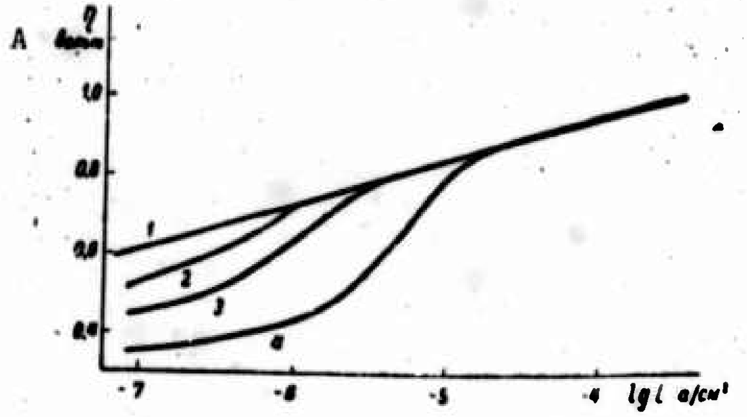

Fig. 80. Effect of surface-active anions on the hydrogen overvoltage at the mercury electrode. Overvoltage as a function of the current density in acidified 1 N solutions of the salts: 1) Na_2SO_4; 2) KCl: 3) KBr; 4) KI. A) Volt.

range from +0.055 v to −1.00 v (relative to the standard hydrogen electrode), i.e., that exactly at a potential of −1.00 v complete desorption of the caproic acid takes place. It follows from this that the effect of organic alcohols and acids and also of other organic substances is connected with an adsorption of these molecules on the electrode surface.

An even greater variation of the hydrogen overvoltage than in the case of adsorption of neutral molecules is observed when surface-active ions are adsorbed.

The adsorption of anions on mercury results in a lowering of the hydrogen overvoltage as can be gaged from Fig. 80, in which the overvoltage curves on mercury for acidified solutions of the salts Na_2SO_4, KCl, KBr and KI [30] are shown. The overvoltage curve for an inactive electrolyte (1 N Na_2SO_4) within the current density range from $5 \cdot 10^{-8}$ to 10^{-2} amp/cm^2 is a straight line. The curves for the solutions containing surface-active halogen ions, at moderate current densities, show a considerable decrease in the overvoltage. At large current densities the effect of the lowering of the overvoltage disappears. As in the case of the organic alcohols and acids, the cessation of the effect of the anions on the process of hydrogen separation is connected with a desorption of the anions from the electrode surface at a fairly large negative surface charge. In accordance with the results of the electrocapillarity measurements, the potential at which the anion ceases to influence the hydrogen overvoltage is the more negative, the greater the adsorption of the anion.

A considerable increase in the hydrogen overvoltage is caused by the adsorption on the surfaces of metallic electrodes of positively charged organic ions, such as, for example, the cations of tetraalkylammonium bases. In contrast to the surface-active anions, these substances are adsorbed on the negatively charged electrode surface and are desorbed at more positive potentials than the zero charge potential. The effect of these substances should therefore be particularly pronounced in the range of fairly high current densities and relatively large overvoltages (see Fig. 81). Some other basic organic substances such as, for example, quinine, diphenylamine, etc., cause a decrease in the hydrogen overvoltage [62]. Further on we shall consider the mechanism of this last effect.

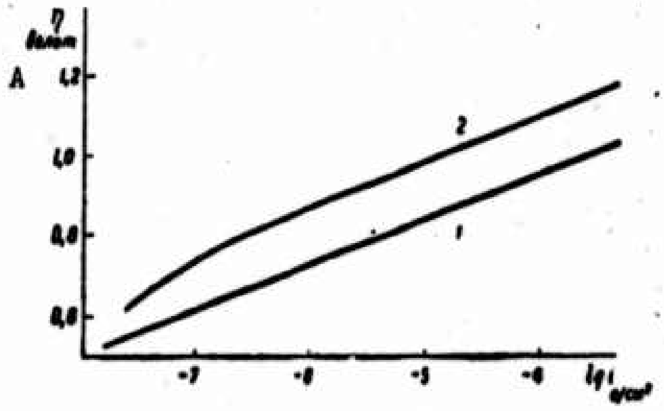

Fig. 81. Effect of surface-active cations on hydrogen overvoltage at the mercury electrode: 1) Overvoltage in 1 N H_2SO_4; 2) in 1 N H_2SO_4 + + 0.0025 N $[N(C_4H_9)_4]_2SO_4$; A) volt.

§6. CAUSES OF THE APPEARANCE OF OVERVOLTAGE

The accumulation of a large number of experimental data on the kinetics of the cathodic separation of hydrogen has led to several attempts at a generalized and theoretical interpretation. During the 50 and more years which have passed since the study of hydrogen overvoltage had begun, numerous theories have appeared trying to explain this phenomenon. Many of these theories are only of historical interest at the present time and we shall not dwell on them in greater detail in the following. Others, conversely, have been widely developed and confirmed by experimental data.

A theory of the hydrogen overvoltage ought to provide a physical explanation for the regularities, found experimentally and should connect these regularities with other known physical and chemical phenomena. A correctly constructed theory enables as yet not investigated regularities to be predicted and to control the electrochemical processes involving hydrogen separation, deliberately.

The electrode reaction during the discharge of hydrogen ions takes place in two sequential stages which can be represented in the following way*:

$$2H^{+} + 2e \xrightarrow{I} 2H \xrightarrow{II} H_2. \qquad (A)$$

In consequence of the existence of repulsive forces between particles with like charge, two hydrogen ions cannot be discharged at the same point of the electrode surface simultaneously; hence, when hydrogen is deposited, atoms are first formed and not hydrogen molecules. The atoms formed during the discharge process then are transformed into hydrogen molecules by a secondary chemical reaction. Only the first of these stages is a real electrochemical process, i.e., connected with an alteration of the charge of the reacting particles. The second stage is a normal chemical reaction, which takes place at the electrode surface.

The most widespread theories of hydrogen overvoltage can be combined into two groups depending on which of these two stages they connect with the cause of the overvoltage.

Let us consider the equilibrium state between the hydrogen ions and atoms and between the atoms and molecules

$$2H^{\cdot} + 2e \rightleftarrows 2H, \tag{A'}$$

$$2H \rightleftarrows H_2. \tag{A''}$$

These equilibria are of a dynamic nature and involve exchange processes. Let us designate the exchange rates for the first and second stage (in electrical units) by i_1^0 and i_2^0. These quantities play for each stage separately the same part as the current exchange i^0, defined in the preceding chapter, plays for the process as a whole.

When current passes through the electrode, the equilibrium is upset; at the cathode, for example, the reactions (A') and (A") proceed from left to right. Let us introduce the quantities $\vec{i}_1$ and $\overleftarrow{i}_1$ which determine the rate of the cathodic and anodic reactions for the first stage (discharge and ionization currents) and the analogous quantities $\vec{i}_2$ and $\overleftarrow{i}_2$ for the second stage (recombination and dissociation currents). According to definition, we have for the equilibrium state

$$\vec{i}_1 = \overleftarrow{i}_1 = i_1^0 \text{ и } \vec{i}_2 = \overleftarrow{i}_2 = i_2^0.$$

In the stationary state the number of H atoms at the electrode surface remains constant; under this condition the density of the external current is equal to the difference of the current densities of the cathodic and anodic reactions for the first and the second stage:

$$i = \vec{i}_1 - \overleftarrow{i}_1 = \vec{i}_2 - \overleftarrow{i}_2, \tag{156}$$

counting the cathodic direction of the current in the external circuit as positive (see remark on page 225).

The kinetic regularities of the reactions are determined by the correlation of the quantities i, i_1^0 and i_2^0. Assuming, for example, that the exchange current of the second stage slightly exceeds the exchange current of the first and that the density of the external current has an intermediate value ($i_1^0 < i < i_2^0$). Because the density of the external current is small compared with i_2^0, the equilibrium of the second stage is not greatly disturbed; the currents $\vec{i}_2$ and $\overleftarrow{i}_2$ are almost compensated as previously. In contrast to this, for the second stage $\vec{i}_1$ becomes considerably greater than i_1^0, and $\overleftarrow{i}_1$ decreases which causes a marked disturbance of the equilibrium. If the difference between the exchange rates of the first and second stage differs sufficiently, the quantity $\overleftarrow{i}_1$ can be neglected over the above-mentioned wide current density range compared with $\vec{i}_1$, i.e., the rate of the over-all process is determined by $\vec{i}_1$, and the first stage becomes irreversible, while the second stage can be regarded as an equilibrium state as previously. Conversely, if i_2^0 is by far less than i_1^0, and i has an intermediate value, the rate of the over-all reaction is determined by the quantity $\vec{i}_2$ and the second stage becomes irreversible, while conditions close to equilibrium are maintained for the first stage. In general it can be said that the rate of the over-all reaction is determined by the kinetic laws of that of its intermediate stages, which has the smallest exchange current and to which we shall refer in the following by the conventional term "slowest stage of the reaction."* If the difference between the exchange currents is sufficiently great the other stages (the fast stages) can be regarded as equilibrium stages as previously.

The appearance of an overvoltage during the cathodic separation of hydrogen is a sign of disturbance of the equilibrium and may be connected with a slowing down of one of the stages of the process. The theories which connect the causes of overvoltage with a slowing down of the second, the chemical stage, were historically the first to be developed. These ideas have been preserved in some form or other to this day and explain part of the experimental data satisfactorily.

The assumption that the kinetic delay of the first, the electrochemical stage, is the cause of the polarization of the electrode has been little used for a long time. In recent years, owing to the work of Soviet electrochemists, these ideas have been reconsidered to a considerable degree and perfected and have been given a firm experimental basis.

These groups of theories we shall consider in their historical sequence, i.e., first the theories involving the concept of the slowing down of the process of removal of adsorbed atomic hydrogen, and then the theories, involving the concept of the slowing down of the discharge process.

§7. RECOMBINATION THEORIES OF HYDROGEN OVERVOLTAGE

The theories in which the appearance of overvoltage is connected with an accumulation of a quantity of adsorbed atomic hydrogen in excess of the equilibrium at the electrode surface, taking place in consequence of a slowing down of its removal, we shall term desorption theories. If it is also assumed in these theories, as has been explained in the foregoing, that the process of removal takes place via a combination of hydrogen atoms to molecules, we shall term these theories recombination theories (sometimes one speaks also of a "catalytic removal mechanism").

During the cathodic separation of hydrogen a certain stationary concentration of adsorbed atoms is established at the electrode surface, depending on the ratios of the rates of their formation and removal from the surface. According to the basic assumption of the desorption theories, the discharge of the hydrogen ions and the ionization of the adsorbed atoms takes place freely and at a fair rate; at any values of the density of the external polarizing current one can assume with sufficient approximation that the equilibrium between the ions and adsorbed atoms is not disturbed. Hence, the discharge stage should not affect the over-all kinetics of the reaction.

The further transformation of the hydrogen atoms into molecules then no longer takes place freely but at a certain limited rate, depending on the surface concentration of the adsorbed hydrogen. During the passage of current the surface hydrogen concentration assumes a value at which the rate of removal of the atoms becomes equal to the rate of their formation, i.e., corresponds to the density of the polarizing current. The higher the density of the cathode current, the greater is the stationary surface concentration of the hydrogen atoms.

The accumulation of the adsorbed hydrogen in quantities, exceeding the equilibrium concentration, shifts the electrode potential to the negative side. This pattern is somewhat reminiscent of the phenomenon of concentration polarization, where the passage of current also alters the stationary concentration of the potential-determining substance near the electrode surface and in consequence of which the electrode potential is shifted. There is a principal difference, however, between these two phenomena. In the case under consideration here we are dealing with the surface concentration of hydrogen atoms which are directly at the electrode, this concentration varying not in consequence of a slowing down of the removal of the reacting substance from the electrode surface via diffusion or migration but in consequence of a slowing down of one of the stages of the electrochemical reaction itself. Hence the use of the term "concentration polarization" is not expedient in this case.

The presence of an excess of adsorbed hydrogen on the surfaces of certain electrodes during their cathodic polarization can be demonstrated by a direct experimental method. For this purpose we can use, for example, the well-known property of certain metals (for example, of iron, palladium, etc.) to not only adsorb, but also to dissolve atomic hydrogen in the volume of the metal.

During cathodic polarization of iron in an acid solution the concentration of dissolved hydrogen which penetrates into the depth of the metal, attains values which exceed many times the concentration corresponding to the solubility of gaseous hydrogen at atmospheric pressure. This follows, in particular, from the fact that in the presence of inclusions in the metal which catalyze the recombination of hydrogen atoms to molecules, the pressure of the hydrogen given off from the metal can attain hundreds of atmospheres, causing a mechanical disintegration of the metal. This phenomenon indicates that in consequence of the increase in the concentration of adsorbed hydrogen at the metal surface its atoms begin to diffuse into the metal lattice or along the grain boundaries.*

If palladium foil is immersed in an electrolyte solution and polarized on one side, its potential on the other, the so-called diffusion side begins to shift to the negative side (see device in Fig. 82) [15, 58]. This "overvoltage transfer" through the metal also points to an excess hydrogen concentration with respect to the equilibrium with the gaseous hydrogen, diffusing from the polarized side to the diffusion side. In the case of palladium this effect is quantitatively not large and is evidently mainly due, not to a slowing down of the recombination of adsorbed atomic hydrogen but to a slowing down of the removal of molecular hydrogen from the solution [15]. In the case of such an "overvoltage transfer" through iron, however, considerable potential shifts can be observed under certain conditions, which could not be explained without the assumption of a variation of the composition of the adsorbed hydrogen layer on the polarization side of the electrode [31].

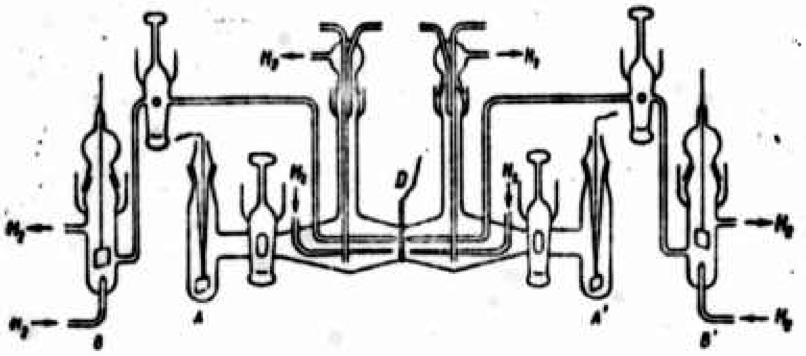

Fig. 82. Device for the study of the polarization of a palladium electrode and the penetration of hydrogen into the palladium: D) Palladium electrode (cathode); A) anode; B) auxiliary hydrogen electrode for the measurement of the potential of the electrode D. A' and B' can also serve as anode and auxiliary electrode.

An increase in the concentration of adsorbed hydrogen on the electrode surface can also be observed indirectly by means of measurement of the rate of change of the electrode potential after the switching off of the polarizing current (overvoltage decay curve). If the overvoltage is due to the accumulation of adsorbed atomic hydrogen, then after the switching off of the current the stationary surface concentration of the hydrogen should decrease and the excess atoms should be removed from the surface. This process is not instantaneous and the potential shifts relatively slowly. On the other hand, if the overvoltage is caused by some other factor, and the concentration of the adsorbed hydrogen has the equilibrium value, then after the switching off of the current only a change in the number of charges in the electrical double layer at the electrode surface can take place. This process is much more rapid because the number of charges in the double layer is small compared with the possible number of adsorbed atoms. Thus, on the basis of the rate of decay of the overvoltage following the switching off of the polarizing current one can infer the presence of excess adsorbed hydrogen on the electrode surface. Measurements of this type indicated the presence of excess adsorbed hydrogen, for instance, on the nickel electrode; according to the data of P.D. Lukovtsev and S.D. Levina [32] the quantity of adsorbed atomic hydrogen on this electrode at an overvoltage of 0.3 v ir 0.5 N NaOH solution is approximately 10^{15} atoms per 1 cm^2 of surface. As N.A. Fedotov [33] showed, adsorbed hydrogen cannot be detected by this method on the mercury electrode, which is in agreement with the data of other electrochemical measurements (see Introduction, §8).*

The stationary surface concentration of atomic hydrogen depends on the rate of removal of the hydrogen atcms formed during the discharge from the electrode surface which can be removed from the surface by different methods, for example, by recombination with formation of molecular hydrogen, by interaction with hydrogen ions, direct desorption from the surface, etc. In this section we shall consider the first of the above enumerated mechanisms of the removal of adsorbed hydrogen.

Before examining the laws whic connect the overvoltage of the electrode with the kinetics of the chemical process of the recombination of the hydrogen atoms, we must recall certain thermodynamic and kinetic properties of atomic hydrogen. The normal electrode potential φ_H^0 of the atomic hydrogen electrode, i.e., an electrode in equilibrium with gaseous hydrogen atoms at atmospheric pressure, as was mentioned in §8 of the Introduction, is 2.096 v.

Thus the potential of the atomic hydrogen electrode at a pressure of the atomic hydrogen of p_H is expressed by the eouation

$$\varphi_H = -2{,}096 + \frac{RT}{F} \ln \frac{a_{H^+}}{p_H}. \qquad (157)$$

The expression for the potential of the hydrogen electrode can be transformed in such a manner that the concentration of the adsorbed hydrogen and not the pressure of gaseous molecular or atomic hydrogen figures in it (Formula 134 or 157). At low adsorption the activity of the adsorbed hydrogen can be considered to be proportional to its surface concentration and this expression assumes the form

$$\varphi_{H_{\text{адс}}} = \varphi^{0}_{H_{\text{адс}}} + \frac{RT}{F} \ln \frac{a_{H^{\cdot}}}{[H]_{s} \cdot a_{H,\text{ac}}}. \qquad (158)$$

Despite the great thermodynamic instability of atomic hydrogen, the process of recombination of the atoms to molecules does not take place instantly (i.e., not at every collision of two atoms) but at a certain measurable, moderate rate. This is due to the fact that the large quantity of energy liberated during the interaction of two atoms is concentrated in the molecule thus formed which is thus fairly unstable and again decomposes into free atoms.

This difficulty is partly overcome on metal surfaces because the excess energy of the reaction of the atoms is drained off by the metal surface and dissipated. Nonetheless, experiments with free hydrogen atoms have shown that the reaction of recombination of the atoms takes place even on metal surfaces at a finite rate and that different metals have different catalytic activity with regard to this reaction. The rate of recombination of the atoms on the surface of different metals can be determined experimentally if a flow of atomic hydrogen (obtained, for example, in an electric discharge) is directed past a metallic wire: the greater the rate of recombination of the atoms at the metal surface, the more is the wire heated [34]. Such experiments have shown that the recombination takes place relatively rapidly on the surface of platinum and nickel, i.e., these metals are good catalysts for the recombination reaction; on a wire of lead or tin this reaction proceeds considerably more slowly.

In the recombination theories of the hydrogen overvoltage the overvoltage is connected with the kinetics of the recombination process of the atoms at the electrode surface. It is not difficult to derive the basic laws of the reaction of hydrogen separation if certain assumptions are made concerning the properties of the atomic hydrogen adsorbed on the electrode surface. Let us designate the surface concentration of the hydrogen atoms at equilibrium potential, when no current passes through the electrode and when it is in equilibrium with molecular hydrogen at atmospheric pressure by $[H]_s^0$. When current passes and the cathodic reaction takes place, the stationary surface concentration of the atoms $[H]_s^i$ will be greater than the equilibrium concentration $[H]_s^0$; during the anodic reaction it will be less.

According to the basic assumption of the recombination theories the overvoltage on a certain electrode depends only on the variation of the surface concentration of the atomic hydrogen during the passage of current. The equilibrium between the solution and the adsorbed atoms is not markedly affected so that the potential shift of the electrode can be calculated by means of thermodynamic formulas.

If the assumption is made that the degree of filling of the electrode surface is low so that the activity of the adsorbed gas is proportional to its concentration, the electrode potential can be expressed by Eq. (158). The overvoltage in this case is

$$\eta_K = -\Delta\varphi = \frac{RT}{F}\ln\frac{[H]_s^i}{[H]_s^0}.. \qquad (159)$$

In order to obtain an expression which would connect the overvoltage with the current density and which could be verified experimentally, it is essential to establish a relationship between the surface concentration of the atomic hydrogen and the reaction rate of the recombination of the atoms to molecules. If we ascribe to the adsorbed atoms the properties of two-dimensional ideal solutions, it is natural to assume that the recombination reaction takes place in accordance with the normal law of bimolecular reactions, i.e., that the reaction rate is proportional to the square of the surface concentration

$$\overrightarrow{i} = k_1([\mathrm{H}]_s^i)^2. \tag{160}$$

The rate of the reverse reaction of dissociation of the molecules is proportional to the surface concentration of the molecular hydrogen: because the adsorption of molecular hydrogen is assumed to be slight, its surface concentration is proportional to the volume concentration and, consequently,

$$\overleftarrow{i} = k_2[\mathrm{H}_2]. \tag{161}$$

We arrive at the same Eq. (161) if we make the more plausible assumption that adsorption of diatomic H_2 molecules from the gas phase is directly followed by their dissociation. The quantity $\overleftarrow{i}$ under these assumptions, according to Eq. (161) is independent of the electrode potential.

In the equilibrium state the rates of the forward and back reaction are equal, i.e., the same number of molecules is formed in unit time as disappear in consequence of dissociation. Thus, in presence of the equilibrium

$$k_1([\mathrm{H}]_s^0)^2 = k_2[\mathrm{H}_2] = i^0, \tag{162}$$

where i^0 expresses the exchange current at equilibrium potential.

This equilibrium is upset when the electrode is polarized. The external current (during cathodic polarization) is equal to the difference between the quantities $\overrightarrow{i}$ and $\overleftarrow{i}$:

$$i_K = k_1([\mathrm{H}]_s^i)^2 - k_2[\mathrm{H}_2] = k_1([\mathrm{H}]_s^i)^2 - i^0. \tag{163}$$

From these equations one can find the connection between the surface concentration of the atoms, the density of the polarizing current and the density of the equilibrium exchange current

$$([H]_s^0)^2 = \frac{i^0}{k_1}; \quad ([H]_s^i)^2 = \frac{i_K + k_2 [H_2]}{k_1} = \frac{i_K + i^0}{k_1}. \qquad (164)$$

By substituting these values into Formula (159) we obtain an equation which connects according to the recombination theory in its simplest form the hydrogen overvoltage with the current density

$$\eta_K = \frac{RT}{2F} \ln \frac{i^0 + i_K}{i^0} = \frac{RT}{2F} \ln \left(1 + \frac{i_K}{i^0}\right). \qquad (165)$$

This general equation can be applied to the entire range of current densities. At high densities, when $i_K >> i^0$, the unit in brackets can be neglected and Eq. (165) is transformed into the simple Tafel equation

$$\eta_K = a_K + \frac{RT}{2F} \ln i_K, \text{ где } a_K = -\frac{RT}{2F} \ln i^0. \qquad (166)$$

At low current densities one can approximately assume

$$\ln \left(1 + \frac{i_K}{i_0}\right) \approx \frac{i_K}{i^0},$$

so that the overvoltage equation assumes the form

$$\eta_K = \frac{RT}{2F} \frac{i_K}{i^0}. \qquad (167)$$

The ratio of η_K to i_K at low current densities we have previously designated by w. It follows from (167) that

$$w i^0 = \frac{RT}{2F}. \qquad (167a)$$

The proportionality between the overvoltage and current density at weak electrode polarization immediately follows as a partial case of Eq. (165) because in its derivation we have already taken into account the existence of the reverse reaction of dissociation of the molecules in addition to the recombination reaction.

By an analogous method we can derive an expression for the overvoltage during the anodic process of ionization of molecular hydrogen at the electrode surface

$$\eta_A = -\frac{RT}{2F} \ln \left(1 - \frac{i_A}{i^0}\right). \qquad (168)$$

It follows from Eq. (168) that the anodic polarization current cannot exceed i^0. In other words, according to this theory, a limit current should exist during anodic polarization, independently of the concentration polarization, which is determined by the rate of dissociation of molecular hydrogen at the metal surface.

The above-described simplest version of the recombination theory explained for the first time the logarithmic relationship between overvoltage and current density over a wide range of current densities.

The circumstance that a parallelism exists between the electrochemical and catalytic activity of metals with regard to hydrogen has also been considered for a long time as a weighty argument in favor of the correctness of the recombination theories. Indeed, if the metals are arranged in a series with increasing hydrogen overvoltage, this series coincides in many cases with the arrangement of the metals in the order of decreasing catalytic activity in the recombination of hydrogen atoms.

Increasing catalytic activity

$$\longleftarrow$$

Pt, Pd, W, Ni, Fe, Ag, Cu, Zn, Sn, Pb

$$\longrightarrow$$

Increasing overvoltage

This means that the separation of hydrogen involves more delay and higher overvoltage if the given metal is a poor catalyst for the recombination reaction of the hydrogen atoms.

One can also attempt to connect the overvoltage on different metals with their adsorption capacity for atomic hydrogen, which is characterized by the work W_{ads} or the heat of adsorption q_{ads}.

The variation of the adsorption energy when going over from one metal to another causes a variation of the equilibrium surface concentration $[H]_s^0$ of atomic hydrogen. Assuming that the adsorption is small and the activity of the adsorbed atomic hydrogen is proportional to its concentration, we can write

$$[H]_s^0 = k p_{H_2}^{1/2} e^{\frac{W_{\text{адс}}}{RT}} = \text{const} \cdot e^{\frac{W_{\text{адс}}}{RT}}, \tag{169}$$

where p_{H_2} is the pressure of the molecular hydrogen; k is a constant: the increase in adsorption energy thus greatly increases the surface concentration of the atomic hydrogen. By substituting into Eq. (159) the expression for $[H]_s^0$ from Eq. (169), we obtain

$$\eta = \text{const} - \frac{W_{\text{адс}}}{F} + \frac{RT}{F} \ln [H]_s^i. \tag{170}$$

Equation (170) has been obtained by N.I. Kobozev and N.I. Nekrasov who were the first to formulate the important inference concerning the connection between overvoltage and adsorption energy [35]. In order to obtain by means of Eq. (170) a quantitative relation between η and W_{ads}, we must make certain assumptions concerning the mechanism of removal of the adsorbed hydrogen and the dependence of the rate of this process on the quantity W_{ads} (in Eq. (170) $[H]_s^i$ also depends on W_{ads} so that this equation in this form does not yet permit the determination of the relationship between η and W_{ads}). Remaining within the framework of the recombination theory, this problem can be solved if a connection is established between the rate constant k_1 of the recombination reaction and the quantity W_{ads}.

It can be assumed that with increase in the bond strength with the metal the reactivity of the adsorbed hydrogen decreases. N.I. Kobozev and N.I. Nekrasov assumed that with increase in W_{ads} the constant k_1 varies in accordance with the law

$$k_1 = k^0 \cdot e^{-\frac{W_{\text{адс}}}{nRT}}, \tag{171}$$

where $n \geq 1$. At fairly high cathodic polarization it follows from Eq. (163) that

$$i_K = k_1 \{[\mathrm{H}]_s^i\}^2,$$

from which the $[\mathrm{H}]_s^i$ as a function of W_{ads} at constant i_k is readily found by means of Eq. (171)

$$[\mathrm{H}]_s^i = \sqrt{\frac{i_K}{k_1}} = \mathrm{const} \cdot e^{\frac{W_{\text{адс}}}{2nRT}}. \qquad (172)$$

If we substitute this relation into Eq. (170), we find

$$\eta = \mathrm{const} - \left(1 - \frac{1}{2n}\right)\frac{W_{\text{адс}}}{F}, \qquad (170\text{a})$$

from which follows that the overvoltage decreases approximately linearly with increase in the adsorption energy at constant i_K.

Little information is available at present on the adsorption energy of atomic hydrogen on different metals*; nonetheless, it may be inferred on the basis of the known data that the overvoltage really decreases with increase in the adsorption energy of the atomic hydrogen. This conclusion could also be regarded as confirmation of the correctness of the recombination theories.

Further study of the kinetics of the process of cathodic separation of hydrogen showed, however, that at least in the above-given elementary form the recombination theory of the hydrogen overvoltage cannot be applied to most metals. This theory suffers from two important defects.

The first great deficiency of the recombination theory consists in the discrepancy between theory and experiment with regard to the magnitude of the factor *b*. Although the recombination theory gives the correct linear relationship between overvoltage and logarithm of current density (at $i_K > i^0$) it nevertheless gives an incorrect value of the coefficient *b*, equal to *RT/2F* (or 29 mv when the logarithm of *i* is expressed in decadic logarithms). As has been explained in the foregoing, the magnitude of the coefficient, determined experimentally, for most metals is *2RT/F* (or 116 mv), i.e., approximately 4 times greater than the quantity, following from the recombination theory.

The second deficiency of the recombination theory becomes evident if we examine the dependence of the overvoltage on the composition of the solution. In the recombination theory the overvoltage depends only on the exchange current between the atomic and molecular hydrogen; neither the pH of the solution nor the presence of other electrolytes in the solution has a direct effect on this quantity. It follows from this, if we do not introduce additional assumptions, that the overvoltage should be independent of the composition of the solution. However, the experiment in most cases indicates the existence of a strong dependence of the overvoltage on the nature of the solution.

Finally, the existence of an anodic limit current determined by rate of adsorption and dissociation of the hydrogen molecules at the surface (and not by the concentration polarization with regard to molecular hydrogen) has not received experimental confirmation to date either, at least in the case of metals with a clean surface which is not covered by foreign adsorption layers.*

Hence a number of attempts were made to modify and improve further the recombination theory.

During the derivation of the formulae of the simplest recombination theory we assumed:

a) that the electrode potential is determined by the surface concentration of atomic hydrogen according to Eq. (158), and

b) that the rate of the chemical recombination reaction of the atomic hydrogen is proportional to the square of its surface concentration (Formula (160)).

Both these assumptions are only crude approximations correct only when the electrode surface is very partially filled with adsorbed hydrogen atoms. The first assumption is equivalent to the assertion that the adsorbed quantity of substance is proportional to its pressure or concentration in the volume phase. This proportionality occurs in the initial part of the adsorption isotherm (the so-called Henry region). With increasing filling of the surface this proportionality is upset; the relation between these two quantities is determined in every individual case by the equation of the adsorption isotherm.

The second assumption also becomes invalid if the filling of the surface is not too small because when the system deviates from the ideal state one cannot equate the kinetic activity of its components (i.e., the effective concentration, figuring in the kinetic equations) with the surface concentration, nor with the thermodynamic activity of these components.

In reality the separation of hydrogen in some case takes place at the electrode surface, on which a considerable quantity of atomic hydrogen has already been adsorbed (see Introduction). In these cases the assumptions made beforehand are not obviously justified, and the corresponding corrections must be introduced into the previous calculations.

If there is moderate filling of the surface, different factors begin to affect the shape of the adsorption isotherm. One of these is connected with the filling of the surface and with the variation of the ratio between the free and occupied sites on the electrode surface. The calculation of the filling leads to the well-known equation of the Langmuir adsorption isotherm

$$[H]_a = Z \frac{\omega p_H}{1 + \omega p_H} \tag{173}$$

(Z is the total number of sites on the electrode surface, ω is the adsorption constant, p_H is the partial pressure of the atomic hydrogen).

In some cases, however, the shape of the adsorption isotherm in the range of medium filling deviates from Eq. (173). This deviation may be connected either with the inhomogeneity of the surface (i.e., with different values of ω at different points of the surface) or with the appearance of interaction forces between the adsorbed particles.

Hence, when taking account of the effect of filling on the kinetics of the electrochemical reaction, two cases must be distinguished:

a) the case in which only the variation of the number of free sites on the surface has an effect and when the kinetic laws are altered only if the surface is filled to a high degree (this case will be considered in §8);

b) the case in which the inhomogeneity of the surface or the interaction forces have an effect and, consequently, the kinetic laws are altered even at medium and even relatively slight filling of the electrode surface.

It has been shown in the Introduction that the equation of the adsorption isotherm of hydrogen for several noble metals has approximately a logarithmic form

$$A = a' + b' \ln p_{H_2}. \tag{174}$$

On the basis of an examination of the kinetics of chemical reactions taking place on an inhomogeneous surface, M.I. Temkin [36] showed that on a surface with logarithmic adsorption isotherm the recombination theory with plausible assumptions leads to the equation

$$\eta_K = \frac{RT}{2\beta F} \ln\left(1 + \frac{i_K}{i^0}\right), \text{ где } 0 < \beta < 1, \tag{175}$$

and at high current densities, respectively, to

$$\eta_K = a + \frac{RT}{2\beta F} \ln i_K. \tag{175a}$$

Equation (175) differs from Eq. (165) which has been derived without taking into account the surface inhomogeneity, by the constant β in the denominator of the coefficient in front of the logarithm. Because $\beta < 1$, taking the surface inhomogeneity into account, results in an increase in the coefficient in front of the logarithm of the current density in the Tafel equation. If it is assumed that $\beta = 1/4$, the coefficient of the slope of the polarization curves assumes the value $b = 2RT/F$, which agrees with the experimental data.

The physical meaning of this correction consists in the following. When the pressure of the adsorbed gas increases, the increase in the filling of the heterogeneous surface takes place in accordance with a very slow logarithmic law in consequence of the fact that in proportion to the pressure increase the adsorption extends to sites with ever decreasing adsorption energy and becomes energetically less advantageous. In an analogous manner, compared with a homogeneous surface, the growth of the filling of an inhomogeneous surface with increase in the overvoltage also slows down. Although this effect is partially compensated by the in-reased reactivity of the atoms adsorbed at the sites with lower adsorption energy, on the whole the increase in the recombination rate with increase in the overvoltage owing to the inhomogeneity of the surface slows down which finds its mathematical expression in the appearance of the quantity β in the denominator of the right part of Eq. (175).

Thus it is evident that under certain assumptions the above-mentioned deficiency of the simplest recombination theory, consisting in a too narrow value of the coefficient b, can be eliminated.

Analogous results can be obtained by taking into account the repulsion forces between the adsorbed particles because the presence of repulsion forces causes the same lowering of the adsorption energy in proportion to the degree of filling of the surface, as the transition to sites with smaller bond energy between the hydrogen atoms and the metal surface. N.I. Kobozev and co-workers [38, 60] have pointed out the lowering of the bond energy of the adsorbed hydrogen atoms during cathodic polarization owing to the existence of repulsion forces. Calculations of the recombination rate taking into account the repulsion forces were carried out by Horiuti and others [37].

We would like to point out that although taking into account the surface inhomogeneity or the repulsion interaction leads to an alteration of *b* in the Tafel equation, the value of the coefficient in the relations between the overvoltage at low current densities and the exchange current (Eqs. 167 and 167a), as a more profound mathematical analysis shows, is not affected by these corrections.

The above-given more precise description of the physical pattern of the recombination process is not applicable to the mercury electrode. By virtue of its liquid state, the surface of the latter is indeed completely homogeneous. Moreover, in this case, taking into account the negligibly low concentration of adsorbed hydrogen atoms, the interaction forces between them can be neglected. Thus, for the mercury electrode it is not possible to amend the incorrect value of the coefficient *b*, on the basis of the recombination theory.

The proposed improvements have no effect either on the second erroneous consequence of the recombination theory, namely the independence of the overvoltage to the composition of the solution.*

§8. OTHER METHODS OF REMOVING ADSORBED ATOMIC HYDROGEN

In the preceding sections we have considered only one of the possible ways in which the adsorbed atomic hydrogen can be removed from the electrode surface, consisting in a direct recombination of two atoms to a molecule.

However, a theory, based on the assumption of the existence of this single removal mechanism, leads to consequences, at high current densities, which are in contradiction with experiment. Indeed the rate of the recombination reaction, determined on the basis of the above-described concepts of the rate of the entire reaction of hydrogen separation, increases with increase in the surface concentration of atomic hydrogen. Thus surface concentration cannot increase indefinitely but attains a limit value corresponding to the covering of the entire surface by a monolayer of hydrogen atoms. For this reason the rate of the cathodic separation of hydrogen should not exceed a certain limit value which is typical for every electrode.* The limit current, under certain additional assumptions, can also be calculated from the recombination theory. It has not been possible, however, to detect reliably the existence of this limit current due to the saturation of the surface by adsorbed hydrogen, experimentally; in any event, it is not observed on the mercury electrode [4, 16]. The use of the concept of the recombination mechanism of the removel of the adsorbed hydrogen also encounters difficulties when the hydrogen concentration at the electrode surface is very small as is the case with the mercury electrode at moderate overvoltage values. Under these conditions the recombination rate, which is proportional to the square of the surface concentration, should also be small and the constant k_1 in Eq. (160) should be ascribed unlikely large values in order that the recombination process could achieve the removal of the atomic hydrogen, formed as a result of the discharge of the hydrogen ions, from the electrode surface.

The above-given concepts compel us to consider, in addition to the recombination, other possible mechanisms of the removal of adsorbed hydrogen from the electrode surface. Among the latter most attention has been given to the so-called electrochemical mechanism. In the electrochemical mechanism the hydrogen atoms are not transformed into molecules by a process of combining with other atoms but in consequence of a reaction with a hydrogen ion; in other words, it is assumed that the discharge of the hydrogen ions is possible not only at the free surface sites but also at the sites where a hydrogen atom is already present. In these cases, in accordance with the scheme

$$H_{\text{адс}} + H^{\cdot} + e \rightarrow H_2 \qquad \text{(B)}$$

the discharge of hydrogen ions does not increase, but on the contrary, reduce the degree of filling of the electrode surface with hydrogen atoms. This mechanism has been first proposed in a slightly different form by Heyrovsky [39]. Later on several variants of scheme B were considered for example, with intermediate formation of the adsorbed ion H_2^+. Although direct experimental data indicating the possibility of the reaction B are lacking to date, various indirect considerations lead to the conclusion that such a mechanism is highly probable.

The possibility that a reaction of hydrogen separation takes place simultaneously in accordance with different schemes was indicated and the dependence of the rate relations of individual parallel stages on the absorption properties of the electrode examined for the first time in the hydrogen overvoltage theory of Kobozev and Nekrasov. In addition to the above-mentioned two mechanisms of hydrogen removal (recombination and electrochemical removal) a third possible mechanism was used in this theory, consisting in a direct desorption of the adsorbed atoms from the electrode surface with their removal into the depth of the solution outside of the sphere of influence of the surface forces (emission mechanism of desorption).*

We find that in the theories of Heyrovsky and Kobozev, as in the earlier described theory, the assumption concerning the equilibrium between the adsorbed hydrogen at the surface and the hydrogen ions in the solution is retained and, consequently, the potential shift of the electrode during polarization is ascribed only to the change in the activity of the adsorbed atomic hydrogen. It will be shown in §12 that the polarization in the electrochemical mechanism can also be regarded from a different point of view, namely on the basis of the theory of the inhibited discharge.

The accumulation of an excess of adsorbed hydrogen at the electrode surface may be connected not with a slowing down of the combination of atoms to molecules but with a slowing down of the process of removal of the molecular hydrogen thus formed from the electrode surface. With this hypothesis, the adsorbed hydrogen is in equilibrium with the molecular hydrogen which accumulates in the solution close to the electrode surface but not with the molecular hydrogen in the depth of the solution or in the gas phase above the solution. Because molecular hydrogen is the end product of the reaction, it is removed from the reaction zone by diffusion or convection and not via a further chemical reaction. Hence the above-described phenomenon should be regarded as a concentration polarization with accumulation of the reaction product, the molecular hydrogen. This theory, as is easy to verify, also leads to Eq. (165), with the only difference that the quantity i^0 in this equation now represents the limit diffusion current of molecular hydrogen which would result if the concentration at the electrode surface were in equilibrium with the molecular hydrogen at atmospheric pressure, and in the volume of the solution would be zero. Indeed, in the case of concentration polarization with respect to molecular hydrogen the potential shift is expressed by the relation

$$\eta = \frac{RT}{2F} \ln \frac{[H_2]_i}{[H_2]_0}, \qquad (176)$$

where $[H_2]_i$ is the concentration of the dissolved hydrogen at the electrode surface during the passage of current, and $[H_2]_0$ is the same concentration under equilibrium conditions. Because the current is determined by the rate of removal of hydrogen from the electrode surface,

$$i = k\{[H_2]_s - [H_2]_0\}, \tag{177}$$

where k is a constant. If we produced an anodic polarization of the electrode and if the concentration of the dissolved hydrogen on its surface dropped to zero, the limit diffusion current would be $(i_d)_a$, where

$$(i_d)_a = k[H_2]_0. \tag{177a}$$

It follows from Eqs. (176, 177 and 177a) that:

$$\eta = \frac{RT}{2F} \ln\left(1 + \frac{i}{(i_d)_a}\right). \tag{178}$$

This theory gives a correct explanation for the polarization phenomenon observed at moderate current densities with very active electrodes (for example, with platinized platinum) on which all stages of the electrochemical process, with the exception of the diffusion of the hydrogen molecules in the solution, proceed fairly rapidly [41].

§9. VALIDATION OF THE THEORY OF DELAYED DISCHARGE

The basis of the theory of the delayed discharge is the assumption that the discharge of the hydrogen ions with formation of adsorbed atoms of hydrogen $H^+ + e \rightarrow H_{ads}$, proceeds at a certain finite rate, depending on the potential difference between metal and solution. Hence to enable a current of given density to pass through the electrode, the potential must be shifted a certain amount from the equilibrium value, which also determines the overvoltage.

The hypothesis of the slowing down of the electrochemical stage of the discharge of the ions (and also the converse stage of ionization of the adsorbed atomic hydrogen during the anodic reaction) has been advanced repeatedly but has not received experimental confirmation for a long time. For this reason the concept according to which this process takes place rapidly and without delay has prevailed in electrochemistry until relatively recently.

In the early Thirties, Erdey-Grüz and M. Volmer [42] and other authors carried out several investigations with the aim of determining the possibility of constructing a quantitative theory of hydrogen overvoltage on the basis of the concept of the delay of the ion discharge. The theory of the delayed discharge saw its full development in the work of the Soviet electrochemists.

It is preferable to begin, as we have done in other instances, the description of this theory with its experimental validation and to pose the problem whether it is possible to show by a direct experimental method that the processes of ion discharge or ionization of the hydrogen atom proceed at a finite, measurable rate.

This task was resolved by B.V. Ershler, P.I. Dolin and A.N. Frumkin [43] who employed the method of measuring the polarization capacitance of a platinum electrode with alternating currents of different frequency. As pointed out already in the Introduction, the capacitance of the platinum electrode in the potential range from 0.05 to 0.3 v (relative to the potential of the reversible hydrogen electrode in the same solution) amounts to several thousand microfarad per 1 cm^2 of true electrode surface and exceeds by far the normal capacitance of the double layer (amounting for the mercury electrode, for example to 18 microfarad/cm^2). This large capacitance is due to the presence of adsorbed hydrogen at the electrode surface: when the potential is shifted, most of the polarizing current is consumed for the variation of the quantity of adsorbed hydrogen via discharge of ions or, conversely, via ionization of the adsorbed atoms. The separation of free molecular hydrogen at such positive potentials is practically impossible and, because these measurements are carried out in a nitrogen atmosphere, the reverse reaction of ionization of molecular hydrogen is excluded. Thus, the entire process consists in a transfer of ions to the adsorbed atoms and vice versa.

Experiments in which the capacitance was measured with high-frequency alternating currents showed that the measured capacitance of the platinum electrode decreases in proportion to the increase in the frequency and tends to the limit capacitance of the ionic double layer (dispersion of capacitance with frequency). Figure 83 shows a typical curve of the electrode capacitance as a function of the frequency of the alternating current in a solution of 1 N H_2SO_4 at a potential of $\varphi = 0.1$ v.

The phenomenon described in the foregoing can be accounted for only by a delay of the ion discharge or atom ionization processes. If the reversible transformation of the hydrogen ions and atoms took place at a very great rate, the atomic covering would be in equilibrium with the ionic double layer under any conditions. In fact, however, owing to the low rate of the electrode reaction, the equilibrium between the atomic and ionic layers is upset; if the potential varies rapidly, the atomic layer cannot change its condition. In the limit case, with very rapid variation of the electrode potential, the transformation of atoms to ions or the reverse process cannot take place at all and the entire current passing through the electrode is used only for the alteration of the state of the double layer. The reaction rates of the ionization and discharge and their dependence on the potential can be directly calculated from the capacitance – frequency curves.*

The measurement results led to the very important conclusion that the exchange process between the hydrogen ions and atoms takes place at a finite, relatively low rate and, in consequence, although only in individual cases, should affect the general kinetics of the electrochemical reaction.

The concept of the delayed electrochemical discharge reaction is attractive because it opens up the possibility of creating a broader basis for electrochemical kinetics. Up to now, starting out from the concepts of the recombination theories, we have concentrated all our attention on the purely chemical stages of the combination of atoms to molecules, which is not of a direct electrochemical nature and is specific for the case of the cathodic separation of hydrogen. By contrast, the theory of the delayed discharge is based on a consideration of the kinetics of the actual electrochemical reaction of addition or delivery of electrons and, with the respective more exact definitions and additions, can be extended to other electrochemical processes as well.

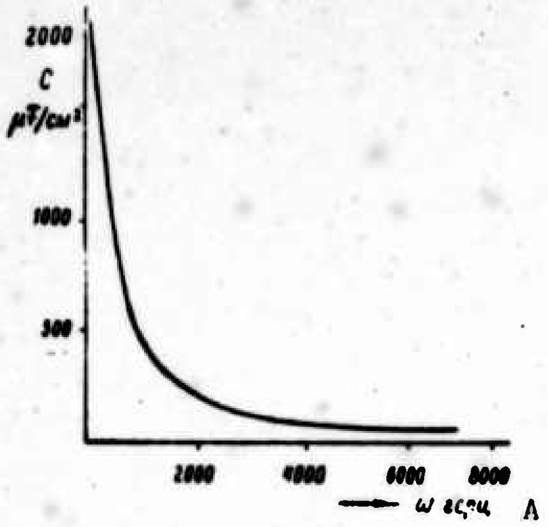

Fig. 83. Capacitance of the smooth platinum electrode as a function of the frequency of the alternating current in 1 N H_2SO_4 at a potential of 0.1 v; A) cycles.

Let us consider the question to which kinetic laws leads the assumption of a slowing down of the discharge stage and how these laws agree with the experimental data.

The slowing down of the stage of hydrogen ion discharge points to the fact that this reaction requires a certain activation energy.

According to the basic equation of chemical kinetics, the rate of a chemical reaction is connected with the activation energy W by the exponential law

$$v=kc_ic_j\ldots e^{-\frac{W}{RT}}, \tag{179}$$

where c_i, c_j, ... are the concentrations of the reactants, and k is a proportionality coefficient, which, as a rule, depends little on the temperature. A peculiarity of electrochemical kinetics compared with normal chemical kinetics is the strong dependence of the reaction rate (current density) on the electrode potential. This dependence can be explained, if it is assumed that the electrode potential affects the activation energy W.

At first sight it may appear surprising that the simple reaction of the combination of the positively charged hydrogen ion with the negative electron should require a certain, even fairly large activation energy. This fact, however, may be due to the strong hydration of the hydrogen ion in solution.

Already at the end of the Seventies in the last century Professor R.A. Kolli of Kazan' University advanced the hypothesis that if the voltage applied to the galvanic circuit is insufficient, the particles (according to the terminology of that time "the atoms of the ion") cannot be separated from the electrolyte molecule and in consequence cannot be discharged at the electrode [44]. The concept of the role of the rupture of a chemical bond in the discharged reaction was formulated by R.A. Kolli with the maximum clarity attainable at that time. The further development of these concepts was made possible by the introduction of the idea of the hydration of ions in aqueous electrolyte solutions into physical chemistry which we owe primarily to I.A. Kablukov (1891) who proceeded from the hydrate theory of D.I. Mendeleyev.

Early in this century Leblanc [45] arrived at the conclusion that the discharge of certain metal ions at the cathode is delayed and connected with a strong polarization in consequence of the fact that these ions form part of stable complexes (for example, with solvent molecules, with anions, etc.), which must be disrupted during the discharge. The decomposition of the complex (or the reverse formation of the complex during the anodic dissolution of metals) takes place with a certain kinetic delay and determines the course of the entire electrode reaction. N.A. Izgaryshev who studied the deposition of metals and somewhat later also that of hydrogen from solutions of different composition [46] arrived at similar concepts in 1915 and used them widely in his investigations.

The hydrogen ion in aqueous solution is a strongly bound complex of a proton with a molecule of water ($H^+ \ldots H_2O$ or H_3O^+) which is sometimes termed the hydroxonium ion. The charge of this ion is uniformly distributed among three hydrogen atoms, which are thus equivalent. The hydroxonium ion as a whole, as any other ion, is surrounded by an additional hydrate envelope.

During the process of discharge of the hydrogen ion considerable interaction forces between the proton and the water molecule must be overcome. The magnitude of these forces can be gaged by the fact that the hydration energy of the proton amounts to 282 kcal per 1 g-ion.

In order to derive the kinetic laws of the reaction of cathodic hydrogen separation we must investigate the problem of the effect of the electrode potential on the activation energy; by substituting into Eq. (179) the functional relation between W and φ, we obtain directly the equation which interests us, which connects the current density with the electrode potential.

The variation of the electrode potential affects directly the heat effect of the discharge reaction. The discharge reaction can be mentally decomposed into a number of separate stages, one of which is the stage of the transfer of an electron from the metal to the solution or a proton from the solution to the metal. The variation ΔE of the electrical energy during this stage involves a jump of the electrostatic potential between the metal and the solution: $\Delta E = \varphi F$. The more negative the electrode potential, the greater is the gain of electrical energy during the reaction between the electron and the hydrogen ion and the greater is the heat effect of this stage. It follows from this that the heat effect $\overline{Q}_1$ of the process of discharge of the hydrogen ion is connected with the electrode potential by the relation

$$\overline{Q}_1 = \overline{Q}_1^0 - \varphi F, \qquad (180)$$

where $\overline{Q}_1^0$ is the value of $\overline{Q}$ at $\varphi = 0$. The heat effect of the reverse reaction of ionization of the hydrogen atoms differs from $\overline{Q}_1$ in sign and increases with a shift of the potential to the negative side

$$\overline{Q}_2 = \overline{Q}_2^0 + \varphi F. \qquad (180a)$$

The heat effect is a thermodynamic quantity and does not directly determine the kinetic parameters of the reaction, as, for example, the activation energy. It is known, however, from chemical kinetics, that a certain relationship exists in some cases between the heat effect and the activation energy. By studying various analogous chemical reactions (i.e., reactions in which one of the components is successively replaced by others, similar in its structure, for example, substitution products or homologs of the same substance) one can often observe that in proportion to the increase in the heat effect of the reaction its activation energy decreases. To these reactions belong, for example, the hydrolysis reactions of various halogen-substituted organic compounds, the substitution of certain groups in organic substances, the saponification of esters under the catalytic influence of hydrogen ions and the undissociated molecules of weak acids, etc. As follows from the experimental data, the lowering of the activation energy in these cases amounts to a certain fraction of the increase in the heat effect of the reaction, i.e.,

$$\Delta W = -\alpha\Delta\bar{Q}, \qquad (181)$$

where α is the proportionality coefficient ($0 < \alpha < 1$). Equation (181) is known in chemical kinetics under the term Broensted relation.*

As A.N. Frumkin already showed [47], the transfer of a proton from the hydroxyl ion to the negatively charged metal electrode may be regarded as a partial case of the reaction of proton transfer from any substance which gives off protons (proton donor or "acid," according to the terminology of Broensted) to a substance which accepts protons (proton acceptor or "base"). The rate of these reactions depends on the heat of dissociation of the respective acids and bases and, as a rule, obey Eq. (181) well. Hence this equation may be also extended to electrochemical reactions involving the discharge of hydrogen ions.

In the case of an electrochemical reaction the heat effect can vary not only because of the replacement of one reaction component by another substance but also because of a variation of the electrode potential. Using Eq. (181) and taking into account (180), we find that in this case

$$\Delta W_1 = -\alpha\Delta\bar{Q}_1 = \alpha F\Delta\varphi \qquad (182)$$

or

$$W_1 = W_1^0 + \alpha F\varphi, \qquad (183)$$

apply, i.e., the activation energy decreases in proportion to the shift of the electrode potential to the negative side.

For the process of ionization of the hydrogen ions, we have, analogously

$$\Delta W_2 = -\beta\Delta\bar{Q}_2 = -\beta F\Delta\varphi \qquad (184)$$
$$(\beta < 1)$$

or

$$W_2 = W_2^0 - \beta F\varphi. \qquad (185)$$

In this case the activation energy decreases in proportion to the shift of the potential to the positive, and not the negative, side.

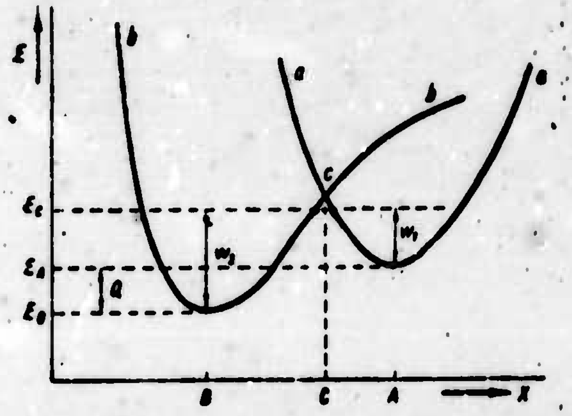

Fig. 84. Potential curves of the hydrogen ion and adsorbed hydrogen atom.

In order to elucidate the physical meaning of the relationship between activation energy and electrode potential, as expressed in the equations (183) and (185), we must consider in greater detail the phenomena which take place during the discharge of hydrogen ions.

The hydroxonium ion can approach the electrode surface only to a certain distance determined by its effective diameter. During the discharge one of the protons, forming part of this ion, is removed from it. Let us designate the point at which the center of the proton is located at the initial moment of discharge, by *A*. During the elementary act of discharge of the ion a neutral hydrogen atom is formed; this atom is adsorbed on the electrode surface because the discharge takes place in the zone of action of the surface forces. The dimensions of the adsorbed atom are considerably smaller than the dimension of the hydrated ion and the point *B* where the center of the atom is during equilibrium is closer to the electrode surface than *A* (see Fig. 84).

During the discharge the proton must be moved in the direction to the electrode surface from *A* to *B*. The first stage of the movement is the stretching of the hydroxonium ion. The potential curves showing the energy *E* of the hydrogen ion and atom as a function of the distance *x* from the electrode surface are given in Fig. 84.

The curve *aa* describes the increase in the energy of the system proton/water molecule when the proton is removed from the stable equilibrium position *A* in the hydroxonium ion. Curve *bb* represents in an analogous manner the energy increase taking place during the displacement of the adsorbed hydrogen atom from its equilibrium position *B*.

During the motion of the proton from *A* to *B* the energy of the whole system increases until the proton is in a certain intermediate position *C*, in which the potential curves intersect. At this point one form of bonding of the hydrogen changes to another; the hydrogen ion is transformed into an atom which is adsorbed on the electrode surface.* In proportion to the further approach of the atom to its equilibrium position *B* the energy again decreases in consequence of the effect of the adsorption forces.

The activation energy of the discharge of the hydrogen ion is equal to the difference of the potential energies of the system in the initial state *A* and in the intermediate position *C*

$$W_1 = E_C - E_A. \qquad (186)$$

Analogously for the reverse reaction of ionization of the adsorbed hydrogen atoms the activation energy, whose existence in this case is due to the necessity of overcoming the adsorption energy of the atom, is

$$W_2 = E_C - E_B. \qquad (186a)$$

During the polarization of the electrode the potential curve *bb* of the hydrogen atom does not change because the atom is not charged. With the hydrogen ion the situation is different. A shift of the electrode potential to the negative side is equivalent to a shift of the potential of the solution to the positive side. The positive H_3O^+ ion present in the solution then goes to a higher energy level, and the curve *aa* for the hydrogen ion is raised parallel to itself (curve *a'a'* in

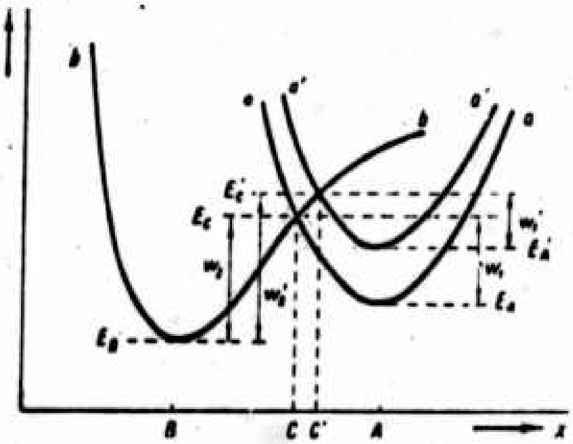

Fig. 85. Displacement of the potential curve of hydrogen ion during variation of the electrode potential.

Fig. 85). The energy of the hydrogen ion is consequently expressed by the relation

$$E_A = E_A^0 - F\varphi, \tag{187}$$

where E_A^0 is the energy of the ion at $\varphi = 0$.*

The heat effect of the discharge reaction, which is evidently equal to the total energy decrease during the discharge process $\overline{Q}_1 = E_A - E_B$, increases during the cathodic polarization of the electrode by the same amount as the energy of the hydrogen ion in the initial state A, i.e.,

$$\overline{Q}_1 = E_A^0 - F\varphi - E_B = \overline{Q}_1^0 - F\varphi. \tag{188}$$

The variation of the activation energy during the polarization of the electrode is due not only to the variation of the potential energy of the ion ΔE_A, but also the variation of the energy ΔE_C in the intermediate position C. This last quantity is less than ΔE_A. As can be readily seen from Fig. 86, when the curve aa is displaced upwards or downwards, the relation

$$\Delta E_C = \beta\Delta E_A = -\beta F\Delta\varphi, \tag{189}$$

applies, where

$$\beta = \frac{\Delta E_C}{\Delta E_A} = \frac{\operatorname{tg}\theta}{\operatorname{tg}\theta + \operatorname{tg}\vartheta} \qquad (190)$$

and, consequently, $\beta < 1$; ϑ and θ are the slope angles of the curves *aa* and *bb*. For the dependence of the activation energy of the discharge on the electrode potential we obtain from (186), (187) and (190)

$$W_1 = (E_C^0 - E_A^0) + (1 - \beta)F\varphi \qquad (191)$$

or, replacing $E_C^0 - E_A^0$ by W_1^0 and assuming that $1 - \beta = \alpha$,

$$W_1 = W_1^0 + \alpha F\varphi, \qquad (192)$$

where

$$\alpha = \frac{\operatorname{tg}\vartheta}{\operatorname{tg}\vartheta + \operatorname{tg}\theta} \qquad (193)$$

and, consequently, $\alpha < 1$.

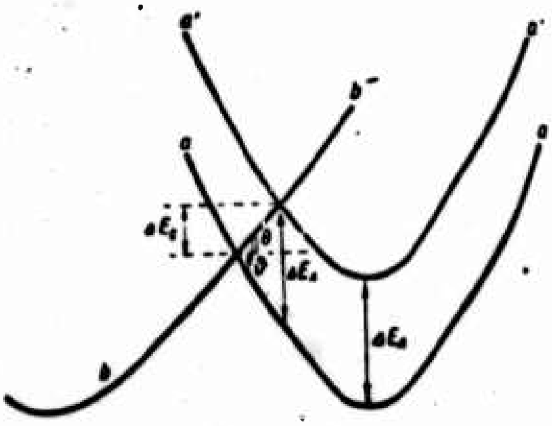

Fig. 86.

The activation energy of the reverse reaction of the ionization of the atoms is

$$W_2 = (E_C^0 - E_B^0) - \beta F\varphi = W_2^0 - \beta F\varphi. \qquad (194)$$

By examining the energetic relations during the discharging and ionization of the hydrogen ions, we have thus arrived at equations which are identical with Eqs. (183) and (185) which follow from the relation (181).

It also follows from this conclusion that the sum of the coefficients which connect the variation of the activation energy with the variation of the electrical energy of the ion for the direct and the reverse reaction, should equal unity

$$\alpha + \beta = 1. \qquad (195)$$

According to (190) and (193) the values of α and β depend on the slope of the potential curves near their intersection.*

As will be evident from the following, these coefficients often but by no means always assume the value $\alpha = \beta = 0.5$, which, according to the above reasoning, should correspond to the same slope of the potential curves of the hydrogen atom and ion near the point of their intersection.

The scheme described in the foregoing contains an assumption concerning the adiabatic nature of the discharge process, which amounts to this: by determining the energy as a function of the distance of the proton from the electrode surface, $E = f(x)$, we have assumed that E is a function only of the position of the proton and not of the possible electronic configuration. In other words, it was assumed that at any position of the nuclei in our system the electrons move in such a way that a state of minimum energy for the given position of the nuclei is maintained. This assumption is not obvious; chemical reactions are known in which it does not apply. However, as the calculations of M.I. Temkin have shown, it is apparently justified in the case of the discharge of the hydrogen ion.

Equation (192) expresses the same dependence of the activation energy of the reaction of transformation of the hydrogen ion into an adsorbed atom as a function of the overvoltage, which we have found above on the basis of the experimental data for the activation energy of the over-all process of cathodic separation of molecular hydrogen (Eq. (149), §3, Chapter 3). This result is natural because in the scheme in which the over-all rate of the process is determined by the rate of the discharge stages, the activation energy of this stage should determine the activation energy of the over-all process.

In the above-described elementary calculation we have considered only the variation of the quantities W_1 and W_2 with potential. Hence the potential at which we considered that $\varphi = 0$ could have been chosen arbitrarily and the physical meaning of the quantity W_1^0 and W_2^0 remained indeterminate. In other words, we have considered how the position of the level E_A in Figs. 84 and 85 varies with variation of the potential curves *aa* and *bb* were known exactly, we could calculate from the position of the point of intersection of these potential curves the quantity which we designated in §3 by W and which cannot be directly determined by experiment. For the calculation of the quantity designated by us as A (Eq. 139b), which is known from experiment, we do not need to know the actual position of the levels *aa* and *bb*. As a more detailed analysis of the energy relations during the discharge of the hydrogen ion shows [23], if the potential curve *aa* of the hydrogen ion at the equilibrium hydrogen potential is placed in such a way that its minimum is above the minimum of the potential curve *bb* of the adsorbed atom at a distance λ, where λ is the heat of adsorption of half an H_2 mole on the metal of the electrode (i.e., so that the H^+ ion in the minimum of the curve *aa* is at the same energy level as the hydrogen atoms in gaseous molecular hydrogen), the discharge activation energy W_1 determined from the intersection of the potential curves coincides with A_0, the value of A at equilibrium potential (Eq. 139b, §3 of Chapter 3). If the curve *aa* is shifted from this initial position with variation of the overvoltage in the manner discussed in the foregoing, it follows from a comparison of Eqs. (192) and (140) that the quantity W_1 determined by the method of potential curves will always coincide with the quantity A at the corresponding overvoltage which can be found from the current-temperature relation.

The method of potential curves makes it possible to examine also the effect of other factors on the activation energy of the processes of discharge and ionization such as, for example, the influence of the electrode material and the nature of the solvent (in nonaqueous solutions).

The influence of the electrode material is exerted primarily via the energy or heat of adsorption q_{ads} of the atomic hydrogen on the given metal. The position of the potential curve of the adsorbed hydrogen atoms, in contrast to the curves for the hydrogen ions, depends on the nature of the electrode: the greater the heat of adsorption q_{ads} of atomic hydrogen, the less is the energy of the adsorbed atoms and the lower down extends the curve *bb*

$$\Delta E_{B} = -\Delta q_{\text{адс}}, \tag{196}$$

where ΔE_B is the variation of the energy of the atom upon variation of the heat of adsorption by the amount Δq_{ads}.

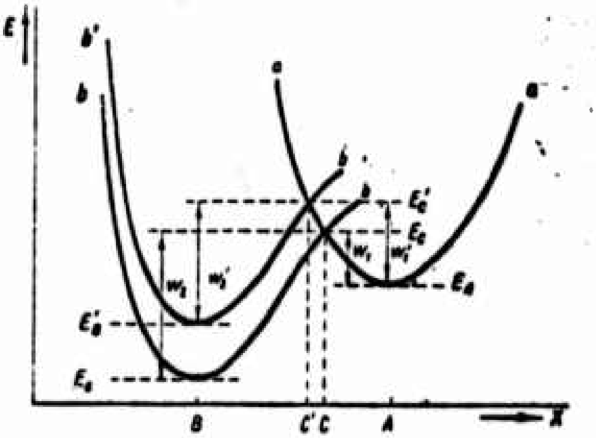

Fig. 87. Displacement of the potential curve of the hydrogen atom by variation of the adsorption energy of the atom.

The energy at the intersection point *C*, as is evident from Fig. 87, then varies as a function of q_{ads} according to the equation

$$\Delta E_C = -\alpha\Delta q_{\text{адс}}. \qquad (197)$$

By substituting these expressions into the equations for the activation energy of the discharge, we find

$$\left.\begin{array}{l}\Delta W_1 = -\alpha\Delta q_{\text{адс}} \\ W_1^{*} = W_1' - \alpha q_{\text{адс}}\end{array}\right\}. \qquad (198)$$

where W_1^{*} is the activation energy at $q_{\text{ads}} = 0$ (it is easy to see that W_1^{*}, like W_1, depends on the electrode potential, compare Eq. (192)). Thus an increase in the adsorption energy of the hydrogen atoms results in a decrease in the activation energy of the discharge reaction, i.e., it facilitates this process.

In exactly the same way an increase in the solvation energy of the proton, when one solvent is replaced by another, impedes the discharge of the ions. The relation between the activation energy of this process and the heat of solvation q_s of the proton has the form

$$W_1 = W_1^{**} + \alpha q_s, \qquad (199)$$

where W_1^{**} is the activation energy at $q_s = 0$.

The above-described method of the potential curves in its original form was used in 1935 by Horiuti and Polanyi [48] for the general case of the reaction of proton transition and, in particular, for the reaction of the discharge of hydrogen ions. Several works appeared later in which the deficiencies of this scheme were pointed out. Reference to the inaccuracy of the assumption concerning the parallel displacement of the potential curve during variation of the electrode potential has been made in the foregoing.

Moreover, this scheme takes into account only the interaction energies due to chemical forces of attraction between the hydrogen atom and the metal (curve *bb*, Fig. 84) and between the proton and the water molecule (curve *aa*, Fig. 84). However, there are other forms of chemical forces, which must be taken into account in a consideration of the energy of the metal-hydrogen-water system, such as, for example, the repulsion forces between the adsorbed hydrogen atom and the water molecule, which cause a marked increase in the potential energy when the H atom comes close to the H_2O molecule and, consequently, to a steeper rise of the right branch of curve *bb*. A scheme which takes into account all three forms of energy has been proposed by O.A. Yesin [49]. In the work of N.D. Sokolov [50] the hypothesis is advanced that the first stage of the discharge reaction is the formation of a hydrogen bond between the H_3O^+ and the metal in presence of which the proton is partially bound to the water molecule as well as to the metal. This means that the proton is partly shielded by the electrons of the water molecule, partly by those of the metal, i.e., as if it did not have the full elementary charge but a smaller charge. Under this assumption the coefficient α is determined by the laws of change of the electrostatic potential and the degree of shielding of the proton on the reaction path from *A* to *B*.

In spite of these deficiencies the method of potential curves gives a satisfactory physical explanation of the experimentally established dependence of the activation energies of various reactions on their heat effect and, in particular, the dependence of the activation energy of the electrochemical reaction of the discharge or ionization of hydrogen on the potential and nature of the electrode; thus, the physical picture, on which it is based, probably reflects the most important features of the observed phenomena correctly.

It should be pointed out that attempts have also been made to approach the interpretation of the elementary act of discharge on the basis of principally different physical concepts. Thus, Gurney [51] developed a theory according to which the discharge of the hydrogen ion takes place via a jump of an electron from a certain energy level in the metal to that of the ion in solution. Examining this electron jump from the quantum mechanical viewpoint, the author arrived at the conclusion that not only ions directly contiguous to the electrode but also those at a certain distance from it are subject to discharge via this "tunnel" transition. This theory fails entirely to take into account the adsorption energy of the hydrogen on the metal. It can be shown that leaving the adsorption energy of the hydrogen atom out of consideration leads to markedly excessive values for the activation energy of the discharge reaction. On the other hand, if the adsorption energy is taken into account, the relative probability of the tunneling of the electrons over short distances is increased and there is no longer any need for considering the discharge of ions at a greater distance from the electrode. Hence the picture proposed by Gurney is not applicable to the case of discharge of the hydrogen ion.

It is not impossible, however, that this picture can nonetheless be applied in some measure to other cases of electrolysis.

§10. KINETIC EQUATIONS OF THE THEORY OF DELAYED DISCHARGE

In the derivation of the kinetic equations of the theory of the delayed discharge use is made of the concept of the existence of a connection between the variation of the activation energy of the discharge reaction and the variation of the electrode potential.

In its original simplest form, developed by Erdey-Grúz and M. Volmer, the theory of the delayed discharge leads to the following laws.

One ion and one electron take part in the elementary act of discharge of the hydrogen ions, i.e., this reaction proceeds as a first-order reaction: the rate of the discharge reaction is proportional to the concentration of the hydrogen ions in the solution.*

$$i_K = k'[H^\cdot]\,e^{-\frac{W_1}{RT}}. \qquad (200)$$

The activation energy W_1 as a function of the potential, according to the generally accepted theory, is expressed by Eq. (183). By substituting this value of W_1 into Eq. (200) we obtain:

$$i_K = k'[H^\cdot]\,e^{-\frac{W_1^0}{RT}}\,e^{-\frac{\alpha F\varphi}{RT}} = k_1'[H^\cdot]\,e^{-\frac{\alpha F\varphi}{RT}}. \qquad (201)$$

It is evident from this equation, which connects the current density with the cathode potential, that with increase in the negative potential the current density increases.

Solving Eq. (201) relative to the potential, we find

$$\varphi = a_K' + \frac{RT}{\alpha F}\ln[H^\cdot] - \frac{RT}{\alpha F}\ln i_K. \qquad (202)$$

The overvoltage is

$$\eta_K = \varphi_p - \varphi = \frac{RT}{F}\ln[H^\cdot] + \varphi_p^0 - \varphi = a_K - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H^\cdot] + \frac{RT}{\alpha F}\ln i_K. \qquad (203)$$

The rate of the reverse reaction of ionization of the atoms depends on the concentration of the adsorbed hydrogen atoms. If this concentration on a given metal depends only on the pressure of the gaseous hydrogen, i.e., if the exchange rate between the gas phase and the atoms on the metal surface is sufficiently large, to preserve the adsorption equilibrium during the passage of current through the electrode, then it can be considered to be constant at constant (for example, atmospheric) pressure. The ionization current in this case is

$$i_A = k''\,e^{-\frac{W_2}{RT}} \qquad (204)$$

or, taking into account (185),

$$i_A = k''\,e^{-\frac{W_2^0}{RT}}\,e^{\frac{\beta F\varphi}{RT}} = k_2''\,e^{\frac{\beta F\varphi}{RT}}. \qquad (205)$$

The constants k'' and k_2'' in the case of slight filling of the surface with adsorbed hydrogen are proportional to its concentration and, consequently, to the square root of the pressure of the gaseous hydrogen.

Solving (205) for the potential, we find

$$\varphi = a'_{A} + \frac{RT}{\beta F}\ln i_{A}, \tag{206}$$

and for the overvoltage of the anodic process

$$\eta_{A} = \varphi - \varphi_{p} = a_{A} - \frac{RT}{F}\ln[H^{\cdot}] + \frac{RT}{\beta F}\ln i_{A}. \tag{207}$$

At the equilibrium potential the rates of the discharge and ionization reactions are equal. Equating the values ln *i* from Eqs. (201) and (205), we find:

$$(\alpha+\beta)\varphi_{p} = \frac{RT}{F}\ln[H^{\cdot}] + \frac{RT}{F}\ln\frac{k'_1}{k''_2}. \tag{208}$$

Because, according to Eq. (195), $\alpha + \beta = 1$, Eq. (208) coincides with the well-known expression for the equilibrium potential of the hydrogen electrode which is used derived by a thermodynamic method (its kinetic derivation has been given by Butler [52]). Substituting the value of φ_p from Eq. (208) into Eq. (201) and (205) instead of φ, we find equal values of the cathodic and anodic currents at equilibrium potential, i.e., and exchange current i^0:

$$i^{0} = (k'_1)^{\beta}(k''_2)^{\alpha}\cdot[H^{\cdot}]^{\beta}. \tag{209}$$

At $\alpha = \beta = 1/2$, according to the above,

$$i^{0} = (k'_1 k''_2[H^{\cdot}])^{1/2} = k_3 p^{1/2}_{H_2}[H^{\cdot}]^{1/2}. \tag{209a}$$

If the cathodic or anodic polarization are not too high, the cathodic and anodic currents must be taken into account simultaneously. The general expression for i_K applicable at any value of the potential, can be obtained from Eqs. (201), (205), (208) and (209):

$$i_{K} = \vec{i} - \overleftarrow{i} = k'_1[H^{\cdot}]e^{-\frac{\alpha F\varphi}{RT}} - k''_2 e^{\frac{\beta F\varphi}{RT}} = i^{0}\left(e^{-\frac{\alpha F(\varphi-\varphi_p)}{RT}} - e^{\frac{\beta F(\varphi-\varphi_p)}{RT}}\right) = i^{0}\left(e^{\frac{\alpha F\eta_K}{RT}} - e^{-\frac{\beta F\eta_K}{RT}}\right). \tag{210}$$

At small values of η_K it follows from Eq. (210) that if we take into account that $\alpha + \beta = 1$:

$$\eta_K = \frac{RT}{F}\frac{i_K}{i^0}. \qquad (211)$$

Equation (211) could also have been obtained from (146) if instead of b_K and b_A the values $RT/\alpha F$ and $RT/\beta F$, which follow from the theory of the delayed discharge, are substituted. Equation (211) differs from Eq. (167) obtained from the recombination theory, by the fact that the coefficient in front of i_K/i^0 is twice as large. The conclusion that the polarization of the electrode is the smaller the greater the exchange current, remains valid.

The theory of the delayed discharge in the above-given simplest form has several consequences which are in good agreement with experiment. The linear relation between overvoltage and logarithm of current density is the same as in the recombination theory. The noncorrespondence between the theoretical and experimental coefficient in front of the logarithm of the current density, however, is eliminated in the theory of the delayed discharge. According to the theory of the delayed discharge this coefficient is $b_K = RT/\alpha F$, where α is a constant less than unity. If $\alpha = 0.5$, which corresponds to an equal slope of the potential curves at the point of intersection, the coefficient b in the overvoltage equation has the value $2RT/F$ which agrees with the experimental data for most metals.

By means of the theory of the delayed discharge we can also explain quantitatively the dependence of the overvoltage on the electrode material. As has been shown in the preceding section, the influence of the nature of the metal is exerted via the energy adsorption of the hydrogen on the given metal. By substituting (198) into the kinetic equation (200) for the discharge of hydrogen ions, we find

$$i_K = k_3'[\mathrm{H}^{\cdot}]\,e^{\frac{\alpha q_{\text{адс}}}{RT}}\,e^{-\frac{\alpha F\varphi}{RT}}. \qquad (212)$$

From this follows for the cathode potential

$$\varphi = \text{const} + \frac{q_{\text{адс}}}{F} + \frac{RT}{\alpha F} \ln [H^{\cdot}] - \frac{RT}{\alpha F} \ln i_{\text{к}} \qquad (213)$$

and for the overvoltage

$$\eta_{\text{к}} = \text{const} - \frac{q_{\text{адс}}}{F} - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln [H^{\cdot}] + \frac{RT}{\alpha F} \ln i_{\text{к}}. \qquad (214)$$

At $\beta = \alpha = 1/2$ Eq. (214) assumes the form:

$$\eta_{\text{к}} = \text{const} - \frac{q_{\text{адс}}}{F} - \frac{RT}{F} \ln [H^{\cdot}] + \frac{2RT}{F} \ln i_{\text{к}}, \qquad (214a)$$

and at constant current density and a certain composition of the solution

$$\eta_{\text{к}} = \text{const} - \frac{q_{\text{адс}}}{F}. \qquad (214b)$$

Thus the adsorption energy of atomic hydrogen enters as an additional term into the expression for the potential of the polarized cathode or (with negative sign) into the expression for the overvoltage: an increase in the adsorption energy lowers the overvoltage of the discharge reaction. Eq. (214b) is reminiscent of Eq. (170) obtained earlier by N.I. Kobozev and N.I. Nekrasov which connects the overvoltage with the adsorption energy on the hypothesis of an equilibrium between the ions and adsorbed atoms. However, apart from the fundamental difference in the interpretation of the adsorption energy for the overvoltage there is also an important difference between these two mathematical relations, namely that in Eq. (214b) the term $RT/F \ln [H]_{s}^{i}$ is absent, whose presence in Eq. (170) led N.I. Kobozev and N.I. Nekrasov to conclude, for example, that η is independent of the adsorption energy for metals with large overvoltage (see page).

The relationship between overvoltage and pH obtained from the theory of the delayed discharge coincides with the relationship observed in solutions with constant total electrolyte concentration (Eq. 149), namely, the overvoltage for the discharge process should decrease by approximately 58 mv if the concentration of the hydrogen ions is increased tenfold, because according to Eq. (203), at $\alpha = 0.5$, the coefficient of log $[H^+]$ is 58 mv. This is not unexpected because we assumed in the derivation of the formula (203) that the discharge rate is proportional to the hydrogen ion concentration, i.e., that the discharge is a first-order reaction; we have arrived at the same conclusion earlier on the basis of the experimental data.

In the above form however, the theory of the delayed discharge is not acceptable. For example, it is not possible to explain on the basis of it the dependence of the overvoltage on the composition of the solution for all other cases, with the exception of the one considered above, such as, for example, in pure acid solutions, in solutions with constant pH, but with varying total electrolyte concentration, in presence of surface-active substances, etc.

This circumstance made it imperative to revise the premises of the original theory of the delayed discharge.

§11. INFLUENCE OF THE STRUCTURE OF THE DOUBLE LAYER ON THE DISCHARGE RATE

In the original form the theory of the delayed discharge considerable use was made of concepts borrowed from general chemical kinetics, in particular, that of the connection between reaction rate and reagent concentration. The specific electrochemical nature of the reactions was taken into account only when the assumption concerning the influence of the electrode potential on the activation energy was introduced. The electrochemical reactions, however, compared with normal chemical reactions, have other specific features as well which must be taken into account when kinetic laws are to be derived.

In the case of homogeneous chemical reactions between uncharged particles the concentration in the volume of the reaction vessel enters into the equation for the reaction rate; in the case of heterogeneous reactions with participation of adsorbed substances the surface concentrations of these substances must be substituted into the kinetic equations. In the case of electrochemical reactions (which proceed at the metal/solution interface and which are thus also heterogeneous) this problem is complicated by the fact that the concentration of the reacting substances in the reaction zone may differ from the volume concentration not only because of the presence of normal adsorption forces but also because of the electrostatic interaction of the electrode with ions in the solution. Whereas the adsorption forces between the metal and the ions in solution are not always acting, the existence of electrostatic forces is indissolubly bound up with the presence of electric charges on the electrode and on the reacting particles and should be taken into account during the examination of any electrochemical reaction. The magnitude of the electrostatic interaction depends on the charge density on the electrode surface, i.e., on the electrode potential, and also on the structure of the double layer (for example, on the degree of its diffusiveness). Hence these factors have an important effect on the surface concentration and thus on the kinetics of the electrochemical reaction. During the transition through the zero charge point (i.e., during the charge reversal of the electrode surface) the electrostatic interaction between the metal and the ions also changes its sign: the attraction forces are transformed into repulsion forces and vice versa.

The influence of the structure of the double layer on the kinetics of electrochemical reactions has been taken into account for the first time by A.N. Frumkin in his theory of the hydrogen overvoltage [53].

The influence of the electrostatic interaction forces between the electrode and the ions on the concentration of the reacting ions in the reaction zone can be quantitatively defined if certain additional assumptions are made concerning the conditions under which the reaction takes place in the surface layer.

Assuming that the electrochemical reaction takes place only by direct contact between the reacting ions or molecules and the metallic electrode because the transition of an electron through the solution to an ion which is at a certain distance from the electrode, is not very probable (see above §9). Hence we should mean by reaction zone not the whole double layer but only part of it which extends from the surface to a distance which does not exceed the effective diameter of the ion. If the filling of this thin surface layer is not too great, i.e., if the ions are sufficiently remote from each other, which is practically nearly always the case, the concentration in the surface layer is connected with the concentration in the volume of the solution by the Boltzmann relation

$$[H^{\cdot}]_s = [H^{\cdot}]e^{-\frac{W_s}{RT}}. \qquad (215)$$

The excess energy W_s of the reacting ion in the surface layer in the case of the action of electrostatic forces only (without adsorption forces) is $W_s = nF\psi_1$ where n is the valency of the reacting ion (for the hydrogen ion $n = +1$) and ψ_1 is the mean electrostatic potential at a distance of approximately one ionic radius from the electrode surface relative to the potential in the depth of the solution. In this case Eq. (215) can be rewritten for the reaction of discharge of H^+ ions in the form

$$[H^{\cdot}]_s = [H^{\cdot}]e^{-\frac{F\psi_1}{RT}}. \qquad (215a)$$

During cathodic polarization of the electrode to potentials which are more negative than the potential of the zero charge point, ψ_1 assumes a negative value, and the surface concentration of the hydrogen ions exceeds their volume concentration. Under the same conditions the surface concentration of the anions ($n < 0$) is less than their volume concentration. At more positive potentials than the zero charge potential the reverse pattern results, which, however, is normally interfered with by the specific adsorption of the anions by chemical forces.

It is evident from Eq. (215a) that the surface concentration of the ions depends on all factors on which the magnitude of the ψ_1 potential depends, i.e., on the total electrode potential, the total electrolyte concentration in the solution and the adsorption of foreign surface-active ions and molecules (relative to the basic laws which the ψ_1 potential obeys, see Introduction).

Having taken into account the surface concentration of the reacting ions and the effect of the double layer structure on this concentration, we are compelled to examine in greater detail also the problem of the effect of the electrode potential on the activation energy of the electrochemical reaction. At the moment of discharge the reacting ion is at a certain point near the electrode surface (point A, Fig. 84; the difference between the potentials at the points A and C is not taken into account here) where the potential differs by the amount ψ_1 from the potential in the depth of the solution. The energy variation of this ion during polarization of the electrode obviously depends not on the total electrode potential relative to the solution but on the quantity $\varphi - \psi_1$. The dependence of the activation energy of the discharge process on the electrode potential is thus expressed by the relation

$$W_1 = W_1^0 + \alpha F(\varphi - \psi_1) \qquad (216)$$

instead of by Eq. (183). In analogy we have for the activation energy of the ionization process, instead of (185)

$$W_2 = W_2^0 - \beta F(\varphi - \psi_1). \qquad (216a)$$

In other words, not the whole potential difference between the electrode and a point in the depth of the solution but only part of the total jump localized in the reaction zone affects the activation energy of the electrochemical process.

It follows from Eqs. (216) and (216a), in particular, that the activation energy can vary not only in consequence of a variation of the electrode potential but also because of a change in the composition of the solution which affects the structure of the double layer.

On the basis of the foregoing we can write down the kinetic equation for the reaction of the discharge of the hydrogen ions in the form

$$i_K = k'[H^{\cdot}]_s e^{-\frac{W_1}{RT}} \qquad (217)$$

or, substituting (215a) and (216),

$$i_K = k'[H^{\cdot}] e^{-\frac{F\psi_1}{RT}} \cdot e^{-\frac{W_1^0 + \alpha F(\varphi - \psi_1)}{RT}} = k_1'[H^{\cdot}] e^{-\frac{F}{RT}[\alpha\varphi + (1-\alpha)\psi_1]} = k_1'[H^{\cdot}] e^{-\frac{F}{RT}(\alpha\varphi + \beta\psi_1)}. \qquad (217a)$$

The equation for the ionization rate of the hydrogen atoms correspondingly takes the form

$$i_A = k'' e^{-\frac{W_2}{RT}} = k_1'' e^{\frac{\beta F(\varphi - \psi_1)}{RT}}. \qquad (218)$$

Solving Eqs. (217a) and (218) for the potential, we obtain

$$\varphi = a_K' - \frac{1-\alpha}{\alpha}\psi_1 + \frac{RT}{\alpha F}\ln[H^{\cdot}] - \frac{RT}{\alpha F}\ln i_K, \qquad (219)$$

$$\varphi = a_A' + \psi_1 + \frac{RT}{\beta F}\ln i_A. \qquad (220)$$

The overvoltages of the cathodic and anodic process are

$$\eta_K = a_K + \frac{1-\alpha}{\alpha}\psi_1 - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H^{\cdot}] + \frac{RT}{\alpha F}\ln i_K, \qquad (221)$$

$$\eta_A = a_A + \psi_1 - \frac{RT}{F}\ln[H^{\cdot}] + \frac{RT}{\beta F}\ln i_A. \qquad (221a)$$

The equations (219)-(221a) differ from the corresponding equations (202), (203), (206), (207) by the presence of the term ψ_1.

As follows from Eqs. (217a) and (218), at positive ψ_1 and given φ the reaction rate is reduced in the case of the cathodic as well as the anodic process compared with the values which would be obtained at ψ_1 =

= 0, and this in the same ratio, equal to $e^{F\beta\psi_1/RT}$. According to Eq. (216a) the slowing down of the anodic process is due to the increase in the activation energy of the ionization reaction. The activation energy of the cathodic process, according to Eq. (216) is reduced if ψ_1 is positive; the rate of this process at a certain potential, however, decreases in spite of this because the effect of the decrease of the concentration of the reacting hydrogen ions, expressed by Eq. (215a) on the rate of the discharge process is greater than the effect of the change in the activation energy (because of the presence of the coefficient α in Eq. (216)). In the case of a negative ψ_1 all these variations obviously proceed in the opposite sense.

The equilibrium conditions between two phases of a given composition and, consequently, also the equilibrium potential cannot depend on the structure of the interface. Indeed, it follows from Eqs. (217a) and (218) that

$$\varphi_p = \frac{RT}{F} \ln [H^{\cdot}] + \frac{RT}{F} \ln \frac{k_1'}{k_1''}$$

and that the value of φ_p consequently does not depend on the quantity ψ_1.

Let us now consider to what modification the new theory leads compared with the original with regard to the problem of the magnitude of the overvoltage.

The dependence of the electrode potential or overvoltage on the logarithm of the current density in the case of the discharge of the hydrogen ion at the mercury electrode remains essentially linear. In the absence of specific adsorption the term ψ_1 causes only a slight deviation from linearity due to the fact that the value of ψ_1 in one and the same solution varies slightly with the total electrode potential: this deviation, as a rule, does not exceed a few per cent if the potential range within which the current measurement is carried out, does not contain the zero charge point (see further on).

Conversely, in the investigation of the problem concerning the effect of the composition of the solution on the hydrogen overvoltage, the above-given overvoltage theory leads to several new conclusions.

Acid solutions. The equation for the overvoltage of the cathodic separation of hydrogen (221) contains two terms which depend on the composition of the solution: the term $-\frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H^+]$, which clearly includes the hydrogen ion concentration and the term $\frac{1-\alpha}{\alpha}\psi_1$, which depends on the total concentration and valency of the electrolyte and also on the presence of surface-active substances in the solution.

In order to elucidate the nature of the dependence of the overvoltage on the composition of the solution, it is expecient to distinguish the different partial cases in the same way as we did in the discussion of the experimental results.

Let us first consider the question of the dependence of the overvoltage on the pH in solutions with constant total electrolyte concentration in the absence of surface-active substances, as, for example, in buffer solutions or in acidified salt solutions. Under these conditions the ψ_1 potential at the same electrode potential is almost independent of the pH of the solution. The only variable quantity in Eq. (221) left is the term $-\frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H^+]$, according to which the overvoltage increases by $\frac{1-\alpha}{\alpha}$ 58 mv (or by 58 mv at $\alpha \approx 0.5$) with unit increase in the pH. In this case Eq. (221) does not differ from the equation which follows from the original theory of the delayed discharge and corresponds equally well to the experimental data. This is a consequence of the fact that at constant value of ψ_1 the surface concentration of the hydrogen ions is proportional to their volume concentration.

Theory, however, leads to an essentially different conclusion with regard to the dependence of the overvoltage on the total electrolyte concentration in the solution. The addition of a neutral salt to the solution of an acid with constant concentration causes a compression of the double electric layer at the electrode surface and to a lowering of the absolute value of the ψ_1 potential. As has been shown in the Introduction, at moderate electrolyte concentration with a univalent cation and at more negative electrode potentials than the zero charge point potential (as is usually the case during cathodic hydrogen separation) the value of ψ_1 obeys the following equation:

$$\psi_1 = -B + \frac{RT}{F}\ln c, \qquad (222)$$

where c is the total concentration of the uni-univalent electrolyte in the solution and B is a constant (compare Eq. (20a)).

Substituting this expression into the overvoltage equation, we obtain

$$\eta = a + \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln c - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln[H^{\cdot}] + \frac{RT}{\alpha F}\ln i, \qquad (223)$$

from which follows that a tenfold increase in the electrolyte concentration of the solution at constant pH should be accompanied by an increase in the overvoltage by about 58 mv at 18°C.

The addition of salts with trivalent and tetravalent cations even in low concentration causes a decrease in the negative value of ψ_1 or even makes it positive, in consequence of which, in accordance with Eq. (221) the overvoltage should increase sharply as is actually observed in the experiment. The cause of the increased overvoltage when a neutral salt is added to the solution is the decrease in the hydrogen ion concentration in the surface layer which, in turn, results in a decrease in the rate of discharge of the hydrogen ions.

In strong acid solutions which do not contain foreign electrolytes, the two terms in Eqs. (217a) and (221) which depend on the composition of the solution vary simultaneously with change in acid concentration. The total electrolyte concentration in this case coincides with the hydrogen ion concentration, i.e., $c = [H^+]$. It follows from Eq. (223) in agreement with experiment that in solutions of pure acids the overvoltage is independent of the acid concentration. This result is a consequence of the opposite effect of two factors: on the one hand, the increase in the hydrogen ion concentration lowers the overvoltage and, on the other, an increase in the total concentration causes a compression of the double layer and an increase in overvoltage. As a result of the compensation of the influence of these two factors, the overvoltage remains constant.

In this case it is also possible to explain clearly the physical meaning of the relation thus obtained. As follows readily from a comparison of Eqs. (215a) and (222), taking into account that $c = [H^+]$, the surface concentration of the hydrogen ion in pure solutions of strong acids does not change but remains constant during changes of the volume concentration of the acid within a fairly broad interval. A more accurate consideration of the problem leads to the conclusion that this constancy is strictly fulfilled if the comparison of solutions of different concentration is carried out at constant overvoltage. The above-indicated consequence from the theory of the structure of the double layer also accounts for the independence of the overvoltage on the acid concentration.

The conclusions presented in the foregoing are well supported by numerous experimental data. Let us take as an example the data on the measurement of the hydrogen separation overvoltage in HCl + KCl solutions at the mercury cathode, given in §5. If the constants a and α are found on the basis of the overvoltage in some other solution, one can calculate the overvoltage as a function of the current density in other solutions by means of Eq. (221) without introducing any new quantities. Such a calculation has been carried out [25, 26] choosing as initial curve the overvoltage curve in 0.1 N HCl which obeys the equation

$$\eta = 1{,}460 + \psi_1 - \frac{RT}{F} \ln [H^{\cdot}] + \frac{2RT}{F} \ln i, \qquad (224)$$

or, in other words, a = 1.460 and α = 0.5. The results of this calculation are reflected in Fig. 76, where the thick line indicates the calculated overvoltage at constant current density as a function of the logarithm of the concentration of the foreign electrolyte for solutions containing 10^{-3} N HCl in presence of different quantities of KCl; the points correspond to the experimental data. As is evident from this diagram, the experimental and calculated values of the overvoltage are in good agreement.

The conclusion as to the independence of the overvoltage in pure solutions of strong acids of the acid concentration holds good only as long as the dependence of ψ_1 on the concentration of the solution obeys Eq. (222). In fairly concentrated solutions and at negative surface charges there occurs a specific adsorption of the anion which results in an increase in the negative value of ψ_1 with increase in concentration and, according to Eq. (221), to a lowering of the overvoltage [7].

Alkaline solutions. During the discussion of the experimental data in §5 it was pointed out that the kinetic laws of the process of hydrogen separation in alkaline solutions differ from the laws observed to apply in acid solutions. Hence it is natural to assume that the reaction mechanism in the alkaline medium is different from the mechanism described in the foregoing.

Indeed, if the above-described laws applied also to the high pH range, the overvoltage should increase when we go from normal acid (pH = 0) to normal caustic (pH = 14) in consequence of the decrease in the hydrogen ion concentration by 14 × 58 mv = 0.81 v. However, such a strong shift of the cathode potential to the negative side makes the occurrence of other electrode reactions at the electrode surface possible.

One of the reactions which is made possible under these conditions is the reaction of hydrogen separation through the combination of electron with a water molecule

$$H_2O + e \rightarrow OH^- + H_{\text{адс}}. \qquad (B)$$

This reaction is energetically much less advantageous than the reaction of discharge of the hydroxonium ions but when we go over to alkaline solutions in which the concentration of the latter is extremely low, it begins to play a predominating role in the total process of cathodic hydrogen separation.

According to the theory of the delayed discharge, the rate of reaction (B) is determined by the equation

$$i = k[H_2O]e^{-\frac{\alpha F(\varphi - \psi_1)}{RT}}, \qquad (225)$$

which is reminiscent of Eq. (217a) for the discharge of hydrogen ions. The basic difference in the kinetics of these two processes consists in the fact that in one of them participates the positively charged hydrogen ion and in the other the neutral water molecule, whose surface concentration is independent of the electrode potential or of the ψ_1 potential; with the exception of very strong solutions, it is also almost independent of the composition of the solution.

We can derive from Eq. (225) an equation for the electrode potential

$$\varphi = a' + \psi_1 - \frac{RT}{\alpha F}\ln i. \qquad (226)$$

In alkaline solutions it is more convenient to express the potential of the equilibrium hydrogen electrode not as a function of the hydroxyl ion concentration

$$\varphi_p = \varphi_U^0 - \frac{RT}{F} \ln [OH^-].$$

The expression for the overvoltage of hydrogen separation in alkaline solutions consequently assumes the form

$$\eta = a - \psi_1 - \frac{RT}{F} \ln [OH^-] + \frac{RT}{\alpha F} \ln i. \qquad (227)$$

It follows from Eqs. (226) and (227) that with increase in the caustic concentration or the pH of the solution at constant value of the ψ_1 potential (i.e., constant total electrolyte concentration) the cathodic potential does not change but the overvoltage decreases in consequence of the shift of the equilibrium potential to the negative side. The independence of the cathode potential of the pH is a consequence of the fact that in alkaline solutions during the delayed stage of the electrochemical process neither hydrogen ions nor hydroxyl ions participate as reacting substances.

The not very numerous experimental data support this conclusion. As is evident from Fig. 75, the overvoltage in acid solutions at the mercury electrode at constant total electrolyte concentration increases with increase in the pH. In neutral solutions the overvoltage attains a maximum and with further increase in pH it decreases again. Approximately the same dependence is also observed, as S.D. Levina and P.D. Lukovtsev [13] showed, within a certain caustic concentration on the nickel electrode. This may serve as an indication of the correctness of the assumption which we made that the hydrogen separation in alkaline solutions takes place from the water molecule.

In solutions of pure caustic which does not contain foreign salts, the value of ψ_1 varies with the caustic concentration in accordance with the equation $\psi_1 = B + \frac{RT}{F} \ln [OH^-]$, which is analogous to Eq. (222). It follows from this that with increase in pH by unity the overvoltage should increase not by 58 but by 116 mv. This conclusion is also confirmed by the experimental data for the mercury electrode [8]. It must be pointed out, however, that for certain electrodes, for example, platinum, the dependence of the overvoltage on the caustic concentration, following from Eq. (227) is not observed in alkaline solutions although on the basis of other data it must be assumed that even in this case the stage which determines the discharge kinetics as a whole is the discharge stage.

In connection with the problem of the dependence of the overvoltage on the acidity or alkalinity of the solution, we must mention the hydrogen overvoltage theory of Eyring, Glasstone and their co-workers [54] which has received wide currency in the American and British literature. Accepting the delay of the discharge stage, these authors applied the kinetic theory of the transitory state [55] to the calculation of the rate of the discharge reaction. Attempting to explain the incorrect data of Bowden on the independence of the overvoltage of the pH in buffer solutions, they proposed that not the H_3O^+ ions but the water molecules are subject to discharge in acid solutions. This conclusion is erroneous, however [56], because the proposition concerning the discharge of the water molecule, as we have shown in the foregoing, leads to an independence of the electrode potential and not the overvoltage on the pH of the solution (see Eqs. (226) and (227)). This theory was subsequently modified several times. Thus, with the aim of eliminating this error, the concept of a division of the potential jump into two parts, one of which determines the surface concentration of the hydrogen ions and the other the activation energy of the discharge, was introduced. Later, in connection with the appearance of more accurate experimental data on the dependence of the overvoltage on pH, the assumption of a separation of hydrogen from water molecules was replaced by the assumption of the discharge of H_3O^+ ions in acid solutions [57]. Thus, this theory was gradually transformed and was finally converted mainly into a reproduction of the physical pattern and the equations of the theory of delayed discharge, formed much earlier by the Soviet electrochemists, differing from the latter only by the arbitrariness of the assumptions concerning the structure of the double electric layer, which the American authors make.

Solutions, containing surface-active ions and molecules. With due regard for the structure of the surface layer the theory of the delayed discharge enables the influence of the surface-active ions or molecules on the hydrogen overvoltage to be elucidated.

The specific adsorption of ions causes important changes in the structure of the double electric layer at the electrode surface and thus a change in the ψ_1 potential.

The surface-active ions are adsorbed in the layer of solution which is directly adjacent to the electrode surface; hence the ψ_1 potential is shifted to the positive side if they are charged positively or to the negative if they are negatively charged. In some cases ψ_1 can change sign (surface charge reversal, see Introduction).

A shift of the potential to the negative side causes an increase in the surface concentration of hydrogen ions and, according to Eq. (217a), an increase in current density. It follows from this that the hydrogen overvoltage in acid solutions should decrease if surface-active anions are adsorbed. The adsorption of surface-active cations, conversely, increases the overvoltage (Eq. 221) [30].

These conclusions from theory correspond with the experimental results given in §5. The variation of the ψ_1 potential through adsorption of surface-active substances in solutions of different composition can be determined by electrocapillarity measurements on the basis of the shift of the zero charge point potential. Comparison of these data with the variation of the hydrogen overvoltage shows that the latter, at least qualitatively, corresponds to the variation of the ψ_1 potential. The absence of completely quantitative agreement is partly explained by the fact that the overvoltage measurements and the measurements of the maximum of the electrocapillarity curve are usually carried out in different ranges of the electrode potential. It should also be pointed out that the absolute values of the ψ_1 potential in presence of surface-active anions are quite considerable, attaining, for example, 0.3 v. Under these conditions the surface concentrations calculated by means of the Boltzmann equation (215a) can exceed by far the limits of applicability of the laws of dilute solutions and it is essential to introduce instead of the concentrations the activities into this equation which causes a certain complication of the theory but does not change the qualitative picture.

The adsorption of ions and the variation of the ψ_1 potential and the overvoltage caused by it depend on the electrode potential. In the case of the adsorption of anions one would expect the appearance of two branches on the overvoltage curve as shown in Figs. 70 and 80. The lower branch is observed in the range of anion adsorption, causing the appearance of large negative values of ψ_1. If the current density is increased and the electrode potential is shifted to the negative side, a desorption of the anions takes place, ψ_1 increases and the quantity η assumes its normal value. If the specific adsorption is only moderate, a sudden variation of the ion adsorption takes place near the zero charge potential. Indeed, as Ya.M. Kolotyrkin [6] found, two branches are observed, as a rule, on the hydrogen overvoltage curve near the zero charge point for metals such as lead, cadmium and thallium, whose zero points are situated in the range of strongly negative potentials (see Introduction, Table 1). In concentrated acid solutions the desorption of the anions from the surface of the mercury electrode takes place gradually with increase in the negative potential, and instead of two branches an increase in the slope of the overvoltage curve is observed in some cases (Fig. 77).

The difference to be expected in the adsorption of surface-active ions in acid and alkaline solutions is of interest. This difference is due to the circumstance that the quantity ψ_1 enters into the overvoltage equations for acid and alkaline solutions with a different sign (Eqs. (221) and (227)). If the adsorption of surface-active cations in acid solutions increases the overvoltage, one would expect a decrease in the overvoltage in alkaline solutions through the adsorption of these same cations. This conclusion, predicted by theory, could really be confirmed by experimental observation [8].

As the experiment shows, an increase in overvoltage occurs in the case of adsorption of the simpler organic molecules, such as, for example, alcohols or acids of the aliphatic series [61, 29]. This may be due to the fact that the access of the hydrated proton to the electrode surface is made more difficult by the layer of adsorbed molecules and to the weakening of the effect of the electric field on the activation energy of discharge in consequence of the increased thickness of the double layer. In fact the adsorbed organic molecules, as is evident from the lowering of the electrode capacitance, dislodges the ions of the double layer from the electrode surface which must impede the discharge process. The increase in overvoltage through the adsorption of large organic cations is also connected not only with the increase in the ψ_1 potential but also with the shielding of the electrode surface.

When the potentials at which desorption of the adsorbed organic molecules begins are reached, the effect of increasing the overvoltage naturally disappears.

When considering the problem of the influence of surface-active organic substances on the overvoltage we should not forget, however, that the above-explained simple theory cannot describe the influence of all factors on the kinetics of the electrochemical process of hydrogen separation. When a complex molecule is adsorbed its interaction with the discharged ion cannot be reduced merely to an alteration of the electrical energy of the ion in the double layer.

Thus, in cases where a cation which can split off a hydrogen ion, i.e., which has the composition BH^+, where B is the molecule of a weak base, is adsorbed, the possibility of a new mechanism of the discharge of the hydrogen ion is given: $BH^+ + e \rightarrow H_{ads}$, $B + H^+ \rightarrow BH^+$, which can lead to a lowering of the overvoltage. This probably accounts for the catalytic acceleration of the cathodic hydrogen separation observed in presence of various organic compounds. The NH_4^+ cations can also serve as proton donors; because, however, the latter are not specifically adsorbed, their effect is manifested only at relatively high concentrations.

§12. DELAYED DISCHARGE IN CASES OF SIGNIFICANT FILLING OF THE SURFACE

The conclusions from theory of delayed discharge presented in the foregoing are correct only for electrodes which adsorb atomic hydrogen only slightly. If the filling of the surface is fairly considerable, new factors come into play which affect the kinetic laws of the electrochemical reaction.

The reaction of discharge of the hydrogen ion with formation of an adsorbed hydrogen atom

$$H^{\cdot} + e \rightarrow H_{адс} \qquad (G)$$

proceeds only at the free sites of the electrode surface. If the surface is homogeneous, the rate of this reaction is proportional to the free electrode area. If we designate the filling of the surface with atomic hydrogen by θ (θ is the ratio of the number of occupied sites to the total number of sites on the electrode surface) and the proportion of free sites by (1 − θ), we find for the discharge rate the expression

$$i = k_1 (1 - \theta) [\mathrm{H}^{\cdot}] e^{-\frac{F}{RT} [\alpha\varphi + (1-\alpha)\psi_1]} \qquad (228)$$

instead of Eq. (217a) which applies if the filling is very slight (θ → → 0).

As pointed out already in §8 of the present chapter, discharge of ions at the sites occupied by adsorbed hydrogen atoms is also possible in addition to this reaction and the ionization of the adsorbed hydrogen atoms; in this case molecular hydrogen is formed directly during the discharge:

$$\mathrm{H}^{\cdot} + e + \mathrm{H}_{\text{адс}} \rightarrow \mathrm{H}_2. \qquad (B)$$

If we assume that the reaction (B) requires a certain activation energy, which depends on the electrode potential in the same way as the activation energy of the reaction (G), its rate can be expressed by the equation

$$i = k_2 \theta [\mathrm{H}^{\cdot}] e^{-\frac{F}{RT} [\alpha\varphi + (1-\alpha)\psi_1]}. \qquad (229)$$

This equation differs from Eq. (217a) by the presence of the factor θ and also a different value of the constant. It is easy to show that if the reactions described by Eqs. (228) and (229) take place simultaneously, the filling of the surface with adsorbed hydrogen during increasing cathodic polarization should tend to a certain limit. This conclusion holds particularly for the mercury electrode, for which, as indicated previously in §8, the mechanism of removal of the adsorbed hydrogen via the reaction (B) and not via combination of hydrogen atoms to molecules, is the most probable. However, the limit concentration of the adsorbed hydrogen on the electrode surface in this case is so small that it cannot be measured with the existing experimental methods: the small value of this concentration is explained by the fact that the activation energy of the reaction (B) is considerably smaller than the activation energy of reaction (G) and, consequently, $k_2 >> k_1$.

The application of the theory of delayed discharge leads to an interesting conclusion in the case of discharge at a surface, whose filling with adsorbed hydrogen varies linearly with the logarithm of the equilibrium pressure. If it is assumed that the removal of the adsorbed hydrogen takes place via recombination, the total overvoltage on the electrode is composed additively of the two components η_1 and η_2 of which the first is determined by the delay in the discharge as in the case of discharge on an unfilled surface; the second component expresses the shift of the equilibrium potential of the adsorbed hydrogen compared with the reversible hydrogen potential under atmospheric pressure in the same solution. These conclusions proved to be quite applicable to the process of hydrogen separation at the palladium electrode. In this case, owing to the high solubility and mobility of the hydrogen in the metal, the equilibrium potential of the adsorbed hydrogen at different degrees of saturation of the metal with hydrogen can be determined by different methods, for example, by direct measurement on the diffusion side of an electrode of palladium foil (see §7). As experiment shows, the overvoltage on palladium observed under different conditions can really be expressed as the sum of two components, of which one depends only on the current density and composition of the solution and the other on the concentration of the hydrogen dissolved in the metal [15].

The shift of the equilibrium potential of the adsorbed hydrogen compared with the reversible hydrogen potential under atmospheric pressure in the same solution, generally speaking, may be connected with a delay in the recombination or a delay in the diffusion of the molecular hydrogen thus formed in the solution. Experiments show that in the case of palladium and platinum electrodes with an active nonpoisoned surface the delay in the diffusion stage is of primary importance; in this case the part of the overvoltage η_2 reflects the concentration polarization due to the dissolved molecular hydrogen and can be expressed by Eq. (178).

If we deduct from the total overvoltage the component η_2, calculated in accordance with the last equation, the remaining part of the overvoltage η_1 satisfies the relations obtained from the theory of the delayed discharge. Thus, for the platinum electrode in alkaline solution, according to the experiments of P.I. Dolin and B.V. Ershler, the following relation obtains for the current density and the quantity η_1

$$i = 0{,}6 \cdot 10^{-3} [e^{0{,}6\eta_1 F/RT} - e^{-0{,}4\eta_1 F/RT}], \qquad (210a)$$

which coincides with the general equation of the theory of the delayed discharge (210), if we assume $i^0 = 0.6 \cdot 10^{-3}$ and $\alpha = 0.6$. The relation (210a) can be applied not only for cathodic but also for anodic polarization over the entire range of current densities accessible to measurement.

When calculating the correction for the concentration polarization due to molecular hydrogen in the case of the anodic process, we must evidently use the following equation instead of Eq. (178)

$$\eta_a = \frac{RT}{2F} \ln \left[1 - \frac{i}{(i_d)_a} \right]. \qquad (178a)$$

because the electrochemical process in this case does not cause an enrichment but an impoverishment of the solution with molecular hydrogen. A dependence on the composition of the solution is typical for the part of the overvoltage η_1 at the platinum and palladium electrode which is connected with the delay in the discharge state. Thus, the quantity n_1 is considerably greater in alkaline solutions than in acid, and in acid solutions in presence of an excess of indifferent electrolyte it increases with decrease in the acid concentration.

As has been shown earlier, it is sufficient for the explanation of the phenomena, observed during the separation of hydrogen at cathodes with large overvoltage and small adsorption energy of atomic hydrogen, whose surface is practically free of adsorbed hydrogen, to take into account the delay in the discharge stage. When going over to cathodes with larger adsorption energies, the reaction rate of the discharge increases and becomes comparable with the rate of other stages of the process. In these cases several successive and sometimes also parallel stages proceeding at comparable rates must be taken into account for the interpretation of the total sum of the experimental data. This results in considerable complication of the pattern of the process and makes the conclusions more ambiguous, all the more as with strong filling of the surface, as explained previously, the nature of the relationship between the concentration of adsorbed hydrogen and the rate of its removal may vary under the influence of several factors. Finally, in the case of solid electrodes with inhomogeneous surface the electrochemical reaction can proceed in accordance with different mechanisms at different sites on the electrode surface. As an example we can point to the platinum electrode in alkaline solutions. It was shown in the foregoing that in alkaline solutions the overvoltage during hydrogen separation on an activated platinum electrode, after correction for the concentration polarization caused by the molecular hydrogen formed in the process, obeys the laws which follow from the theory of the delayed discharge. It follows from this that the rate of formation of molecular hydrogen should coincide with the rate of transformation of the hydrogen ion to an adsorbed hydrogen ion or of a water molecule to an adsorbed atom and the OH^- ion. The rate of the discharge process in the case of the platinum electrode can be measured by an independent method (see page 163) which opens up a possibility for verifying this conclusion. It is found that in 1 N HCl solution the rate of separation of hydrogen really coincides with the rate of formation of adsorbed atoms, but in alkaline solutions the former is much less than the latter. This contradiction can be eliminated only by assuming that on some part of the electrode surface the rate of separation of molecular hydrogen is limited by the rate of recombination of the adsorbed atoms to such a degree that these parts of the surface are practically not used for the separation of molecular hydrogen, while the deposition of the adsorbed atoms on them may take place at a fairly high rate. This is then the cause of the difference in the rates of the two processes. Conversely, at the active parts the removal is unimpeded and the kinetics of the process as a whole are determined by the discharge stage.

The measurement of the decrease in the overvoltage with time following the switching off of the current and the observations on the penetration of hydrogen during electrolysis into the metal lattice lead us to the conclusion that on nickel or iron electrodes the delay of the removal stage must be taken into account in addition to the delay of the discharge stage. This conclusion is confirmed by observations on the influence of surface-active substances on the hydrogenation of iron during the evolution of hydrogen on its surface [31]. In some cases the addition of surface-active substances to the solution causes a decrease in the quantity of hydrogen, passing into the metal lattice and in others (for example, β-naphtoquinoline) it is increased, while the overvoltage increases in all these cases. This difference in the behavior of different adsorbed substances can be explained by assuming that the increase in the overvoltage in the first case is due to a slowing down of the discharge and in the second case to a slowing down of the hydrogen removal. The delay in the removal of the adsorbed hydrogen causes an increase in its concentration at the surface and intensifies its penetration into the depth of the metal.*

As follows from §§ 7 and 10, the product of the exchange current at the equilibrium potential i^0 and the "polarizability" w of the electrode which is equal to the ratio of the overvoltage η and the current density i at small values of η can serve as a criterion for the determination of the mechanism of the hydrogen separation reaction. Whereas in the case of a delayed recombination, according to Eq. (167a), the quantity wi^0 should be equal to $RT/2F$, in the case of a delayed discharge $wi^0 = RT/F$. Because metallic nickel does not dissolve spontaneously in alkaline solutions, and the overvoltage in this case is not excessive, the range of small overvoltages can be successfully investigated on nickel in alkaline solutions and the quantity wi^0 can be determined (see § 3) with sufficient accuracy. It is found that depending on the composition of the solution this quantity varies within the limits of 15 to 27 mv, which indicates a variation of the nature of the slow stage. In order to explain all the results obtained in experiments with nickel in alkaline solutions it may be assumed that, as in the case of the platinum electrode in alkaline solutions, the ratio of the rates at different parts of the electrode is different. On the nickel surface there are sites for which the slower stage is the discharge stage and also sites on which the rate of the process is determined by the rate of recombination, and the exchange of adsorbed hydrogen between the different sites is also a slow process** [32].

As is evident from the above-stated, the pattern according to which the process of separation of molecular hydrogen proceeds in the case of electrodes with low overvoltage, proves to be much more complex than in the case of electrodes with high overvoltage where the single assumption of a delay of the discharge stage was sufficient to account for the totality of experimental data. However, it may be taken as proved that in the case of electrodes with low overvoltage, in addition to the delay of the discharge stage, a delay of the stage of removal of molecular hydrogen must be assumed.

It is possible that there are cathodes for which the recombination stage is so slow over the entire electrode surface that it alone determines the kinetics of the process of hydrogen separation as a whole: however, this assumption has not yet been experimentally confirmed.

It follows from the above-stated that the supposed antithesis found in some works of the views concerning the delay of the discharge state and the delay of other (chemical or diffusion) stages, as mutually exclusive, is incorrect. Depending on the electrode material and the experimental conditions one or other of these factors can influence the kinetics of the process. This comment applies not only to the reaction of hydrogen separation but also to other electrochemical reactions in which in some cases the electrochemical discharge or ionization stage and in others the chemical stages are delayed.

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194 In some cases it is necessary, however, to take into account the slowness of the adsorption stage which precedes the electrochemical reaction proper. Further on we shall examine such examples.

We remember that when comparing the data of polarization measurements on electrodes of any arbitrary dimension it is more convenient to consider not the current intensity but the current density (i.e., the relation of current intensity to electrode surface). The true surface of a solid electrode, however, nearly always exceeds the visible, geometrical surface. For example, for a metal with normal smooth surface the true surface is 2-3 times greater than the visible surface. Because of this the ratio is usually not known with sufficient accuracy, the current density in most works is related to the unit of visible metal surface. In the case of platinized platinum and other electrodes which are coated with a layer of disperse metal, the true surface is many times greater than the visible surface and the true current density is that many times less than the conventional density, calculated for the visible surface. Hence the overvoltage on such electrodes at normal current densities is also greatly reduced.

207 The values a and b for many technical metals have been measured by A.G. Pecherskaya and V.V. Stender [5].

208 The results of the comparison of the heats of melting and evaporation and also of the work function of the electron with the values for a for several metals are given by N.I. Kobozev [60].

225 In the following sections in which the experimental data mainly for the cathodic reaction of hydrogen separation will be considered (and not of the anodic reaction of the ionization of hydrogen) we shall omit in the places where this cannot cause any misunderstanding, the subscript K in the expressions for the cathodic overvoltage η_K, for the constants a_K and b_K and for the cathodic current i_K (i without subscript with negative sign will correspond in this case to the anode current).

232 The surface concentration of the ions $[H^+]^s$ which varies in consequence of the passage of current, as already pointed out in §1 of Chapter 1, must not be confused with the concentration of the hydrogen ions, adsorbed in the double layer, which we shall designate by $[H^+]_s$.

234 We must also point out that in the case of an irreversible electrochemical reaction Eq. (155), strictly speaking, cannot be applied to the drop electrode. Indeed, Eq. (153) from which Eq. (155) is derived, is correct only if the quantity $[H^+]^s$ is constant in time. At constant $[H^+]^s$, according to Eq. (151), the density of the discharge current i should also be constant. Instead, as has been shown in Chapter 2, the density of the diffusion current towards the drop surface decreases in proportion to $t^{-1/2}$, where t is the time elapsed since the moment of the beginning of its increase. Thus the condition of a constancy of the concentration of H^+ at the drop surface cannot be met in the case of an irreversible electrode process, if the growth of the drop takes place at constant potential, while it is automatically fulfilled if the polarization is of a purely concentration nature. It can be shown, however, that the error which results from the use of Eq. (155) for the process of hydrogen separation at the drop electrode is not very large if i and i_d stand for the mean current density and limit current [28].

235 Because the hydrogen ion concentration was 2 eq/liter, a potential of the polarized electrode of approximately –1.00 v corresponds to an overvoltage of 1.02 v.

238 Another possible decomposition into two stages for the reaction of H_2 formation will be described further on.

240 Indeed if the reaction proceeds in one direction the rates of all the individual subsequent stages, established under stationary conditions, will be the same.

243 To cause the appearance of dissolved atomic hydrogen in iron it is not necessary to polarize the iron by an external current source. For this purpose the negative potential which is spontaneously established during the action of acids on iron is sufficient (see Chapter 8). The dissolved hydrogen is the cause of the "hydrogen embrittlement" of the metal well known in engineering. The penetration of hydrogen is much more pronounced with normal technical iron than in the case of the perfectly pure metal. Among the studies which deal with the problem of the penetration of hydrogen into iron, we must make special mention of the work of D.Alekseyev and co-workers [59].

245 The measurement of the overvoltage drop may be regarded as the determination of the capacitance of the electrode *C* at potentials at which separation of hydrogen is already possible. Indeed, after opening of the circuit the current *i* in the external circuit becomes zero. The discharge of hydrogen ions at the electrode, however, continues and the positive charges of the discharged ions displace the cathode potential to the anodic side. It is obvious that under these experimental conditions the total charging current corresponding to the potential variation at a certain rate, and the current of the hydrogen ion discharge should be zero and consequently,

$$C\frac{\partial\eta_t}{\partial t}+i_t=0, \qquad \text{(a)}$$

where η_t and i_t are, respectively, the overvoltage and the discharge current at the time *t* elapsed after the opening of the circuit. Assuming that the quantity *C* can be considered as constant and assuming in Eq. (a) in accordance with (136),

$$i_t=ke^{-\eta_t/b}, \qquad \text{(b)}$$

we find after integration

$$\eta_t=-b\ln\left(\frac{kt}{Cb}+\text{const}\right). \qquad \text{(c)}$$

Because at $t = 0$, $\eta_0 = b \ln i_0/k$, where η_0 and i_0 are the overvoltage and current density prior to the opening of the circuit, the integration constant in Eq. (c) is

$$\text{const}=\frac{k}{i_0} \qquad \text{(d)}$$

and, consequently,

$$\eta_0 - \eta_t = b \ln\left(\frac{ti_0}{Cb} + 1\right). \qquad (e)$$

Equation (d) allows us to determine C from the dependence of η_t on time. In the case of the mercury electrode we obtain values of C of about 18 microfarads/cm^2, i.e., corresponding to the normal double layer capacitance in the case of a negatively charged electrode surface [33]. The same calculation method, applied to electrodes with low overvoltage, however, gives higher values of C which point to the presence of adsorbed hydrogen.

252 In particular, we do not know the relations between the adsorption energy and the quantities typical for the electrode material for which a connection with the constant a in the Tafel equation has been established experimentally which makes the theoretical interpretation of the regularities described in §3 more difficult.

253 There are some indications relative to the existence of such "limit adsorption currents" in presence of a passivating film on the metal surface.

257 Whilst the dipole nature of the bond between metal and adsorbed hydrogen can also be taken into account within the framework of the recombination theory to yield a certain relationship between overvoltage and composition of the solution, these effects should be one order of magnitude smaller than those observed experimentally.

258 This result naturally cannot be derived from Eq. (170) because the latter was obtained on the assumption of a slight degree of filling.

259 With metals with small overvoltage and, consequently, large adsorption energy of the hydrogen atoms (see Eq. 170) the electrochemical desorption is of special importance according to this theory. If the energy of the bond between the metal and the hydrogen atoms is fairly small (for example, less than 10 kcal), i.e., in the case of metals with large overvoltage, according to Kobozev and Nekrasov, the hydrogen atoms should predominantly evaporate into the solution. The rate of this last process, as follows from the kinetic theory of evaporation, is expressed by the equation

$$v_{\text{эмисс}} = \nu [\mathrm{H}]_s^i e^{-\frac{W_{\text{адс}}}{RT}}, \qquad (a)$$

where ν is a coefficient (frequency factor) of the order of 10^{11}-10^{12} sec^{-1}; to this rate corresponds a current

$$i_{\text{эмисс}} = \nu F [\mathrm{H}]_s^i e^{-\frac{W_{\text{адс}}}{RT}}. \qquad (b)$$

However, as calculations have shown, carried out on the basis of Eq. (a), the rate of desorption by evaporation at practically attainable overvoltages is negligibly small and cannot have a marked effect on the over-all kinetics of the reaction or lead to the appearance of observable quantities of hydrogen atoms in the solution.

From a comparison of Eqs. (170) and (b) follows:

$$\eta = \text{const} - \frac{RT}{F} \ln \nu F + \frac{RT}{F} \ln i_{\text{эмисс}}, \qquad (c)$$

where the value of the constant is the same as in Eq. (170). The latter can be calculated from the free energy of dissociation of the hydrogen molecule into atoms. Having found the value of the constant, one can find from Eq. (a) the quantity i_{emiss} at a given η. This calculation gives the above-indicated result [40].

As is evident from Eq. (b), if the desorption mechanism is purely one of emission, the overvoltage at a given current density should be independent of the adsorption energy and, consequently, of the nature of the metal, and the coefficient b should equal RT/F which does not agree with the experimental data. N.I. Kobozev [60], starting out from the assumption of the presence of a repulsion interaction between the adsorbed atoms, which does not vanish even with extremely slight filling, has recently derived a new, more complex relation between the overvoltage, the adsorption energy of the hydrogen atoms and the evaporation rate, on which we cannot dwell here in greater detail.

263 In §12 of Chapter 1 it as shown that the additional capacitance, observed in measurements on an electrode which is immersed in a solution of potential-determining ions, also decreases with increase in the frequency in the case of pure concentration polarization. This effect is connected with the slowness of the diffusion of the ions while the effect described here is connected with the slowness of the reaction itself. In the experiments described here the hydrogen ion concentration in the solution was so great that the slowness of the diffusion towards the electrode at the frequencies used could not yet affect the magnitude of the measured capacitance.

268 For an explanation of the theory of Broensted see A.I. Shatenshteyn. Teoriya kislot i osnovaniy. Istoriya i sovremennoye sostoyaniye [Theory of Acids and Bases. History and Modern Position]. Goskhimizdat [State Publishing House for Chemical Literature], 1949.

270 The concepts of a quantum-mechanical nature, on which we shall not dwell here, lead to the conclusion that the energy of the whole system consisting of metal and electron, proton and water molecule, near the point C is somewhat less than would follow from the position of the curves aa and bb, taken separately (the dotted part of the curve in Fig. 84, omitted in Figs. 85-87). We shall not take into account either the "zero" energies of the particles owing to whose existence the true energy level of the particles is higher than that which follows from the position of the minima on the poten-

tial curves. It should be pointed out, however, that if we review some more subtle electrochemical problems, such as, for example, the theories of electrolytic separation of hydrogen isotopes, the zero energies play an important part.

So long as we consider the variations of the quantities E_A and E_C and not their absolute values, the value of the potential at which we consider that $= 0$ can be chosen arbitrarily.

273 The above conclusion is based on the assumption of a parallel displacement of the potential curve *aa* of the ion during the variation of the potential drop and does not take into account the variations of the potential in proportion to the approach of the center of gravity of the charge of the ion to the electrode surface within the field of the double layer. The last circumstance also affects the magnitude of the coefficients α and β. Thus, if we assume that the double electric layer has a dense structure and that the point of intersection of the curves *aa* and *bb* is in the center of it, then, as is easily verified, $\alpha = \beta = 0.5$ with vertical position of the ascending branch of the curve *bb* ($\theta = 90°$) while, according to Eqs. (193) and (190) in this case α should have been 0 and $\beta = 1$.

278 We assume initially that we are far from the equilibrium potential and shall assume that the cathodic current i_K is equal to the discharge current which we shall designate by $\vec{i}$, and the anodic current i_A is equal to the ionization current $\overleftarrow{i}$.

305* N.I. Kobczev and V.V. Monblanova [38] connect the influence of surface-active substances on the penetration of hydrogen with a lowering of the energy of hydrogen adsorption in the presence of foreign adsorbing substances. The lowering of the energy of adsorption, according to the theory of N.I. Kobozev and N.I. Nekrasov, results in an increase in the overvoltage and facilitates the transition of the hydrogen atom from the surface into the depth of the metal lattice. According to this scheme the addition of surface-active substances should in all cases intensify the penetration of the hydrogen into the metal during its electrolytic separation.

305** The behavior of the nickel hydrogen electrode in alkaline solutions near the equilibrium potential and in presence of anodic polarization is complicated further by the appearance of oxide films on its surface. As will be shown in Chapter 7, the latter have an important influence on the hydrogen overvoltage.

Manuscript Page No.	[Transliterated Symbols]
233	= n.v.e. = normal'nyy vodorodnyy elektrod = normal hydrogen electrode
246	= ads = adsorptsiya = adsorption
314	= emiss = emissiya = emission

Chapter 4

REACTIONS OF ELECTROCHEMICAL REDUCTION AND OXIDATION

§1. GENERAL INFORMATION

Any electrochemical reaction can be regarded either as an oxidation, when the reacting substances give off electrons to the electrode (anode), or as a reduction, when they acquire electrons (at the cathode).

In the present chapter we shall limit consideration to the reactions whose initial components and products are dissolved substances. This category of electrochemical reactions also includes reactions taking place with the participation or resulting in the formation of dissolved molecules of gaseous substances but do not include the reactions of electro-deposition or dissolution of metals or other solids. We thus assume that the metallic electrode merely plays the part of an electron transmitter and that its chemical modifications, if they take place, are limited to the surface layer.

The reaction of the cathodic reduction of hydrogen, which has been examined in detail in the previous chapter, is typical and one of the most important examples of reducing reactions.

Other redox reactions have been studied to a lesser extent than the reaction of hydrogen separation, although many of these are also of practical importance and frequently form the basis of entire branches of industry. As examples we can mention the anodic separation of oxygen and halogens, the cathodic reduction of dissolved oxygen. the anodic oxidation of the sulfate ion to persulfate ion, on which the industrial production of hydrogen peroxide is based, the production of chlorates and perchlorates and many others.

The number of known oxidation and reduction electrode reactions is very large. Nearly all metal cations existing in solution in several oxidation stages (for example, the ions of iron, chromium, titanium, etc.), can be subjected to redox reactions. A number of oxygen-containing inorganic ions ($Cr_2O_7^{--}$, MnO_4^-, AsO_3^{---}, etc.) are reduced at the cathode; many anions which do not contain oxygen (Cl^-, Br^-, S^{--}, etc.) are oxidized at the anode. A large number of reactions in which organic substances participate is also known; for example, compounds containing the carbonyl group, such as aldehydes and ketones, are fairly readily reduced at the cathode. The anions of organic acids are oxidized at the anode with splitting off of carbon dioxide and formation of hydrocarbons; various unsaturated organic compounds are hydrogenated at the cathode.

The first experiments in the electrolysis of organic compounds were carried out in 1803 by Academician V.V. Petrov [1]. A large number of important oxidation and reduction reactions with participation of organic substances were discovered and studied by the great Russian chemists N.N. Beketov [2] (reduction of bicarbonate to formic acid, 1869), A.M. Butlerov [3] (electrosynthesis of butylene, 1870) and others. It is particularly important to mention the work of N.A. Bunge [4] at Kiev, who carried out comprehensive investigations on the influence of various factors (current intensity, temperature, concentration) on the course of different processes of anodic oxidation of organic substances. The work of N.D. Zelinskiy, N.A. Shilov [5] and L.V. Pisarzhevskiy [6] also dealt with the oxidation of organic substances by electrolysis (for more details on these works see N.Ye. Khomutov [38]).

It would be in order to give a classification of all known electrochemical reactions based on the difference of the mechanisms by which they proceed. However, the currently available experimental data do not yet permit such a broad generalization. Nonetheless, certain common regularities can be pointed out even now which characterize their kinetics and mechanism.

In the following we shall consider phenomena connected mainly with the reactions of cathodic reduction. The study of the reactions of anodic oxidation of dissolved substances is greatly complicated by the fact that the surface of the metallic anode, as a rule, is oxidized (even in the case of platinum), and the oxide film thus formed to some degree affects the course of the reaction.

§2. REVERSIBLE AND IRREVERSIBLE REDOX REACTIONS

It is generally accepted to divide the redox reactions or redox systems* into reversible and irreversible. Reversible systems, as a rule, are termed the systems which satisfy the following conditions:

a) when an inert electrode is immersed in a given solution, a certain potential is established in it which is independent of the material and the surface condition of the electrode, depending only on the concentration and nature of the oxidized and reduced reaction components, in correspondence with their thermodynamic properties;

b) when current is passed through the electrode, i.e., during the course of the oxidation or reduction reaction, the electrode potential practically remains at the equilibrium value as long as the current density is so low that the concentration polarization need not be considered; in other words, these reactions do not show electrochemical polarization.

The systems quinone/hydroquinone, I_2/I^- or Fe^{++}/Fe^{+++} with platinum or gold electrode are usually cited as classical examples of reversible redox systems. To these belongs also the reversible hydrogen electrode, i.e., the system H^+/H_2 with an electrode of platinized platinum.

A large number of irreversible systems is known which do not satisfy the above-indicated conditions. Thus, for example, aldehydes are relatively readily reduced at the cathode or oxidized at the anode to the corresponding alcohols or acids. If, however, a platinum electrode or inert electrode of some other metal is immersed in a mixture of aldehyde and alcohol, the potential established on it depends on the material and condition of the electrode and cannot be regarded as the thermodynamic equilibrium redox potential of the system aldehyde/alcohol. The oxygen electrode behaves in the same way; if a platinum electrode is immersed in an aqueous solution saturated with gaseous oxygen, the equilibrium oxygen potential is not established on it.

Every electrochemical reaction taking place at a measurable rate, i.e., every passage of current through the electrode, causes a certain disturbance of the thermodynamic equilibrium and should thus cause a certain shift of the electrode potential. The different redox systems differ by the degree of their irreversibility. The overvoltage can serve as a characteristic of the degree of irreversibility of the reaction; since the overvoltage depends on the current density, it can be compared for different reactions only at the same current density. The reactions with low activation energy take place at a fairly high rate and the overvoltage for them at moderate current densities can be less than the sensitivity limit of the method used for the measurement of the electrode potential; hence it may seem that the electrochemical reaction does not disturb the equilibrium. At high current densities the concentration polarization assumes primary importance in these cases. However, even for such classical reversible systems, as Fe^{++}/Fe^{+++}

or I_2/I^-, it can be shown that the polarization during the passage of current is not of a purely concentration nature and that, consequently, the electrochemical process proper takes place at a measurable rate [7]. Strongly irreversible reactions at low current intensities also involve a considerable overvoltage, attaining values of 1 v and over.

Reactions are often conventionally termed reversible if their overvoltage is much less than the shift of the electrode potential, caused by concentration polarization under normal mixing conditions.

Another criterion of the reversibility of a reaction can be the intensity of the exchange current at the equilibrium potential of a given redox system. The reversibility of the process is the greater the greater the exchange current. The exchange current of practically irreversible reactions is immeasurably small. The degree to which condition a) can be fulfilled depends on the magnitude of the exchange current. In order that an inert electrode assumes the equilibrium potential of a certain redox system it is essential that the exchange current of this system should considerably exceed the exchange current of the electrochemical side reactions which can take place at the same electrode, for example, those connected with the presence of traces of oxygen in the solution.

Closely bound up with the problem of the degree of irreversibility of different redox reactions is the problem of the electrochemical reducibleness or oxidability. Various substances are difficult to reduce by an electrochemical method. The saturated monocarboxylic acids, e.g., acetic acid, may serve as examples. During polarization of the electrode in an acetic acid solution to a strongly negative potential (for example, during the recording of polarographic curves by means of the mercury drop electrode) reactions of its reduction to acetic aldehyde or ethyl alcohol are not observed although thermodynamically the reduction process would be quite feasible. This means that the reaction of reduction of acetic acid involves such a large overvoltage that it would proceed at a measurable rate only at potentials which are more negative than the potential of hydrogen separation.

We ought to point out that the rate of a redox reaction depends not only on the nature of its components or on the type of reaction but to a very considerable degree also on the electrode material. This had been clearly evident already during the discussion of the reaction of the cathodic separation of hydrogen which takes place on the platinized platinum electrode under conditions close to reversible, and on other metals with a varying delay.

The process of the electrolytic reduction of nitric acid and its salts can also serve as an example of the effect of the nature of the electrode metal; on cathodes of different metals different compounds are obtained with different current yields.

The influence of the cathode material on the course of the electrolytic reduction process of organic substances has been studied in the works of S.A. Fokin (1906) [8]. S.A. Fokin showed that the process of cathodic reduction of oleic acid and other unsaturated organic compounds takes place most readily on metals of the platinum group and also on nickel and cobalt, i.e., precisely on the metals which are the best catalysts in the hydrogenation of these compounds with gaseous hydrogen, which have the maximum adsorption of atomic hydrogen and low hydrogen overvoltages. In other cases, however, such a parallelism between the hydrogen overvoltage on metals and their behavior in other electrolytic reduction reactions is not observed. Whilst the reduction of oleic acid proceeds most readily on electrodes of catalytically active metals with low hydrogen overvoltage, other electrolytic reduction reactions can be realized only on cathodes with large overvoltage.

Thus, for example, as was shown by N.A. Izgaryshev and A.A. Petrova [9], the reduction reaction of nitromethane to methylhydroxylamine or methylamine takes place readily on lead or tin electrodes, i.e., on metals which have a large hydrogen overvoltage. L.I. Antropov [10] found, as a general rule, that the electrolytic reduction of unsaturated organic compounds with double bond proceeds more readily on catalytically active metals, while the electrolytic reduction of oxygen-containing polar compounds (for example, aldehydes, ketones, etc.) takes place more readily on metals with large overvoltage.

As has been shown in the previous chapter, the slowing down of the reaction of the discharge of the hydrogen ion upon transition from a metal with low overvoltage to metals with high overvoltage is connected with a decrease in the adsorption energy of the hydrogen atom on the metal. Let us assume that the adsorption energy of the particle formed during the elementary act of electrolytic reduction of some organic substance is less or depends on the nature of the metal in a different way than the adsorption energy of the hydrogen atom. Then when we go over to metals with large hydrogen overvoltage the corresponding reduction reaction at a given potential will not be slowed down as much as the reaction of hydrogen separation or may not be slowed down at all. On the other hand, on cathodes with high hydrogen overvoltage, owing to the delay in the hydrogen separation, it is possible to produce much more negative potentials than on cathodes with low overvoltage. This enables the rate of the reaction which interests us to be considerably increased. Thus, in the case under consideration the reaction of electrolytic reduction should really proceed more readily on cathodes with large hydrogen overvoltage. Analogously, a large oxygen separation overvoltage facilitates in many cases other oxidation reactions at the anode. Platinum has the largest overvoltage during the separation of oxygen (in acid and also alkaline solutions), whereas lead has a lower one, being covered, for example, in sulfuric acid solution with a film of PbO_2, and even less iron and nickel (in alkaline solutions) and also graphite. Reactions which require a high anode potential can be achieved only on a platinum anode (for example, production of persulfates or perchlorates) while chlorates, whose production requires a lower oxidation potential, can be produced on graphite anodes.

Depending on the anode potential different organic substances can be obtained from the same initial product, for example, in the oxidation of ethyl alcohol on smooth platinum acetic acid is obtained, and on platinized platinum acetaldehyde.

The effect of the nature of the electrode on the course of the electrochemical process may be connected in some cases with the formation of intermediates of the reacting substance with the electrode metal. For example, the reduction of the compounds of the acetylene series is easily achieved on copper and silver electrodes with which they obviously form unstable chemical compounds.

Various external conditions, above all the temperature, also affect the degree of irreversibility of the different reducing and oxidizing reactions. As a rule, increasing the temperature lowers the overvoltage and the degree of irreversibility of all reactions and brings the system close to the equilibrium state.

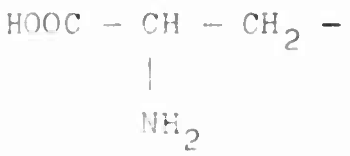
§3. STAGES OF THE REDUCTION REACTIONS. INTERMEDIATE PRODUCTS.

Using the reaction of the reduction of the hydrogen ion as an example, we have become acquainted with a reaction in the course of which the reacting particle (the hydrogen ion) combines with a single electron. As a result of this reaction a particle with unsaturated valency is formed, the adsorbed hydrogen atom, which combines with another atom during the subsequent chemical reactions with formation of a hydrogen molecule. In other cases the combination of a single electron with a stable molecule or ion can also give a particle which contains an odd number of electrons, i.e., at least one unpaired electron in the outer electron shell. In consequence of this a particle (atom or free radical) is obtained which, as a rule, possesses a high reactivity and enters into further reaction either via combination with a second electron or via combination with another identical particle (dimerization reaction). In either case a compound is formed containing an even number of valency electrons and which is stable.

Examples of reactions consisting in the combination or emission of only one electron with formation of stable products are the reduction or oxidation reactions of metal ions existing in solution in several oxidation stages, such as, for example,

$$Fe^{\cdot\cdot\cdot} + e \rightarrow Fe^{\cdot\cdot}$$
$$MnO_4^- + e \rightarrow MnO_4^{--}.$$

As an example of a reaction which takes place via dimerization of primarily formed atoms or free radicals, we can mention, apart from the reaction of hydrogen separation or the analogous reaction of chlorine separation, the reaction of the oxidation of cysteine to cystine $2RSH \rightarrow RS - SR + 2e + 2H^+$, where R means



$HOOC - \underset{NH_2}{\underset{|}{CH}} - CH_2 -$

or the reaction of the formation of pinacols during the reduction of aldehydes.

The majority of redox reactions of inorganic or organic substances, however, takes place with the summary participation of at least two electrons per reacting particle. As examples we can mention the reaction of the reduction of quinone to hydroquinone

$$C_6H_4O_2 + 2H^{\cdot} + 2e \rightarrow C_6H_4(OH)_2$$

or the reaction of the reduction of oxygen to hydrogen peroxide

$$O_2 + 2H^{\cdot} + 2e \rightarrow H_2O_2.$$

Reactions which take place with the summary participation of more than two electrons can often be divided into separate stages in each of which two electrons take part. Thus, the reaction of the reduction of organic nitro compounds to the corresponding amines requires the participation of six electrons:

$$RNO_2 + 6H^{\cdot} + 6e \rightarrow RNH_2 + 2H_2O.$$

By varying the experimental conditions it is possible to isolate individual intermediate stages of this reaction and to obtain intermediates:

$$RNO_2 \xrightarrow{+2e} RNO \xrightarrow{+2e} RNHOH \xrightarrow{+2e} RNH_2.$$

To elucidate the mechanism of a reducing (or oxidation) reaction it is important to know the physical and chemical properties of the intermediates and free radicals produced in it. Of primary interest is the elucidation of the problem of their thermodynamic and kinetic stability.

The thermodynamic stability of intermediates means that they can exist at least in a certain potential range in measurable concentrations in equilibrium with the initial and final reaction products. The problem of the thermodynamic stability of the intermediate products can be comprehended by using the example of the reduction of trivalent iron ions to metallic iron or of the ions of divalent copper to metallic copper.

The normal redox potential of the system Fe^{++}/Fe^{+++} is +0.77 v (n.v.e.). At potentials which are more negative than this value, the equilibrium concentration of the ions of divalent iron exceeds the concentration of the ions of trivalent iron; for example, at a potential of 0.65 v the ratio $[Fe^{++}]/[Fe^{+++}]$ is 100, at more negative potential it is even larger. The normal electrode potential of the system Fe/Fe^{++} is −0.44 v. Hence, in presence of metallic iron the Fe^{+++} ions are unstable and are reduced to Fe^{++} ions. The ions of divalent iron in turn are stable and do not undergo any changes (oxidation to Fe^{+++} or reduction to metallic iron) within a wide potential range from the region of the equilibrium potential of the system Fe^{++}/Fe^{+++} to the region of the equilibrium potential of the system Fe/Fe^{++}. Thus during the reduction of trivalent iron the Fe^{++} ions can accumulate as a stable intermediate product to considerable concentrations; only at potentials which are more negative than the equilibrium potential Fe/Fe^{++} are they reduced further to metallic iron.

In the system $Cu^{++}/Cu^{+}/Cu$ we are faced with a different situation. In presence of metallic copper the lower oxidation stage of copper, Cu^{+}, is unstable in solution. Indeed the reduction of the ions of divalent copper to the univalent state should occur close to the normal electrode potential of the system Cu^{++}/Cu^{+} of 0.16 v (n.v.e.); because, however, this potential is much more negative than the potential Cu/Cu^{+} (0.52 v), the ions of monovalent copper can exist near the electrode only in negligibly small concentration. Thus in consequence of the low thermodynamic stability of the Cu^{+} ion they cannot accumulate in the solution in measurable quantities during the reduction of divalent copper to metallic copper. Closely connected with this, in particular, is the well-known property of the salts of monovalent copper to decompose spontaneously in solution into salts of divalent copper and metallic copper

$$Cu_2SO_4 \rightarrow CuSO_4 + Cu.$$

Summarizing the above, we can say that the intermediate products of reduction or oxidation reactions are thermodynamically stable if the equilibrium redox potential of the system oxidized component – intermediate product has a more positive value than for the system intermediate product-reduced component. In the polarographic analysis of solutions of such substances two separate polarographic waves are formed (or a greater number of waves in presence of a greater number of intermediate reduction stages). Conversely, during the polarographic analysis of a solution, containing an oxidant of the type of Cu^{++}, only one wave can be recorded on the polarogram, corresponding to the summary process $Cu^{++} + 2e \rightarrow Cu$. However, if a substance is added to the solution which increases the stability of monovalent copper by forming complexes with it, for example, ammonia or chlorine ions, the monovalent copper is enabled to accumulate to a measurable concentration and the polarographic wave of Cu^{++} is decomposed into two waves.

We have considered here the thermodynamic conditions of the stability of the intermediate products of electrolytic reduction reactions. The accumulation of thermodynamically unstable reduction products to measurable concentrations, however, is frequently observed. Thus, during the reduction of dissolved molecular oxygen to water, hydrogen peroxide is formed as an intermediate on several electrode materials. The normal potential of the system O_2/H_2O_2 in acid medium is 0.682 v, the potential of the system H_2O_2/H_2O is 1.77 v, i.e., the reduction potential of the substance with the lower oxidation stage (hydrogen peroxide) is considerably more positive. In spite of this two waves are observed during the polarographic determination of oxygen, of which the first is due to the reduction of oxygen to hydrogen peroxide and the second to the reduction of the peroxide to water. The cause of the appearance of the intermediate stage is the fact that both reactions (the reduction of oxygen and the reduction of hydrogen peroxide) are strongly irreversible and take place only in presence of a considerable overvoltage. The overvoltage of the second stage (reduction of hydrogen peroxide to water) is considerably greater than the overvoltage of the first stage; in consequence of this the reduction of hydrogen peroxide to water takes place at a more negative potential than the reduction of oxygen although the equilibrium potential of the system in the second stage of the process is more positive. The accumulation of peroxide to concentrations exceeding the thermodynamic equilibrium concentration thus takes place in consequence of the kinetic delay of the process of further reduction of the peroxide. The appearance of thermodynamically unstable intermediate reduction products is also observed in other instances.

The reaction of reduction of oxygen to water is an example of a complex four-electron reaction which can be divided as a result of the action of kinetic factors into two simpler two-electron stages. Of considerable interest is the problem of the possibility of a further subdivision of the two-electron processes into individual stages and the detection of the intermediate products obtained as a result of the combination or emission of a single electron. Single-electron intermediate products are obviously formed in the course of many complex reduction or oxidation reactions (although they cannot always be detected), i.e., in every elementary electrochemical stage, as a rule, only a transition of a single electron takes place but not of two or more electrons simultaneously.

The reaction of the reduction of quinone to hydroquinone has been given above as a typical example of a reaction of electrolytic reduction with addition of two electrons. However, during the chemical reduction of some more complex quinones an intermediate formation of products of one-electron addition has been observed, the so-called semiquinones," which have many of the properties of free radicals [11].

As long aso as 1870, the professor of Kiev University N.A. Bunge

[4] pointed out the possibility of the formation of intermediate unstable products during the electrolysis of solutions of organic compounds which are subsequently transformed into stable electrolysis products via dimerization or other reactions. The single electron intermediates have unsaturated valencies and their thermodynamic and kinetic stability is low. Hence they cannot accumulate in important quantities during the reaction and in many cases participate in the reaction only in the adsorbed state on the electrode surface, as, for example, during the cathodic separation of molecular hydrogen. On the whole the problem of the transition of the valency-unsaturated intermediates, radicals or atoms, into the volume of the solution has not yet been sufficiently studied. Cases are known in which such a transition appears to occur although only to a slight extent. The appearance of valency-unsaturated radicals in the solution can be detected if they cause chemical chain reactions. Particularly suitable for this purpose are the polymerization reactions of unsaturated compounds which are readily initiated by valency-unsaturated particles. This method of detecting free radicals can also be applied to electrochemical reactions. Thus, during the electrolytic reduction of acrylic acid $CH_2 = CH - COOH$ or its esters a polymerization of the dissolved unsaturated compound is observed which can be explained by assuming that the intermediate product of the electrolytic reduction, for example, the radical $-CH_2 - CH_2 - COOH$, going into solution in very small quantities, initiates the polymerization reaction [12].

The radicals which form as intermediate products during the reduction of more complex organic compounds, may be relatively stable and, correspondingly, may accumulate to a marked degree within a certain potential range. The polarographic wave which characterizes the over-all two-electron process is separated in these cases into two individual waves with equal height.

§4. KINETICS OF THE INDIVIDUAL STAGES OF THE ELECTROCHEMICAL PROCESS. REACTIONS WITH PARTICIPATION OF INTERMEDIATE REDUCING AGENTS OR OXIDANTS

It has been shown, using the reaction of hydrogen separation as an example, that the over-all rate of the electrochemical reaction depends on the rates of the individual intermediate stages; in particular, if the rate, or, more correctly, the rate constant of one of the stages is slightly less than that of the others, and if parallel stages are absent, the over-all rate of the whole reaction is determined only by the rate of this delayed stage.

In the following we shall examine mainly the simplest cases of the kinetics of reducing or oxidation reactions, in which only one stage is limiting. In this case the kinetic laws of the over-all reaction can be derived from the kinetics of the delayed stage.

In the case of reversible redox systems, as, for example, quinone/hydroquinone, the slow stage, as follows from the foregoing discussion, is the diffusion of the reacting substance to the electrode surface or the diffusion of the reaction products from the surface to the interior of the solution. The laws observed in these cases do not differ in principle in any way from those discussed by us earlier and we shall not dwell on them here.

In the chapter which deals with the reaction of cathodic hydrogen separation, it was shown that for some metals the delayed stage which limits the kinetics of the over-all process is the electrochemical stage of the discharge of the hydrated hydrogen ion.

In this connection the question naturally arises how much the electrochemical act of addition or emission of an electron can be rate-limiting in other reduction or oxidation reactions. It must be pointed out that this possibility of the slowing down of a reaction has normally not been considered in the older works on electrochemical kinetics; all experimentally observed polarization phenomena were explained by a possible inhibition of chemical reactions, i.e., stages which take place without the participation of electrons. The hypothesis has been repeatedly advanced in the interpretation of the kinetics of electrochemical transformations, according to which the electrochemical reaction itself, which leads to the formation of some active intermediate product, takes place quickly and is reversible; the delayed stage is the chemical transformation of the unstable intermediate product into the stable end product of the reaction without the participation of charges, for example, via polymerization. In this case the electrode potential is determined in accordance with the equations for the equilibrium potential by the concentrations of the initial substances and the intermediate products in analogy to the situation in the recombination theory of the hydrogen overvoltage. The kinetics of the over-all process are determined by the laws of transformation of the intermediate product into the final reaction product.

It has been shown recently, based on the results of the experimental study of the kinetics of electrochemical reactions, that several important reduction or oxidation reactions of inorganic or organic substances are limited by the electrochemical stage, i.e., the stage of electron addition to the molecule of the reduced substance or the emission of an electron by the molecule of oxidized substance. In the following sections we shall become acquainted with several such reactions.

Numerous reactions of reduction of organic and inorganic substances take place with participation of electrons and hydrogen ions.

In these cases, in addition to the above-considered scheme, according to which an electron is primarily added to the reacting molecule (which after or simultaneously with the addition of the electron reacts with a hydrogen ion), there is also possible a mechanism of the process, in which the electron combines first with a hydrogen ion with formation of a hydrogen atom (discharge of the hydrogen ion), and the atom thus formed, which is a strong reducing agent, then reacts with a molecule of the substance being reduced and reduces it:

$$H^{\bullet} + e \rightarrow H$$
$$R + H \rightarrow RH \xrightarrow{+H} RH_2$$

The concept of the participation of atomic hydrogen as an intermediate product in the reactions of cathodic reduction has received wide currency in the electrochemical literature. According to these views the primary stage of any electrochemical reaction of reduction is the reduction of the hydrogen ion to atomic or some other active state (hydrogen *in statu nascendi*, at the moment of separation), with its subsequent chemical reaction with the substance to be reduced. Thus, Foerster [39] wrote in 1923: "The electrolytic reduction consists in this, that the hydrogen atoms, formed during the discharge of hydrogen ions at the cathode, instead of reacting with each other and forming molecules, enter into reaction with the oxidants in the solutions and reduce them. Hence we shall consider hydrogen as the sole carrier of the reducing action." N.I. Kobozev and co-workers assumed that the electrolytic reduction reaction cannot proceed without the participation of some form of active hydrogen (atomic or molecular-excited) [13].

However, the participation of free (i.e., not adsorbed) atomic hydrogen in the reduction reactions is not very probable for the same reasons as its participation in the process of hydrogen separation, namely, the reserve of free energy of atomic hydrogen is too large to permit its accumulation in concentrations sufficient for permitting a measurable reaction rate. On the contrary, it is highly probable that in many cases of reduction reactions which take place readily on electrodes, which strongly adsorb hydrogen, the adsorbed atomic hydrogen really participates. As has been shown in the Introduction, this hydrogen, however, differs greatly in its properties from free atomic hydrogen. According to L.I. Antropov, the reaction of reduction of compounds on cathodes with high overvoltage takes place via addition of hydrogen ions and electrons, while in the reactions of the reduction of compounds with separate double bonds on platinum and nickel cathodes adsorbed hydrogen atoms take part [10].

The concept of the obligatory participation of an active intermediate product in the electrochemical process has also been repeatedly advanced with regard to the anodic oxidation reactions. According to the theory developed by the British electrochemists Glasstone and Hickling [14], the primary stage of all oxidation reactions is the discharge of hydroxyl ions at the anode with formation of the free hydroxyl radical OH. This free hydroxyl, like atomic hydrogen, having a great reactivity, is dimerized with formation of molecules of hydrogen peroxide which then enter into chemical interaction with the substance to be oxidized. According to these ideas, the reaction of oxidation of the hyposulfite ion to the tetrathionate ion takes place, for example, in the following way:

primary reaction

$$2OH^- \rightarrow 2OH + 2e \qquad (A)$$

$$2OH \rightarrow H_2O_2 \qquad (B)$$

secondary reaction

$$H_2O_2 + 2S_2O_3^{--} \rightarrow S_4O_6^{--} + 2OH^-. \qquad (C)$$

The above-presented mechanism of the oxidation reactions has been repeatedly questioned in the literature [15] and is not very probable. Indeed, hydrogen peroxide is not directly obtained* during anodic polarization of electrodes, i.e., in the course of oxidation reactions on normal electrodes. On the other hand, a large number of oxidation reactions is known which proceed readily by electrolysis but which do not take place under the chemical action of hydrogen peroxide added to the solution.

Summing up it can be said that the theories which regard to above-considered oxidation and reduction reactions as purely chemical reactions, brought about by some active intermediate product, are at least one-sided. It is not possible to reduce all cases of chemical oxidation and reduction reactions to a single mechanism. It is possible that some reactions really proceed in accordance with such schemes but the correctness of this claim must be shown for every reaction separately.

Attention should be given to the cases of action of other intermediate reducing agents or oxidants than atomic hydrogen or hydrogen peroxide. Certain metal ions existing in solution in several oxidation stages, such as, for example, the ions of titanium or chromium, can be such intermediate agents. The addition of such substances accelerates various electrode reactions, in which mainly organic substances take part, considerably and enable reactions to take place which do not proceed in their absence. It is natural to visualize the action of these substances to be such that they are reduced at the cathode to a lower valency and then interact with the substance to be reduced which for some reason is reduced directly at the cathode only with difficulty. The intermediate product is then again reduced cathodically so that the same metal ion can repeatedly enter into reaction.

The reaction of the reduction of acetylene to ethylene which takes place in presence of chromium ions [16] may serve as an example of such an effect:

at the cathode $Cr^{\cdot\cdot\cdot} + e \rightarrow Cr^{\cdot\cdot}$,

chemical reaction $2Cr^{\cdot\cdot} + 2H^{\cdot} + C_2H_2 \rightarrow 2Cr^{\cdot\cdot\cdot} + C_2H_4$,

at the cathode $Cr^{\cdot\cdot\cdot} + e \rightarrow Cr^{\cdot\cdot}$, etc.

As follows from the above, it is necessary for determining the mechanism of oxidation and reduction reactions, as in the case of hydrogen separation, to carry out an all-sided study of the reaction rates as a function of potential and composition of the solution, making use if possible of independent data on the adsorption of individual components on the electrode surface. To obtain such data is one of the future tasks of electrochemical kinetics.

§5. REACTION OF ELECTROLYTIC REDUCTION OF OXYGEN

The reaction of the cathodic reduction of dissolved molecular oxygen is encountered in a large number of important processes, for example, in the operation of galvanic cells with electrodes with depolarization by atmospheric oxygen, in the corrosion and dissolution of metals in presence of air, etc. This reaction has been studied by N.D. Tomashov [17], who investigated the effect of the electrode material on the course of the reaction, by Z.A. Iofa [18], V.S. Bagotskiy [19], A.I. Krasil'shchikov [20] and others and we have some information on its mechanism.

The summary reaction of the reduction of oxygen can be visualized in the following form:

in acid solution $O_2 + 4e + 4H^+ \rightarrow 2H_2O$,

in alkaline solution $O_2 + 4e + 2H_2O \rightarrow 4OH^-$,

i.e., four electrons participate in the summary reaction. The entire reaction can be divided into two two-electron stages with intermediate formation of hydrogen peroxide

$$O_2 \xrightarrow{+2e+2H^+} H_2O_2 \xrightarrow{+2e+2H^+} 2H_2O. \qquad (D)$$

As indicated previously (§3), hydrogen peroxide under these conditions is a thermodynamically unstable intermediate product and can accumulate in measurable quantities only for kinetic reasons. The formation of hydrogen peroxide is observed during the cathodic reaction of oxygen reduction only on certain electrodes (mercury, silver, aluminum, activated carbon and some others). Only small quantities of peroxide are obtained on other electrodes and sometimes its presence cannot be detected at all.

The first stage of the reduction of oxygen is the state of reduction to the peroxide which has been studied in greatest detail on mercury and silver electrodes. The phenomena observed on both these electrodes in acid and alkaline medium differ.

Polarization measurements in acid solutions give a linear relationship between potential and logarithm of current density. The slope factor of the curves, as for the reaction of hydrogen separation, is close to $2RT/F$. The polarization measurements cannot be continued to high current densities because in consequence of the low solubility of oxygen in aqueous solution the concentration polarization begins to show its effect fairly soon.

Lowering of the partial pressure of the oxygen shifts the reduction potential to the negative side, and the coefficient $(\partial\varphi/\partial \ln p_{O_2})_i$ which is also close to $2RT/F$, can be found from the magnitude of this shift. This relationship has been confirmed over a wide range of measurements of oxygen pressure from 70 to 0.01 atm.

The question of the dependence of the reduction potential on the pH of the solution is of great interest for the determination of the reaction mechanism. In weakly acid and in neutral solutions (in the pH range from 2-3 to 8) the reduction potential for the silver and mercury electrode is independent of the pH; at large pH values the reduction potential is shifted to the negative side and the process begins to proceed in accordance with other laws which will be described further

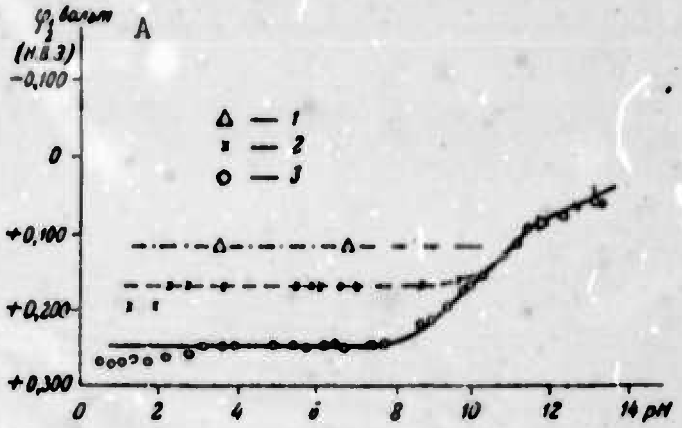


Fig. 88. Halfwave potential of the reduction of oxygen to hydrogen peroxide on the mercury electrode as a function of the pH of the solution: 1) 0.1 N K_3PO_4 + H_2SO_4 (or KOH) + 0.45 N KBr + 0.45 N Na_2SO_4; 2) 0.1 N K_3PO_4 + H_2SO_4 (or KOH) + 0.9 N KCl; 3) 0.1 N K_3PO_4 + H_2SO_4 (or KOH) + + 0.9 N Na_2SO_4. A) Volt (n.v.e.).

on. In strongly acid solutions a certain, although weak dependence of the reduction potential on the pH is evidently also observed (see Fig. 88, curve 3).

The experimental data in the medium pH range can thus be expressed by the equation

$$\varphi = a + \frac{2RT}{F} \ln [O_2] - \frac{2RT}{F} \ln i \tag{230}$$

or

$$i = k [O_2] e^{-\frac{F\varphi}{2RT}}. \tag{230a}$$

The equality of the coefficients $\partial\varphi/\partial \ln i$ for the reactions of cathodic hydrogen separation and for the reactions of oxygen reduction cannot in itself serve as an unequivocal indication that both these reactions are based on the same mechanism, because, as has been shown in Chapter 3, such values of $\partial\varphi/\partial \ln i$ can be due to a delay of the electrochemical stage of the reaction (i.e., the discharge or ionization stage) as well as the delay of other, nonelectrochemical stages, if they take place on a nonhomogeneous metal surface or if the surface is occupied to a significant degree with adsorbed atoms or molecules.

However, in the case of the reaction of oxygen reduction on the mercury or silver electrode the factors of occupation or inhomogeneity of the surface are excluded. The absence of any effect of the surface occupation follows, in particular, from the experimental fact that the reaction rate at a given potential is proportional to the partial oxygen pressure above the solution (E.230a), i.e., that the reaction proceeds in accordance with the kinetic laws of a first-order reaction over a relatively wide range of partial oxygen pressures. Such an order in the case of heterogeneous reactions is normally observed only when the surface concentration of the adsorbed reacting substances is proportional to their volume concentration, i.e., in the initial part of the adsorption isotherm in presence of slight adsorption. In the case of the reduction of oxygen this order of the reaction means, first, that the surface concentration of adsorbed oxygen is low and proportional to its volume concentration, and second, that oxygen molecules and not atoms participate in the delayed reaction stage. Further, as is evident from Eq. (230a), neither hydrogen ions nor atoms take part in the elementary act of the electrochemical process.

Thus, the above-indicated experimental laws can be explained only by the assumption that the stage of electron addition to an oxygen molecule with formation of the negatively charged ion O_2^- is the delayed stage

$$O_2 + e \rightarrow O_2^-, \qquad (E)$$

i.e., the electrochemical reaction in which the molecular oxygen takes part (possibly adsorbed on the electrode surface) but in which the hydrogen does not participate.*

The assumption concerning the existence of the molecular ion O_2^- has been advanced earlier, in particular, in connection with the interpretation of the kinetics of the catalytic decomposition of hydrogen peroxide and photochemical processes. The ion O_2^- can be regarded as the anion of the unstable acid HO_2. As the works of I.A. Kazarnovskiy and co-workers showed in particular, the nonhydrated ion O_2^- forms part of the higher oxides of the alkali and alkaline earth metals, for example, KO_2 [21].

If we follow the general concepts of the theory of inhibited discharge, taking into account the influence of the structure of the double layer, the rate of the reaction rate (E) can be expressed by the equation

$$i = k[O_2]e^{-\frac{\alpha F(\varphi - \psi_1)}{RT}}, \qquad (231)$$

where α, as previously, is a coefficient which assumes a value between zero and unity. If we take α as equal to 0.5, and consider ψ_1 to be approximately constant, Eq. (231) coincides with Eq. (230a), i.e., reflects correctly the kinetic laws observed in weakly acid and neutral solutions.

The assumption of a delay of the electrochemical stage (E) is supported by several consequences of Eq. (231). Of special interest is the influence of adsorbed surface-active ions (for example, the ions Cl^- or Br^-) on the kinetics of oxygen reduction at the mercury electrode. As follows from the data presented in Fig. 88, curve 2, the presence of chlorine ions in a concentration of 0.9 equ/liter at $pH < 9$ causes a shift of the oxygen reduction potential to the negative side of 0.075 v compared with the reduction potential in sulfate solutions. This phenomenon can be accounted for by the influence of the ψ_1 potential, which is made more negative by adsorption of anions. As follows from the electrocapillarity measurements, the ψ_1 potential varies by –0.080 v when going over from sulfates to chlorides. Solving Eq. (231) for φ, we find

$$\varphi = \frac{RT}{\alpha F}\ln k + \psi_1 + \frac{RT}{\alpha F}\ln [O_2] - \frac{RT}{\alpha F}\ln i. \qquad (232)$$

It is easy to see that at constant current density the variation of the ψ_1 potential should correspond to the variation of the electrode potential in the same direction and by the same amount which is very well confirmed by the above-given experimental data. In presence of strongly adsorbed ions, such as I^- or CN^-, the oxygen reduction potential is shifted to the negative side by some tenths of a volt [37].

The reactive anion O_2^- readily reacts further with hydrogen ions and with a second electron with formation of hydrogen peroxide

$$\begin{aligned} O_2^- + H^\cdot &\rightleftarrows HO_2, \\ HO_2 + e &\rightleftarrows HO_2^-, \\ HO_2^- + H^\cdot &\rightleftarrows H_2O_2. \end{aligned} \qquad (F)$$

It can be assumed that the equilibrium

$$O_2^- + 2H^\cdot + e \rightleftarrows H_2O_2.$$

is established between the ion O_2^- and the peroxide molecule. It follows from this that the concentration of the ion O_2^- in the solution at the given potential is determined by the equation

$$[O_2^-] = K\frac{[H_2O_2]}{[H^\cdot]^2} = K'[H_2O_2][OH^-]^2. \qquad (233)$$

In strongly acid medium where the hydrogen ion concentration is high, it is possible that the hydrogen ion also participates in the stage of electron addition to the oxygen molecule (E); in this case the free radical HO_2 should be obtained directly. Naturally the participation of the hydrogen ion in the delayed stage causes a certain dependence of the reduction potential on the pH.

Of considerable interest are the regularities observed during the reduction of oxygen in alkaline solutions. In this case the polarization curves on a semilogarithmic scale are straight lines with a slope factor of 30-40 mv. With unit increase in pH, the reduction potential is shifted to the negative side by approximately 58 mv at pH < 11 and by 29 mv at higher pH values (see Fig. 88). This regularity can be explained in two ways. If it is considered that, as in acid solution, the electrochemical stage is delayed, it follows from the slope factor of the polarization curves that the reaction of addition of the second and not the first electron should be delayed, i.e., the electrochemical stage

$$HO_2 + e \rightarrow HO_2^-, \qquad (G)$$

and not the stage

$$O_2 + e \rightarrow O_2^- \qquad (E)$$

with the subsequent reaction

$$O_2^- + H^+ \rightarrow HO_2. \qquad (H)$$

Indeed, to an inhibited stage (G) would correspond a reaction rate of

$$i = k[HO_2]e^{-\frac{\alpha F\varphi}{RT}}, \qquad (234)$$

where, as previously, $0 < \alpha < 1$. If it is assumed that the formation of HO_2 according to the reactions (E) and (H) takes place rapidly compared with the subsequent reduction according to (G), the HO_2 concentration is determined by the equilibrium conditions

$$[HO_2] = K_1[O_2][H^+]e^{-\frac{F\varphi}{RT}}. \qquad (235)$$

Substituting this value into (234), we find for the reaction rate

$$i = k'[O_2][H^+]e^{-\frac{(1+\alpha)F\varphi}{RT}} \qquad (236)$$

and for the potential

$$\varphi = \frac{RT}{(1+\alpha)F}\ln k' + \frac{RT}{(1+\alpha)F}\ln[O_2][H^+] - \frac{RT}{(1+\alpha)F}\ln i. \qquad (237)$$

As follows from this conclusion, the inhibition of the addition of the second electron in the two-electron process gives a value of the slope factor of the polarization curves between $RT/2F$ and RT/F, i.e., when decadic logarithms are used, between 29 and 58 mv. This interpretation of the kinetics of oxygen reduction in alkaline medium has been proposed by A.I. Krasil'shchikov for the case of the silver electrode [20].

A comparison between the oxygen reduction potential and the thermodynamic equilibrium potential of the system O_2/H_2O_2, however, leads to the conclusion that the overvoltage of the process of oxygen reduction to hydrogen peroxide, at least in the case of the mercury electrode, is very low in alkaline medium, and that the polarization phenomena observed in this case are mainly due to concentration polarization and not to a delay of the actual electrochemical stage. This means that under these conditions the process is very close to reversible and that during passage of current the equilibrium of the system O_2/H_2O_2 is hardly affected. The observed variation of the mechanism of the process upon transition from acid to alkaline solutions is easily accounted for. Indeed, according to Eq. (233), the stationary concentration of the O_2^- ions in the solution increases with the pH. The rate of the reaction

$$O_2^- \rightarrow O_2 + e. \qquad \text{(I)}$$

which is the reverse of reaction (E), should increase in the same proportion. At a certain pH the rate $\overleftarrow{i}$ of the anodic reaction (I) becomes comparable to the rate of the cathodic reaction (E), and the system O_2/H_2O_2, because of the increase in the exchange current, becomes reversible.

As a quantitative calculation indicates, the transition of this system from the irreversible to the reversible state begins on the mercury electrode at pH values close to 9. In the reversible state the electrode potential, i.e., the potential of oxygen reduction, varies upon increase in pH in the same manner as the potential of the reversible oxygen-peroxide electrode. This variation, as readily derived from the general thermodynamic relations for the potential of reversible electrodes, is 58 mv per unit of pH up to pH values of 11, and 29 mv per unit of pH in more alkaline solutions (in which the hydrogen peroxide is present in the form of HO_2^- ions. The slope of the polarization curves in alkaline solutions, according to the laws of concentration polarization, should be 29 mv. All these conclusions are quantitatively confirmed by the experimental data.

It must be pointed out that the interpretation of the laws observed in alkaline solutions is a consequence of the basic assumption on the delay of the stage (E) in weakly acid and neutral solutions and does not require any new assumptions. The good agreement of the experimental data obtained in alkaline solutions with these conclusions is thus an additional confirmation of the correctness of the concept of the delay of the electrochemical stage of the formation of the molecular oxygen ion. The approximation of the system oxygen/hydrogen peroxide from the irreversible state to the reversible upon increase in the pH is also observed on the carbon electrode.

The second stage of the reduction of oxygen, the reduction of the hydrogen peroxide to water, has been studied in less detail. A typical feature of this stage is the large slope coefficient $\partial\varphi/\partial \lg i$ which is 220-240 mv (in decadic logarithms) which corresponds to a value of α in the kinetic equation of nearly 0.25. The absolute magnitude of the coefficient $\partial\varphi/\partial \lg [H_2O_2]$ is also close to this value. This signifies that, as in the case of oxygen, the rate of the reaction of hydrogen peroxide reduction at a given potential is proportional to the concentration of this substance.

In acid solutions and up to pH values of 11, the reduction potential of hydrogen peroxide is independent of the pH of the solution; in more strongly alkaline solutions, a marked shift of the potential to the negative side is observed.

The kinetic laws over the entire pH range (including also alkaline solutions) are completely covered by the equation

$$\varphi = a + \frac{4RT}{F} \ln c_{H_2O_2} + \frac{4RT}{F} \ln \frac{[H^+]}{[H^+] + K_{H_2O_2}} - \frac{4RT}{F} \ln i, \qquad (238)$$

where $K_{H_2O_2}$ is the dissociation constant of hydrogen peroxide and $c_{H_2O_2}$ is its total analytical concentration (dissociated and undissociated parts). Taking into account that the concentration of the undissociated hydrogen peroxide molecules $[H_2O_2]$ is expressed by the relation $[H_2O_2] = [H^+]c_{H_2O_2}/([H^+] + K_{H_2O_2})$, found experimentally, Eq. (238) can be rewritten in the form

$$\varphi = a + \frac{4RT}{F} \ln [H_2O_2] - \frac{4RT}{F} \ln i \qquad (239)$$

or

$$i = k [H_2O_2] e^{-\frac{F\varphi}{4RT}}. \qquad (240)$$

These laws are completely accounted for by the assumption that the delayed stage in the process of hydrogen peroxide reduction is the stage of electron addition to the hydrogen peroxide molecule. As in the case of reduction of the molecule O_2, this stage takes place without participation of hydrogen ions in consequence of which the reduction potential is independent of the pH in acid solutions. The addition of an electron to a hydrogen peroxide molecule probably is accompanied by a simultaneous splitting of the molecule into an ion and the free hydroxyl radical

$$H_2O_2 + e \rightarrow OH + OH^- \qquad (K)$$

Even in alkaline solutions, in which the hydrogen peroxide is strongly dissociated, undissociated molecules are not hydrogen peroxide ions are subjected to cathodic reduction. The shift of the reduction potential of the peroxide to the negative side in alkaline solutions is thus due to the decrease in the concentration of the undissociated molecules with increase in the pH of the solution. The more difficult reduction of the peroxide ions compared with the reduction of the molecules is probably explained by the fact that the negative peroxide ions are repelled from the electrode surface which is also negatively charged (see §6).

The summary reaction of the reduction of molecular oxygen to water also proceeds via a different pathway, in addition to that given in the scheme (D); for example,

$$\left.\begin{array}{l} O_2 \rightarrow 2O_{\text{адс}} \\ O_{\text{адс}} + 2H^{\cdot} + 2e \rightarrow H_2O \end{array}\right\}. \qquad (L)$$

In this case the intermediate product is not hydrogen peroxide but the adsorbed oxygen atom. The reduction of oxygen on carbon under certain conditions can also proceed in accordance with the scheme (L) [22]; the same is possibly the case with some other electrodes.

§6. REACTIONS OF ANION REDUCTION

Many inorganic anions (for example, CrO_4^{--}, MnO_4^-, AsO_3^{---}, BrO_3^-, IO_3^-, $S_2O_8^{--}$) are reduced at the cathode. The process of anion reduction is interesting because the negative charge of the particle which is reduced, in cases when the electrode surface is also negatively charged, superposes certain specifics on its kinetics.

Some anions such as NO_3^- and NO_2^- can be reduced at the mercury electrode under normal conditions only at very large negative potentials. If, however, a small quantity of salts with polyvalent cations (for example, salts of Ba^{++}, La^{+++} or Th^{++++}) are added to the solution, the reaction of reduction of these ions is facilitated, its rate being the greater, the higher the concentration and valency of the added cations* [40]. In the case of the anions BrO_3^- and IO_3^- the addition of multivalent cations also accelerates the reaction considerably, i.e., it reduces the overvoltage at a certain current density.

The peculiarities of the electrolytic reduction of anions are more clearly apparent in the case of the reduction of $S_2O_8^{--}$ on the mercury electrode, first studied by T.A. Kryukova [24]. Figure 89 gives the cathodic polarization curve for the rotating amalgam electrode in dilute $K_2S_2O_8$ solution. As can be seen from this diagram, the process of reduction of the $S_2O_8^{--}$ ion in this solution begins at a potential close to the n.k.e. potential; if the polarization is increased the limit diffusion current is soon attained which depends only on the concentration of these ions in the solution. However, if the cathode potential is increased further, the reduction current decreases sharply (curve 4) and drops to a very low value. Over a wide potential range the reduction process is markedly delayed. Only at strongly negative potentials it is again accelerated and a new rise of the current is observed in the polarization curve to values corresponding to the limit diffusion current of the $S_2O_8^{--}$ ions.

The sudden decrease in current begins at a potential which is slightly more negative than the potential of the zero charge point, i.e., −0.5 v (n.k.e.).

Addition of an indifferent electrolyte has the consequence that the current drops much less suddenly: thus, if the concentration of the Na_2SO_4 in the solution is sufficiently high, a current drop is not observed at all, and the curve of the $S_2O_8^{--}$ reduction assumes the normal form (curve 1). In this case also the influence of the added electrolyte is apparent at lower concentrations if the valency of the cation is greater.

The above-described phenomena can be explained by the action of repulsion forces between the negatively charged metal surface and the anions [24]. These repulsion forces are naturally manifested only in

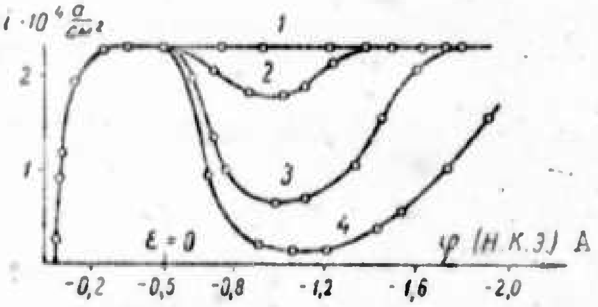


Fig. 89. Polarization curves of the reduction of the $S_2O_8^{--}$ ion from $K_2S_2O_8$ solutions in presence of different quantities of Na_2SO_4 (on the rotating amalgam electrode); $c_{K_2S_2O_8} = 10^{-3}$ equ/liter. The Na_2SO_4 concentrations are: 1) 1 N; 2) 0.1 N; 3) 0.008 N; 4) 0. The rate of rotation of the electrode is $m = 3.8$ rps (the potentials were measured relative to the normal calomel electrode).

the range of potentials which is more negative than the potential of the zero charge point. If the reduction process begins at a more positive potential, as in the case of $S_2O_8^{--}$ ions, the attraction forces are replaced by repulsion forces after the zero charge potential has been passed, and the process may cease or at least slow down. In other cases, when the process does not begin until the zero charge potential has been reached, the presence of repulsion forces at more negative potentials inhibits the process so that it either does not take place at all or takes place only at very strongly negative potentials (NO_3^-, BrO_3^-).

The influence of the negative surface charge on the anions can be manifested in a different manner depending on the rate of the electrochemical discharge stage. If this stage is slow, the effect of the repulsion forces is only to lower the concentration of the reacting particles in the surface layer, and the pattern of the phenomenon becomes to some degree similar to that observed during the discharge of hydrogen ions in presence of adsorbed cations. Thus, for example, at a concentration $[S_2O_8]_s$ of the $S_2O_8^{--}$ ion in the surface layer the relation

$$[S_2O_8^{--}]_s = [S_2O_8^{--}]e^{\frac{2F\psi_1}{RT}} \qquad (241)$$

applies.

The rate of discharge of the $S_2O_8^{--}$ ion under the simplest assumptions should be

$$i = k[S_2O_8^{--}]_s e^{\frac{-\alpha F(\varphi-\psi_1)}{RT}} = k[S_2O_8^{--}] e^{\frac{(2+\alpha)F\psi_1}{RT}} e^{\frac{-\alpha F\varphi}{RT}} \qquad (242)$$

Thus a negative value of the ψ_1 potential reduces the rate of discharge of the anion, this effect being particularly pronounced because the ψ_1 potential enters into the numerator with the factor $(2 + \alpha)$, i.e., both effects produced by it (the lowering of the concentration of the ion and the reduced effect of the field of the double layer on the activation energy) are superposed. As is evident from Eq. (242) the influence of the field on the rate of the anion reduction reaction is expressed by the product of two factors contained in the right part of Eq. (242). If the negative values of the potential increase, the factor $e^{-\alpha\varphi F/RT}$ increases monotonously which also determines the acceleration of the reaction, observed with the usual dependence of reaction rate on potential. The right part of Eq. (242), however, contains another factor $e^{(2+\alpha)F\psi_1/RT}$ which decreases with increasingly negative values of φ. Thus increase of the cathode polarization causes a variation of these factors in opposite senses and the trend of the quantity i depends on which of them affects it more strongly.

As we know from §3 of the Introduction, the quantity ψ_1 varies particularly strongly with variation of the quantity φ near the zero charge point, hence, as calculation shows, i decreases near this point, if the potential is shifted to the negative side. Conversely, at a considerable distance from the zero charge point at large negative values of φ the quantity ψ_1 varies little with φ and the trend of i is mainly determined by the factor $e^{-\alpha\varphi F/RT}$ which is also the reason for the second rise of the quantity i. If the electrochemical discharge reaction is rapid, in presence of a negative ψ_1 potential the penetration of the anion to the electrode surface through the diffusion part of the double layer can become the slow stage of the reaction, requiring an activation energy which is greater if the ψ_1 potential (in absolute magnitude) is higher. In this case the second rise with further shift of the potential to the negative side is no longer possible [41]. In either case the addition of a foreign electrolyte, which lowers the absolute value of the ψ_1 potential and thus reduces the magnitude of the repulsion forces, should increase the reaction rate. Particularly effective in this sense, as is also observed in the experiment, should be polyvalent cations which not only lower the absolute values of the ψ_1 potential but also reverse its sign.

An anomalous trend of the polarization curves, like that described here, is also observed during the reduction of $S_2O_8^{--}$ on cathodes of Cd and Pb and also during the reduction of various other anions on the Hg electrode, as, for example, the ions $Fe(CN)_6^{---}$, $PtCl_6^{--}$, $Pt(NO_2)_4^{--}$, etc.

§7. REACTIONS OF THE REDUCTION OF ORGANIC COMPOUNDS

Several thousand oxidation or reduction reactions are described in the literature which take place with participation of organic substances. Electrochemical reactions assume ever increasing importance for the synthesis of new organic substances, for qualitative and quantitative analysis and also for the study of various peculiarities of the structure of organic substances. However, detailed systematic investigations on the influence of different factors on the kinetics of the process have been carried out to date only for a small number of such reactions.

An example of a relatively simple and fairly well studied reaction is the reduction of oxalic acid at the mercury electrode to glyoxalic acid. This reaction proceeds in accordance with the equation

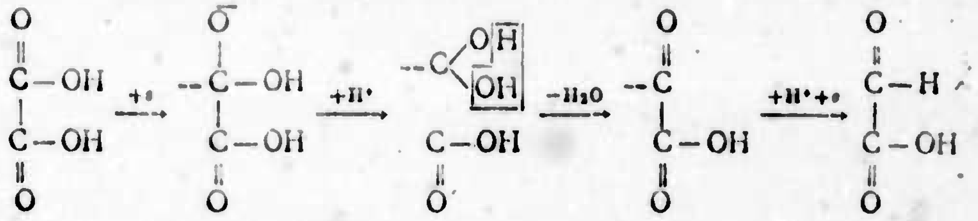
$$(COOH)_2 + 2H^{\cdot} + 2e \rightarrow COOH \cdot CHO + H_2O.$$

A study has been made of the reduction potential of this reaction as a function of the concentration of the components in the solution and the current density on the amalgamated lead [42] and the mercury drop electrode [25]. It follows from the results of the last measurement that the reduction potential varies linearly with the logarithm of the current density, the slope factor $-(\partial\varphi/\partial \lg i$ of the polarization curve being 0.090 - 0.100 v (in the pH range from 1.5 to 4). The observed dependence of the reduction potential on the total concentration of the oxalic acid and the hydrogen ion concentration is complex. If, however, one calculates the reduction potential not as a function of the total oxalic acid concentration but of the concentration of the undissociated molecules (which naturally depends on the pH of the solution at constant total concentration), a constant value is found for the coefficient $\partial\varphi/\partial \lg [H_2C_2O_4]$ close to 0.100 v. Further it is found that at constant concentration of the undissociated molecules the reduction potential is independent of the pH of the solution (within the indicated pH range). Thus the measurement results can be expressed by the equation

$$i = k[H_2C_2O_4]\, e^{-\frac{\alpha F\varphi}{RT}}, \qquad (243)$$

where k and α are constants ($\alpha = 0.6$).

This kinetic dependence can be explained by the assumption that the addition of an electron to the oxalic acid molecule is the rate-determining step in the pH range of 1.5 to 4 for the reduction of oxalic acid at the mercury electrode. The hydrogen ions do not take part in this stage and only later they combine together with the second electron with the formed ion-radical with formation of a molecule of glyoxalic acid. The successive stages of the reduction of oxalic acid to glyoxalic can be represented by the following scheme:



The fact that the oxalic acid molecules are reduced on the mercury electrode more easily than the anions of this acid is in full agreement with the statement in §6 concerning the reduction of negative ions at an electrode surface with like charge. It should be mentioned that the glyoxalic acid can be further reduced with formation of glycolic acid $CH_2(OH)COOH$. The radicals formed during the reduction of oxalic acid can also dimerize; the reduction of the dimerization products gives rise to the formation of succinic acid

$$COOH-CH_2-CH_2-COOH.$$

The phenomena involved in the reduction of nitrocompounds are more complex. It has been mentioned previously in §3 that the summary process of the reduction of organic nitrocompounds to the corresponding amines takes place with participation of six electrons; the over-all process can be divided into separate two-electron stages with formation of nitroso compounds and hydroxylamines as intermediate products.

A large number of investigations carried out during the last 50 years have shown that different reduction products accumulate on different metals as a result of electrochemical reactions [26]. Thus, on zinc or mercury electrodes the process of the reduction of nitrobenzene goes to completion, and the main reaction product is aniline. On electrodes of platinum or nickel the reduction of nitrobenzene does not go to completion, and a mixture of intermediate products is obtained as a result of the reaction. These intermediate products form various new substances (azo and hydrazo compounds) as a result of interactions between them or with the starting materials. Thus a complex series of different redox systems is obtained during the reduction of nitro compounds instead of a definite redox system. The production and accumulation of any intermediate product obviously depends on the ratio of the reaction rates of its formation and further transformation.

The quantitative study of the kinetic laws of the reduction of organic nitrocompounds is difficult because of the complexity of this process. For this reason the measurement data of different authors are not always in good agreement.

As measurements made on the mercury electrode have shown the relationship between the reduction potential and the logarithm of the current density in this case can be represented by an equation of the same type as for other electrochemical reactions, with the slope $-(\partial\varphi/\partial \ln i)$ close to $2RT/F$. A marked influence of the pH of the solution on the reduction potential is observed, namely, increase in the pH by unity shifts the potential at a given current density to the negative side by about 60 mv. According to the data of older works the dependence of the rate of reduction of nitrobenzene on its concentration in the solution corresponds to a constant coefficient $\partial\varphi/\partial \ln c_{\text{n.b.}}$ of $2RT/F$ as well as in the case of the coefficient $-(\partial\varphi/\partial \ln i)$.

According to L.I. Antropov [27] a more complex dependence of the potential on the concentration of the nitrobenzene is observed; the measurement results of this author can be represented by a kinetic equation of the form

$$\varphi = a - \frac{2RT}{F}\ln i + \frac{RT}{F}\ln[\mathrm{H}^{+}] + \frac{2RT}{F}\ln(1 + kc^{\beta}_{\text{н. б.}}) \qquad (244)$$

This kinetic equation can be interpreted on the basis of the assumption that the slow stage of the reduction reaction is the stage of interaction of a molecule of nitrobenzene adsorbed on the electrode surface with an electron and a hydrogen ion. The more complex nature of the last term in Eq. (244) is explained by the relatively good adsorption of intro compounds on the surface of a mercury electrode and in connection with this by the considerable degree of occupation of the electrode surface with adsorbed molecules. Like other authors, L.I. Antropov observed on the platinum electrode a lower slope of the polarization curve equal approximately to *RT/F.* The data obtained by this author on the platinum electrode are explained by him by means of the hypothesis that the nitrobenzene molecule is reduced by hydrogen atoms adsorbed on the electrode surface. N.A. Izgaryshev and A.A. Petrova [9], who investigated the process of electrolytic reduction of nitromethane on electrodes of different metals, did not observe a parallelism between the polarization of the electrode during this reaction and during hydrogen separation. On this basis the authors arrived at the conclusion that the process of reduction of nitromethane is due to a direct interaction between the adsorbed nitromethane molecules and electrons and that the intermediate effect of the hydrogen atoms at the electrode surface is not very probable.

These examples show that the rate of electrochemical reactions in which organic substances take part can be limited by the purely electrochemical stage of interaction of the substances being reduced with electrons during their direct contact with the electrode surface. This conception is in contradiction with the view widely held in the older electrochemical literature according to which every electrochemical stage, involving a change in the number of charges, is rapid and reversible. Indeed, the kinetic laws of various investigated reactions do not leave any doubt that the process of transition of an electron to the reacting molecule not only takes place slowly in individual cases but more slowly than any other purely chemical stage of the process. In some cases it is also possible to observe an effect of the position of the reduction potential relative to the zero charge point on the mechanism of the reduction reaction [10].

On the other hand, however, a number of reactions is known, whose rate is indeed limited by the chemical stages which are thus slower than the electrochemical stage proper. Of great interest is the case in which the slow stage of the chemical transformation precedes a rapid electrochemical reaction. Such reactions have been studied in recent years by the Czech researcher Prdicka and co-workers and also by M.B. Neyman [28]. Among these are reduction reactions of numerous organic substances, such as, for example, formalin, certain sugars, etc. If a solution containing glucose is subjected to reduction at the mercury drop electrode, a small polarographic wave is obtained whose height is much less than that calculated by means of the formula for the limit diffusion current towards the drop electrode (Eq. 117). With increase in the temperature the limit current rises sharply. The dependence of the limit current on temperature is expressed by the exponential formula

$$i_d = ke^{-\frac{E}{RT}}. \qquad (245)$$

These experimental laws can be explained by the assumption that the substance being reduced is present in the solution in two (for example, tautomeric) forms and that only one of them is subject to cathodic reduction. If these two forms were in equilibrium and this equilibrium were established quickly, the existence of two forms should not be reflected in the polarization curve of the reduction reaction. Indeed, in proportion to the reduction of the more reactive form its concentration should remain constant owing to the reaction of transformation of the unreducible to the reducible form.

In the cases mentioned in the foregoing, however, the reaction of the chemical transformation is delayed. As a result of this the concentration of the reducible form is only partly reestablished, and the limit reduction current depends on two quantities: on the rate of diffusion of the reducible form of the organic substance and on the rate of the chemical transformation. If the rate of the latter is very small, the limit current is entirely determined by the rate of the chemical reaction. Because the rates of chemical processes are connected with temperature by an exponential law, the limit current under these conditions should obey the same law. During the reduction of solutions containing anions of certain weak organic acids, the rate of the process evidently depends on the rate of the reaction of formation of the acid molecule from its anion and a hydrogen ion [28, 43].

§8. OXIDATION REACTIONS

The experimental investigation of anodic reactions is made difficult by the circumstance that these reactions, depending on the nature of the electrode and the electrolyte solution, are often accompanied by anodic dissolution of the electrode metal or formation of oxide films on its surface. These processes cause a change in the condition of the surface which makes the analysis of the measurement results more difficult. The strong dependence of the kinetic laws on the surface condition of the electrode often has the consequence that the experimental data of different authors who have studied the same anodic reaction contradict each other and cannot be reconciled. As a result the mechanism of the anodic reactions in redox systems has been elucidated to a much lesser degree than the mechanism of the cathodic reactions.

One of the most important anode reactions is the reaction of oxygen separation. This reaction has been studied in acid solutions particularly on platinum and gold electrodes; other metals are often insufficiently stable in acid solutions. Of much greater practical importance is the separation of oxygen from alkaline solutions. In this case nickel and iron (steel) can be used as electrode materials because they are passivated under the corresponding conditions in alkaline solution and are not subject to anodic dissolution.

The overvoltage of the process of oxygen separation on platinum and gold is relatively large. Lower overvoltage values are observed on nickel and iron. In the investigation of the reactions of oxygen separation semilogarithmic polarization curves are observed in some cases. However, in contrast to the process of cathodic hydrogen separation and other electrochemical reduction reactions, the linear dependence of the potential or overvoltage on the logarithm of the current density range. Some sections with different slope are frequently observed on the polarization curves of oxygen separation; in some cases these sections are fairly sharply divided, in others they show a continuous transition. A typical feature observed in a number of cases of oxygen separation is the strong dependence of the electrode potential on time during polarization with a current of constant density.

The polarization laws observed on electrodes during anodic oxygen separation depend greatly on the preceding treatment of the electrode surface, in particular, on the duration of the preceding cathodic or anodic polarization of the electrode.

All these phenomena indicate that oxygen separation does not take place on a clean metal surface but on a surface which is covered to a varying degree with oxides, which is easily demonstrated by using the method of recording charging curves, described in §4 of the Introduction. As will be shown in Chapter 7, the presence of oxygen atoms on the electrode surface, even in very small quantities, causes a marked alteration of the kinetics, mechanism and even direction of the electrode reactions. Hence the theoretical interpretation of the process of anodic oxygen separation is impossible without taking into account the surface condition, nature and properties of the oxide films formed on it.

As a result of the experimental study of the oxygen separation reaction a number of hypotheses has been advanced concerning the mechanism of its course and the possible cause of the appearance of an overvoltage. Nearly all theories connect the process of oxygen separation with an intermediate formation of higher oxides of the metal which serves as the electrode, which has already been pointed out by N.P. Sluginov [44]. According to these ideas, there are two main stages of the process of oxygen separation: the stage of interaction between the discharged oxygen atom (hydroxyl ion) with metal atoms, as a result of which a higher oxide is formed, and the stage of the decomposition of the higher metal oxide with formation of a lower oxide and molecular oxygen. These oxides are considered in this hypothesis now as compounds of a definite composition, the properties of a phase, now as adsorbed layers with a different degree of saturation of the surface with oxygen.

The so-called oxide theory of the oxygen overvoltage described here is relatively old. In its original variant the appearance of an overvoltage was connected exclusively with the slowness of the second stage, the stage of decomposition of the metal oxides [29]. In many later works, particularly those of Soviet electrochemists, the oxide theory was subjected to considerable modifications. Several authors assumed that the slow stage is not the stage of the decomposition of the metal oxide but the stage of the discharge of the hydroxyl ion and the formation of the higher oxide [30].

In the case of the platinum electrode the slowness of the discharge stage during which the oxygen atoms, which are adsorbed on the surface, arise, has been demonstrated by direct measurements [31]. The same method was used for this purpose as that used for the study of the discharge reaction of the hydrogen ion with formation of adsorbed hydrogen (see Chapter 3), namely, the kinetics of oxygen deposition on the surface at potentials at which separation of free molecular oxygen does not yet take place. Such measurements were carried out with alternating current as well as with the method of recording charging curves with high density currents. It was found that the electrochemical deposition of oxygen atoms proceeds not only at a measurable but also relatively low rate compared, for example, with the deposition of hydrogen atoms.

The soundest statement and that which agrees best with the experimental data is evidently that the ratio of the rates of the individual stages varies as a function of the electrode potential and the experimental conditions, in consequence of which it is impossible to give a single kinetic scheme for the reaction of oxygen separation. Thus, according to L. Yelina [32], the reaction rate at low current densities and moderately positive potentials is determined by the rate of decomposition of the highest oxide. With increase in the current density and shift of the electrode potential to the positive side the stage of the discharge of the hydroxyl ions becomes the limiting step.

An example of an anode reaction which is not complicated by the formation of oxide layers on the surface of the electrode metal and thus lends itself to a relatively simple interpretation, is the reaction of anodic nitrogen separation on the platinum electrode during the electrolysis of a solution of an ammonium salt in liquid ammonia as solvent [33]. At a temperature of -50° the polarization of the platinum electrode varies over the entire measurement range linearly with the logarithm of the current density, and the slope factor $-(\partial\ /\partial \lg i)$ of the straight lines varies within the limits 0.080-0.090 v. This slope factor is close to the value $2RT/F \cdot 2.3$ (−0.088 v at $T = 223°$). As follows the measurements of the rate of decay of the overvoltage after the switching off of the polarizing current the capacity of the double layer on the electrode surface under the experimental conditions was approximately 30 $\mu F/cm^2$. This capacitance indicates the absence of a marked chemosorption of nitrogen or other reaction components on the electrode surface.

The experimental data can be explained by means of the hypothesis that the stage of splitting off of electrons from the reacting ammonia molecule, $NH_3 \rightarrow NH_3^+ + e$, is the controlling step in the process of nitrogen separation. Compared with this stage the other transformation stages, expressed by the summary scheme

$$NH_3^{\bullet} + 3NH_3 \rightarrow 3NH_4^{\bullet} + {}^1/_2N_2 + 2e,$$

evidently proceed at a fairly rapid rate.

Fairly complex are the laws applying to the separation of chlorine from aqueous chloride solutions. As follows from the measurements of S.V. Gorbachev and N.P. Zhuk [34], a linear dependence of the electrode potential on the logarithm of the current density is observed within a certain narrow range of current densities (approximately from 10^{-6} to 10^{-3} amp/cm^2) while at higher current densities the kinetic laws are modified. This modification may be connected either with a change in the state of the surface or, as the above-mentioned authors assume, with a change in the reaction mechanism at different potentials.

The effect of impurity components on the course of an electrochemical reaction, which we have often encountered in the discussion of reduction processes, is often very marked also in the case of anodic reactions. Thus, in the case of the anodic oxidation of ammonium sulfate or alkali sulfates on the platinum electrode with formation of persulfates a slight addition of fluorine ions greatly increases the current yield of the reaction. This effect is obviously due to the strong shift of the anode potential to the positive side in presence of fluorine ions, i.e., the increase in the oxygen overvoltage. Chlorine ions and many organic compounds, such as, for example, thiocyanates, have the same kind of effect. By means of the method of recording of charging curves it is possible to show that the quantity of oxygen at the platinum surface is decreased under these conditions; thus, the increase in the oxygen overpressure in this case is connected with a slowing down of the stage of discharge of the hydroxyl ion.

A dependence of the course of the reaction of oxidation of the SO_4^{--} and Cl^- anions on the nature of the cation, present in the solution, has been found in the works of N.A. Izgaryshev and co-workers [35]. The reaction of oxidation of the sulfate ion to a persulfate ion takes place most readily in presence of ammonium ions; the salts of alkali metals, particularly lithium, give much lower current yields of this reaction. Even lower values are observed in the case of divalent ions or in the case of aluminum. The opposite is observed in the case of the oxidation reaction of the Cl^- ion to chlorate or perchlorate ions. The highest current yield for this reaction is observed during the electrolysis of lithium chloride or calcium chloride. Other ions promote the oxidation reaction less so that the current yield is greatly decreased.

N.A. Izgaryshev explained this specific effect of the cations by the different degree of their hydration. Because strong hydration of the cation reduces the hydration of the anion, it was inferred from the observation data that strong hydration of the anion promotes the reaction of its oxidation in the case of the SO_4^{--} ion and inhibits it in the case of the Cl^- ion. However, in addition to the variation in the degree of hydration of the ions, the observed phenomena may also be caused by the effect of the cations on the surface layer of oxides on the platinum electrode, because the surface oxidation imparts to it the ability to adsorb cations even at high positive potentials.

In the case of certain oxidation reactions on the platinum electrode, as, for example, the oxidation of aniline [36], an anomalous trend of the polarization curves is observed. With increase in the positive potential of the electrode the current intensity initially, as usual, increases, attains a maximum and then decreases. Only at very positive potentials does another rise of the current density take place. The anomalous trend of the polarization curve is observed within a potential range in which a layer of adsorbed oxygen atoms appears on the electrode surface and is possible also connected with changes in the structure of the electric double layer which accompany the appearance of adsorbed oxygen. This problem, however, requires further detailed investigation.

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Manuscript Page No.	[Footnotes]
320	By redox system we mean an inert electrode immersed in a solution containing reduced as well as oxidized reaction components, for example, a platinum electrode in a solution of salts of divalent and trivalent iron.
335	The reactions (A) and (B) can be realized by means of the so-called "air electrode" [14]. In this case the anode is placed into the air space outside the electrolyte, and the passage of current is achieved by the application of a large potential difference, causing ionization of the air. The electrolyte ions are discharged at the air interface without coming into contact with the electrode metal.
340	On the contrary, the electrolytic reduction of oxygen on the Pt electrode takes evidently place with participation of adsorbed hydrogen.
347	This reaction has unfortunately not been sufficiently investigated. According to some data, the current yield of the reaction products of the NO_3^- ion is less than theoretical because the current is partly consumed for the separation of hydrogen [23].

Manuscript Page No.	[Transliterated Symbols]
328	н.в.э. = n.v.e. = normal'nyy vodorodnyy elektrod = = standard hydrogen electrode
347	адс = ads = adsorbirovanny = adsorbed
348	н.к.э. = n.k.e. = normal'nyy kalomel'nyy elektrod = = standard calomel electrode
354	н.б. = n.b. = nitrobenzol = nitrobenzene

Chapter 5

EVOLUTION OF GAS BUBBLES AT THE ELECTRODE AND WETTING OF METALS BY ELECTROLYTES

§1. EVOLUTION OF GAS BUBBLES AND OVERVOLTAGE

During the initial stage of development of the science of electrode reactions attempts were made to connect the overvoltage of the process of hydrogen evolution with the gaseous nature of the reaction products. It was assumed that the process of formation and separation of the gas in the form of bubbles is an important factor in the appearance of the hydrogen overvoltage, and that a large oversaturation of the solution with the gas is necessary for this process. Thus it was thought that during the polarization of the electrode molecular hydrogen accumulates on the metal surface to very high oversaturation and that only when this high oversaturation, to which a very high pressure would correspond in the gas phase under equilibrium conditions, is attained, can the evolution of the bubbles begin. A more negative potential that at atmospheric pressure would naturally correspond to the increased concentration of molecular hydrogen in the solution.

Hence arose the concept of overvoltage arising during the initial stage of the separation of bubbles an attempt to find this value experimentally. Actually, although the process of gas bubble separation is of importance for various phenomena, the accumulation of hydrogen or other gas in the solution up to the initial moment of bubble formation cannot be the cause of the large overvoltages which are observed in the experiment. Only in the case of electrodes with low overvoltage and, particularly, with a strongly developed surface, for example, the hydrogen electrode of platinized platinum, is the entire cathodic polarization of the electrode at moderate current densities which do not exceed some ten millivolts, explained by oversaturation of the solution with hydrogen. The hydrogen which is not separated in the form of bubles is removed from the electrode surface by diffusion or, when bubbles are separated, reaches the bubble surface by diffusion. The relationship between overvoltage and current density is expressed in this case by the equation

$$\eta = \frac{RT}{2F} \ln i + \text{const}, \qquad (246)$$

which follows from Eqs. (176) and (177) under condition that the hydrogen concentration at the electrode surface is high compared with its concentration in the depth of the solution.

At the present time we know well that overvoltage is observed in electrochemical processes independently of whether the reaction products at a given temperature are in the gaseous state or not. Thus the process of bubble separation at the electrode is generally not directly connected with electrochemical kinetics, but indirectly, as we shall see further on, it is nevertheless connected with it.

§2. DIMENSIONS OF THE GAS BUBBLES SEPARATED AT THE ELECTRODE

Even superficial observation leads to the conclusion that under different electrolysis conditions the evolving gas bubbles are of quite different sizes. Probably everyone who had anything to do with electrolysis for the production of hydrogen and oxygen has paid attention to the fact that in an electrolyzer with cathode and anode of the same material the solution has a different appearance at the cathode and anode. Thus, in an alkaline electrolyte, the hydrogen is separated at the cathode in the form of very small bubbles which form a milky turbidity in the whole electrolyte in the cathode space, while at the anode the oxygen is evolved in the form of relatively large bubbles which rise rapidly, leaving the electrolyte transparent. If the electrolyzer is filled not with alkali but with acid, the difference in the bubble dimensions is not so great; in this case the oxygen bubbles are smaller than the hydrogen bubbles.

The difference in the dimensions of the evolving bubbles is of importance in the technology of electrolytic production of oxygen and hydrogen. The formation of small hydrogen bubbles (in alkaline electrolyte) results in a greater "filling of the electrolyte with gas" because of the slow rate of their ascent to the surface. This in turn causes an increase in the effective resistance of the solution and the penetration of hydrogen bubbles through the diaphragm into the anode space and, consequently, to contamination of the oxygen.

In order to account for this difference in the dimensions of the evolving bubbles, Coehn advanced the hypothesis of the connection of these phenomena with the presence of an electric charge on the surface of the gas bubbles in electrolyte solutions [1]. The existence of this charge is confirmed by the electrophoresis of the bubbles, i.e., their movement in the electric field. According to Coehn, the cause of the difference in the size of the bubbles separated at the electrode, was the different electrostatic interaction of the charged bubbles with the electrode. It was assumed that depending on the sign of the charge of the electrode and bubble the latter is either pressed against the electrode or repelled from it and, correspondingly can attain varying sizes before the breakaway from the electrode. However, if the magnitude of these effects is calculated, it is easy to show that they cannot exert any influence whatever on the size of the gas bubbles.

This follows, for example, from the fact that the electrophoretic force, calculated from the electrophoresis speed according to the Stokes law,* with which the electric field acts on the charged bubbles, is negligibly small compared with the force of hydrostatic buoyancy (particularly in media with good conductivity, such as the electrolyte solutions). To this attests also the fact that the bubbles rise almost vertically in the electric field, without any noticeable deflection. Hence, under normal conditions of electrolysis one can neglect the electrophoretic force, and the explanation of Coehn should be rejected.

In order to understand the interaction of the different forces which act on the bubble let us consider the simple case of a bubble which is sessile on a horizontal electrode surface as shown in Fig. 90.

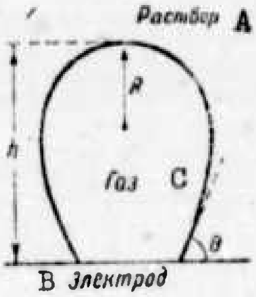

Fig. 90. Bubble sessile on a horizontal surface. A) Solution; B) electrode; C) gas.

The force F_σ of adhesion of the bubble with which it is held by the electrode surface, acts along the perimeter of attachment of the bubble and is equal to the product of the length of this perimeter πa and the vertical component of the surface tension $\sigma_{23}\sin\theta$, i.e.,

$$F_\sigma = \pi a \sigma_{23} \sin\theta, \qquad (247)$$

where a is the diameter of the circle along which the bubble is held to the electrode surface, θ is the contact angle at the interface metal/solution/gas (see Fig. 90), σ_{23} is the surface tension at the phase boundary solution/gas.

According to the law of Archimedes the force of hydrostatic buoyancy of the bubble in the liquid is

$$F_A = vg\rho, \qquad (248)$$

where v is the bubble volume, ρ the density of the liquid, g the gravity acceleration. For small bubbles $F_\sigma > F_A$. With increase in the bubble dimension F_A increases more rapidly than F_σ, because F_A is proportional to the third power of the linear dimensions of the bubble and F_σ to the first power. It follows that there is a certain critical bubble size at which the bubble should break away from the surface.

To determine the equilibrium conditions we must also take into account that the pressure within the bubble is greater than the hydrostatic pressure in the ambient medium by the amount $2\sigma_{23}/R$, where R is the radius of curvature of the bubble surface at a given point,* i.e., the gas inside the bubble is compressed by the surface. If R indicates the curvature of the bubble surface at its apex (Fig. 90), the pressure difference in the liquid and the gas at the base of the bubble amounts to

$$\frac{2\sigma_{23}}{R} - hg\rho,$$

where h is the height of the bubble, because when we go from the level of the bubble top to the level of the base, the pressure in the liquid increases by $hg\rho$ while the gas pressure remains practically the same. This difference in pressures results in the appearance of an additional breakaway force, equal to the product of the area of the base $\pi a^2/4$ and the quantity $([2\sigma_{23}/\ ] - hg\rho)$.**

Thus the full equilibrium condition has the following form:

$$\pi a\sigma_{23}\sin\theta = vg\rho + \frac{\pi a^2}{4}\left(\frac{2\sigma_{23}}{R} - hg\rho\right). \qquad (249)$$

All quantities entering into this equation are accessible to direct measurement. As measurements, carried out on bubbles of different dimensions, sessile on a mercury surface in an electrolyte solution, have shown, the correctness of Eq. (249) is fully confirmed by the experiment. It follows that the equilibrium of the bubbles is wholly determined by the effect of the capillary forces and the force of gravity [3]. By means of the theory of capillarity one can determine, on the

a

b

Fig. 91. Micrograph of bubbles with different contact angles θ prior to breakaway from the electrode (6 × magnification): a) $\theta = 18°$; b) $\theta = 75°$.

basis of Eq. (249), the shape of the bubble surface at a given value of θ. Such an analysis, like the above-given elementary argument, leads to the conclusion that there is always an upper limit for the size of a bubble at which the capillary forces no longer can hold the bubble at the surface and it breaks away. It is easy to show that the limit size of the bubble depends on the contact angle. If the contact angle is very small, for example 18° (in other words, if the metal surface is readily wetted by water), the bubble sits on a small base whose perimeter of attachment to the surface is small and in consequence of this, the bubble is readily torn off without being able to grow to considerable size (Fig. 91a).

If the contact angle is larger, for example, 75° (Fig. 91b), the perimeter of attachment to the surface, and consequently, also the force which holds the bubble on the surface, are greater; in consequence of this the bubble can grow to considerably greater size than in the first case prior to breakaway.

Thus, the size of a bubble which can be retained on the surface is the greater, the larger the contact angle. The size and shape of the bubble as a function of the contact angle at the moment of breakaway from the mercury electrode is shown in Fig. 91a, 91b and 92. The mathematical theory of capillarity permits us to establish a quantitative relationship between the contact angle and the bubble dimensions at breakaway. As Fig. 93 shows, this relationship is very well confirmed by experiment.

Fig. 92. Micrograph of bubble with contact angle θ = 97° before breakaway from the electrode (7.5 × magnification).

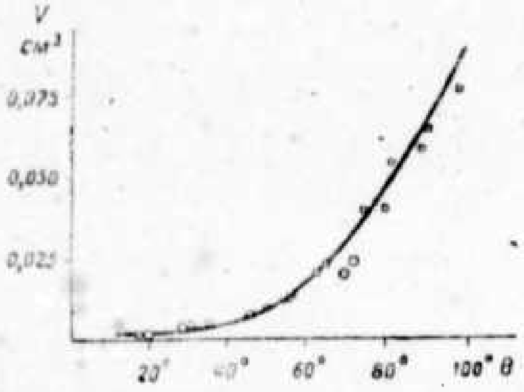

Fig. 93. Volumes v of bubbles at the moment of breakaway from the electrode as a function of the contact angle θ: o) Bubbles on silver electrode; ×) on platinum; ⊡) on mercury. Thick line: theoretically calculated maximum volumes of bubbles held at the electrode at the corresponding contact angles.

§3. WETTABILITY OF ELECTRODES BY THE ELECTROLYTES

The dependence of the bubble dimensions on the contact angle θ has the consequence that the electric field of the double layer exerts an important influence on the adhesion. Thus, the electrical field plays an important part here, although in a quite different sense as in the theory of Coehn.

Let us dwell on this in somewhat greater detail. The size of the equilibrium contact angle can be expressed as a function of the surface tensions at three interfaces: solution/metal, solution/gas and metal/gas. From the equilibrium conditions of the forces of surface tension (Fig. 94) follows:

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \cos \theta \quad \text{and} \quad \cos \theta = \frac{\sigma_{13} - \sigma_{12}}{\sigma_{23}}, \qquad (250)$$

where σ_{12} is the interfacial tension between metal and solution, σ_{23} is the surface tension between solution and gas which is practically independent of the nature of the gas for this solution; σ_{13} is the surface tension between metal and gas, saturated with water vapor.

In the case of a liquid mercury surface the bubble pulls the metal surface slightly outwards so that it ceases to be horizontal. This requires the introduction of a certain correction into Eq. (250) which we omit here.

When the metal, for example, mercury, is polarized, the quantity σ_{12} varies in accordance with the law represented by the electrocapillarity curve, i.e., it decreases when the potential deviates from the zero charge potential of the surface. The surface tension σ_{23} between the solution and gas is independent of the polarization. The quantity σ_{13} should not vary in first approximation with change in the electrode potential because, as it would seem, there are no ions at the metal/gas interface and thus a potential change cannot take place. This conclusion, however, is not accurate because the metal under the bubble is not completely dry but covered with a thin film of solution which contains ions. Hence, a variation of the quantity σ_{13} during polarization of the electrode is possible but because σ_{13} varies less with the potential than σ_{12}, the pattern of the phenomenon is determined in first approximation by the variation of σ_{12} If the cathodic polarization increases to a fairly large value, σ_{12} decreases, consequently the difference $\sigma_{13} - {}_{12}$ and cos θ increase and the contact angle θ decreases.

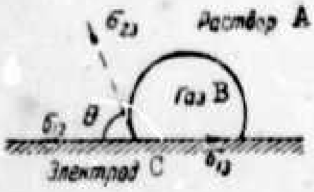

Fig. 94. Equilibrium of the tensions at the interfaces solution/gas (σ_{23}), solution/metal (σ_{12}) and metal/gas (σ_{13}). A) Solution; B) gas; C) electrode.

Together with it decrease the adhesion and the size of the bubble at breakaway. The same takes place during anodic polarization. Physically this can be visualized in this way, that when the charge density of the double layer increases, the wettability of the metal by water increases and the water, wetting the surface, expels the bubble. Correspondingly the contact angle θ of the bubble is a maximum when the surface charge is zero (Fig. 95). The method of determining the zero charge potential of metals by means of measurement of the contact angles of bubbles at different potentials, as mentioned in the Introduction [4], is based on this phenomenon.

If the separation of gas takes place at a potential close to the zero charge potential of the metal in the given solution, then σ_{12} is ovviously large, the difference $\sigma_{13} - \sigma_{12}$ and cos θ are small and can even have a negative value, and the contact angle is large. The bubbles at breakaway are large.

This can be ascertained if a bubble of an indifferent gas, for example, nitrogen, is placed on the surface of the mercury electrode and this electrode is then polarized. The bubble breaks away from the surface at the moment when the force of hydrostatic buoyancy becomes equal to the adhesion force of the bubble. It is then possible to place artificially bubbles of different size on the electrode and to determine the potential at which the bubble breaks away from the electrode surface.

This potential may obviously be more negative or more positive than the zero charge potential of mercury. On the basis of the data thus obtained it is possible to plot the curve of the dimensions of the bubble at breakaway as a function of potential. This curve has approximately the same shape as the electrocapillarity curve (Fig. 96). In order to encompass a larger potential range, the measurements in the cathodic range were carried out in alkaline, and in the anodic range in acid solution [3].

It should be pointed out that the addition of surface-active organic substances to the solution alters all three surface tensions σ_{12}, σ_{13} and σ_{23} at a given potential, and this can increase or decrease the wettability of the metal surface.

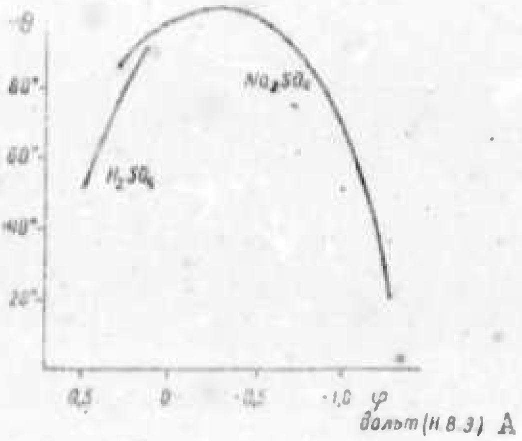

Fig. 95. Contact angle of the bubble on mercury in 1 N solutions of sulfuric acid and sodium sulfate as a function of the potential. A) Volt (n.v.e.).

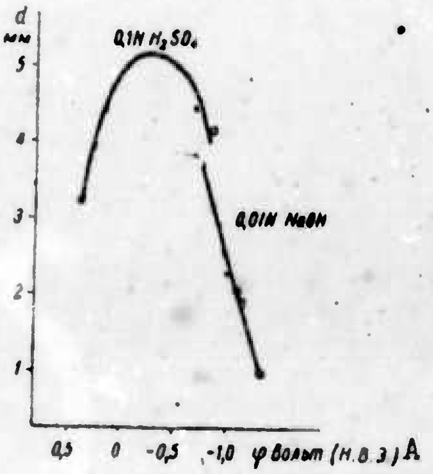

Fig. 96. Diameter *d* of the bubbles at breakaway as a function of the mercury electrode potential: o) bubbles separated electrolytically; ×) bubbles, placed mechanically. A) Volt (n.v.e.).

Turning now to the problem raised at the beginning of this chapter concerning the dimensions of the gas bubbles evolved during electrolysis, we can now conclude that the small size of the hydrogen bubbles separated at the cathode in alkaline solutions is connected with the negative potential of hydrogen separation in these solutions at which the metal is well wetted by water and the bubbles have small contact angles. On the other hand, the separation of oxygen at the anode in alkaline solution takes place at a slight positive potential (counting from the neutral point) at which the surface charge is less in absolute magnitude and the wettability is less. The converse situation exists in acid solutions: the hydrogen evolution takes place at a less negative potential and at a smaller negative surface charge than in alkaline solutions; the oxygen is separated at a large positive potential at which the electrode surface carries a strong positive charge [3].

The increase in the wettability of the electrode in consequence of the increase in the charge of the double layer on its surface plays an important part in different electrochemical processes. Thus, for example, graphite anodes in chloric electrolytic cells are more intensely attacked at large polarization owing to the increase in wettability and the penetration of electrolyte into the depth of the electrode pores [6]. The carbon electrode with "atmospheric depolarization" which is used in certain galvanic cells, for example, the cell of P.M. Spiridonov, is a porous membrane at which oxygen should arrive continuously from one side and electrolyte from the other side. At the same time, the membrane should not be wetted right through. In a certain potential range the charge of the double layer on this electrode is small and the membrane is not wetted for long periods. If the current density is increased or the composition of the solution is varied, the wettability increases and the solution penetrates into the pores. As a result, the three-phase boundary solution carbon/air required for the work of the electrode disappears, and the electrode ceases to function. The dependence of the soaking rate on the potential is a curve which is analogous to the electrocapillarity curve, with a minimum soaking rate in the range of potentials which is close to the zero charge point potential [7].

The adhesion of the hydrogen bubble to the metal during electroplating, for example, with zinc, leads to the formation of honeycombs on the deposited metal, whose depth sometimes extends over the entire thickness of the layer of deposited metal. The number and depth of the honeycombs is less if the polarization of the electrode is greater, i.e., the greater the charge of the double layer and, consequently, the wetting of the metal. The dependence of the wettability on polarization is also of great importance in molten salt electrolysis [5].

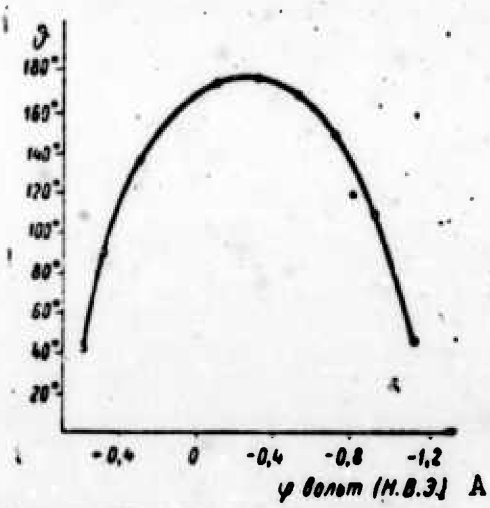

Fig. 97. Contact angle of a drop of toluene, sessile on mercury in 1 N Na_2SO_4 solution, as a function of the potential of the metal. A) Volt (n.v.e.).

An analogous phenomenon of contact wetting angle variation with variation of the electrode potential takes place when instead of a gas bubble a drop of oil or some other organic liquid which is not miscible with water is placed on the metal surface (Fig. 97). If the metal surface with the sessile oil drop is polarized, the shape of the drop changes and then a partial and finally complete breakaway of the drop from the electrode takes place. The process of breakaway of the drop has been recorded photographically in Fig. 98. If the polarization is strong, a complete cleaning of the electrode from oil takes place in consequence of an increase in the wettability of the electrode by the solution. This phenomenon is analogous to the well-known phenomenon of drawing in of a dielectric with large dielectric constant in the field between the plates of a capacitor. In the presence of the charges of the double layer on the surface the body with the greater dielectric constant, the water repels the oil from the surface in the same way as it repels adsorbed molecules of organic compounds [8].

The effects described in the foregoing explain the following phenomena. Graphite anodes, which, as mentioned above, are rapidly destroyed under conditions of high wettability, are used in chlorine electrolysis. To protect them from destruction, they are impregnated with oil. However, if the electrode is impregnated with a liquid. for example, vaseline oil, the latter is dislodged by the electrolyte solution which penetrates into the graphite through the capillaries during polarization. However, if the anode is impregnated with a substance which cannot be removed even from surface pores (for example, paraffin), the potential of such an electrode, owing to the large current density, increases greatly (approximately by 1 v) which causes rapid destruction of the electrode also in this case. With correct impregnation, the surface and part of the pores close to the electrode surface are freed of oil and the electrolyte does not penetrate further [6].

Technical methods of cathodic and anodic degreasing of metals, which are widely used in the metalworking industries, are based on the increase in wettability during polarization. The degreasing of metals is carried out during the preparation of the metal surface for electrochemical deposition of metals and certain methods of surface treatment of metals. The cathodic degreasing is promoted by the presence of hydrogen bubbles at the interface between the oil layer and the solution: the hydrostatic buoyancy of the bubble, in combination with a certain quantity of oil adhering to it, results in an additional cleaning of the metal surface [8].

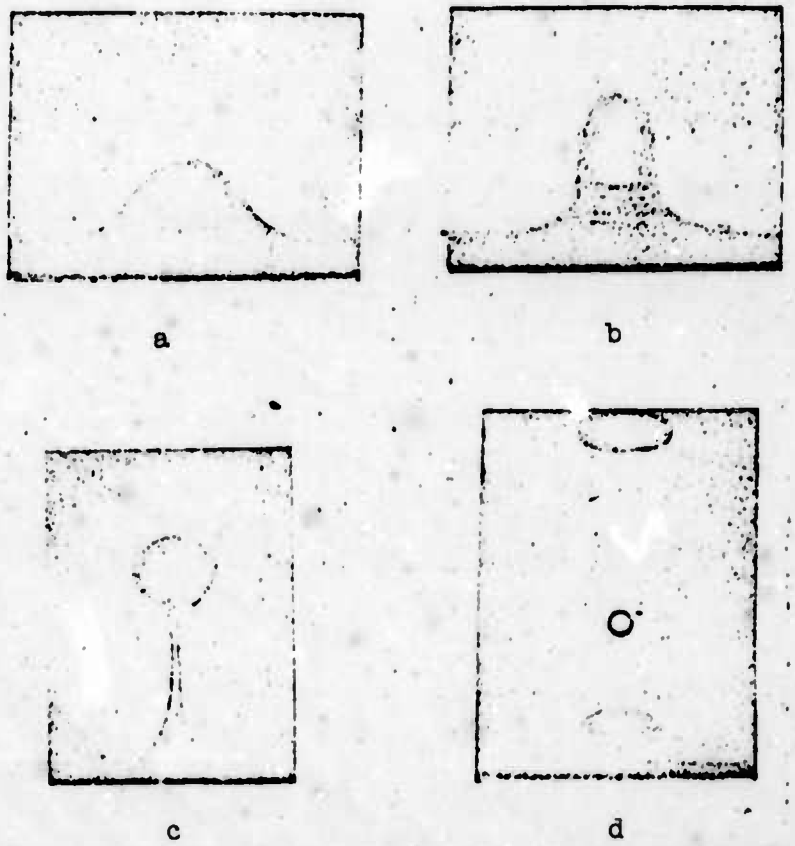

Fig. 98. Variation of the shape and breakaway of an oil drop from the electrode during application of a negative potential (photograph, natural size).

§4. WETTABILITY AS A FUNCTION OF POTENTIAL AND FLOTATION

The breakaway of bubbles from a metal surface is a kind of reserved elementary act of flotation. In flotation the bubbles should adhere to the surface of the floated particle and should not break away from it. Interesting relationships exist between the mechanisms of these two groups of phenomena.

As pointed out previously, based on a mathematical analysis of the conclusions from Eq. (249) one can determine the limit dimensions of a bubble which is still held by a horizontal surface of a solid at a given value of θ. At the same time, obviously, we determine its maximum buoyancy, i.e., the maximum weight of the particle which can be floated by the bubble, i.e., lifted by it to the liquid surface. Thus the verification of the relationship between the contact angle and the dimensions of bubble at breakaway, which can be carried out owing to the strong dependence of the contact angle on the polarization of the metal, is also of great interest for the development of flotation theory.

A decrease in the contact angle which facilitates the breakaway of the bubble, reduces the floatability of the solid. Hence in some cases of flotation precisely the same dependence of the floatability on the surface charge is observed as the one which we found for the dimensions of the bubbles at breakaway. Thus, it was shown that powdered $BaSO_4$ and AgI are most readily floated near their isoelectric point, when their surface carries only a negligible charge. The magnitude of the surface charge in this case can be varied by variation of the composition of the solution [9].

Ore particles are normally made to float by addition of flotation agents into the solution, which are adsorbed on the ore surface and reduce its wettability, i.e., increase the contact angle θ. An increase in surface charge, as we have seen repeatedly, can have the effect that organic substances are no longer adsorbed and thus result in a decrease in floatability. The effect of the so-called flotation depressants which, when added to the solution, modify the potential difference at the surface of the mineral particle in such a manner that its charge density increases, is based on this in some cases. The selective inhibition of flotation makes it possible to separate different minerals during the flotation process [10].

It must be pointed out, however, that the flotation phenomena with all their complexity cannot be explained merely from the point of view of the concepts concerning the equilibrium of surface forces. In order that the elementary flotation act can take place, the bubble which encounters a particle must adhere to it within the short collision time.

It can be shown that in the case of incomplete wetting, i.e., when the contact angle is finite, either the relatively thick liquid layers between the solid and the gaseous phase or the very thin layer of molecular dimensions is stable. Layers with intermediate thickness are unstable. When the bubble approaches the surface of the solid under the surface of the solution, the layer of solution between the surface and the bubble first gets gradually thinner until it enters into an unstable state; the layer is then ruptured which causes the adhesion of the bubble. Thus, the kinetics of the adhesion process are of great importance. Observations of the adhesion of bubbles to a mercury surface have shown that the lower the electrolyte concentration and the larger the surface charge, the longer the bubble takes to adhere. The stabilizing effect of the charge of the double layer on the water film is basically due to the electric repulsion of the ions of the double layer from the free surface of the water which prevents the film from thinning out [11].

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[Footnotes]

371 The resistance offered by a fluid to a sphere with diameter r, which moves with a velocity v, is $6\pi r\eta v$, where η is the viscosity of the fluid.

372* More accurately, by the amount $\sigma_{23}(1/R_1 + 1/R_2)$, where R_1 and R_2 are the main radii of curvature of the surface [2]. At the top of the bubble $R_1 = R_2 = R$.

372** This is easily proved in the following way. Through the bubble we draw an imaginary plane parallel to the electrode surface but somewhat higher than this. If the plane formed the lower physical limit of the bubble and the space under it were filled with solution, the sum of the hydrostatic pressures of the liquid on the bubble, according to the law of Archimedes, would be exactly equal to $vg\rho$. In reality, the part of the bubble above our imaginary plane is acted on, not by the pressure of the fluid, but the gas with a pressure which exceeds that of the fluid, which must be taken into account by introducing the term

$$\frac{\pi a^2}{4}\left(\frac{2\sigma_{23}}{R}-hg\rho\right).$$

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[Transliterated Symbols]

377 н.в.э. = n.v.e. = normal'nyy vodorodnyy elektrod = standard hydrogen electrode

Chapter 6

ELECTRODEPOSITION OF METALS

§1. GENERAL INFORMATION

The processes of the electrodeposition of metals, like the reverse processes of anodic dissolution of metals, are of great practical importance. The first practical application of the electrodeposition of metals, galvanoplastics, was discovered by the Russian Academician B.S. Yakobi in 1837 [1]. The discovery of B.S. Yakobi led to the development of a new branch of technology, electroplating; subsequently, the method of galvanic coating found widespread application, in particular, for the protection of metals against corrosion. The electrochemical deposition of metals is used in hydroelectrometallurgy. A combination of anodic dissolution and subsequent electrodeposition forms the basis of the refining of metals by electrolysis. Also of great importance are these reactions in the processes which take place at the electrodes of storage batteries and primary cells. Important methods of producing metals such as aluminium and magnesium are based on their separation by means of electric current from molten electrolytes. An important part in the development of the industrial utilization of the reactions of electrodeposition and electrolysis of melts in our country played the researches of several electrochemists: P.P. Fedot'yev, N.A. Izgaryshev, Yu.V. Baymakov, P.F. Antipin, A.F. Alabyshev, N.P. Fedot'yev, N.T. Kudryavtsev and others.

In the present account we shall limit consideration to the mechanism of the processes which take place in electrolyte solutions and shall not deal with the electrolysis of melts.

The processes of cathodic separation and anodic dissolution in the case of solid metals have certain peculiarities compared with other electrochemical reactions which are connected with the fact that the end products or starting substances are in the crystalline state. However, before considering this aspect of the problem of electrodeposition, we must consider the question of the kinetics of the discharge of the metal ions under the conditions when the metal is separated not in the crystalline but in the liquid state. A study of this problem will assist in the further elucidation of the peculiarities connected with the crystal structure of the electrode.

§2. ELECTRODEPOSITION OF METALS ON A LIQUID CATHODE

Of great interest for the study of the mechanism of the discharge of metal ions is the mercury electrode on which the separation of metals takes place with formation of amalgam, for example, zinc or copper amalgam, for example, zinc or copper amalgam.

The existing experimental data lead to the conclusion that the reaction of discharge and formation of metal ions at the mercury electrode take place in many cases at a considerable rate. Hence the polarization phenomena which are observed here are to a large extent connected with the concentration polarization.

The serivation of the formula of the polarographic wave, corresponding to a reversible process, as has been shown in Chapter 1, is based on the assumption that the rate of the processes of ion discharge and metal ionization is fairly high and that the rate of the over-all electrode process is determined by the rate of diffusion of the reduced substance towards the electrode. This formula is well supported by experiment in the case of the discharge of many metal ions which is a confirmation of the correctness of this assumption.

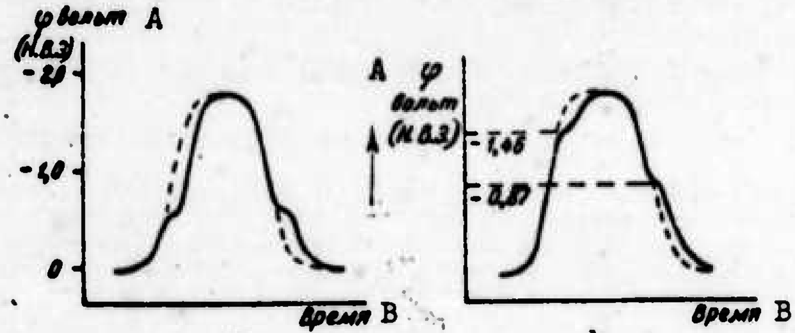
An exception are some metals (for example, of the iron group), which will be discussed further on.

When investigations are carried out, however, by means of more perfect experimental methods, it is found that for a large number of metals the reaction of the discharge of the ions on the mercury takes place at a relatively large, but measurable rate. In order to make the electrochemical polarization accessible to investigation, it is desirable in these cases to use relatively large current densities. Hence it is important to avoid as far as possible an impoverishment of the solution with regard to the reacting ions near the electrode surface which takes place with prolonged passage of a direct current with high current density, or, in other words, it is essential to lower the concentration polarization. This result can be achieved by the use of alternating current.

It has been shown in Chapter 1 that in the absence of marked electrochemical polarization during the application of an alternating current, a certain dependence of the amplitude of the potential fluctuation and the phase shift on frequency is observed. In this case the electrochemical polarization is manifested as a kind of additional resistance between the electrode and solution which can be detected by measuring the amplitude and phase shift as a function of frequency [2].

Another method consists in determining the electrode potential variations during the passage of a direct current during a short interval of time. In this case the impoverishment of the solution cannot propagate to a great distance from the electrode which enables relatively large current densities to be achieved and to determine whether the process is accompanied by electrochemical polarization. After a certain interval of time the direction of the current is reversed and the potential variation during the anodic process is determined. A convenient device, based on this principle, was designed by A.T. Vagramyan and used by him for the study of the polarization phenomena which occur during the electrodeposition of solid metals [3].

J. Heyrovsky used a similar method for the study of the processes of discharge of various metal cations on the mercury electrode [4]; in this case the potential variation was observed by means of an oscillograph which permitted the use of short current pulses. In the absence of discharging ions the record of the potential variation during the passage of current pulses with alternating direction obviously gives the cathodic and anodic charging curves for the mercury surface. In the presence of such ions at a potential at which the electrode process is possible, the current begins to be consumed for the discharge of ions (cathodic curve) or the ionization of the atoms of the metal which forms the amalgam (during the recording of the anodic curve); the curve of the potential as a function of time then shows a delay. With further passage of time, in consequence of the impoverishment of the layer near the electrode, the discharge current decreases and the supplied current is sufficiently large to produce a further potential shift. The dotted line in Fig. 99a shows the cathodic and anodic charging curves of mercury, taken with the oscillograph; the thick lines show the potential as a function of time in the presence of lead ions in the solution, the left curve corresponding to the cathodic process of discharge of the lead ions, and the right one, to the ionization of the lead amalgam which is formed. The delays on the cathodic and anodic curves are observed at the same potential which indicates the reversibility of the process (absence of electrochemical polarization). A different pattern is observed with solutions containing Zn^{++} ions (Fig. 99b). In this case the discharge potential is strongly shifted to the negative side



a b

Fig. 99. Reversible and irreversible phenomena during the discharge of metal ions on the surface of the mercury drop electrode. Dotted lines: oscillograph record of the potential variation with time in the absence of discharging ions. Thick line in Fig. a: the same in the presence of Pb^{++} ions; thick line in Fig. b: the same in presence of Zn^{++} ions. A) Volt (n.v.e.); B) time.

while the ionization potential is shifted to the opposite side; this shift indicates the presence of a considerable electrochemical polarization in these processes.

The discharge of the ions Tl^{+}, Ag^{+}, Hg_2^{++}, Cd^{++}, Cu^{+}, Pb^{++} is practically reversible, while a marked irreversibility of the process is observed during the deposition of metals on the mercury electrode from solutions of the salts of Zn^{++}, Mn^{++}, Cr^{++} and from plumbite solutions.

Heyrovsky advanced the hypothesis that the polarization during the discharge of the Zn^{++} ion is due to an accumulation of an intermediate univalent ion which is slowly disproportioned into the ion Zn^{++} and a Zn atom:

$$Zn^{++} + e \rightarrow Zn^{+} \qquad (A)$$

$$2Zn^{+} \rightarrow Zn^{++} + Zn \qquad (B)$$

However, according to the statements in the chapter on the reduction and oxidation reactions (see Chapter 4), the electrical reduction of the hypothetical unstable single-charge Zn^{+} ion would probably proceed more readily and not with greater difficulty than the reaction (A) and it is more logical to assume that the electrochemical polarization occurring during the discharge of zinc ions is connected with the first elementary act (A) of the electrode process and not with the subsequent stages [32]. It can be assumed that similar relationships obtain in the inhibited discharge of other metal ions, although there is as yet an insufficient number of data to permit final conclusions.

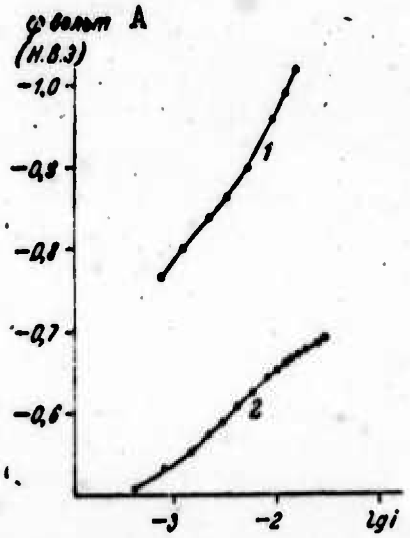


Fig. 100. Polarization during the discharge of Ni^{++} ions from a solution of $NiSO_4$ + + H_3BO_3. Curve 1: mercury cathode; curve 2: nickel cathode; A) volt (n.v.e.).

During the deposition of the metals of the iron group from aqueous solutions on the surface of the mercury electrode, considerable overvoltages are observed. In this case the overvoltage is approximately a linear function of the logarithm of the current density: $\eta = a + b \lg i$. Figure 100 [5] gives the overvoltage as a function of the logarithm of the current density for the case of the separation of nickel from a solution $NiSO_4 + H_3BO_3$. It is highly probable that the relatively large overvoltage, observed for these metals, is due to a delay of the stage of discharge of the ions. However, other hypotheses have also been advanced. Thus, it was proposed that during the separation of ions on the mercury cathode the metal is first present in an "active," highly disperse state, because it is only very slightly soluble in mercury [6]. The high energy content of this "active" iron, according to this hypothesis, causes the anomalously large electrode polarization. This circumstance is possibly of some significance; however, as has been indicated previously, a strong polarization is also observed during the discharge of the ions of metals which are fairly soluble in mercury, such as, for example, in the case of zinc. On the other hand, during the separation of metals of the iron group in the solid crystalline state (Fig. 100, curve 2) under conditions which exclude the formation of a highly disperse system, the discharge of the ions also requires a relatively large potential shift (see also §4).

In addition to the polarization measurements, the method of isotope tracers [29] can be applied with success to the study of the kinetics of the processes of discharge of metal ions at the mercury electrode. Their use is based on the same principles as the use of deuterium in studies of the process of discharge of hydrogen ions. If an amalgam of a metal, for example, zinc, containing radioactive zinc, is brought into contact with a zinc salt solution, the exchange rate can be gaged on the basis of the increasing radioactivity of the solution with time and consequently, the magnitude of the exchange current between amalgam and solution, which is equal to the rate of discharge of the Zn^{++} ions or the ionization of zinc amalgam at the equilibrium potential.

If the corresponding electrochemical processes take place at a sufficient rate, the exchange currents can be very large. Thus, the exchange current in 2 N $ZnSO_4$ attains 0.08 amp/cm^2. The addition of a complexing agent, for example, KCN, to the solution causes a marked decrease in the exchange current.

§3. PHENOMENA OBSERVED DURING THE APPEARANCE AND GROWTH OF A NEW PHASE

In cases where a new phase is obtained as a result of the process of electrodeposition, the ion discharge conditions show typical features. At the initial moment of the appearance of the new phase these features appear in the case of the formation of a solid metal crystal as well as during the formation of a drop of liquid metal, for example, mercury; during further growth, however, the crystal surface and the liquid surface behave differently in certain respects. The points of the liquid surface are on the average energetically equal so that it is a matter of indifference at what point of the surface of the liquid metal the atom formed during the discharge of the ion is deposited. The situation is different during the growth of a crystal of solid metal as a result of the electrodeposition of ions.

Before we pass on to a discussion of the conditions under which the process of the appearance and growth of metallic crystals takes place as a result of the discharge of ions (electrocrystallization process), let us recall certain basic concepts concerning the mechanism of normal crystallization which does not involve the passage of electricity through the interface. The basis of this trend in science has been laid by the work of J.V. Gibbs and the Russian scientist G.V. Vul'f. During the last decase the theory of the nucleation and growth of crystals has been greatly developed thanks to the investigations of Volmer, Stransky and others. Here we can tough only upon a few of the most elementary aspects of this important problem [7, 8, 9].

A typical and long-known peculiarity of the process of the appearance of a new phase is the presence of an initial supersaturation. Assuming we wish to cause the crystallization of a salt from its solution by cooling. If the solubility of the salt decreases with decrease in temperature we can achieve a state by cooling of the solution, in which the concentration of the solution corresponds to saturation, i.e., the solution can be in equilibrium with the solid crystal. At this stage, however, the separation of a new phase does not yet take place. To achieve this within a measurable interval of time it is essential that the concentration of the solution exceeds in a certain ratio the equilibrium concentration, or, as it is commonly said, that a certain degree of oversaturation is attained. The oversaturation is considerably reduced if a small crystal of the same substance is introduced into the solution on which the further deposition from the solution can take place. The crystallization can also be promoted by some other solid if its crystal lattice is fairly similar to the lattice of the crystals which are to be separated, in particular, if it can form isomorphous mixtures with the substance to be separated from the solution.

The oversaturation phenomenon is explained in the following way. The conditiion of equilibrium between two phases is determined by the equality of the chemical potentials of each component in the two phases. The chemical potential of the crystal which is formed under conditions close to equilibrium thus should be equal to the chemical potential of the same substance in the saturated solution. However, the chemical potential of the crystal, if it is fairly small, depends on its dimensions; if the size of the crystal is greatly reduced, the chemical potential increases. This takes place in consequence of the fact that the proportion of atoms in a small crystal which are at the surface and are less strongly bound to the other atoms than the atoms in the center of the crystal, is relatively large. Hence small crystals are unstable with respect to a saturated solution which is in equilibrium with large crystals. Very small crystals formed in such a solution in consequence of fortuitous concentration fluctuations, again decompose. In order that the crystal can grow in a solution even if the concentration of the latter is higher than the saturation concentration, it is essential that the dimensions of the crystal should exceed a certain critical size at which its chemical potential is equal to the chemical potential of the dissolved substance in the ambient medium, i.e., at which the solution is supersaturated with respect to a crystal of this size. Thus, the process of the appearance of a crystal begins with the creation of a nucleus of minimum size for which a certain amount of work must be expended (see further on). Obviously this work will be less and, consequently, the appearance of a nucleus more probable, if the critical dimensions of the nucleus are smaller. This condition can be fulfilled if the chemical potential of the dissolved substance is increased, i.e., if the degree of oversaturation of the solution is increased. It follows from this that the beginning of crystallization is promoted by an increase in the supersaturation because of the fact that the critical dimensions of the nucleus, and, consequently, also the work required for its creation, are reduced in proportion to the increase in supersaturation and that the probability of its appearance is increased.

The conclusions presented so far are not connected with the regular arrangement of the atoms in the crystal lattice and are thus equally applicable to the case of the formation of a liquid phase, for example, of drops from oversaturated vapor. Let us consider the quantitative relationships first for the latter example because they are simpler in this case. We designate the concentration of the saturated vapor at a given temperature by c_s. Then the radius r of the drop which can be in equilibrium with the supersaturated vapor with the concentration c at the same temperature and which can thus serve as a nucleus for the growth of large drops, is defined by the Thomson (Kelvin)* relation:

$$RT \ln \frac{c}{c_s} = \frac{2\sigma v}{r}, \qquad (251)$$

where σ is the surface tension of the liquid, and v its molecular volume. This relation is easily derived thermodynamically. In order to create such a nucleus drop from the ambient medium, the work A, equal to

$$A = \frac{1}{3}\sigma S, \qquad (252)$$

must be expended, where S is the surface of the drop, equal to $4\pi r^2$. At first sight it may be incomprehensible that this work is equal to $(1/3)\sigma S$ and not to σS. The last value would indeed be correct if the drop were formed from the liquid phase or, at constant volume of the system, from the saturated vapor in equilibrium with a liquid phase which has a flat surface. However, when a drop is formed from supersaturated vapor, work can initially be gained by transforming it from the supersaturated to the saturated state. This gain is equal to $RT\ln(c/c_s)$ per mole and, consequently, amounts to

$$\frac{4}{3}\frac{\pi r^3}{v}RT\ln\frac{c}{c_s} \qquad (253)$$

for the quantity of substance necessary for the formation of a drop with radius r. Substituting into the expression (253) the value $RT\ln(c/c_s)$ from Eq. (251), we obtain

$$\frac{4}{3}\frac{\pi r^3}{v}RT\ln\frac{c}{c_s}=\frac{8}{3}\pi r^2\sigma=\frac{2}{3}\sigma S. \qquad (254)$$

Subtracting the quantity $(2/3)\sigma S$ from the work σS, which must be expended for the formation of the drop from saturated vapor, we obtain the value A given in Eq. (252). Substituting into (252) the value $S = 4\pi r^2$, calculated by means of Eq. (251), we find

$$A\doteq\frac{16\pi\sigma^3v^2}{3R^2T^2\left(\ln\frac{c}{c_s}\right)^2}. \qquad (255)$$

It is apparent from Eq. (255) that the work of formation of the nucleus decreases in proportion to the increase in the degree of supersaturation c/c_s which is fully understandable because the size of the drop nucleus decreases in this case.

It follows from statistical mechanics that between the work A necessary for the formation of the drop and the probability W of this event exists the relationship

$$W=B\cdot e^{-\frac{A}{kT}}, \qquad (256)$$

where k is the Boltzman constant, i.e., R/N (N is the number of molecules in one mole) and B is a certain proportionality factor. Of decisive importance for the magnitude of W is the expression in the exponent from which follows that the probability of the appearance of a nucleus of a new phase should markedly increase with increase in supersaturation.

The above-presented concepts are also applicable to a crystalline nucleus, with the sole difference that the surface tensions of the different faces in this case have different values. Hence, instead of the expression for A, given in Eq. (252), we must write

$$A = \frac{1}{3}\sum \sigma_i S_i, \qquad (257)$$

where the summation is carried out with respect to all equilibrium facets of the crystal.*

The values for the work of formation of the nucleus, the drop or crystal in Eqs. (252) and (257) relate to the case of nuclei, which appear within the volume of the phase. These values can be considerably lowered (i.e., the probability of appearance of the nucleus can be increased) if the appearance of the new phase takes place on a preexisting interface. This last circumstance is again most easily explained by using the example of a liquid drop.

Assuming that the liquid drop appears not in the volume but on a solid flat wall. We designate by σ_1 the surface tension of the liquid, by σ_2 the surface tension of the solid surface in the atmosphere of the vapor, by σ_{12} the interfacial tension at the liquid/solid interface, by S_1 the free surface of the drop and by S_{12} the interfacial area drop/solid. Then, using the same arguments which in the case of the free drop lead to Eq. (25), it can be shown that

$$A = \frac{1}{3}(\sigma_1 S_1 + \sigma_{12} S_{12} - \sigma_2 S_{12}). \qquad (260)$$

With complete wetting $\sigma_2 = \sigma_1 + \sigma_{12}$, $S_1 = S_{12}$, and A vanishes; in other cases it will decrease compared with the value defined by Eq. (252) and this decrease will be greater if the solid wall is well wetted by the liquid. The physical meaning of this effect is that the work of formation of the nucleus decreases owing to the gain of energy connected with the interaction between the particles of the solid and the liquid. Analogously, the appearance of a three-dimensional crystalline nucleus is facilitated by the presence of a solid surface, the magnitude of this decrease depending on the nature of the surface on which the formation of the nucleus occurs. In order to obtain an idea of the effect of the nature of the surface, we can use Eq. (260) from which it is evident that the work A will be less if the quantity σ_{12} at the interface between the existing and newly formed phases is less. Hence a similarity between the crystal lattices of the two phases facilitates the formation of a crystalline nucleus.

As is evident from the foregoing, the phenomena observed during the formation of a nucleus of a new crystalline phase are in many respects analogous to those observed during the formation of a drop, although large quantitative differences can exist between these two cases, even if they are merely due to the fact that the surface tension σ of solid bodies is much greater than that of liquids.

An important difference between the liquid and solid phase is found when we examine the conditions of their further growth. While in the case of the liquid surface a further combination of particles with the previously formed drop takes place without impediment, the formation of every new layer at the face of a growing crystal encounters difficulties somewhat similar to those which appear during the formation of a crystal nucleus. This is due to the circumstance that different atom positions (here we limit consideration to the case of an atomic lattice) at the faces of a growing crystal are energetically nonequivalent. Let us elucidate this by means of several simple examples.

Let us visualize the facet of a crystal in the cubic system, divided into several elementary cells like a chessboard. Let us consider the different positions of an atom on this facet from the point of view of their bond strength. Assuming the atom, represented in the form of a cube, is in the middle of the face (Fig. 101a); such an atom has only one near neighbor, namely the atom which is under it. The interaction of this atom with the surface is determined to a large extent by the interaction with this single atom which is directly below it and not with the more remote atoms which form the crystal lattice. It is obvious that the position of the atom shown in Fig. 101a is not energetically advantageous. The position of the deposited atom is more favorable if it adjoins a complete row (the atoms marked with a cross in Fig. 101b) because in this case it has two near neighbors. An even greater energy gain is obtained when the atom is deposited in the position marked with a cross in Fig. 101c, when the atom continues a row which has already been started and is contiguous to a previously completed row; in this case the atom has three nearest neighbors. If the filling of a new plane with fairly large dimensions takes place consecutively, one row after another, the deposition of most atoms takes place under conditions corresponding to the last case examined by us (the so-called case of the repeating step).

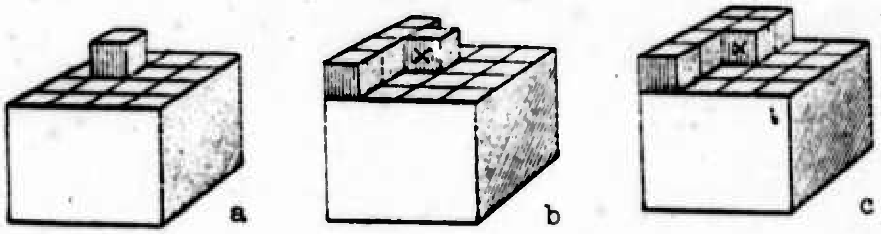


Fig. 101. Di-ferent positions of an atom on growing facet of a crystal.

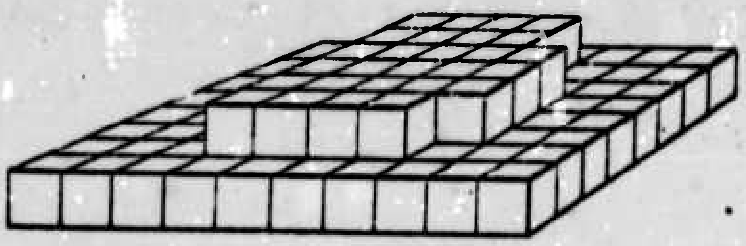


Fig. 102. Schematic representation of a two-dimensional nucleus on a growing crystal face.

It is clear from the foregoing that the atoms on a partly filled surface of a crystal face are not energetically equal; the atoms at the edges of the filled section have an excess of free energy compared with the atoms which are in the center. In the case of a three-dimensional body the energetic inequality of the atoms in the volume and at the surface causes the appearance of surface tension; for "two-dimensional" bodies, i.e., for formations consisting of a single molecular layer, we must analogously introduce the concept of the peripheral tension ρ. The product of the peripheral tension and the length of the perimeter l, bounding the occupied surface of the face (Fig. 102) defines the excess free energy in such a two-dimensional body compared with the energy contained in the same quantity of substance which forms part of a filled plane of infinite size. In the case of a two-dimensional crystal which interests us, the magnitude of ρ naturally depends on the direction of the linear boundary in the same way as the magnitude of σ depends on the orientation of the crystal face.

Using these concepts we can find several relations analogous to Eqs. (251), (256) and (257) but relating to a two-dimensional crystal. Thus it can be shown that between the oversaturation and the linear dimensions of the two-dimensional crystal, which is thermodynamically stable at the given oversaturation, exists a relationship analogous to Eq. (251), which, however, contains instead of the surface tension the peripheral tension ρ. This relation determines the size of the two-dimensional crystal which can serve as nucleus for the formation of a new layer on the given face. For the work of formation A_1 of such a nucleus we obtain an expression which differs from the expression for the work of formation of a three-dimensional nucleus (257) only by the numerical coefficient:

$$A_1 = \frac{1}{2} \sum \rho_i l_i. \qquad (261)$$

The summation in the right part of Eq. (261) must be carried out over the entire length of the perimeter which limits the two-dimensional nucleus. Between the probability of the appearance of a two-dimensional nucleus and the quantity A_1 exists a relation which is completely analogous to Eq. (256),

$$W_1 = B_1 e^{-\frac{A_1}{kT}}, \qquad (262)$$

where B_1 is also a proportionality factor.

The concepts presented here give the following picture of crystal growth. In presence of a certain (slight) oversaturation two-dimensional nuclei of a new layer can be formed fairly frequently on the terminal layer. Such a nucleus appears, etc. Thus, the growth of the crystal takes place in layers, each layer having a thickness of the order of molecular dimensions.

In some cases, for example, during the growth of paratoluidine crystals from its vapor, it has actually been possible by means of perfected optical methods to observe the appearance of mono- or dimolecular layers with constant thickness on the surface of the growing crystal. More frequently, however, these layers form a thicker layer; several successive layers fuse into a single layer whose boundary moves along the surface of the growing face. The cause of this transition to relatively thick layers has not yet been fully elucidated; we shall consider one possible cause of this phenomenon in the following.

It must be pointed out that the pattern of crystal growth as presented in the foregoing is extremely simplified. In particular, we have constantly assumed that the shape of the growing crystal is ideally regular. Real growing crystals invariably show deviations from this ideal structure, particularly in the case of marked oversaturation. As a more detailed theory shows, the presence of such deviations reduces the work of formation of the two-dimensional nuclei and lowers the supersaturation limit at which crystal growth at a noticeable rate is still possible [9].

§4. FORMATION AND GROWTH OF THE METALLIC PHASE DURING THE PROCESS OF ELECTRODEPOSITION

The basic conclusions which we have derived during the examination of the conditions of the appearance and growth of crystals, can be applied to the processes of electrodeposition. However, whilst the probability of the formation of three-dimensional and two-dimensional nuclei during the normal crystallization process is determined by the oversaturation, in this case, in which the transition of a particle from the solution into the metal lattice is effected by imparting an electrical charge to it, the role of the oversaturation is played by the additional (with respect to the equilibrium potential) potential difference at the metal/solution interface, i.e., the electrode polarization. The difference of the chemical potentials $\mu - \mu_s$ of the substance in the state of an equilibrium nucleus and in the massive form in the case of crystallization from supersaturated solutions is equal to $RT\ln(c/c_s)$, whereas in the case of electrodeposition this quantity can be expressed by the difference of the electric potentials, i.e., the magnitude of the polarization η_K. Thus, according to Eq. (259),

$$\mu - \mu_0 = nF\eta_K = \frac{2\sigma_{10}v}{h_i}. \qquad (263)$$

This equation enables us to establish a relationship between the dimensions of the nucleus and the polarization η_K which is specifically connected with the formation of the nucleus [7]. In the case when an impoverishment of the solution with regard to the metal ions takes place at the same time, the quantity η_K is added to the concentration polarization.

The relations (257) and (256) which define the work of formation of the nucleus and the probability of its appearance, remain in force for the case of electrodeposition as well. Thus we are enabled to determine the minimum polarization at which separation of a metal on a foreign surface can take place within an observable interval of time. Using this approach, Volmer calculated the minimum overvoltage during the separation of mercury from a dilute solution of mercuric acetate on carbon. It was necessary in this case to introduce a correction for the fact that mercury, although only slightly, nevertheless wets carbon and, consequently, the work of nucleus formation is reduced. The minimum polarization thus calculated was 0.34 v; the experimental value was about 0.2 v.

The concepts used here are somewhat analogous to those mentioned by us in Chapter 5 of the theory of hydrogen overvoltage which connected the polarization during the separation of hydrogen with the oversaturation, necessary for the formation of gas bubbles. However, the work required for the formation of a gas bubble is relatively small, and the polarization connected with this stage of the process of hydrogen separation can be neglected compared with the electrochemical polarization involved in the discharge of the hydrogen ion (with the exception of the case in which the gas evolution takes place at a cathode with very low overvoltage). The situation is different in the case under consideration here of the formation of a nucleus of the metallic phase, because the work of formation of such a nucleus, due to the large value of the interfacial tension, is large while the electrochemical polarization (for example, during the discharge of mercury ions) can be very small.

The polarization phenomena occurring during the separation of a new crystalline phase were studied by A.G. Samartsev and K.S. Yevstrop'yev [10]. According to the data of these authors, the cathode potential during the electrodeposition of solid metals on a foreign base with constant current intensity is a function of time, similar to that shown in Fig. 103. The quantity of electricity supplied from outside is first consumed for the charging of the cathode surface, whose potential is shifted to the negative side (and also in the formation of an adsorbed layer of the atoms of the separated metal, see further on). When a certain "initial overvoltage" is attained, sufficient for the separation of the nucleus and the appearance of crystallization centers, the discharge of the metal ions begins. Because the growth of a previously formed crystal can take place at a considerable rate at an overvoltage which is less than that required for the formation of the nucleus, part of the overvoltage is taken off and the potential assumes a less negative value.*

By substituting the value of η_K from Eqs. (263) and (259) into Eq. (255), we can find the relation between the quantity A and η_K:

$$A = \frac{16\pi\sigma^3 v^2 n^2 F^2}{3\eta_K^2}. \qquad (255a)$$

From Eqs. (255a) and (256) follows

$$W = Be^{-\frac{k_1}{\eta_K^2}}, \qquad (256a)$$

where k_1 is a constant. Assuming that the time τ required for the formation of a nucleus on the electrode during constant overvoltage η_K is

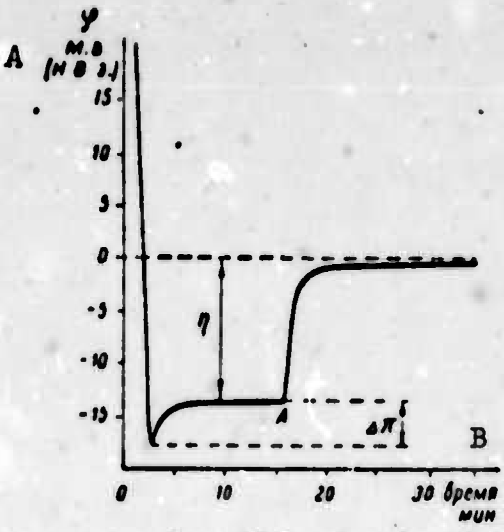


Fig. 103. Polarization curve for the electrodeposition of a metal on a foreign surface; Δπ) Initial increase in overvoltage; η) stable overvoltage during prolonged passage of current. The point *A* corresponds to the moment of interruption of the current. A) mv (n.v.e.); B) time, minutes.

inversely proportional to its probability *W* of appearance, the Bulgarian scientists R. Kaishev, A. Sheludko and R. Bliznakov [11] subjected Eq. (256a) to experimental verification for the case of the deposition of silver on a platinum electrode, by measuring the value of τ and confirmed its correctness.

In the case of incipient electrodeposition of ions on the surface of the same metal, a direct continuation of the lattice of the base is not always possible and the process can often take place only by formation of new three-dimensional nuclei as in deposition on a foreign base. This can be observed, for example, when the metal surface is covered with an oxide film; in other cases, as will be shown further on, the presence of adsorbed organic substances is sufficient.

At potentials at which the formation of a three-dimensional nucleus is not yet possible, the metal ions can be discharged with the formation of atoms which are adsorbed on the electrode surface or dissolved in its surface layer. These phenomena are in many respects analogous to the formation of adsorbed layers of hydrogen on platinum at potentials at which separation of hydrogen into the volume does not yet take place. The electrochemical properties of such adsorbed layers can be successfully studied, as has been shown in particular by the investigations carried out in the laboratory of the French scientist F. Joliot-Curie [30], when solutions containing compounds of radioactive elements in strong dilution are used as electrolytes. The quantity of deposited substance is determined in this case on the basis of the radioactivity acquired by the electrode.

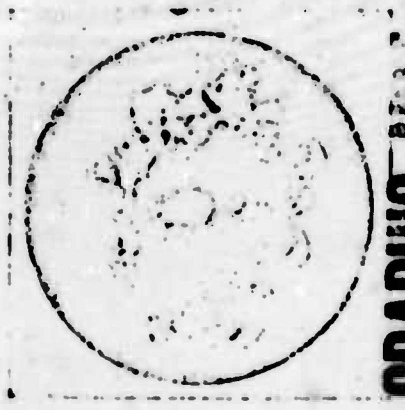


Fig. 104. Formation of a "halo" around a growing crystal in consequence of the lowering of the probability of formation of new nuclei caused by impoverishment of the solution.

During the growth of a newly formed nucleus an impoverishment of the solution around it takes place, i.e., concentration polarization takes place which inhibits the formation of new nuclei in its vicinity. Hence when metal is deposited on a cathode on which the formation of new crystal nuclei is made possible by an increase in current density, "haloes" are observed around the growing crystals which are free of new crystallization centers (Fig. 104) [12].

According to Erdey-Gruz and Volmer, crystal growth during electrodeposition, as in the case of normal crystallization, takes place in layers in consequence of the formation of two-dimensional nuclei, which grow and fill the surface of the crystal face. On the basis of Eqs. (261) and (262) it is possible to connect the probability of the formation of a two-dimensional nucleus and, consequently, the growth rate of the crystal, with the polarization. Several attempts have been made in this direction [13], but the relations obtained to date have not been sufficiently confirmed in the interpretation of the experimental polarization curves. There is no doubt that the phenomena observed during the growth of real crystals are much more complex than the simplified pattern discussed in the foregoing.

Fig. 105. Layerwise growth of the basis face of a zinc crystal (1280 × magnification).

Observations on the faces of growing crystals show that not layers of molecular dimensions but relatively thick "packets" which are readily visible under the microscope (Fig. 105, according to K.M. Gorbunova) extend over the surface of the crystal face. The growth front of this packet can have a stairway structure which is easily visible in the diagram, but even the individual steps consist of many hundreds or thousands of elementary layers. By means of microkinematography it is possible to observe the movement of the growth front of the packet along the crystal face. At the growth front of the packet a rapid discharge of metal ions takes place and an impoverishment of the solution occurs which causes concentration polarization. If the dissolved electrolyte is replenished, for example, by directing a flow of solution against the growth front, the direction of propagation of the packet can be influenced [14].

The question as to why the individual elementary two-dimensional nuclei aggregate to thicker packets is of considerable interest. This aggregation should reduce somewhat the surface energy of the growing crystal and in this sense it is energetically advantageous but the problem of its molecular mechanism has not yet been elucidated. It is possible that the existence of passivation phenomena, which will be discussed in §5 of the chapter, promotes the almost simultaneous appearance of a large number of two-dimensional nuclei arranged one above the other. The phenomena observed during layerwise growth were discussed by K.M. Gorbunova and P.D. Dankov, taking into account the work required for the formation of the two-dimensional nucleus and the concentration polarization [14].

A large number of studies has been devoted to the elucidation of the dependence of the polarization on the current density during the electrodeposition of metals. The interpretation and comparison of the data thus obtained presents great difficulties, connected primarily with the determination of the true current density. On a growing crystal face the discharge of ions at any moment of time takes place along the growth front of the packets and, probably, predominantly at the end of the unfinished rows of atoms and not over the entire area of the face. Moreover, as will be discussed further on, all faces of the crystal normally do not grow simultaneously. Hence the mean current density relating to the total geometrical surface of the crystal often does not have a definite physical meaning. Nonetheless various qualitative conclusions in this area can be indicated which have been fairly strongly established.

In some cases the polarization during the electrodeposition of metals is very low and is mainly concentration polarization. This has been shown in particular detail for the case of the deposition of silver from solutions of silver nitrate [12]. According to N.T. Kudryavtsev, the polarization is mainly of a concentration nature also in the case of the deposition of zinc from zincate solutions [15]. O.A. Yesin [16] believes that during the separation of zinc from complex cyanide solutions the polarization observed in this case is due to a delay of the discharge and during the separation of copper from similar solutions only concentration polarization is observed. The predominant concentration nature and the small total polarization during the separation of silver from an $AgNO_3$ solution shows that the work of formation of the two-dimensional nucleus on an uncontaminated face of a growing silver crystal is small. The temperature dependence of the polarization occurring during the electrodeposition of metals has been studied by S.V. Gorbachev [31].

During the electrodeposition of the metals of the iron group, a considerable electrochemical polarization is observed and an approximately linear relation between the polarization and the logarithm of the current density, if the polarization is fairly high. The polarization in this case, however, is somewhat less than during the deposition of the same metals on the mercury cathode (curve 2, Fig. 100). At low polarization, as in the case of hydrogen separation, the polarization is a linear function of the current density.

V.A. Royter, V.A. Yuza and B.S. Poluyan compared the polarization during the electrodeposition of iron, which they consider to be due to a delay of the discharge, with the polarization during the electrodeposition of zinc [18. In order to avoid the effect of surface variations caused by crystal growth during electrodeposition, the authors used the oscillographic method. According to these authors, the discharge of iron ions takes place 1000 times more slowly than the discharge of the zinc ions at the same polarization.

It should be pointed out, however, that the polarization during electrodeposition, for example, of nickel, cannot be completely explained by a delay of the discharge stage [19].

The determination of the laws which connect the polarization during the electrodeposition of metals with other physicochemical properties, is made difficult not only by the inaccuracy of the measurement of the true current density but also by the strong influence exerted on the process of electrodeposition by oxide films which are present on metal surfaces in many cases and which increase the work of formation of crystal nuclei compared with their work of formation on a clean metal surface.

Up to now we have almost exclusively dwelt on the individual elementary stages of the process of electrodeposition, the discharge of ions and the appearance and growth of an individual crystal. The problems which we encounter when we consider the conditions of formation of galvanic coatings, are much more complex.

B.S. Yakobi has already pointed out the need for a detailed study of the influence of the electrolysis conditions on the properties of the metallic coatings obtained by electrodeposition. A beginning in the modern investigations in this field in our country was made by the work of N.A. Izgaryshev and co-workers. The practically useful coatings are formed from a large number of fine crystals which frequently show a certain preferred orientation. If the coating should have good protecting properties it is essential that the crystals are strongly adhering to each other and to the base to which the coating is applied; furthermore, the coating must be free of pores. The nature of the deposit is obviously determined by the conditions of the formation and growth of the individual crystals, and all factors which influence these processes (such as temperature, composition and concentration of the solution, current density, mixing conditions, presence of complexing agents in the solution, which increase the electrochemical polarization, the presence of adsorbed organic compounds in the form of a true or colloidal solution) affect also the quality of the coatings thus formed. We cannot dwell here in greater detail on these questions which are considered in special courses on electroplating.

Investigation of the crystal structure of the metallic coatings by x-ray diffraction, electron microscopic and particularly electron diffraction leads to interesting conclusions. If the electrodeposition is carried out on the surface of a metal crystal, the crystal lattice of the deposit is orientated in such a way that the layer of atoms is parallel to the atom layers in the original crystal. The orientating effect of the base takes place if the difference in the lattice constants of the original metal and that formed during the process of electrodeposition is not too great (not exceeding about 15%); the orientation extends over a relatively large distance in the depth of the growing deposit, amounting to some tenths of a micron or even several microns. This effect disappears at greater distances so that the orientation of the crystallites is now determined by the electrodeposition process and is independent of the structure of the base. The orientating effect also disappears when large current densities are used, in which case a large number or randomly orientated crystallites are formed [20].

The phenomena of electrodeposition are also complicated by another circumstance. At the potentials at which the electrodeposition of many metals takes place, a discharge of hydrogen ions (particularly when the pH of the solution is not too high) can also take place in addition to the discharge of the metal ions. The relative distribution of the current between the reactions of metal ion and hydrogen ion discharge is determined by the ratio of their concentrations in the solution and also by the magnitude of the hydrogen overvoltage [21]. The simultaneous separation of hydrogen not only lowers the current yield of the metal but can also cause a disturbance of the conditions of growth and adhesion of the crystallites of the deposit. In some cases in which a large hydrogen overvoltage prevents the separation of hydrogen in molecular form, the dissolution of hydrogen in the metal lattice and formation of adsorbed layers of hydrogen atoms can disturb the regularity of the crystal lattice of the metal. During the deposition of antimony from acid solutions at high current densities the growth delay of the crystals, caused by the presence of adsorbed hydrogen and dissolved hydrogen has the result that the deposits have an amorphous structure. Dissolved hydrogen has a strong effect on the properties of electrolytically deposited Fe and Ni by slowing down the process of their transformation into ions [22].

§5. EFFECT OF SURFACE-ACTIVE SUBSTANCES ON THE ELECTRODEPOSITION OF METALS

As indicated in the foregoing, the electrochemical reaction of the discharge of the ions of various metals can be very fast but this reaction can be inhibited by the adsorption of impurity substances on the electrode such as, for example, the adsorption of oxygen (with formation of oxide layers) and particularly the adsorption of organic compounds. The source of the organic surface-active substances are either special additions to the solution or fortuitous contamination of the solution. The processes of the formation and growth of metal crystals are highly sensitive to the adsorption of organic substances, and deposits with special properties can be obtained in some cases, for example, bright deposits, only if certain surface-active compounds are added.

Various results of general interest were obtained during the study of the comparatively simple reaction of the electrodeposition of silver from silver nitrate solution. The phenomenon which is often termed cathodic passivation of the faces of the growing crystal [12] is particularly clearly evident in this case although its mechanism differs from the mechanism of the normal passivation of metals which will be discussed in the next chapter.

This phenomenon can be observed, for example, under the following conditions. Assuming that we interrupt the current for a certain length of time during the growth of the silver crystal. If it is then again switched on, the overvoltage proves to be higher. The increase in the overvoltage is due to the fact that the nature of the growth has changed. Instead of a continuance of the growth of the crystal face which has grown up to the moment of switching off of the current, a new crystallite appears on it which is sometimes microscopically distinguishable from the original crystal. In other cases, for example, if the interruption of the current is shorter, only part of the growing crystal face may prove to be passivated. This phenomenon depends on the presence of foreign adsorbed substances in the solution and disappears if the solution is very carefully purified. An adsorption of the dissolved impurities takes place on the surface of the metal and these accumulate on the surface in relatively large quantity when the current is interrupted. This makes a normal growth of the faces with formation of two-dimensional nuclei practically impossible and to continue the growth the potential must be increased to a value at which new three-dimensional nuclei appear. If a part of the surface remains unpassivated, the increased effective current density in this case also results

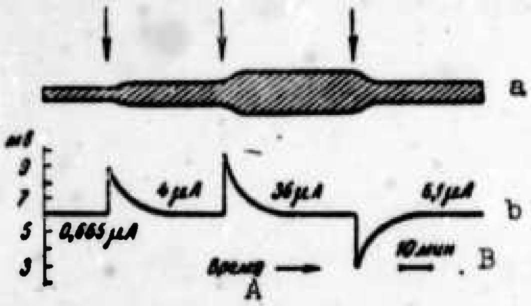


Fig. 106. Variation of the diameter of a growing silver crystal (a) and of the p - larization with variation of current intensity (b). The moments of the increase and decrease of the current density are indicated by arrows. A) Time; B) minutes.

in an increase in the overvoltage [12].

The influence of the adsorption of impurities is also felt during normal growth without interruption of the current. If the deposition of silver from a solution of silver nitrate is carried out with weak current, only a single crystal grows at the electrode and its growth is accomplished in such a way that a thin filament (dendrite) is formed. This form of growth depends on a difference in the adsorption of surface-active substances at different faces of the crystal. The faces of the crystal on which the substance is strongly adsorbed, do not grow, and the face with a relatively clean surface grows without hindrance [12].

A typical phenomenon, detected by A.G. Samartsev [24] is observed during variation of the current intensity. It would be natural to expect that when the current intensity is increased, the growth rate of the filament would also increase. Actually, however, this is not the case. When the current density increases, at least within a certain interval, the cross section of the crystal increases proportionally to the current (Fig. 106a, according to A.T. Vagramyan) so that the current density and, consequently, the growth rate, remain constant.

According to A.T. Vagramyan [12] and K.M. Gorbunova [17] this peculiarity of the electrochemical growth of a filamentary single crystal can be explained in the following manner. The newly appearing metal surface is contaminated by the substance adsorbed from the solution at a certain rate. If the rate of formation of the new surface is less than the rate of passivation, further separation of the metal on this surface is impossible. Hence, if the current density is decreased, growth stops at the edges of the growing face where the rate of passivation is greater because of the more favorable conditions of supply of the adsorbed substance from the solution and the growth front is narrowed while the linear growth rate of the filament returns to the previous value. If, conversely, the intensity of the cathodic current is increased, passivation cannot occur at the edges of the face either and the face will be enlarged as long as the current density and the linear growth rate of the filament do not return to the previous value. Thus the same current density is always established in time, i.e., a certain linear growth rate of the crystal fiber which corresponds to stationary passivation conditions.

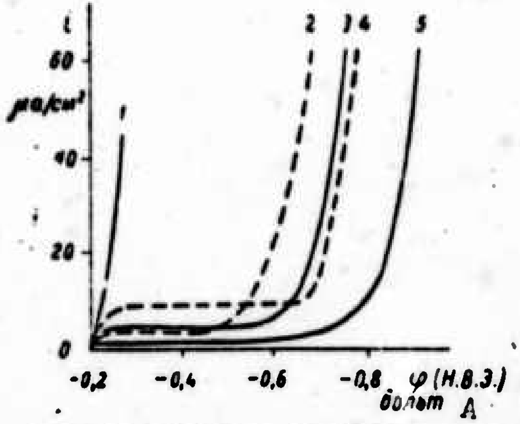


Fig. 107. Polarization curves during the electrodeposition of tin in presence of surface-active substances: 1) Pure solution of 0.25 N $SnSO_4$; 2) in presence of 0.005 M diphenylamine; 3) 10 g/liter cresol sulfonic acid and 1 g/liter gelatin; 4) 0.005 M α-naphtol and 1 g/liter gelatin. A) Volt (n.v.e.).

The conclusion that the growing part of the surface always has a constant activity was confirmed by A.T. Vagramyan by polarization measurements. If the current intensity is increased, the overvoltage first increases sharply but then in proportion to the increase in the surface area of the face it gradually comes down to the previous moderate value; analogous polarization variations, but in the reverse sequence, take place when the current intensity is decreased (Fig. 106b).

The phenomena of contamination described here are not observed in cyanide solutions, in which, as follows from direct experiments, the adsorption of organic substances is inhibited (evidently because of a structure of the double layer which is unfavorable for the adsorption process). A surface which had previously been passivated by contact with silver nitrate solution, can be again activated by immersion in a solution of potassium cyanide. This causes a desorption of the organic substances, and the normal growth can be continued in the previous solution after the potassium cyanide has been washed off [12].

Organic substances can affect the processes of electrodeposition in two ways. If the rate of adsorption of the organic substance is fairly low compared with the rate of formation of the new surface, then, as is evident from the foregoing, the uncontaminated part of the surface grows. The overvoltage varies only as a function of the variation of the true current density but calculated for the true current density it remains constant. At the value of the overvoltage established under these conditions the probability of the formation of new nuclei on the passivated part of the surface is too small so that growth ceases on this part of the surface.

Another case is also possible, where the rate of adsorption is fairly high and the ions must be discharged at a surface, covered with an adsorbed layer. In this case one can expect a considerable increase in the overvoltage of the electrodeposition process. N. A. Izgaryshev and co-workers were the first to study the influence of surface-active substances, particularly of colloids, such as, for example, gelatin, on the polarization during the discharge of metal ions and discovered various typical features of this phenomenon [23]. N.A. Izgaryshev believed, however, that the principal cause of the overvoltage variation is the complexing of the metal ions by the organic substances in the volume of the solution.

The laws observed during the electrodeposition of metals on a surface covered with an adsorption layer were established in the works of M.A. Loshkarev [25] which were based on the following observation. Addition of certain surface-active substances to tin salts causes the formation of fine-grained, dense deposits. In this case, particularly when a mixture of several surface-active substances, such as, for example, β-naphtol + diphenylamine + thymol, is used, polarization curves with unusual shape are observed: over a broad potential range the current remains constant independently of the polarization and begins to increase markedly only upon further increase in the polarization (Fig. 107). This limit current density is by far less than the limit diffusion current under experimental conditions and cannot be explained by impoverishment of the solution.

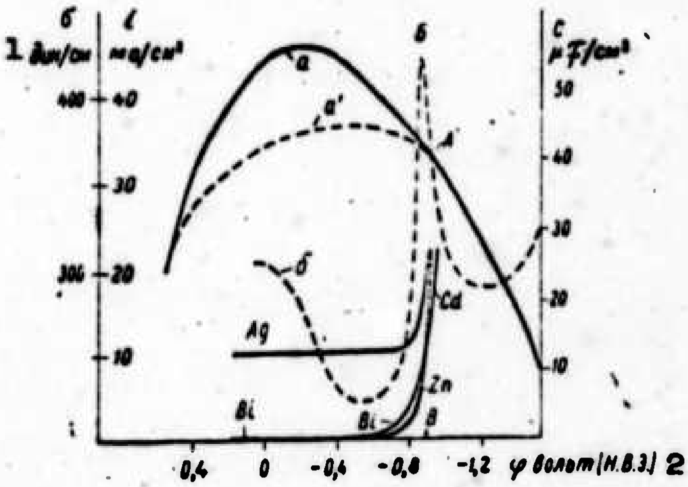


Fig. 108. Polarization curves measured on the mercury drop electrode in 0.05 N solutions of Bi, Cd, Zn and Ag salts in presence of 0.1 H_2SO_4 and surface-active additions. The rise of the polarization curves occurs at the potential *V* corresponding to the limit of the adsorption range. At this same potential the curve of the differential capacitance *b* has a maximum *B* and the electrocapillarity curves (at the point *A*) of the pure Na_2SO_4 solution *(a)* and the same solution saturated with β-naphtol, thymol and diphenylamine *(a')* fuse. 1) Dyne/cm; 2) volt (n.v.e.).

Later it was found that these phenomena are not only observed in the case of electrodeposition of metals (lead, copper, bismuth, cadmium) in the solid state but also during the separation of various metals on the mercury drop electrode. A comparison of the polarization curves with the capacitance measurements showed that the increase in the current density is observed within the potential range in which there is a maximum on the capacitance curve (Fig. 108). As has been explained in the Introduction, the appearance of a sharp maximum on the curve of the capacitance as a function of potential indicates the limit of the adsorption range of the organic substances. This range, as is evident from Fig. 108, is at the same time the range of low values of the limit current. Thus, a low limit current is observed only in presence of an adsorbed layer. When the adsorbed layer disappears owing to an increase in the negative potential difference, the current intensity increases. This conclusion applies to the case of a liquid as well as a solid metal surface.

It could have been assumed that the adsorbed layer contains pores and that the discharge of ions takes place only in these pores. This hypothesis is contradicted, however, by the circumstance that the effect of the surface-active substances on the discharge of metal ions is highly selective. Thus, for example, for a large number of organic additives (although not for all of them) it is slight or altogether absent in the case of the discharge of mercury or univalent thallium ions. It is easy to show that the presence of these ions does not destroy the adsorbed film. Indeed in presence of octyl alcohol during the electrolytic reduction of a solution containing at the same time $S_2O_8^-$ and Hg_2^{++} ions, the adsorbed layer of octyl alcohol completely inhibits the discharge of the $S_2O_8^-$ ions and, consequently, is not impaired. In spite of this the discharge of the mercury ions takes place without

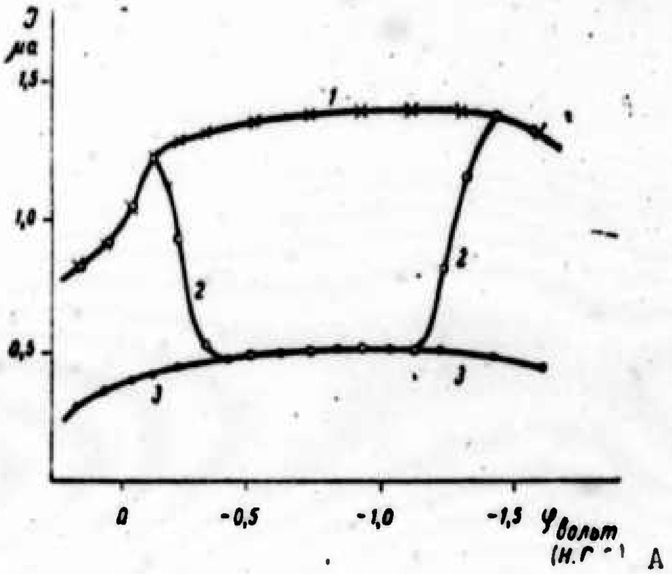


Fig. 109. Effect of an adsorbed layer of normal-octyl alcohol during the simultaneous discharge of $S_2O_8^{=}$ and Hg_2^{++} ions. The polarization curves were obtained on the mercury cathode in the solutions: 1) 1 N Na_2SO_4 + 7.10^{-5} N $Hg_2(ClO_4)_2$ + 1.2 M $K_2S_2O_8$; 2) the same solution, saturated with normal octyl alcohol; 3) 1 N Na_2SO_4 + $7 \cdot 10^{-5}$ N $Hg_2(ClO_4)_2$. In the range of adsorption of the octyl alcohol the curves 2 and 3 coincide, i.e., the reduction of the $S_2O_8^{=-}$ ions ceases completely while the reduction of the Hg_2^{++} ion takes place unimpeded. A) Volt (n.v.e.).

hindrance (Fig. 109).

Analogous phenomena are observed during the electrolysis of solutions containing two metal cations, for example, Cu^{++} or Cd^{++} and Tl^{+}; one of these is strongly inhibited by the adsorption layer and the other only slightly.

This selectivity cannot be explained on the basis of the assumption of the presence of pores in the adsorbed layer and the sole possible explanation is that the discharge of the ions requires their prior penetration to the electrode surface through the adsorption layer for which a certain activation energy is necessary, depending, obviously, on the nature of the ion as well as the nature of the adsorption layer. In this case the kinetics of the process as a whole are determined by the stage which precedes the electrochemical process proper; in the potential range in which a fairly strong adsorption layer exists, the rate of this stage should naturally be independent of the potential difference metal/solution, which also accounts for the appearance of the practically constant limit current.* The applicability of the last conclusion is limited by the fact that the adsorption intensity and, consequently, the structure and permeability of the adsorption layer themselves depends on the limit potential difference (see §7 of the Introduction). This becomes particularly evident when the desorption potential is approached: the work of adsorption of the adsorbed molecules decreases in this case which facilitates the penetration of ions into the absorbed layer and leads to a regular increase in the current. When the desorption potential is reached, the film of adsorbed substance is removed and the rate of the electrochemical process is then limited only by the limit diffusion current.

§6. THROWING POWER

Let us briefly examine one other practically important quantity which characterizes the processes of electrodeposition. Assuming that it is required to coat a surface with a certain relief on which, for example, there are deep recesses, with a smooth layer of a metal deposit. It is obvious that under otherwise equal conditions, owing to the presence of ohmic resistance of the solution, the mean current density on the bottom of these recesses should be less than on the remainder of the surface and the thickness of the deposit is also correspondingly less. However, as experience shows, the degree of nonuniformity of the distribution of the coating differs depending on the electrolyte composition. Some solutions give a relatively smooth coating even in presence of a deep relief; in such cases it is said that the electrolyte has a great "throwing power" or "works well in depth"; other electrolytes do not have this practically valuable property.

Let us explain on the basis of a simplified example the physical factors, which characterize the passage of current through the system, on which the throwing power depends. To this end let us imagine that

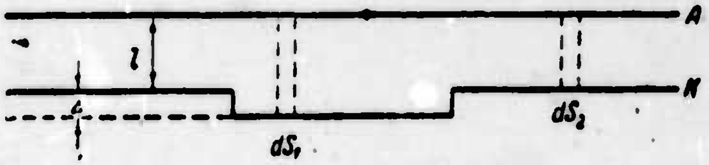


Fig. 110. Current distribution in presence of recesses in the electrode.

the cathode has the profile shown in Fig. 110, i.e., that it has a wide (compared with its depth Δ and the distance between the electrodes l) depression with a flat bottom, and let us examine the current distribution in this system. We isolate two surface elements of the cathode dS_1 and dS_2, in the recession and on the level surface which are fairly remote from the edge of the recession. When this condition is fulfilled, the current lines passing from the anode to the cathode are directed perpendicularly to the cathode surface, and the potential variation along their path is easy to calculate. We designate by φ_A the potential difference anode/solution (considering the anode unpolarized), by $(\varphi_K)_1$ and $(\varphi_K)_2$ the potential differences cathode/solution at the parts dS_1 and dS_2, by i_1 and i_2 the corresponding current densities and by w the specific resistance of the solution. Owing to the high electrical conductivity of the metal the potential within the cathode and anode has practically a constant value at all points, from which follows that

$$(\varphi_K)_1-(l+\Delta)\,i_1w-\varphi_A=(\varphi_K)_2-l\,i_2w-\varphi_A. \qquad (264)$$

The quantity $(\varphi_K)_2$ can be expressed by $(\varphi_K)_1$ if φ_K as a function of i is known. Assuming that the potential variation is slight, we find:

$$(\varphi_K)_2 = (\varphi_K)_1 + \frac{\partial\varphi_K}{\partial i}(i_2 - i_1). \tag{265}$$

From Eqs. (264) and (265) follows

$$\frac{i_2 - i_1}{i_1} = \frac{\Delta}{-\frac{1}{w}\frac{\partial\varphi_K}{\partial i} + l} = \frac{\Delta}{\frac{1}{w}\left|\frac{\partial\varphi_K}{\partial i}\right| + l}. \tag{266}$$

It can be concluded from Eq. (266) that the relative nonuniformity of the current distribution and, consequently, the relative variation of the thickness of the deposit, equal to $(i_2 - i_1)/i_1$ depends on the ratio of the polarization of the cathode $|\partial\varphi_K/\partial_i|$ and the specific resistance of the solution.* If this ratio is small compared with l (i.e., $1/w|\partial\varphi_K/\partial_i| << l$), the first term in the denominator of the right part of Eq. (266) can be neglected compared with the second, and consequently,

$$\frac{i_2 - i_1}{i_1} \sim \frac{\Delta}{l}. \tag{267}$$

In this case the current distribution depends only on the ohmic resistance along its path and the quantity $(i_2 - i_1)/i_1$ attains the maximum possible value. The cathode is covered with a nonuniform deposit and the bath, as it is termed, has a low throwing power.

A different pattern results when the ratio $1/w|\partial\varphi_K/\partial_i|$ is large compared with l. In this case, as is evident from Eq. (266), the quantity $(i_2 - i_1)/i_1$ can be made as small as desired, which gives any desired degree of uniformity of the deposit thickness. Formally, the same result could have been obtained if the cathode surface had been covered with a thin layer of a substance with large specific resistance. The quantity $|\partial\varphi_K/\partial_i|$ whose dimension is ohm × cm^2, plays the part of a surface resistance although the physical nature of the inhibition of the current penetration in this case is different than in the case of ohmic resistance. The quotient obtained by dividing this quantity by the specific resistance w of the solution can be regarded as a measure of the throwing power; it has obviously the dimension of length. The pattern of the current distribution, however, depends not on the absolute magnitude of $1/w|\partial\varphi_K/\partial_i|$ but on the ratio of it to the quantities l and Δ which determine the geometrical dimensions of the system. The greater l and Δ with their ratio constant, the greater should be the quantity $1/w|\partial\varphi_K/\partial_i|$ in order to attain a uniform current distribution. This can be easily verified by presenting Eq. (266) in the following form:

$$\frac{i_2-i_1}{i_1}=\frac{\frac{\Delta}{l}}{\frac{1}{wl}\left|\frac{\partial\varphi_K}{\partial i}\right|+1}. \qquad (266a)$$

These conclusions were derived for an extremely simplified geometrical model. It can be shown, however, that for other, more complex cases, the nature of the current distribution is also determined by the relation between the quantity $1/w|\partial\varphi_K/\partial_i|$ and a certain length, depending on the linear dimensions and shape of the system. Thus, if the internal surface of a narrow tube serves as cathode, opposite to the opening of which there is an anode [26], it is essential for a uniform current distribution over the tube surface that the quantity $1/w|\partial\varphi_K/\partial_i|$ should be large compared with l^2/r, where l is the length and r the radius of the tube. The following method can be used in practice to determine the throwing power in relative units: a Z-shaped bent electrode is coated with metal in a given bath, and the thickness of the metal deposit thus formed is measured at different points of the electrode. The throwing power of the bath is gaged by the degree of uniformity of the coating [27]. It should be pointed out that for reasons analogous to those given in the foregoing, the current distribution on the electrode also depends on the shape and disposition of the second electrode and on the presence of nonconducting bodies in the electrolyte solution [28].

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[Footnotes]

395 See, for example, N.K. Adam, Fizika i khimiya poverkhnostey [Physics and Chemistry of Surfaces], Gos. izd-vo tekh.-teor. lit-ry [State Publishing House for Technical and Theoretical Lit.], Moscow-Leningrad, 1947, page 27; E.K. Rideal, Khimiya poverkhnostnykh yavleniy [Chemistry of Surface Phenomena], Gos. izd.-vo tekh.-teor. lit-ry., Leningrad, 1936, page 36.

397 A certain modification must obviously be introduced also into Eq. (251) because the concept of radius is not applicable to a solid crystallite. For a crystallite of thermodynamic equilibrium shape we can always find a point whose distance h_1, h_2, ..., h_i from the crystal face satisfies the condition

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \ldots = \frac{\sigma_i}{h_i}, \qquad (258)$$

where σ_1, σ_2, ..., σ_i are the surface tensions of the corresponding faces (G. Vul'f). The value σ/r in Eq. (251) must be replaced in the case of a crystal by any of the ratios σ/h:

$$RT \ln \frac{c}{c_0} = \frac{2\sigma_i v}{h_i}. \qquad (259)$$

404 During the deposition of a metal on a foreign cathode under the influence of a current with constant intensity one can observe at the first moment of time after switching on of the current, in addition to the polarization due to the formation of nuclei, a noticeable electrochemical and concentration polarization, due to the fact that the current density on the newly formed very small nuclei attains considerable values.

420 In other cases the presence of adsorbed compounds, for example, aliphatic alcohols during the discharge of metal cations

does not cause a lowering of the limit current but only an increase in the overvoltage as is also observed during the discharge of the hydrogen ion under the same conditions (Chapter 3) [32].

422 Here we shall limit consideration to the simplest case when the cathodic process involves considerable electrochemical polarization as this is always the case in electrolytes with good throwing power. If the polarization is mainly of a concentration nature, the quantity $\partial\varphi_K/\partial_i$ can have different values at different points of the cathode because of the differences in the conditions of supply of substance which complicates the pattern of the phenomenon. We encounter such cases in the theory of the positive and negative polarographic maxima on the mercury drop electrode.

Manuscript Page No.	[Transliterated Symbols]
390	н.в.э. = n.v.e. = normal'nyy vodorodnyy elektrod = standard hydrogen electrode

Chapter 7

PASSIVATION AND KINETICS OF ELECTRODE PROCESSES

§1. PASSIVITY OF METALS AND OXIDE FILMS

In analogy to the acceleration of the discharge of metal ions upon transition to more negative potentials, the anodic processes of metal dissolution should be accelerated when the potential is shifted to the positive side. This phenomenon is indeed observed, for example, during the anodic polarization of nickel or iron in hydrochloric acid but in many cases a marked slowing down of the rate of metal dissolution takes place at sufficiently large values of positive potential and sometimes even simply when the duration of anodic polarization is increased.

Thus, for example, strong nitric acid is a powerful oxidant which can impart a high positive potential to a metal. At this potential a rapid dissolution of iron should take place if the relations between the rate of dissolution and potential were the same as during slight anodic polarization of iron in acid solutions. Actually, however, the chemical reaction which occurs when iron is immersed in strong nitric acid continues only for a short time, then stops, and the iron then remains practically completely stable. The accepted explanation is that the iron has gone over into a passive state (in contrast to the active state of iron which dissolves in hydrochloric or dilute nitric acid). The transition from the active to the passive state is termed passivation and the reverse process activation or depassivation of the metal.

The passivity of metals is of great practical importance because it is an important factor in the stability of metals such as iron and aluminum in many media. Hence it is natural that a very large number of studies deal with the problem of the origin of the passive state.

M.V. Lomonosov was the first to observe the phenomenon of passivation of metals. In the work of M.V. Lomonosov [1] "O deystvii khimicheskikh rastvoriteley" [On the Effect of Chemical Solvents] in §33 there is the following statement: "When one takes two different portions of the same acid spirit for the dissolution of metal, but one of them is slightly diluted with water, this dissolves a greater quantity of metal than the first ...," and a few lines further on in §34: "When fairly strong spirit of nitre is used for the dissolution of metal, the dissolution soon ceases ...." It is obvious from the foregoing that Lomonosov observed and described the phenomenon of passivation of a metal in strong nitric acid.

Faraday advanced a hypothesis according to which the passive state is caused by the presence of chemically bound oxygen at the metal surface. The "oxygen" theory of passivity was subsequently widely developed thanks to the work of numerous scientists, among whom we must mention specially the academician V.A. Kistyakovskiy, Evans and others.

Schoenbein and Hittorf advanced another hypothesis according to which a passive metal must be regarded as a special chemically inactive form of the metal. Views similar to this point of view are still defended by some German and American authors. Thus, V. Mueller [2] and his successors maintain an opinion which differs little from the Schoenbein hypothesis; according to Mueller a completely passive metal is the result of a "modification of the electron state" of the metal at the bottom of the pores in an insulating film which is formed in consequence of the passage of high-density current through the pores.

Uhlig [3] believes that passivity is due to the distribution of the electrons in the metal atoms: the passivity of the metals of the iron group arises as a result of the removal of electrons from the *d*-shell of the metal atom. Thus, the passivity of homogeneous alloys, according to Uhlig, is determined by the component which does not readily yield the electrons in its *d*-shell, the passivating component taking the electrons from the other component, which yields them more easily and the activation of the alloys takes place by the filling of this shell. The activating effect of oxygen is explained by Uhlig by the fact that the oxygen collects some of the electrons from the *d*-shell of the surface atoms of the metal. To prove his theory, Uhlig attempted to use the fact that the passivity of alloys (for example, Ni-Cu) is a function of their composition. However, as a more detailed analysis of the problem showed [4], the consequences of this theory often contradicted by the experimental data. Thus, according to these ideas, the passivity of stainless steel should increase with increase in the content of iron and not that of chromium.

The general objection to the explanation of passivity by a special allotropic or electronic state of the metal is based on the fact that the phenomenon of passivation is not accompanied by variations of the physical properties of the metal itself but by a variation of the stability of the adsorbed or phase films on its surface. From the thermodynamic point of view a passive metal is not more noble than an active metal. In all investigated cases of passivation, either a layer of salt or oxides is formed on the metal surface which forms a separate phase, or oxygen or some other substance is adsorbed in varying quantity.

The theory which connects the passivation with the formation of oxide or other layers on the metal surface has been completely recognized in the USSR, primarily due to the many-sided researches of Academician V.A. Kistyakovskiy and also the work of N.A. Izgaryshev, G.V.

Akimov and others.

V.A. Kistyakovskiy [5] discovered and studied the phenomena of partial and complete passivation which take place when a solution, containing a passivator (motoelectric phenomena). The mixing increases the supply of the substance which causes the transition of the metal to the passive state, to the metal surface, thus facilitating the onset of passivity. The important role of the composition of the solution in the passivation phenomena was demonstrated at the same time. It also follows from the work of V.A. Kistyakovskiy that the strong variation of the electrode potential taking place in consequence of the mixing of the solution is an indication that the electrode is not in equilibrium.

In the first works, passivity was regarded as a complete cessation of the anodic process of dissolution of the metal. Actually cases are observed and have great practical importance, in which the passivation of the metal does not result in a complete cessation of the anodic process (which, strictly speaking is not possible in principle) but to a strong inhibition. V.A. Kistyakovskiy was the first [5] to point out the significance of partial passivity of a metal. Thus, the problem of passivity gave rise to another problem, that of determining the connection between the state of the metal surface and the rate of the electrochemical processes which take place on the metal.

N.A. Izgaryshev showed by experiments in alcoholic and pyridine solutions that the passivity of Zn, Cd, Cu and other metals caused by dissolved atmospheric oxygen depends on the nature of the solvent; in solutions of salts in the above-indicated solvents the passive state is more readily attained than in aqueous solutions which is due to the lower rate of the electrode processes in these solvents. When oxygen reacts with the metal surface in presence of an organic solvent, a coupled oxidation of the molecules of the latter with formation of compounds of a peroxide nature takes place simultaneously [6]. The literature gives different definitions of the concept of passivation. The most correct definition is one according to which passivation consists in an increase in the overvoltage or in a delay of the anodic process of metal dissolution in consequence of an alteration of its surface, the formation of adsorbed or phase layers of oxides or salts.

The study of the passivity phenomena consists either in the measurement of the rate of the electrode processes which take place on the surface of the passive metal or in a study of the nature of the passivating layers. For the study of the variation of the rate of the anodic process of metal dissolution one uses the normal electrochemical methods of recording the polarization curves and charging curves, sometimes in combination with analytical measurements and the oscillographic method (for the study of fast processes). For the determination of the mean thickness of the passivating films one uses, in addition to the method of charging curves, the method described in the introductory chapter of capacitance measurement by means of alternating current and optical methods. A method has been proposed for the determination of the ohmic resistance and the breakdown voltage of the protective films on the metal surface, according to which drops of mercury are applied to the surface and the intensity of the direct current passing between the mercury and the test metal when a dc voltage is applied between them [7] is measured.

Different metals differ greatly with regard to the degree of their tendency to passivation. The creation of alloys on whose surface a stable passivating film, which increases their resistance to chemical action is readily formed, is of special importance from an engineering point of view. To these alloys belong primarily the so-called stainless steels which normally contain, in addition to iron, chromium and nickel or manganese and also small addition of various other elements such as, for example, titanium or niobium. A chemically and mechanically stable oxide film which practically stops corrosion of the steel under different conditions, for example, in air, in 10% HNO_3 or in sea water, is formed on parts of such alloys under the action of atmospheric air or water.

In the following we shall examine the problems of the passivation of metals predominantly in connection with the kinetics of electrochemical processes. A number of studies dealing with this aspect of the passivation phenomena on iron, lead and light metals were carried out by B.N. Kabanov and co-workers [8, 15]. Let us give some typical examples for the existence of a connection between the passivation of a metal the presence of oxide on its surface.

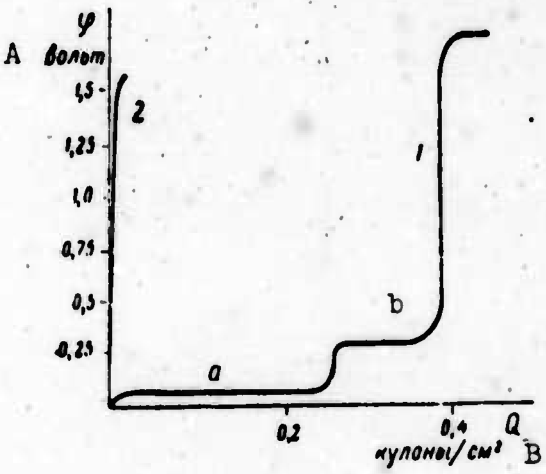

Fig. 111. Potential φ as a function of the quantity of electricity Q passed through for an iron electrode in 2 N NaOH: 1) Electrode surface freed of the oxide film by reduction in hydrogen; a) transition of the metallic iron to divalent iron; b) transition of the divalent iron to trivalent; 2) electrode subjected to the action of air for several seconds before immersion in the solution. The potential was measured against a hydrogen electrode in the same solution. A) Volt; B) coulombs/cm^2.

Figure 111 shows the potential of an iron anode in 2 N NaOH solution such as a function of the quantity of electricity passed through it. Curve 1 was obtained during the anodic polarization of iron from whose surface the oxide film had been previously removed by reduction in hydrogen at high temperature. The unpassivated iron continues to go into solution for a long time according to the reaction

$$Fe + 3OH^- = HFeO_2^- + H_2O + 2e$$
$$HFeO_2^- + H_2O = Fe(OH)_2 + OH^-.$$

The ferrous hydroxide which is only sparingly soluble in 2 N NaOH, is precipitated in the form of a deposit which envelops the electrode with a loose layer. The transformation of the iron into $Fe(OH)_2$ takes place at almost constant potential in consequence of which the horizontal section *a* is obtained in the curve 1. This process takes place during the discharge of the iron electrode of the alkaline battery. Curve 2, which almost fuses with the ordinate, was obtained during the polarization of iron which had been exposed to the effect of atmospheric oxygen at room temperature after the hydrogen reduction. As the diagram shows, this iron does not dissolve during anodic polarization, i.e., it is completely passivated. During the passage of current in this case the potential increases until it attains values at which the discharge of the hydroxyl ions becomes possible with evolution of molecular oxygen.

It is evident from the trend of curve 1 in Fig. 111 that in the case of an electrode with a surface which has been previously freed of oxygen, a passive state also supervenes in time. The area *a* of this curve has a finite length; in other words, the above-described reaction continues only for a certain time after which the process of formation of $Fe(OH)_2$ stops and the potential begins to increase. At higher potentials, other electrochemical processes can take place at the electrode, for example oxidation of the ferrous hydroxide $Fe(OH)_2$ to ferric hydroxide $Fe(OH)_3$ (area b), and at higher potentials separation of molecular oxygen. In the case under consideration here the passivation is due to the accumulation of passivating oxides on the surface which takes place simultaneously with the formation of the nonpassivating layer of $Fe(OH)_2$ [8].

An example by means of which we can readily trace the relationship between the degree of passivation and the quantity of oxygen on the surface, is the anodic dissolution of platinum in hydrochloric acid [9]. When platinum is anodically polarized in solutions containing a sufficient quantity of chlorine ions, it goes into solution at a moderate but nonetheless measurable rate. The latter can be determined from the intensity of the current passing through the platinum electrode at a certain potential. It is found that the current intensity drops in time, i.e., the rate of the electrochemical process decreases. As B.V. Ershler showed, this decrease conforms to the slow accumulation of oxygen on the platinum surface which takes place simultaneously with the dissolution of the platinum. The method of charging curves, described in §4 of the Introduction, was used to determine the quantity of oxygen on the platinum surface. After the electrode had been subjected to anodic polarization at constant potential during a certain time, and the intensity of the anodic current had dropped to a certain fraction of its initial value, the anodic polarization ceased and the cathodic charging curve was recorded with a high-density current. The quantity of oxygen which had accumulated on the platinum surface was determined by means of the lag on the charging curve and the relationship between the quantity and the density of the anodic current of platinum dissolution prior to the cessation of the anodic polarization could be determined. It was found that when the quantity q of oxygen on the surface increases, the rate of dissolution i decreases in accordance with the exponential law $i = ae^{-bq}$, where a and b are constants, a quantity of oxygen sufficient only for the filling of 6% of the platinum surface already causing a decrease of the rate of dissolution of the platinum by a factor of 4; filling of 12% of the surface slowed down the dissolution 16 times, etc. Thus, quantities of oxygen which were far from sufficient for forming a monatomic layer on the metal surface, produced a considerable passivation.

Let us examine in somewhat greater detail the conditions under which the passive state appears and disappears. If the anodic dissolution of platinum is carried out at constant current density, the potential increases gradually with time. In other cases, conversely, the passivation occurs suddenly. Thus, it is evident from the trend of curve 1 in Fig. 111, that the potential of the iron electrode varies little over the entire extent of the area *a* and then increases rapidly.

An increase in the anodic current density promotes the passivation process. In many cases when a certain current density is attained, a sudden transition of the electrode to the passive state takes place. The behavior of iron in concentrated alkali during increase in temperature may serve as an example [32]. The lower curve in Fig. 112 shows the increase in the potential during increase in the current density on an active iron electrode in 10 N NaOH at 80°. To a current density of $2 \cdot 10^{-3}$ amp/cm^2 corresponds a sudden rise in the curve which is due to passivation of the iron. The electrochemical process Fe → FeO_2^{--}, i.e., the transformation of the metallic iron to the divalent state then ceases.

The cessation of one anodic process which occurs as a result of passivation of the electrode often does not prevent the occurrence of other anodic processes at the same electrode, which result in the formation of compounds with higher valency. For example, on passive iron in a caustic solution, on which the formation of divalent iron has ceased, another electrochemical process begins at higher potentials:

2 Fe → $Fe_2O_4^{--}$, i.e., the transformation of metallic iron to trivalent iron. The upper curve in Fig. 112 corresponds to this process.

Under certain conditions, for example, during the anodic polarization of iron in moderately strong caustic solutions, the passive state which arises at high current density is retained at low current densities. In many cases, however, activation of the metal takes place after a certain interval of time when the current density is sufficiently decreased. Thus, it can be seen in Fig. 112 (dotted line) that at a current density of $3 \cdot 10^{-6}$ amp/cm^2 an activation of the iron takes place which results in the renewed formation of divalent iron and a lowering of the potential. This activation during reduction of the density of the anodic current may be due to dissolution of the passivating layer in the electrolyte.

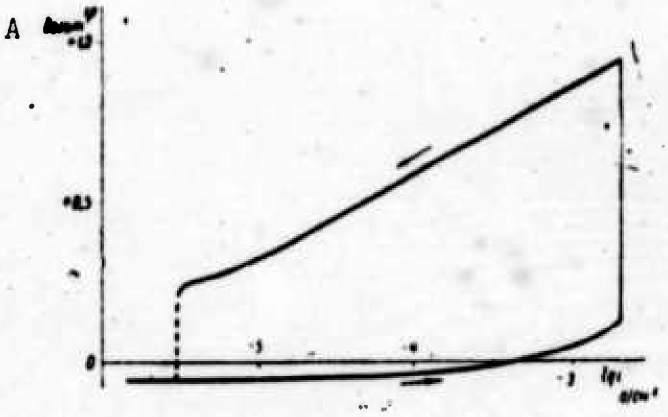

Fig. 112. Polarization curves during the dissolution of iron in 10 N NaOH at 80°. When the current density is increased to $2 \cdot 10^{-3}$ amp/cm^2, the electrode is passivated and when it is subsequently reduced to $3 \cdot 10^{-6}$ amp/cm^2, it returns to the active state. The potential φ was measured against a hydrogen electrode in the same solution. A) Volt.

In other cases the anodic activation is evidently due to displacement of the passivating oxygen from the metal surface by anions present in the solution. Thus, iron and magnesium in alkaline and aluminum in neutral solutions of chlorides are activated by increase in the anodic current within certain limits. This will be discussed in greater detail in §4 of this chapter.

The activation is rapid during cathodic polarization of a passive electrode if it results in a reduction of the passivating oxides. For example, during the cathodic polarization of passive chromium in acid its activation and rapid self-dissolution occurs.

On various metals, for example, iron, magnesium and aluminum, the oxide film can be preserved at potentials at which hydrogen separation occurs. In the case of iron and magnesium in caustic solutions it was shown that the presence of an oxide film causes an increase in the hydrogen overvoltage; in other words, the reaction of discharge of the proton from a water molecule is delayed on an oxidized surface compared with an unoxidized surface. The more negative the potential, the greater is the inhibiting effect of the oxide film [8]. By prolonged cathodic polarization or mechanical cleaning of the surface it is possible to remove the oxide film and thus to lower the hydrogen overvoltage. These relationships are illustrated in Fig. 113, where the curves of the hydrogen overvoltage in caustic solutions as a function of current density are given for the case of iron with an oxidized (1) and reduced (2) surface.

Thus, the anodic process of metal dissolution as well as the cathodic process of hydrogen separation are delayed in the passive state. However, the anodic process is in most cases much more strongly delayed than the cathodic process. Correspondingly, when the passivating layer is removed, the anodic process is much more strongly accelerated than the cathodic process. As will be shown in the next chapter, the ratio of the rates of the anodic and cathodic processes determines the stationary potential of a metal which dissolves without passage of an external current; the acceleration of the anodic process causes a shift of the stationary potential to the negative and acceleration of the cathodic process, to the positive side.

Numerous measurements of the potentials of metal electrodes during mechanical cleaning of their surfaces while immersed in a solution were carried out by G.B. Klark and G.V. Akimov [10]. These showed that when the passivating film of many metals is destroyed, the potential shifts strongly to the negative side. The potential shift during cleaning in a caustic solution is particularly large in the case of strongly passivated metals of the iron group, chromium, manganese, magnesium, etc.

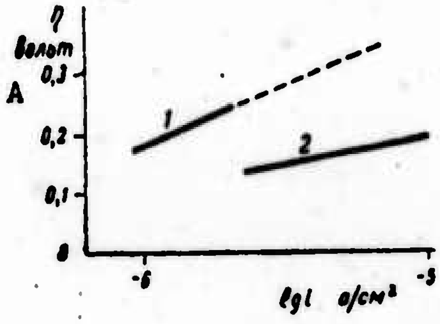

Fig. 113. Hydrogen overvoltage η as a function of the current density on an oxidized (1) and reduced (2) iron surface in alkaline solution. A) Volt.

The potential shift, discovered by G.B. Klark and G.V. Akimov indicates an activation of the metals during the cleaning of their surfaces.

TABLE 1

Effect of Mechanical Cleaning of the Surface in the Stationary Potential of Metals in 0.1 N NaOH

a Металл	B Стационарный потенциал в вольтах относительно н. в. э.	
	C до зачистки	D во время зачистки
a Железо	−0,1	−0,57
b Кобальт	−0,08	−0,53
c Никель	−0,03	−0,45
d Хром	−0,05	−0,86
e Марганец	−0,35	−1,2
f Магний	−0,9	−1,5

A) Metal; B) stationary potential in volts relative to n.v.e.; C) before cleaning; D) during cleaning; a) iron; b) cobalt; c) nickel; d) chromium; e) manganese; f) magnesium.

In aqueous solutions or in an atmospheric oxygen medium the saturation of the free valencies of the surface atoms on the metal takes place primarily through the formation of oxide layers whose formation is of basic importance in the phenomena of passivity. The oxide layers, formed in aqueous solutions, can contain chemically bound water. However, other groups of atoms or molecules which are sufficiently strongly bound to the metal, can also participate in the formation of passivating layers. We shall consider such examples in the following.

§2. ADSORPTION AND PHASE PASSIVATING LAYERS

With individual exceptions there is at present not much disagreement between the different researchers on the question concerning the role of oxide layers in the passivation phenomena. The situation is different, however, with regard to the ideas on the structure of these layers. While some researchers believe that the formation of a monomolecular layer or even only the filling of part of the metal surface is sufficient for passivation, others assume that the passivating oxides form a layer, which is a separate phase and insulates the metal mechanically from the ambient medium. Here we shall touch on this problem only briefly, starting out from the most unequivocal experimental data and limit ourselves as far as possible to those of its aspects which are significant for chemical kinetics.

The experiments described in the previous section show that even if only a relatively small part of a platinum surface is occupied by oxygen atoms, its rate of dissolution is considerably slowed down. Such passivation obviously cannot by any means be explained by an insulating film. A hypothesis has been advanced, according to which the modification of the kinetics of the anodic process in this case is wholly determined by an alteration of the structure of the double electric layer [9]. As follows from the adsorption experiments, described in the Introduction, the formation of a layer of adsorbed oxygen on the metal surface, owing to its dipole properties, causes a profound change in the structure of the double layer which markedly lowers the part of the potential difference metal/solution which depends on the free charges on the metal surface and the ions of the double layer or even reverses its sign.

It was pointed out in §8 of Chapter 4 that in the case of some other oxidation processes the appearance of oxide layers is accompanied by a decrease in the reaction rate. Although the existence of a connection between the variation of the structure of the double layer and passivation is beyond doubt, it should be pointed out that the explanation of the passivation effect on the basis of the variation of the electric field at the metal surface alone is less justified than, for example, the analogous explanation in the case of the increase in the hydrogen overpressure due to adsorption of cations (see Chapter 3). Indeed, while the valency-saturated and hydrated ions affect the course of the electrochemical process primarily because of the electric field created by them, the combination of an oxygen atom with the metal surface modifies its chemical nature and can affect its reactivity via different pathways.

The circumstance that passivation is often accompanied by other parallel anodic processes must be taken into account in the investigation of the nature of the passivating layers. As an example let us consider the quantitative relationships during the passivation of iron in alkaline solutions. The quantity of oxygen required for transforming the iron (whose surface has previously been freed of oxide layers) to the passive state, was determined by recording the anodic charging curves. If this measurement is carried out in a relatively concentrated caustic solution, it is necessary to use a relatively large quantity of electricity. Thus, for example, with anodic polarization of an active iron electrode in 2 N NaOH (see curve 1, Fig. 111) passivation occurred only after 0.26 coulombs/cm^2 had passed through the electrode, instead of approximately $0.5 \cdot 10^{-3}$ coulombs, required for the formation of a monolayer of oxygen. This quantity of 0.26 coulombs/cm^2, however, is not a measure of the quantity of passivating oxides on the surface.

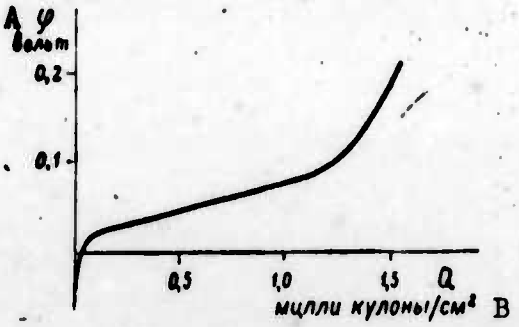

Fig. 114. Passivation of an iron electrode in 0.05 N NaOH at a current density of $4 \cdot 10^{-6}$ amp/cm^2. The diagram gives the potential φ as a function of the quantity of passed electricity Q. The potential was measured against a hydrogen electrode in the same solution. A) Volt; B) in millicoulombs/cm^2.

During the anodic polarization of iron in alkali, two reactions take place simultaneously. The first of these results in the formation of a deposit of $Fe(OH)_2$ via the intermediate formation of the ferrate ion $HeFeO_2^-$ in the solution and does not directly passivate the metal. The second reaction consists in the formation of passivating surface oxides. The ratio of the rates of the first and second process decreases in proportion to the decrease in the concentration of the OH^- ions in the solution and increase in the current density. In consequence of this the total quantity of electricity required for the passivation of an iron electrode in caustic solutions also decreases with decrease in its concentration and with increase in current density. Thus, in 0.05 N NaOH solution at a current density of $4 \cdot 10^{-6}$ amp/cm^2 a quantity of electricity is used for the passivation and dissolution of iron which is equivalent to the formation of only a single monatomic oxygen layer (Fig. 114); at a higher current density a quantity of electricity is sufficient for passivation which is even less than that corresponding to a monatomic layer of oxygen [8].

If an electrode is passivated under these conditions and the solution is then replaced by a more concentrated one, the passive state remains. It can be assumed that even in more concentrated caustic, in which iron can remain active and pass into solution for a long time even during anodic polarization, the passivation is also achieved by a very small quantity of oxygen.*

Of great importance for an understanding of the mechanism of the passivation phenomena is a consideration of the kinetics involved in the deposition of oxygen atoms on the metal surface and the reverse reaction of ionization of adsorbed oxygen atoms. It has already been shown in Chapter 4 (§8) that the kinetics of this reaction can be investigated by measurement of the electrode capacitance by means of alternating currents of different frequency. In the case of the platinum electrode it is found that these reactions are slow.

The existence of a large overvoltage which is typical for the inhibition of the reactions of deposition and removal of adsorbed oxygen atoms is well illustrated by the oscillographic records of the charging curves on a smooth platinum electrode within the potential range of the existence of the oxide film, given in Fig. 115 [12]. The anodic charging curve began in all cases at a potential of 0.5 v at which the platinum surface is relatively free of adsorbed layers. When an anodic polarizing current is applied, a marked potential shift is observed which is the greater, the greater the current density (curves 1 and 2, Fig. 115). The magnitude of this potential shift is determined by the over-

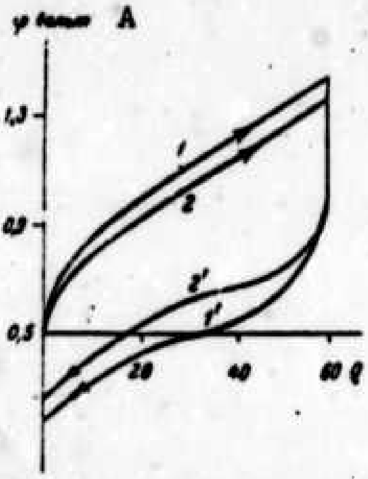

Fig. 115. Oscillographic record of the process of oxidation of a platinum surface (upper curves) and the reduction of the oxide film (lower curves) in 0.01 N H_2SO_4 + 1 N Na_2SO_4; curves 1 and 1': $i = 4.2 \cdot 10^{-2}$ amp/cm^2; 2 and 2': $i = 9.4 \cdot 10^{-3}$ amp/cm^2. The curves represent the potential φ (measured against a hydrogen electrode in the same solution) as a function of the quantity Q of electricity passed through (in microcoulombs/cm^2). A) Volt.

voltage during the deposition of oxygen atoms. If the direction of the polarization current is reversed, the potential shifts to the opposite side as a result of which the anodic and cathodic charging curves form a loop, whose size characterizes the degree of irreversibility of the processes of formation and removal of the oxide film. The overvoltage of the cathodic process of reduction of the oxide film increases with the time elapsed after the deposition of oxygen which indicates a gradual increase in the bond strength of the oxygen atoms with the metal.

The passivity caused by the adsorbed layers is the result of a modification of the chemical properties of the surface in consequence of the saturation of the free valencies of the metal by impurity atoms. This modification can affect the kinetics of the electrochemical processes in various ways, for example, via an alteration of the structure of the double layer or a variation of the adsorption energy of the reacting particles.

The specific chemical role of the atoms adsorbed on the metal surface becomes particularly clearly obcious when we consider the influence of these atoms on the kinetics of the anode processes which take place on the metal surface when the latter is in an active state. The same atoms or groups of atoms, whose adsorption under other conditions results in the formation of passivating layers, can accelerate the anodic process. As we shall see further on, the adsorption of small quantities of oxygen on an iron surface from the gas phase does not reduce but increase the reactivity of the iron in the anodic process.

A comparison of the rates of the anodic dissolution of iron in NaOH and HCl solutions gives an analogous result. For the purpose of such a comparison we must determine the law connecting the rate of dissolution of the iron in acid with the potential and extrapolate it to the potential values at which the dissolution of iron takes place in caustic (Fig. 116). It is found that at equal potential the rate of dissolution of the iron in caustic (curve b) is much higher than in HCl (curve a); this rate is approximately proportional to the 0.7*th* power of the OH^- concentration. The processes of anodic dissolution are irreversible in both solutions and their rate is determined by the electrochemical reaction and not by diffusion. The observed difference in rates cannot be accounted for in any other way than by assuming that in the caustic solution the first stage of the anodic process of dissolution of the iron is the formation of adsorbed groups, containing hydroxyl. The subsequent interaction of these groups with the solution results in the ionization and passing into the solution of the surface atoms of the iron [8]. Thus, the adsorption of oxygen in this case causes an acceleration of the anodic reaction.

We encounter an interesting case of the accelerating effect of an oxide film on the kinetics of the electrode process when we examine the action of light on the overvoltage of oxygen separation and the anodic oxidation of a metal. Illumination of metals with an oxidized surface lowers, for example, the oxygen overvoltage on platinum and silver and the overvoltage of the oxidation of silver, or, in other words, it accelerates the anodic electrochemical reaction. As V.I. Veselovskiy [13] has shown, the oxide film in this case serves as a receiver which intercepts a light quantum and transmits its energy to the particles which participate in the electrochemical act.

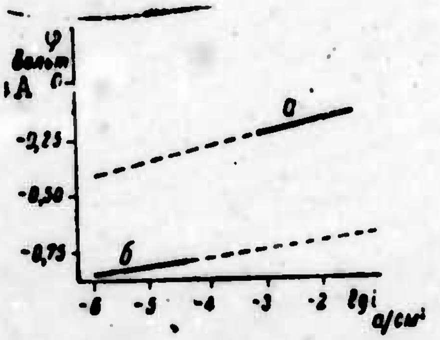

Fig. 116. Comparison between the rates of anodic dissolution or iron in HCl (a) and NaOH (b) solutions. The potential φ was measured against the standard hydrogen electrode. A) Volt.

Passivation of a metal can be produced not only by the adsorption of oxygen but also of other atoms. For example, in analogy to the oxygen passivation of iron in caustic, a passivation of iron takes place in acid solutions through adsorption of halogens. The strongest passivating effect has iodine, followed by bromine, and the much weaker one chlorine [14]. With increase in the concentration of the acid, for example, sulfuric, the effect of passivation of an iodine or bromine compound increases noticeably.

This action is reflected in a marked inhibition of the cathodic reaction, the separation of hydrogen, and the anodic reaction, the ionization of iron. As in the case of the passivation of iron by oxygen in caustic, a formation of an adsorbed iron compound with halogen obviously takes place here. As direct measurements have shown, the adsorbed quantity of the haloid i less than the quantity required for the filling of a monolayer.

It is of interest to call attention to the fact that the halides, like oxygen, cause a passivation of metals under certain conditions and activate them under others. Thus, in presence of adsorbed anions the intensity of the exchange current between zinc amalgam and the solutions of its salts increases (Chapter 6, §2). Chlorine ions in alkaline solutions depassivate iron (see further on, §4). The halogens exert an activating effect by being adsorbed in the forms of ions, retaining, although in a deformed state, their hydrate envelope. These effects can be interpreted on the basis of the theory of the double layer taking into account the ψ_1 potential as has been shown in the chapter on hydrogen overvoltage. The passivating effect is probably connected with a more profound reaction between the halogens and the metal, resulting in the formation of surface compounds. We do not have at the present time a simple theory which would fully explain the kinetic effects observed in this case. It is possible that in some cases the formation of adsorbed compounds with halogens does not cause a slowing down but an acceleration of the anodic process on the metal. Otherwise it would be difficult to account for the fact, for example, that the rate of the anodic dissolution of platinum at constant potential is proportional to the concentration of the chlorine ions in the electrolyte [9].

Let us now turn to an examination of passivation due to the formation of a relatively thick layer which shields the electrode surface. This kind of passivation can be termed "mechanical"* in contrast to the "chemical," i.e., connected with chemical adsorption, which has been discussed in the foregoing. The works of L.Yu. Kurts, A.G. Samartsev, B.N. Kabanov and also various foreign authors have been devoted to the problems of mechanical passivation.

Electrode systems such as silver in solutions of halides and lead in sulfate solutions are covered during anodic polarization with a layer of the corresponding salt. As a typical example let us take the practically important case of the passivation of lead in sulfuric acid solutions which has been studied in great detail [15]. The practical importance of this case consists in the fact that the passivation of lead limits the process of discharge of the lead electrode of the sulfuric acid battery. This electrode consists of spongy lead the pores of which are filled with electrolyte, the sulfuric acid solution. During discharge the reaction

$$Pb + SO_4^{--} = PbSO_4 + 2e \qquad (A)$$

takes place and insoluble lead sulfate is formed. During the reaction the SO_4^{--} ions are used up and the H^+ ions are removed by transfer, in consequence of which the concentration of the sulfuric acid at the negative electrode decreases.

The reaction (A) in the battery never goes to completion: only a certain proportion of the quantity of lead present is used, determined by the capacitance of the electrode.* When the current density is increased and the temperature lowered, the capacitance of the lead electrode decreases. This phenomenon is usually ascribed to the decrease in the sulfuric acid concentration in the pores, which, as it was believed, should have a greater effect at low temperatures in consequence of the slowing down of diffusion. A study of the behavior of the smooth lead electrode has shown, however, that the important factor which limits the possibility of using metallic lead, is the passivation taking place in consequence of the coating of a large proportion of the lead surface with a nonconducting layer of $PbSO_4$ crystals, and that the polarization of the same electrode is determined by the overvoltage of the anodic process.

Figure 117 shows the potential of the lead electrode in a H_2SO_4 solution as a function of the quantity of electricity passed through it. The origin of the ordinate axis corresponds to the reversible potential of lead in a sulfuric acid solution, saturated with lead sulfate. During anodic polarization the potential shifts to the positive side. The electrochemical polarization during the reaction of ionization of the lead at low current densities is slight, and the potential shift is caused mainly by the increase in the concentration of the Pb^{++} ions near the electrode surface. When a certain oversaturation of the solution with lead sulfate has been attained, crystals of lead sulfate begin to be deposited on the electrode surface which causes a reduction of the oversaturation and the appearance of a potential shift in the opposite direction on the curve (section A on curve Fig. 117). On the curve potential-quantity of electricity (at constant density of the polarization current) in its initial stage there is thus observed a certain potential jump of a magnitude corresponding to the steady-state process of the formation of $PbSO_4$ crystals which is represented by the horizontal section of the curve. In contrast to the analogous phenomenon which is observed when oxide layers are removed from the surface of platinum and rhodium (Figs. 35 and 36), this jump is due to the inhibition of the process of crystallization of the dissolved substance while in the previously described case we were dealing with a pure surface reaction. However, when the first $PbSO_4$ crystals appear on the electrode surface, the potential does not revert to the equilibrium value, and the solution remains oversaturated although somewhat less than prior to the formation of the $PbSO_4$ layer. The oversaturation depends, on the one hand, on the density of the polarizing current and, on the other, on the rate of crystallization of the $PbSO_4$.

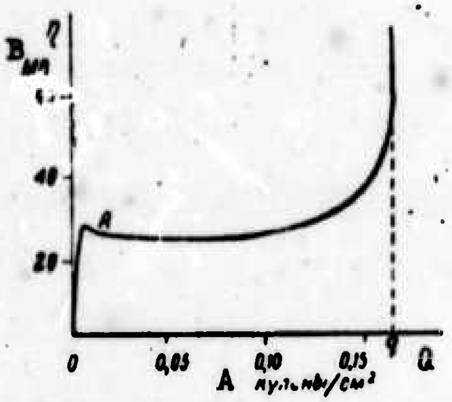

Fig. 117. Overvoltage η (in mv) of a lead electrode in 10 N H_2SO_4 as a function of the quantity of electricity *Q* passed through it. The passivation of the electrode takes place as a result of the passage of the quantity of electricity *q*. A) Coulombs/cm^2; B) mv.

Following the passage of a certain quantity of electricity *q* (Fig. 117), further passage of current causes the electrode potential to rise slightly at first and then shifts it to the positive side, i.e., passivation has occurred. This increase in potential which appears to be sudden is caused by the increase in the current density in the pores of the insulating salt layer at the end of the process of covering of the surface. Measurements showed that the capacitance of the double layer decreases during the anodic passivation of lead by a current with constant intensity approximately linearly with time (Fig. 118) and, consequently, the lead surface is uniformly covered with a layer of lead sulfate. If the surface is covered uniformly with time, the potential, in accordance with the logarithmic dependence of the potential on the current density, should increase in the manner observed experimentally (Fig. 117). The quantity of electricity, required for the complete passivation of lead under these conditions, corresponds to the formation of a layer of salt over most of the metal surface with a thickness of the order of one micron [15].

The presence of crystalline layers of insoluble salts on the electrode surface in the case of this "mechanical" passivation can also be detected by the phenomenon of double refraction in reflected light.

The above-described passivation of iron in alkaline solutions also involves the formation of a layer of the insoluble compound $Fe(OH)_2$ around the electrode. The passivation of lead, however, differs from the passivation of iron by the fact that the flocculent layer of $Fe(OH)_2$ does not impede access of electrolyte to the electrode. The formation of this layer does not directly affect the electrochemical properties of the metal which depend mainly on the appearance of a much thinner layer of passivating oxide. In contrast, the formation of a layer of $PbSO_4$, which adheres tightly to the electrode, greatly reduces its active surface and thus causes a decrease in its electrochemical activity.

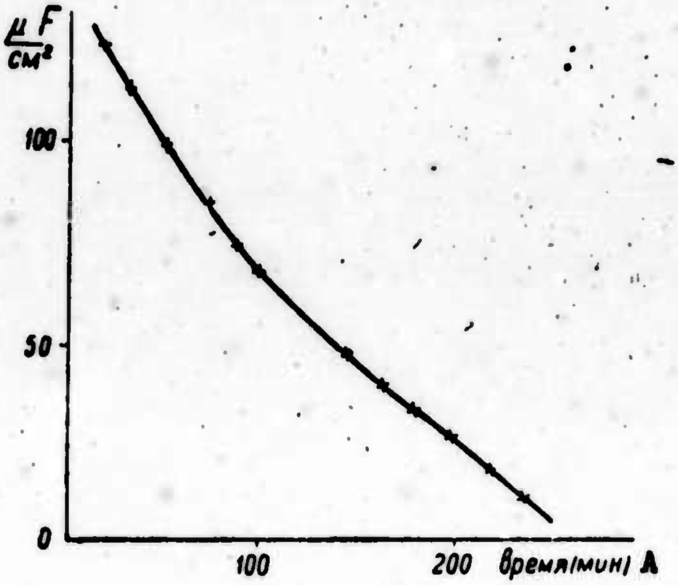

Fig. 118. Capacitance of a lead electrode, measured by means of alternating current, as a function of the duration of anodic polarization. A) Time (min).

Apart from these fundamental differences between the course of the process of passivation in these two cases there are also certain similar features. In both cases the quantity of electricity *q* required for the passivation of the electrode is reduced by a decrease in temperature and an increase in current density. The following relationship obtains between the quantity of electricity $q = ti$ (where t is the interval of time, required for the passivation of the electrode) and the density of the anodic polarization current i

$$qi^n = ti^{n+1} = \text{const}, \qquad (268)$$

in which the exponent n is approximately constant. In the case of the passivation of lead n is 1-0.4, and in the case of passivation of iron in NaOH it is 0.3-0.5. This quantitative coincidence of the exponents in the two cases is unexpected because in the passivation of lead q expresses the quantity of electricity consumed for the formation of the passivating $PbSO_4$ layer, which is proportional to the thickness of the passivating layer, while in the case of iron passivation the predominating part of the quantity of electricity imparted to the electrode is consumed in the formation of the nonpassivating porous deposit of $Fe(OH)_2$, and only a small fraction of it is consumed for the formation of the passivating ferrous oxide.

The thickness of the passivating layer of $PbSO_4$ is determined by the conditions of crystallization of the $PbSO_4$ on the lead surface. If the growth of the $PbSO_4$ crystallites takes place mainly parallel to the electrode surface, it is covered sooner and a thinner passivating layer is formed. Conversely, a relative increase in the growth rate perpendicularly to the surface results in a thickening of the passivating layer. The ratio of the growth rates in a direction parallel and perpendicular to the surface is evidently connected with the solubility of the $PbSO_4$ and the degree of oversaturation of the solution with $PbSO_4$ formed at the lead surface. Conditions which promote a high supersaturation (such as, for example, increase in the current density, or at a given current density, lowering of the solubility of the $PbSO_4$ because of a variation of the sulfuric acid concentration or lowering of the temperature) result in the formation of thinner passivating layers (Fig. 119). Because of the decrease in the thickness of the passivating $PbSO_4$ film the quantity of electricity which can be obtained during the discharge of the lead battery decreases. Surface-active substances have a great influence on the thickness of the passivating layer, for example, gelatin causes a thickening of the layer.

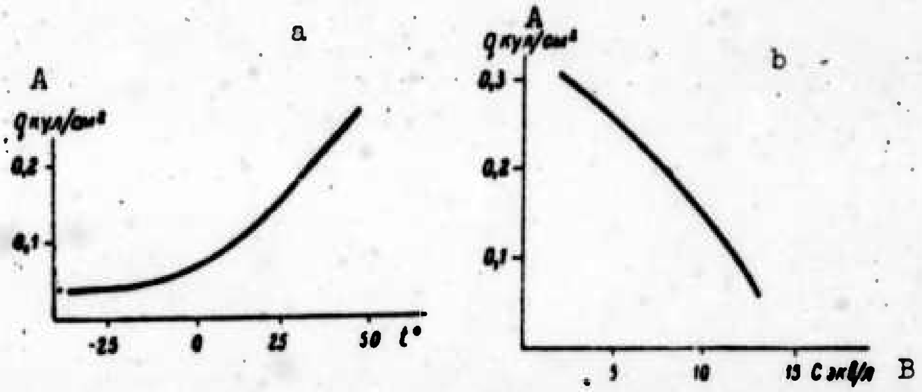

Fig. 119. Variation of the quantity of substance *q* in the passivating layer of lead sulfate on lead, expressed on coulombs per cm^2 or surface, as a function of temperature (a) and the sulfuric acid concentration (b). A) Coulombs/cm^2; B) equ/liter.

An analogous passivation mechanism is obviously involved in some other cases, for example, that of the anodic passivation of silver in a solution of halides [16].

As Fig. 117 shows, once the greater part of the lead surface is covered by a layer of $PbSO_4$, further passage of current causes a strong potential shift to the anodic side. However, this does not cause the electrochemical process to cease because some pores remain in the $PbSO_4$ or are newly formed. The potential shift to the positive side during the covering of the electrode with a passivating film has often been explained by the ohmic potential drop due to the high resistance of the electrolyte in the pores. This point of view has been particularly defended by V. Mueller [2]. Although the ohmic potential drop in the electrolyte in the pores can attain considerable values for certain systems, this explanation is not correct in most cases. In the case of lead in H_2SO_4 solutions the ohmic potential drop is negligibly small, and the observed potential shift is caused by a polarization of the electrode due to the high current density in the pores.

The large potential shift to the anodic side has the consequence that a new anodic process begins in which the lead no longer goes over into the divalent but the tetravalent form, namely PbO_2. The formation of compounds with higher valency, which takes place in consequence of the potential shift to the positive side, is often observed in passivation phenomena, independent of the nature of the passivating film. Thus, during the passivation of chromium the normal process of transformation of the chromium into ions of divalent (and partly trivalent) chromium ceases, but at sufficiently high positive potentials the formation of chromate ions is observed in which the chromium is hexavalent. When iron in concentrated alkaline solutions has been passivated with regard to the process of formation of divalent iron compounds, it can go into solution depending on the experimental conditions, as pointed out above, with formation of ferrites in which the iron is trivalent or, at still more positive potentials, with formation of ferrates, compounds of hexavalent iron.

Passivating phase layers which separate a varying part of the electrode surface from the solution can modify the conditions under which the electrochemical reactions take place on the remaining uncovered surface. If this layer has a considerable metallic conductivity (as, for example, a layer of Fe_3O_4 on iron), an electrochemical process can take place even on the covered surface under suitable conditions. Thus, if the solution contains oxygen, it can be reduced not only on the bare metal but also on the surface of the oxide layer (see following chapter).

In some cases the passivation of an anodically soluble metal depends to a large extent on the crystal form of the deposit appearing on it. For example, during the anodic dissolution of zinc in alkalis at moderate current densities such as are used in galvanic cells, passivation of the zinc occurs only when the rhombic modification of zinc hydroxide [17] is deposited from the saturated zincate solution. This is the case in concentrated alkali at low temperatures or in caustic solutions of medium concentration at room temperature. The passivation of the electrode is due to the fact that this modification of zinc hydroxide covers the electrode with a compact tightly adhering layer. The formation of non-hydrated zinc oxide, however (in concentrated caustic potash solutions at room temperature) or of the prismatic modification of zinc hydroxide (in relatively dilute solutions at low temperatures) does not cause passivation of the zinc electrode because the crystallization of these compounds and the growth of their crystals does not lead to the formation of a tightly adhering compact passivating film on the electrode.

Despite the wide distribution of the phenomena of "mechanical" passivation, it should be remembered that a large number of the phenomena observed in passivation cannot be interpreted on the basis of the concepts which take merely the shielding effect of the passivating layer into account. As previously emphasized, the diverse effects observed in the presence of foreign atoms on the electrode surface, attest to the profound chemical changes of its properties and cannot be reduced to mere mechanical covering of the surface. However, it would be entirely incorrect to infer from this that the shielding of the surface does not play an important part in the phenomena of passivity. The state of the surface layer depends on the density of the current passing through it. The latter, however, evidently increases many times if a large part of the electrode surface is shielded by a nonconducting oxide film or insoluble salts and the electrochemical processes are concentrated only in the pores. Moreover, the mixing of the solution in the pores is inhibited which facilitates alterations in its composition. Hence when a complete theory of passivation is to be constructed, it is essential to take into account not only the chemical nature of the adsorbed or other passivating layers whose thickness is close to molecular, but also the diverse structural properties of thinner films present on the electrode surface.

The historical merit to have stated this part of the problem of passivity broadly belongs to Academician V.A. Kistyakovskiy [5] whose film theory of passivity and corrosion encompassed a large number of processes, which take place in oxide films and affect their protective properties. V.A. Kistyakovskiy emphasized that the protective films should have a colloidal structure and believed that the destruction of the film takes place via the formation of corrosion centers reminiscent of crystallization; at the present time we cannot agree with the hypothesis concerning the disappearance of the protective properties upon crystallization of the film.

In his examination of the passivity of stainless steel, G.V. Akimov [18] arrived at the conclusion that the greater part of the surface is covered with a thin, dense (phase) film, below which (and in its pores) there are oxygen atoms which are strongly adsorbed on the surface. The combination of a thin, elastic and strong film with an adsorbed layer of oxygen determines the high corrosion resistance of the stainless steels in media containing oxidants.

Of great importance for the further development of our ideas on the passivation phenomena is the investigation of the crystal structure of these surface films [19], their porosity, the distribution of defects in them, etc. [20], by means of the methods of electron diffraction, electron microscopy and electrochemical measurements.

§3. FORMATION OF PASSIVATING LAYERS ON THE METAL-ELECTROLYTE INTERFACE AND OXIDATION OF METALS BY GASEOUS OXYGEN

A comparison of the phenomena which take place during the formation of oxide films at the metal-electrolyte interface, on the one hand, and during the reaction of metals with gaseous oxygen, on the other, is of considerable interest.

Let us first dwell briefly on the basic kinetic laws which govern the latter.

Of great importance for the kinetics of the interaction between metals and gaseous oxygen is the ratio of the atomic volume of the metal and the molecular volume of the oxide formed from it. When the latter is greater than the first, as is the case, for example, in the oxidation of iron or aluminum, a compact oxide layer is often formed as a result of the oxidation which has protective properties to some extent. In consequence of the volume decrease connected with the transition from the atom of the metal to the ion contained in the oxide, a volume increase through oxidation of the metal does not always take place; for example, it does not occur in the oxidation of the alkali metals. In this case a compact oxide layer is not formed and the oxidation goes to completion without hindrance, at least at temperatures which are not too low.

In the presence of compact oxide films the rate of oxidation decreases with time in accordance with typical laws. The simplest relationship is obtained when the thickness of the film thus formed exceeds the molecular dimensions and the rate of the process as a whole is determined by diffusion of the reacting substance through the film in which case a constant value can be ascribed to the diffusion factor D, which does not vary with increase in the film thickness x. Because the diffusion rate is inversely proportional to the layer thickness, through which the diffusion takes place, it is obvious in this case that

$$\frac{dx}{dt}=\frac{KD}{x}, \qquad (269)$$

where K is a proportionality factor, and t the time. Integration of Eq. (269) gives the relation

$$x^2=2KDt, \qquad (270)$$

which expresses the parabolic law of growth of the film. Equation (270) is correct only at not too small values of x because the above-given arguments are not applicable to films of molecular dimensions [21].

Because of the slowness of the diffusion processes in solids the diffusion in compact oxide films, covering the metal, can be observed in practice only at elevated temperatures. Some sorts of steel (for example, chromium steels with additions of silicon, molybdenum or other elements) remain stable to oxygen at high temperatures up to 1000°C.

Of special interest is the elucidation of the question of the precise nature of the particles which diffuse through the film. As experiment shows, in many cases when films grow under the action of oxygen (and other aggressive agents, for example, sulfur, halogens), a diffusion of the metal from the metal/film interface to its external surface takes place, where the metal does not diffuse in the form of atoms but in the form of ions with simultaneous movement of electrons. The electrons combine at the outer surface of the film with the oxygen with formation of oxygen ions. Thus both metal ions and oxygen ions arrive in the film and the film grows as a result of the electrochemical process, the closing of this unique electrical circuit takes place by the movement of the electrons through the film [22].

The passage of metal through the film is possible only if its composition differs from stoichiometrical, these deviations being of different kinds. Thus, in the case of the oxidation of zinc the oxide film near the metal surface contains an excess of zinc ions compared with the composition which would accurately correspond to the formula ZnO and an equivalent number of electrons. The excess Zn^{++} ions are distributed between the lattice points. At the external surface the concentration of these excess ions drops almost to zero. During the oxidation process a diffusion of zinc ions and electrons takes place from the internal to the external surface of the film.

A different picture is observed in the case of the oxidation of copper with formation of cuprous oxide. The composition of the oxide formed in this case also differs from the stoichiometric composition Cu_2O but no longer in the direction of an excess of metal but in the direction of an excess of oxygen. Part of the sites in the Cu_2O lattice which should be occupied by Cu^+ ions, are vacant and the shortage of positive charges compared with the charges of the O^{--} anions is compensated by a replacement of part of the Cu^+ ions by Cu^{++} ions. The latter may be regarded as sites of electron deficiency or electron "holes." The deficiency of Cu^+ ions and the concentration of the holes is evidently greater at the external boundary of the layer than at the internal. During oxidation a diffusion of Cu^+ ions from the internal to the external surface takes place in consequence of successive transitions of Cu^+ ions from occupied sites to vacant sites and the exchange of electrons between the Cu^+ and Cu^{++} ions, which may be regarded as a movement of holes from the external to the internal surface. A more profound analysis of the conditions of movement of charged particles in the two cases leads to the conclusion that the rate of oxidation of copper should be greater than the rate of oxidation of zinc and depends more on oxygen pressure than the latter.

The use of the theory of diffusion and electrical conductivity in ionic conductors and semiconductors, created primarily by Soviet scientists, in particular, by Ya.I. Frenkel', makes it possible in other cases as well to analyze the phenomena taking place during the growth of oxide and other layers on metals. Experiments, however, have shown that in addition to taking into account the movement of cations and electrons, the movement of anions must generally also be considered and, according to some authors, also that of oxygen atoms. The quantitative development of these concepts leads to a relation from which Eq. (270) can be derived under certain simplifying assumptions.

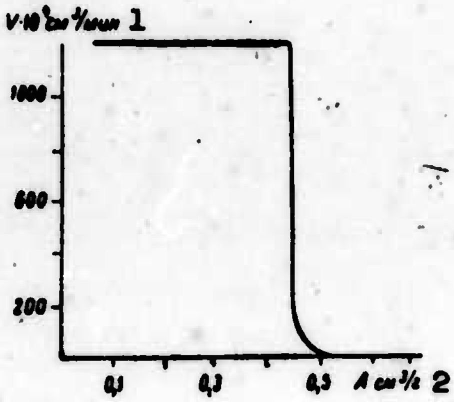

Fig. 120. Rate of oxidation *v* of iron powder as a function of the quantity *A* of adsorbed oxygen. The rate of oxidation is expressed in cm^3 of adsorbed oxygen per minute. 1) cm^3/min; 2) cm^3/g.

In some systems one has to take into account not only the slowness of the diffusion but also the slowness of the reaction at the interface between the film and the gas (or between the film and the metal). In these cases the rate of growth is determined by the reaction rate for small thicknesses and by the diffusion rate for great thicknesses [21].

Of special interest for electrochemistry are the deviations from the parabolic growth law expressed by Eq. (270) in the case of very thin films, consisting only of a single or several crystal cells of oxide. Such deviations have been observed during the oxidation of iron, aluminum, stainless steels and other metals at moderate temperatures. Figure 120 gives the oxidation rate of iron as a function of the absorbed quantity of oxygen [23]. In these experiments the oxygen was brought into contact with the iron in successive portions at 20°C, and the absorption rate was observed. This was initially very high but after the absorption of a certain quantity of oxygen, i.e., the formation of a film with a certain thickness, the rate dropped sharply to a very small value. At low temperatures this value is so small that film growth is practically completely arrested after the attainment of the above-mentioned limit value. At higher temperatures one can observe further film growth even during the second, slow stage of the oxidation process which gradually slows down with increase in the thickness of the oxide film as has been discussed in the foregoing. Finally, at even higher temperatures, the growth rate during the second (slow) stage increases so strongly that the borderline between the first and second stage disappears.

Thus there exists a limit film thickness over a relatively wide temperature range, at which the reaction with oxygen is greatly slowed down or practically arrested. The cessation of the oxidation reaction at a certain thickness of the oxide film is superficially similar to the transition to the passive state and the term metal passivation is also often applied to it. The existence of a fast and slow oxidation stage in the case of iron was discovered by Langmuir; this phenomenon was later studied by A.A. Kochetkov and others [24].

As R.Kh. Burshteyn showed, the thickness of the limit layer on iron depends greatly on temperature. Within the range of temperatures from −130° to −70°C the oxidation reaction is arrested by the formation of a coating containing two oxygen atoms for every surface atom of iron (Fig. 121), at room temperature the thickness of the limit layer is twice as great and at 200°C it is about 10 times greater than at −70° [23].

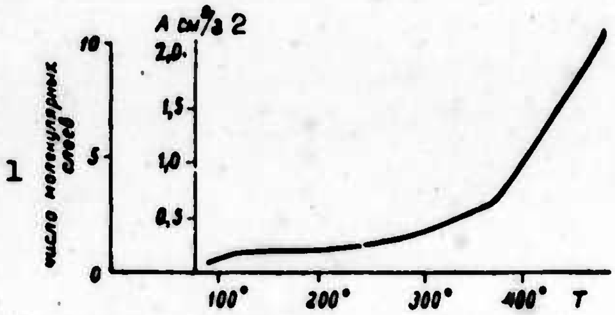

Fig. 121. Quantity of absorbed oxygen, corresponding to the end of the first stage of adsorption, as a function of temperature (in ° Kelvin) during the oxidation of iron. 1) Number of molecular layers; 2) cm^3/g.

Various attempts have been made to explain the rapid drop of the oxidation rate occurring when a certain thickness of the oxide film is reached. Mott used a concept which is to some degree analogous to that used for the interpretation of the action of the field in the theory of delayed discharge, assuming that the positive charge on the metal surface and the negative charges of the oxygen ions at the outer surface of the film form a double layer whose field facilitates the penetration of metal ions through the film. In proportion to the thickening of the film, the intensity of this field decreases and the penetration of ions is inhibited which results in a decrease in the growth rate of the film [25].

Other explanations have been advanced by I.A. Smirnov [26] and P.D. Dankov [27]. P.D. Dankov connects the slowing down of the growth rate of the oxide film with a decrease in time of the number of defects in the oxide lattice which make the diffusion of the metal atoms possible.

The mechanism of this phenomenon cannot yet be considered as finally explained. In any case, the sudden slowing of the growth rate, occurring when a certain thickness has been attained, shows that the movement of ions and atoms during the growth of very thin films takes place in accordance with a mechanism which differs from the normal diffusion observed in thicker layers. In spite of a certain similarity existing between the formation of protective films during the oxidation of metals with gaseous oxygen in the absence of moisture and the passivation through the action of dissolved oxidants or during anodic polarization, these phenomena cannot be considered as identical.

The quantity of electricity required for the passivation of an iron electrode depends on the conditions of formation of the surface oxide. Whilst a passivation of the electrode can be achieved during the deposition of oxygen by anodic polarization with quantities corresponding to the formation of a fraction of a monolayer, a much greater quantity of oxygen is required during the oxidation of iron by gaseous oxygen for passivation. It has been shown that the electrochemical activity of the electrode can be gaged by the length of the lag on the curve of the potential as a function of the quantity of electricity passed through (Fig. 111). If the iron is completely passivated beforehand in air, this lag disappears, i.e., $Fe(OH)_2$ is not formed on such an electrode during anodic polarization in alkaline solutions and the electrode goes over into the range of more positive potentials almost immediately.

In the case of the action of gaseous oxygen this result is attained only after the iron has absorbed quantities of oxygen, which, although not large, nonetheless are much greater than the quantity required for filling of a monolayer. Thus a quantity of oxygen corresponding to $2 \cdot 10^{15}$ molecules per square centimeter of true electrode surface does not markedly passivate the electrode at room temperature although it is sufficient for the formation of a layer of γ Fe_2O_3 oxide, with a mean thickness of approximately 6 A. Complete passivation is attained only by the deposition of $4 \cdot 10^{15}$ molecules. Furthermore, during anodic polarization in dilute caustic solutions the preliminary deposition of small quantities of oxygen, insufficient for complete passivation, from the gas phase, causes also a considerable increase in the quantity of $Fe(OH)_2$ formed during further anodic polarization [23]. This peculiar activating effect of small quantities of oxygen, deposited from the gas phase, may be connected with their penetration under the outer layer of atoms in the iron lattice which can be detected on the basis of the variation of the sign of the work function of the electron during the adsorption of small and large quantities of oxygen from the gas phase (see Introduction, §8). It is possible that during the formation of an oxide film by anodic polarization in electrolyte solution the oxygen atoms remain bound to water molecules which would prevent them from sliding under the top layer. The problem of the cause of the difference in the passivating effect of oxygen in these two methods of formation of a surface layer requires some further study.

In the case of aluminum there are also great differences between the phenomena observed during oxidation by gaseous oxygen and during anodic polarization. The oxidation of aluminum in gaseous oxygen at room temperature practically ceases as soon as a very thin protective oxide film has been formed. At the same time if anodic polarization is carried out in various electrolytes, for example, in sulfuric acid, the thickness of the oxide layer on the aluminum can be much greater than that of a monomolecular layer. As Fig. 122 shows, the capacitance of the double layer on aluminum in sulfuric acid decreases with increase in the potential. If we assume the dielectric constant of alumina on the aluminum surface as 10, it can be calculated from the above data that at the potential of oxygen separation the thickness of the oxide layer is approximately 70 A.

With stronger and more prolonged anodic polarization of aluminum relatively thick oxide films can grow on it, with a thickness of microns and hundreds of microns which finds widespread application in practice (the so-called anodizing of aluminum). A potential difference of some ten volts is applied to the aluminum electrode during anodizing. This causes an increase in the thickness of the oxide layer because a very large potential gradient is created in the surface layer which promotes the movement of ions in the layer. In chemically inactive electrolytes of the type of bicyrbonates or borates the process ceases when relatively thin and dense layers have been formed; such layers find application as insulating layers in electrolytic capacitors and rectifiers. In chemically more active media, for example, in solutions of sulfuric or oxalic acid, in consequence of the destruction of the

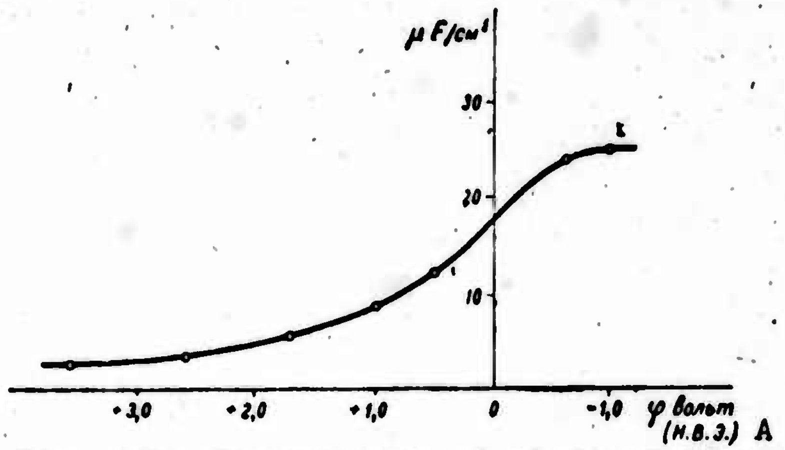

Fig. 122. Capacitance of aluminum electrode in 8 N H_2SO_4 as a function of the electrode potential. A) Volt (n.v.e.).

film by the action of the electrolyte, the process of anodic oxidation of aluminum continues longer. This gives thicker, porous layers which are used as anticorrosion protective coverings, usually after the pores have been filled with suitable fillers [28]. Professor N.P. Sluginov of Kazan' University was the first to propose in 1877 to use the oxide layers obtained by anodic polarization for the anticorrosion protection of aluminum [29].

§4. ACTIVATION OF PASSIVATED METALS BY CHLORINE IONS

The disintegration of the passivating layer and, consequently, the transition of the metal into the active state is greatly facilitated by the presence of certain anions, for example, chlorine ions, in the solution. Thus, chromium, which had been in contact with atmospheric air, placed into a solution of H_2SO_4, remains passive; after addition of NaCl to the solution the dissolution of the chromium begins after some time with simultaneous evolution of hydrogen [30].

The activating effect of chlorine ions is also observed in alkaline solutions and can therefore not be explained by the more rapid dissolution of the oxide film in hydrochloric acid compared with its dissolution in sulfuric acid.

Typical polarization curves are obtained during the anodic polarization of metals which can be passivated in solutions containing chlorine ions, which shed some light on the mechanism of this phenomenon [31]. Figure 123 gives the potential of an iron electrode as a function of the quantity of electricity passed through in alkaline solutions, containing chlorine ions. The electrode surface was previously subjected to different treatments. Curve 1 corresponds to the case of an electrode with an oxide film, formed during the contact of the iron with air at room temperature; in the case of curve 2 the electrode was freed of the oxide film before polarization by heating in hydrogen and was passivated only after some anodic polarization. For purposes of comparison curve 3 is also given which was obtained during the polarization of a similarly prepared iron electrode in a caustic solution which did not contain chlorine ions. It can be seen that the curves representing the potential as a function of the quantity of electricity passed through in the presence of chlorine ions have initially a normal trend which can be expected in the case of the passive (curve 1) and initially active (curve 2), respectively, iron electrodes. However, when a sufficiently high positive potential is attained (points A and B) in the presence of chlorine ions, a disturbance of the passive state is observed which is manifested in a sudden potential shift to the negative side. After this the potential settles down at a certain value at which the dissolution of the metal can continue indefinitely. The dissolution does not take place uniformly over the entire anode surface but is localized at certain points, in which pits appear (so-called

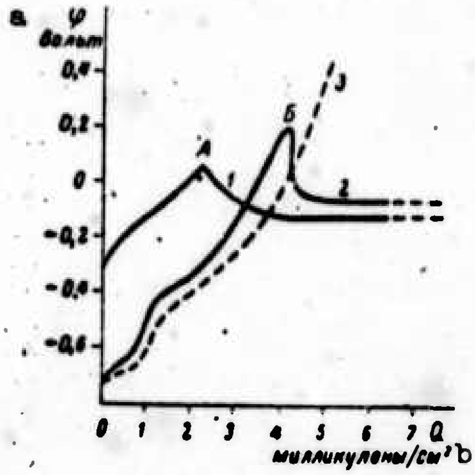

Fig. 123. Activating effect of chlorine ions during the anodic polarization of an iron electrode in caustic solutions. Curve 1: polarization in 2 N NaCl + 0.2 N NaOH after oxidation in air. Curve 2: polarization in 2 N NaCl + 0.05 N NaOH after removal of the oxide film by reduction in hydrogen. Curve 3: polarization in 0.05 N NaOH after removal of the oxide film (no activation). The potential was measured against the standard hydrogen electrode. a) Volt; b) millicoulombs/cm^2.

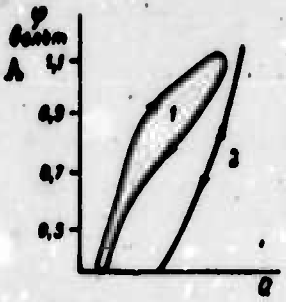

Fig. 124. Influence of chlorine ions on the adsorption of oxygen during the polarization of platinum: 1) Charging curve in 5 N H_2SO_4; 2) in 5 N H_2SO_4 + 0.02 N HCl. The direction of the potential variation is indicated by arrows. The potential was measured against the standard hydrogen electrode. A) Volt.

point or "pitting" corrosion). Analogous phenomena are observed in presence of other anions. The anions can be arranged in the order of their capacity to activate passive electrodes in the following sequence: $Cl^- > Br^- > I^- > F^- > ClO_4^- > OH^- > SO_4^{--}$. The sequence of this series can be slightly modified depending on conditions.

Evans et al. connect the activating effect of anions with their ionic radius and their ability to penetrate the passive layer. The latter is regarded in this case as a membrane, permeable for ions with small radius and impermeable for ions with large radius. This notion, however, does not stand up to criticism. For example, in alkaline solution the activating effect of anions on iron takes place only at a fairly high positive potential. This indicates clearly that we are dealing here with a surface phenomenon which depends on the potential difference within the double layer.

Indeed, it can be shown by direct experiment that in presence of chlorine ions the adsorbed oxygen is displaced from the metal surface. Figure 124 shows the oscillographically recorded anodic and cathodic charging curves of a platinum electrode in 5 N H_2SO_4 (1) and 5 N H_2SO_4 + 0.02 N HCl (2) solutions. An oxygen lag is clearly apparent in the upper part of curve 1 during cathodic as well as anodic polarization which is completely absent in curve 2. In other words, the presence of chlorine ions in the solution prevents the adsorption of oxygen on the platinum surface [9]. At a certain fairly high positive potential, a similar adsorption displacement of oxygen by chlorine also takes place at some parts of the iron electrode, in consequence of which the passivating film is destroyed at these points and activation of the iron electrode occurs.

The activating effect of chlorine ions may be manifested not only during anodic polarization but also in presence of oxidants which shift the potential of the metal to the positive side. At certain ratios between the concentrations of the passivator and activator in the solution, periodic fluctuations of the metal potential can be observed in many cases, going over from the passive state to the active and vice versa. According to V.A. Kistyakovskiy, the explanation of these periodic phenomena is that in consequence of the convective mixing of electrolyte, impoverished and enriched in oxidant, a periodic change of the processes which result in the formation or destruction of a passivating film takes place [5].

The problem concerning the conditions of the appearance and stability of passivating layers is undoubtedly one of the most important ones in electrochemistry, however, in spite of the considerable accumulation of experimental data, it has not yet been fully resolved. A complete theory of passivity must obviously take into account not only the kinetics of the deposition and ionization of individual oxygen atoms but also the laws of interaction between them, the probability of the destruction of the passivating layer by the dissolution of the metal under it, etc.

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[Footnotes]

445 An argument in favor of the correctness of the hypothesis that the passivation of iron is already achieved by a monolayer of adsorbed oxygen is the determination of the quantity of electricity required for the activation of iron, passivated in nitric acid. As Bonhoeffer and co-workers [11] found, a very small quantity of electricity is sufficient in this case for activation, equal to $0.2-0.5 \cdot 10^{-3}$ coulombs/cm^2 which corresponds to the removal of only part of the monolayer of iron oxide. Bonhoeffer assumed, however, that this quantity of electricity during activation is consumed for the removal of the oxide film from part of the surface only, while the remainder of the surface is reduced by the simultaneous self-dissolution of the metal at the active parts.

449 It must be pointed out that some authors interpret the term "mechanical" passivation somewhat differently.

450 The term "capacitance" is used here not in the sense in which we have often used it in the preceding chapters (i.e., the capacitance of the double layer, analogous to the capacitance of a capacitor) but in the sense in which it is used in the literature on chemical current sources. In other words, capacitance here means the quantity of electricity which is given off by the electrode upon discharge. The term "capacitance" in this sense can also be replaced by the expression "yield of the electrochemical process."

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[Transliterated Symbols]

467 н.в.э. = n.v.e. = normal'nyy vodorodnyy elektrod = standard hydrogen electrode

Chapter 8

KINETICS OF THE DISSOLUTION OF METALS

§1. CHEMICAL AND ELECTROCHEMICAL MECHANISM OF THE DISSOLUTION OF METALS

The process of the spontaneous dissolution of metals in electrolyte solutions is one of the fundamental causes of corrosion (chemical destruction) of metals.

In view of its enormous practical and economic importance, the problem of metal corrosion has long ago engaged the attention of many researchers. Several important observations in this field have already been made by M.V. Lomonosov. A comprehensive literature is extant which includes theoretical as well as numerous practical problems on metal corrosion and methods of protection against it. In this book we cannot dwell in greater detail on the existing rich experimental material which can be found in special courses on metal corrosion (see the general reference list in this chapter) and we shall merely touch upon some fundamental, principal aspects of the theory of the dissolution of metals.

The process of the dissolution of metals in electrolyte solutions (in contrast to the processes of dissolution in water of substances such as sugar or salt) is accompanied by chemical changes: the metal goes into solution with the formation of ions or not very highly dissociated metal compounds; at the same time gaseous hydrogen is evolved or substances present in the solution are reduced. Thus, for example, the dissolution of zinc in sulfuric acid involves the formation of a solution of zinc sulfate and hydrogen separation; when copper is dissolved in concentrated nitric acid, copper nitrate and products of the reduction of nitric acid, nitrogen oxides, are formed.

In contrast to the processes of the anodic dissolution of metals under the influence of an external electric current (in electrolytic cells or in chemical current sources), the dissolution of metals taking place during simple contact of a metal with a solution are often termed self-dissolution of metals.

The reaction of interaction of a metal with other substances can take place according to two mechanisms:

a) in the form of a chemical reaction without participation of free electrons,

b) in the form of an electrochemical reaction.

Thus, the reaction of sodium with gaseous hydrogen chloride takes place in one stage in accordance with the equation

$$Na + HCl \rightarrow NaCl + H.$$

The separation of the over-all process into independent separate stages, involving, for example, a preliminary splitting off of an electron from the sodium atom ($Na \rightarrow Na^+ + e$), transition of the electron to a HCl molecule ($HCl + e \rightarrow H + Cl^-$) and subsequent reaction of the Na^+ and Cl^- ions with formation of a molecule of NaCl would be energetically too disadvantageous in this case because of the necessity of the creation of free ions in the gas phase. Hence this is a purely chemical reaction which does not involve electrochemical reactions with participation of electrons.

In an aqueous solution of hydrochloric acid the same reaction proceeds via an electrochemical mechanism: the sodium goes into solution in the form of ions, leaving the corresponding number of free electrons in the metal; in addition to this anodic reaction, the cathodic reduction of hydrogen ions takes place with the participation of the free electrons.

One of the principal differences between these two mechanisms consists in the fact that in the electrochemical mechanism the over-all process consists of two or several parallel stages taking place simultaneously and at the same rates (i.e., with participation of the same number of electrons), which are otherwise independent of each other. Such parallel electrochemical reactions are commonly termed conjugated. The mutual independence of the conjugated reactions is expressed in the fact that, as will be evident from the following, the course of one of these reactions can be influenced without affecting the basic kinetic laws of the other. By variation of the composition of the solution and other experimental conditions it is possible, for example, to replace the reaction of reduction of hydrogen ions by a reaction of reduction of other substances without changing thereby the nature of the anodic process of the ionization of the metal. The quantitative relationships observed in this case will be defined more precisely in the following description.

If the surface of the dissolving metal is heterogeneous (for example, in presence of inclusion of other metals or intermetallic compounds in the metal), a spatial separation of the conjugated cathodic and anodic processes can take place in the electrochemical mechanism of dissolution of the metals in consequence of this independence of the individual stages. In this case the process of the anodic dissolution of the pure metal takes place predominantly on some parts (for example, on the surface of the pure metal); the remaining electrons travel through the metal to the places on which the cathodic reactions predominate (for example, on the exposed areas of foreign inclusions). This pattern is reminiscent of the function of a galvanic element in which the negative electrode (for example, zinc) dissolves when it is connected by a conductor with a second electrode and the hydrogen ions or other substances are reduced on the latter. In the galvanic element the basic cathodic and anodic processes are spatially completely separated.

In contrast to this pattern, the transition of the metal into the solution and the separation of hydrogen during the dissolution of a metal according to a chemical mechanism take place in a single act on the same area of the surface.

When we consider different reactions it is often difficult to say beforehand whether they proceed by a chemical or an electrochemical mechanism. A purely chemical dissolution mechanism is obviously observed during the reaction of metals with certain nonaqueous solutions, for example, with a solution of hydrogen chloride in benzene or with an iodine solution in dry chloroform.* When metals are dissolved in aqueous solutions of electrolytes, an electrochemical mechanism of dissolution with participation of free electrons takes place in most cases. True, even in these cases the possibility cannot be excluded that in addition to the electrochemical reactions, purely chemical interaction of the metal with the electrolyte takes place to some extent, but the importance of the latter is subordinate, and in all practically important cases of the dissolution of metals in aqueous solutions we can limit consideration to electrochemical mechanism. N. Kayander who carried out a systematic study of the rate of dissolution of metals in different electrolytes [1] arrived at this conclusion concerning the electrochemical mechanism of dissolution in 1880.

The basic problems of the theory of the electrochemical dissolution of metals concern the interrelations between the anodic and cathodic processes which take place on the metal surface.

As far back as 1830, De la Rive [3] found that the process of metal dissolution depends on the presence of inclusions or other surface heterogeneities which together with the clean metal surface form a large number of short-circuited galvanic elements of microscopic dimensions, the so-called local elements or microelements. The dissolution of the base metal takes place as a result of the operation of the local elements. In these elements the anodic process takes place on the clean metal surface, and the cathodic process on the inclusions. The laws of the distribution of the cathodic and anodic processes in other cases may of course differ considerably from the simplest example discussed here.

The first quantitative formulation of the theory of local elements was given by N.P. Sluginov who connected the rate of disintegration of the metal with the electromotive force and the resistance of the local elements [4]; an analogous relationship was proposed much later by Palmaer [5].

The theory of the local elements was subsequently widely developed; a particularly valuable contribution was made to it by the Soviet researchers G.V. Akimov and co-workers [6].

As will be evident from the following, the presence of short-circuited microelements, i.e., the spatial separation of the cathodic and anodic reaction, whose possibility follows from the electrochemical nature of the over-all corrosion process, causes a marked acceleration of the latter in many practically important cases. Hence, the incorrect conclusion is often arrived at in classical corrosion theory that a metal with a completely pure and homogeneous surface is chemically completely stable. Actually, however, the surface homogeneity of a metal is not an impediment to the simultaneous occurrence of anodic and cathodic processes on it so that even a chemically pure and homogeneous (for example, liquid) metal can dissolve in an electrolyte solution. If the physical and chemical properties are the same at all points of the surface, cathodic and anodic processes can take place with the same probability at any point and cathodic and anodic areas cannot be distinguished. The possibility of the dissolution of pure metals leads to the conclusion that even on a heterogeneous (nonuniform) surface a complete differentiation of the cathodic and anodic processes does not take place; the operation of the local elements on such a surface and the metal dissolution connected with it are superposed on the dissolution taking place as a result of a conjugation of the reactions within the limits of each of the homogeneous surface areas. Depending on the degree of heterogeneity of the surface in different cases the degree of differentiation of the cathodic and anodic processes may differ.

In addition to the problem of the interconnection of the cathodic and anodic processes in the study of metal dissolution, problems often arise connected with the accumulation of the corrosion products. If the corrosion products are highly soluble (for example, in the dissolution of iron in hydrochloric acid), they are removed from the reaction zone via diffusion and convection; in such cases the surface concentration of these substances can be calculated by means of the equations of diffusion kinetics (see Chapter 1). However, the corrosion products are very frequently insoluble and are deposited on the metal in the form of a film with varying density. The formation and growth of such films on metal surfaces and also of adsorbed passivating layers naturally affects the dissolution reaction strongly and may lead to a slowing down or almost complete cessation of the latter. Thus the passivity phenomena, considered in Chapter 7, are of great importance for the course of corrosion processes which has been particularly strongly emphasized in the work of V.A. Kistyakovskiy.

In the present chapter we shall consider the fundamental laws of metal dissolution first by using the example of metals with a homogeneous surface; later on, in §7, we shall discuss the peculiarities observed during the dissolution of metals with heterogeneous surface. In the examination of these questions we shall give attention mainly to the cases of metal dissolution in acid solutions in which the reaction products are frequently highly soluble. In our exposition we shall consider only the simplest system and, in particular, we cannot touch upon the practically important case of corrosion at the three-phase boundary, which has been studied by V.A. Kistyakovskiy and co-workers [2].

§2 CONJUGATED ELECTROCHEMICAL REACTIONS AND STATIONARY ELECTRODE POTENTIALS

In the discussion of the laws of the reactions of hydrogen separation we have pointed out that on a platinized electrode, immersed in an electrolyte solution, saturated with hydrogen, two electrode reactions can take place simultaneously: the reaction of hydrogen ion discharge $H^+ + e \rightarrow 1/2\ H_2$ and the reverse reaction of ionization of the hydrogen $1/2\ H_2 \rightarrow H^+ + e$; the rates of these two reactions (in electrical units) we have designated by $\overrightarrow{i}$ for the discharge reaction and by $\overleftarrow{i}$ for the ionization reaction.

In the equilibrium state, when the electrode is not polarized, the discharge and ionization reactions are mutually compensating and their rate is equal to $\overrightarrow{i} = \overleftarrow{i} = i^0$ (i^0 = equilibrium exchange current). When current passes through the electrode, the equilibrium is upset and the equality of the rates of the straight and reverse reaction is also upset. The rates of these reactions depend on the electrode potential, the hydrogen ion concentration, the pressure of the molecular hydrogen and other factors. This connection is expressed by the kinetic equations of the given electrochemical reaction. The form of the equations and the numerical values of the constants in them depend on the nature of the electrode reaction and the nature of the electrode.

It has been shown in Chapter 3 that for a number of electrodes the reaction of hydrogen separation obeys the kinetic equation*

$$\overrightarrow{i} = k_1 [\mathrm{H}^{\cdot}] e^{-\frac{\alpha F \varphi}{RT}}, \qquad (271)$$

while the equation

$$\overleftarrow{i} = k' p_{\mathrm{H}_2}^{1/2} e^{\frac{\beta F \varphi}{RT}}. \qquad (272)$$

applies to the reverse reaction of hydrogen ionization.

In the theoretical examination of the reaction of hydrogen separation we made the assumption that the kinetic laws of each of these reactions can be considered independently of the course of the other reactions; in other words, it was assumed that the simultaneous occurrence of another reaction does not affect the rate of an electrochemical reaction. As pointed out previously (Chapter 3), the correctness of this hypothesis can be demonstrated experimentally, for example, by determining the exchange current at the equilibrium potential.

The sole requirement for the kinetic equations for the direct and reverse reactions is that at the equilibrium potential and at any concentration of the components the rates of the two reactions should be equal. If we substitute in Eqs. (271) and (272) instead of the variable φ the equilibrium potential in this system φ_r, the right parts of these equations should assume the same value.

The last conditions can also be formulated thus: if the kinetic equation of the direct and reverse reactions is known and if the equilibrium potential is unknown, the latter value can be found as the solution of the equation which expresses the condition of the electrochemical equilibrium: $\overrightarrow{i} = \overleftarrow{i}$.

As has been shown in Chapter 3, the solution of this equation really gives the expression for the equilibrium potential, well known in thermodynamics.

The above described picture is applicable to any electrode, on the surface of which only one pair of electrochemical reactions takes place (i.e., the direct and reverse reaction), as, for example, for a zinc electrode immersed in zinc sulfate solution (reactions of discharge and ionization of zinc), for a platinum electrode, immersed in a mixture of salts of divalent and trivalent iron (reactions of oxidation of Fe^{++} and reduction of Fe^{+++}). However, cases are often encountered in which a greater number of reactions takes place on the electrode simultaneously. We find such phenomena, for example, in the processes of metal dissolution in electrolyte solutions.

Let us visualize a metal electrode, immersed in an acid solution which is saturated with hydrogen. Two pairs of electrochemical reactions can take place on the surface of this electrode (with participation of hydrogen and metal)

$H^{+} + e \rightarrow {}^{1}/_{2} H_2$, reaction rate $\vec{i}_1$
${}^{1}/_{2} H_2 \rightarrow H^{+} + e$ » » $\overleftarrow{i}_1$
$Me^{n+} + ne \rightarrow Me$ » » $\vec{i}_2$
$Me \rightarrow Me^{n+} + ne$ » » $\overleftarrow{i}_2$

The rates of these reactions depend on the electrode potential and on the concentrations of the reaction components. Some of these reactions can take place at a rate which is immeasurably smaller than the rate of the others; if, for example, the concentration of the metal ions in the solution at the initial moment is zero, the rate of the discharge reaction of these ions must naturally also be zero.

Many metals when placed in an acid, dissolve with formation of the corresponding salts and gaseous hydrogen. This means that the rate of the reactions of the ionization of metal and of the hydrogen ion discharge exceeds the rate of the corresponding reverse reactions in the absence of an external current. The effective rate of dissolution of the metal can be expressed as the difference between the current density of the ionization and discharge reaction of the metal ions $i_2 = \overleftarrow{i}_2 - \overrightarrow{i}_2$ while the rate of hydrogen separation is expressed as the difference between the densities of the discharge and ionization current of the hydrogen $i_1 = \overrightarrow{i}_1 - \overleftarrow{i}_1$.

If the electrode is not inserted in an electrical circuit and an external current does not pass through it, the separation of hydrogen and the dissolution of the metal takes place in equivalent quantities, i.e., the rates of the two processes i_1 and i_2 are equal

$$i_1 = i_2 = i_c \tag{273}$$

(i_s is the rate of self-dissolution of the metal) or, if we substitute the rates of the individual electrochemical reactions, $\overrightarrow{i}_1 - \overleftarrow{i}_1 = \overrightarrow{i}_2 - \overleftarrow{i}_2$, and, consequently,

$$\overrightarrow{i}_1 + \overrightarrow{i}_2 = \overleftarrow{i}_1 + \overleftarrow{i}_2. \tag{274}$$

The sum of the rates of all cathodic reactions is equal to the sum of the rates of all anodic reactions; the number of electrons freed in the course of one reaction is equal to the number of electrons which enter into the second reaction. An accumulation of electric charges on the electrode surface does not take place, and the electrical state of the system does not vary with time, i.e., it is stationary. Eq. (273) expresses the stationarity conditions.

In contrast to the above-considered example of the platinized hydrogen electrode, the absence of an external electric current in the last case cannot by any means serve as an indication of equilibrium. Although a balance of the electric charges is observed on the electrode surface, the quantity of metal decreases continuously, and gaseous hydrogen accumulates continuously, i.e., the chemical composition of the system is gradually altered.

The rate of these chemical changes (i.e., the rate of the self-dissolution of the metal) can be calculated if the kinetic laws of the individual electrochemical reactions taking place at the electrode surface are known. In addition to the concentrations of the components we must also know the electrode potential in order to calculate these quantities.

On a metal electrode which is immersed in an acid solution, a certain stationary potential is established which differs from the equilibrium potential of this metal and from the equilibrium potential of the hydrogen electrode. In the same way as the equilibrium potential of the hydrogen electrode can be derived from the condition of equality of the rates of hydrogen discharge and ionization, the stationary potential of the metal electrode in the acid solution can be determined, at least in principle, by means of Eq. (274) which expresses the conditions of compensation of the four electrochemical processes. To this end we must substitute into Eq. (274) the expression for the rates of the individual reactions as a function of potential and concentration and solve the equation thus obtained for the potential. If it is assumed that the kinetic laws of the discharge and ionization reactions of the metal have the same form as for the reaction in which the hydrogen participates, Eq. (274) will assume the form:

$$k_1[\mathrm{H}^+]e^{-\frac{\alpha_1 F\varphi}{RT}}+k_2[\mathrm{Me}^{n+}]e^{-\frac{\alpha_2 F\varphi}{RT}}=k'_1 p_{\mathrm{H}_2}^{1/2}e^{\frac{\beta_1 F\varphi}{RT}}+k'_2 e^{\frac{\beta_2 F\varphi}{RT}}. \qquad (275)$$

Knowing the stationary electrode potential, we can easily find the rate of self-dissolution i_s of the metallic electrode in the acid solution.

$$i_c = k_1[\mathrm{H}^+]e^{-\frac{\alpha_1 F\varphi_c}{RT}}-k'_1 p_{\mathrm{H}_2}^{1/2}e^{\frac{\beta_1 F\varphi_c}{RT}} = k'_2 e^{\frac{\beta_2 F\varphi_c}{RT}}-k_2[\mathrm{Me}^{n+}]e^{-\frac{\alpha_2 F\varphi_c}{RT}}. \qquad (276)$$

The concentrations entering into these equations can be predetermined or determined from the diffusion conditions in the system under consideration.

Equation (285) in this form, however, is not used as a rule for the calculation of the stationary potential. As will be evident from the following, the rate of certain electrochemical reactions is in many cases much less than the rate of other, simultaneously occurring reactions. In these cases we can neglect in Eq. (275) the terms corresponding to the slower reactions, in consequence of which the solution of the equation is simplified. A particularly simple solution is obtained in the case when only two terms remain in Eq. (275), i.e., when the rates of all reactions with the exception of one cathodic and one anodic reaction can be neglected.

The stationary potential and the rate of self-dissolution of the metal can be readily found by a graphic method. In Chapter 3 (Fig. 68) we have already become acquainted with the method of graphic representation of the rate of a direct and reverse electrochemical reaction as a function of the electrode potential. Figure 125 gives on a semilogarithmic scale the same relationship between the reaction rates and the electrode potential but now for an electrochemical reaction in which the hydrogen as well as the metal participate. In the case here presented the curves for the reactions in which the metal participates are shifted far into the region of negative potentials compared with the curves relating to the separation and ionization of hydrogen. The thick lines give the curves of the effective rate of hydrogen separation (i_1) and the dissolution of the metal (i_2) as a function of the electrode potential. In the absence of a current these two rates are identical, i.e., the electrode assumes the stationary potential. φ_s corresponding to the point of intersection of the curves i_1 and i_2. The rate of the self-dissolution i_s of the metal is defined by the abscissa of this point.

As will be obvious from the following sections, the conclusions from the above-given theory of the electrochemical dissolution of metals is in good agreement with the experimental data. This fact confirms the correctness of the above assumption concerning the independence of the course of separate electrochemical reactions. These concepts remain valid even in the case of metals with heterogeneous surface (this question will be discussed in greater detail in §7).

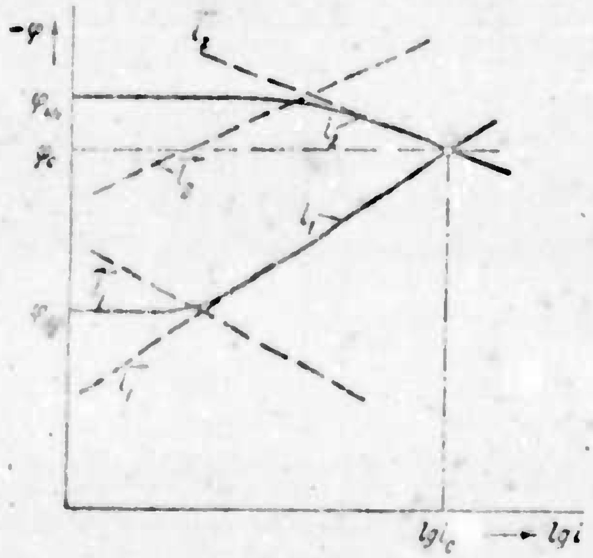

Fig. 125. Rates of the reactions of discharge and ionization of hydrogen ($\overrightarrow{i}_1$ and $\overleftarrow{i}_1$) and the metal ($\overrightarrow{i}_2$ and $\overleftarrow{i}_2$) and also the over-all rate of hydrogen separation i_1 and the dissolution of the metal i_2 as a function of potential. φ_{Me} and φ_{H_2} are the equilibrium potentials for the metal and hydrogen in the given solution; φ_s is the stationary potential of the dissolving metal and i_s is the self-dissolution current.

The concepts of the course of conjugated electrochemical reactions on the surface of a homogeneous metal were used first in the interpretation of the kinetics of the decomposition of alkali metal amalgams by A.N. Frumkin in 1932 [7].

The theory of the conjugated electrochemical reactions was further developed in the work of Wagner and Traud [8].

The same assumptions are used in works on kinetics of metal dissolution of a number of Soviet researchers: Ya.V. Durdin [9], A.I. Shultin [10], Ya.M. Kolotyrkin [11, 12], and others.

§3. DECOMPOSITION OF AMALGAMS

An important branch of electrochemical industry is the production of chemically pure alkalis by electrolysis, based on the formation and subsequent decomposition of the amalgams of alkali metals. For this reason the elucidation of the reaction mechanism of amalgam decomposition is not only of theoretical but also practical interest.

It has been found in several works that the rate of decomposition of sodium amalgam by aqueous buffer solutions in the absence of atmospheric oxygen is proportional to the square root of the sodium concentration in the amalgam [13]. This dependence of the reaction rate on the concentration of the reacting substances is fairly rarely encountered. On the basis of the usual laws of chemical kinetics one would have assumed that an amalgam decomposes at a rate proportional to its concentration, i.e., in accordance with a monomolecular law. On the basis of the ideas on the electrochemical mechanism of solution, however, this unusual relationship is easily interpreted and, as will be clear from the following, the reaction rate can be calculated theoretically.

The following electrochemical reactions are possible on the amalgam surface:

$$\begin{array}{lll} H^{\cdot} + e \rightarrow H & \text{rate} & \overrightarrow{i}_1 \\ H \rightarrow H^{\cdot} + e & \text{»} & \overleftarrow{i}_1 \\ Na^{\cdot} + e \rightarrow Na & \text{»} & \overrightarrow{i}_2 \\ Na \rightarrow Na^{\cdot} + e & \text{»} & \overleftarrow{i}_2 \end{array}$$

In this case the examination of the mechanism is simplified by the circumstance that the reverse reaction of the ionization of hydrogen can be neglected, because sodium amalgam has a strongly negative potential and $\overleftarrow{i}_1$ is very small. Thus, only the direct hydrogen reaction need be considered.

Two reactions are possible for the sodium: a transition to the state of ions, and the reverse reaction, the formation of sodium atoms from the ions. The transition into the ionized state should be somewhat faster because the over-all reaction proceeds in the direction of decomposition of the amalgam. The effective dissolution rate of sodium i_2 is the difference between the rates of ionization and discharge of sodium $i_2 = \overleftarrow{i}_2 - \overrightarrow{i}_2$.

In the absence of a current supplied from outside the amalgam electrode assumes a stationary state which is determined by the equilibrium of the rates of hydrogen separation and sodium dissolution

$$\overrightarrow{i}_1 = \overleftarrow{i}_2 - \overrightarrow{i}_2. \tag{277}$$

By substituting into Eq. (277) the expressions for the dependence of the rate of each individual electrochemical reaction on the electrode potential and on the composition of the solution and solving this equation for the potential, one can find the stationary potential of the amalgam electrode and by means of it the rate of decomposition of sodium amalgam.

In this case, however, the rate of the self-dissolution of the metal can be found by an even simpler method. As experiment shows, when an electrical current of moderate intensity from an outside source is passed through the amalgam electrode, immersed in a solution which contains Na^+ ions, the potential of this electrode remains almost unchanged. This means that the sodium discharge and ionization currents separately are very large and their relative variation during passage of an external current is so slight that it does not affect the state of the electrode. The same is the case when the amalgam electrode is not polarized by an external current source but if hydrogen is evolved on it. Because the hydrogen overvoltage on the amalgam (as on pure mercury) is large, the rate of hydrogen separation is relatively small even at strongly negative potentials of the amalgam electrode. Hence the left part of Eq. (277) is small compared with the terms of the right part each of which separately is very large. Thus the simultaneous reaction of hydrogen separation varies the reaction rate of the sodium exchange relatively little and the equilibrium between the sodium amalgam and the sodium ion is hardly affected. For this reason one can assume with a sufficient degree of approximation that the potential of the dissolving amalgam electrode is the same as the equilibrium potential of the amalgam electrode in a solution of sodium ions of the same concentration.

This assumption of the approximate equality of the stationary and equilibrium potential is justified in all cases in which the exchange current between metal and ions is large and the rate of hydrogen ion discharge is small as is the case, in particular, in the case of the decomposition of sodium amalgam.*

Let us find the expression for the rate of dissolution of sodium amalgam in acid buffer solutions, containing a considerable quantity of sodium ions (for example, in solutions of sodium ions (for example, in solutions of sodium phosphate). The variation of the concentration of the Na^+ and H^+ ions which takes place in consequence of the ionization of sodium and the separation of hydrogen can be left out of account in first approximation in these solutions and these concentrations can be regarded as constant.

If we consider the amalgam to be dilute with regard to sodium, we can write for the equilibrium potential:

$$\varphi_{Na} = \varphi^0_{Na} + \frac{RT}{F} \ln [Na^{\cdot}] - \frac{RT}{F} \ln [Na] = \varphi'_{Na} - \frac{RT}{F} \ln [Na], \qquad (278)$$

where [Na] is the concentration of the metallic sodium in the amalgam.* φ^0_{Na} (normal potential of sodium amalgam), according to the most reliable data, is 1.844 v.

With regard to hydrogen the system is obviously far from equilibrium because the hydrogen ions are discharged at the amalgam at the rate $\vec{i}_1$ and ionization of the hydrogen does not take place.

In order to find the quantity $\vec{i}_1$, we must substitute into the kinetic equation of the reaction of hydrogen separation

$$\vec{i}_1 = k_1 [H^+] e^{-\frac{\alpha \varphi F}{RT}} = k_1' e^{-\frac{\alpha \varphi F}{RT}} \qquad (279)$$

the value of the equilibrium potential of the amalgam electrode according to Eq. (278).

Taking into account that the rate of hydrogen separation is proportional to the rate of decrease in the sodium concentration in the amalgam $i_1 = i_2 = -k_2(d[Na]/dt)$ we obtain after substitution into Eq. (279)

$$-\frac{d[Na]}{dt} = \frac{k_1'}{k_2} e^{-\frac{\alpha F}{RT}\left(\varphi^0_{Na} - \frac{RT}{F}\ln[Na]\right)} = k'[Na]^{\alpha}, \qquad (280)$$

where

$$k' = \frac{k_1'}{k_2} e^{-\frac{\alpha F \varphi^0_{Na}}{RT}}. \qquad (281)$$

As has been shown in Chapter 3, the constant α in the case of hydrogen separation on mercury is close to 1/2. It can be assumed that this also applies to dilute amalgams. At α = 1/2 Eq. (180) assumes the form

$$\frac{d[Na]}{dt} = k'[Na]^{1/2} \qquad (282)$$

Thus, starting out from the concept of the electrochemical mechanism of the process of amalgam dissolution and from the equation for the hydrogen overvoltage, we obtain an expression according to which the rate of decomposition of amalgam is actually proportional to the square root of the amalgam concentration, as has been found experimentally.

If we integrate the differential equation (282), taking into account the initial condition according to which at $t = 0$ the quantity $[Na]$ is equal to the initial concentration $[Na_0]$, we obtain:

$$t = \frac{2}{k'}\left(\sqrt{[Na]_0} - \sqrt{[Na]}\right) \tag{283}$$

or

$$\sqrt{[Na]} = \sqrt{[Na]_0} - \frac{k'}{2}t. \tag{284}$$

As is evident from Eq. (284), the square root of the amalgam concentration decreases linearly with time. In consequence of this the reaction under discussion is completed within a finite length of time, equal to $\tau = \frac{2}{k'}\sqrt{[Na]_0}$. This result is unusual; for chemical reactions of the first, second and higher orders the concept of the end of the reaction, as we know, is indeterminate; the rate of these reactions tends asymptomatically to zero, or, in other words, these reactions taper off gradually and do not terminate abruptly.

The correctness of the above-deduced law of the kinetics of amalgam decomposition has been confirmed experimentally in the work of S.I. Sklyarenko [14] and Z.A. Iofa [15]. In other cases of amalgam decomposition, slightly different relationships can be observed; thus, it is easy to show that for the amalgams of divalent metals, for example, barium or zinc, the same reasoning leads to a law according to which the decomposition rate is proportional to the fourth root of the amalgam concentration [8].

The relations presented in the foregoing apply when only the amalgam concentration varies during the reaction while the concentrations of the other components of the system (hydrogen ions, metal ions in solution, etc.) remain constant.

In the case of the decomposition of amalgam by solutions in which the concentration of the components does not remain constant, the reaction equations assume a slightly more complex form; these equations can be derived in an analogous manner but it is essential, of course, to take into account the variations of the ion concentration in the equation for the kinetics of the hydrogen ion discharge. Moreover, if the total electrolyte concentration in the solution varies at the same time the influence of the ψ_1 potential must also be taken into account and the corresponding modifications introduced into the kinetic equations [16].

In practice we have to deal more often with the decomposition of amalgams by alkaline solutions in which hydrogen separation takes place via discharge of a water molecule. On the basis of the principles reviewed in the foregoing, we can derive differential equations for the reaction of amalgam decomposition for this case as well. The equation for the hydrogen overvoltage on the mercury cathode in alkaline solutions (see Eq. 227) and the equation for the equilibrium potential of the amalgam electrode must be used for this purpose. The absolute value of the rate constant of the amalgam decomposition in alkaline solutions, as follows from the above, can be calculated from the normal potential of the amalgam electrode and the hydrogen overvoltage on the mercury cathode in alkaline solutions. The equations thus obtained for the rate of decomposition of the amalgams of the alkali metals agree well with experiment. Conversely, the hydrogen overvoltage in alkaline solutions can be found from the decomposition rate of amalgams, as has been pointed out already in Chapter 3.

§4. DISSOLUTION OF SOLID METALS WITH SEPARATION OF HYDROGEN

The above considered reaction of amalgam decomposition is characterized by the fact that a gradual variation of the concentration of the metal dissolved in the amalgam takes place in the course of the process. Let us now turn to the process of dissolution of pure metals in which an alteration of the composition of the metallic phase does not take place.

Let us examine two different extreme cases of dissolution of solid metals in acid solutions (in the absence of atmospheric oxygen).

First let us discuss the case in which the rate of discharge of the ions and the ionization of the metal is high and the rate of the discharge of ions and the ionization of hydrogen is small. This case is analogous to that observed during the decomposition of the amalgams of the alkali metals.

As a typical example we can use the process of the dissolution of lead in sulfuric acid, which takes place, for example, in the lead battery. In the charged battery, the negative plates consist of spongy metallic lead which is normally immersed in 8 N sulfuric acid. During standing of the battery, a dissolution of the lead takes place with evolution of hydrogen, which causes its spontaneous discharge.

In this case the same four electrochemical reactions can take place as those indicated in the foregoing. In this case we can also neglect the rate of the ionization of the hydrogen because the potential of lead in 8 N sulfuric acid is much more negative (by about 0.37 v) than the reversible potential of the hydrogen electrode in this solution. Three processes remain whose rates are connected by the relation $\overrightarrow{i}_1 = \overleftarrow{i}_2 - \overrightarrow{i}_2$.

We must then take into account that compared with the rate of hydrogen separation the rates of the discharge and ionization of lead are large. Under these conditions, as in the case of the decomposition of amalgams, the solution of the problem can be found fairly easily because the electrode potential is practically very close to the equilibrium potential of the lead electrode which is defined by the thermodynamic expression

$$\varphi=\varphi^0+\frac{RT}{2F}\ln[\mathrm{Pb}^{\cdot\cdot}], \qquad (285)$$

where $\varphi^0 = -0.13$ v relative to the standard hydrogen electrode.

When lead is dissolved in sulfuric acid solution, the sparingly soluble lead sulfate is formed. Within a short time the solution is saturated and the salt is precipitated in the solid form.

Figure 126 shows the potential as a function of the logarithm of the current density for the case of cathodic (curve 2) and also anodic (curve 1) polarization of a lead electrode [17]. The dotted line gives the equilibrium potential of lead in sulfuric acid solution saturated with lead sulfate. It can be seen that the potential of the anodically polarized lead electrode in this solution varies only slightly over a broad range of current densities and that it is very close to the equilibrium potential of Pb in H_2SO_4 solution, saturated with $PbSO_4$.

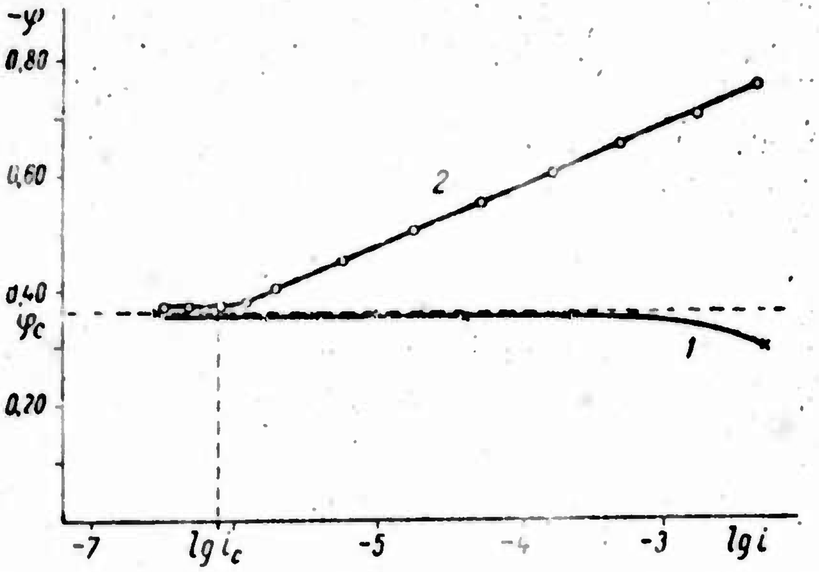

Fig. 126. Polarization curves of the processes: 1) Dissolution of lead; 2) hydrogen separation; i_s is the self-dissolution current of lead. The potential was measured relative to the hydrogen electrode in the same solution.

The slight positive shift, amounting to a few millivolts, is explained by the fact that during the dissolution of metallic lead the process of crystallization of the sulfate does not take place at an infinite rate but requires a certain time. In consequence of this, a supersaturated solution of lead sulfate is formed, and the concentration of the lead ions at the electrode surface is somewhat higher than the concentration in the saturated solution. At large anodic current densities the overvoltage of the process of ionization of the lead begins to play an important part, and the electrode potential is shifted to the negative side [38]. In order to resolve the problem of the rate of dissolution of lead one has to know the laws of the cathodic hydrogen evolution on lead in the solutions of interest to us. At moderate current densities, the hydrogen overvoltage is an almost linear function of the logarithm of the current density for the lead electrode.

The rate of hydrogen separation is independent of the simultaneously occurring dissolution of the lead, i.e., these two reactions do not affect each other (provided that an alteration of the surface condition of the electrode does not take place). The point of intersection of the polarization curves for the reaction of hydrogen ion discharge and the reaction of the anodic dissolution of lead gives the stationary potential φ_s on the ordinate and the rate of self-dissolution i_s of the lead on the abscissa (see Fig. 126).

The experimentally observed rates of self-dissolution of the lead electrode are in good agreement with the values found by the above-described method from the polarization curves [11].

Different relationships obtain in the case of dissolution in acids of metals for which the processes involved in the ionization and discharge of the metal take place slowly, such as, for example, in the case of the metals of the iron group.

The normal iron potential relative to its divalent ions is −0.44 v. However, if this metal is immersed in 1 N hydrochloric acid solution, its stationary potential is −0.26 v. It is immediately evident that this potential cannot be regarded as the equilibrium potential relative to the ferrous ions (to this value of the equilibrium potential would correspond an activity of the Fe^{++} ions of approximately 10^6 which is devoid of any physical meaning).

Let us examine the over-all process consisting, as in the previously discussed cases, of four electrochemical reactions. The stationary potential of the iron electrode during dissolution in acid is approximately 0.26 v more negative than the potential of the reversible hydrogen electrode in this solution, hence the rate of ionization of the hydrogen $\overleftarrow{i}_1$ on this electrode is negligibly small and can be neglected. Moreover, another simplification is possible in this case, connected with the fact that the exchange current of the iron at its equilibrium potential is relatively small. At more positive potentials than the equilibrium potential the rate of the cathodic process of discharge of the ferrous ions $\overrightarrow{i}_2$ decreases further and it can also be neglected by way of a first order of approximation relative to the rates $\overrightarrow{i}_1$ and $\overleftarrow{i}_2$. Then only two out of four terms remain in Eq. (277), $\overrightarrow{i}_1 = \overleftarrow{i}_2$, corresponding to the reaction of iron ionization and hydrogen ion discharge. The dependence of the rate of these reactions on potential can be studied separately if during polarization of the electrode one measures at different potentials not only the total current but also the quantity of iron dissolved in unit time for the first reaction and the quantity of hydrogen separated for the second.

The polarization curve of hydrogen separation on iron can be expressed by an equation of the same type as for the mercury electrode (at least within a certain range of current densities and concentrations):

$$\vec{i}_1 = k_1[H^{\cdot}]e^{-\frac{\alpha\varphi F}{RT}}. \qquad (286)$$

If the electrode surface remains unchanged, the rate of ionization of the iron is also connected with the electrode potential by the exponential relationship

$$\overleftarrow{i}_2 = k_2 e^{\frac{\beta\varphi F}{RT}}. \qquad (287)$$

By graphic representation of the polarization curves of the hydrogen separation or ionization of the iron it is possible, as in the case of the amalgam and lead electrodes, to determine on the basis of the point of intersection the stationary potential and the rate of self-dissolution of the iron electrode (see Fig. 127).

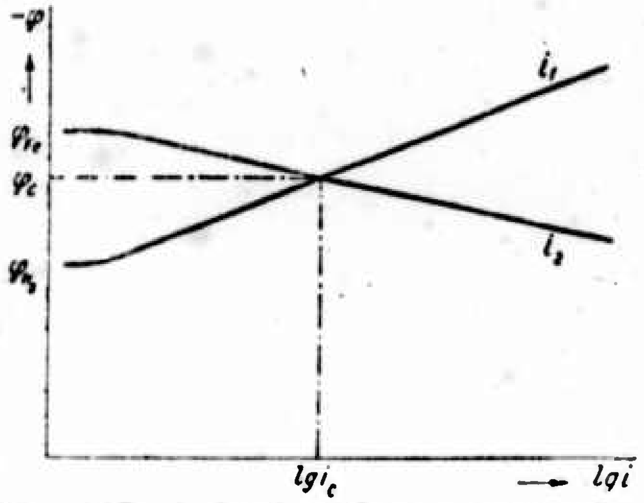

Fig. 127. Polarization curves of the processes of hydrogen separation (i_1) and iron dissolution (i_2) in acid solutions.

The problem of finding the rates of self-dissolution of iron can also be resolved by a direct analytical method because only two exponential terms remain in Eq. (274) which expresses the stationarity conditions. By substituting into it the expressions for $\vec{i}_1$ and $\overleftarrow{i}_2$ from (286) and (287), we find

$$k_1[H^+]e^{-\frac{\alpha_1\varphi F}{RT}} = k_2 e^{\frac{\beta_2\varphi F}{RT}} \qquad (288)$$

and, solving this for φ, we obtain the expression for the stationary potential

$$\varphi_c = A + \frac{RT}{(\alpha_1+\beta_2)F}\ln[H^+], \qquad (289)$$

where

$$A = \frac{RT}{(\alpha_1+\beta_2)F}\ln\frac{k_1}{k_2}.$$

Substituting the value for $_s$ into the equation for $\vec{i}_1$ and $\overleftarrow{i}_2$, we find, after some simple transformations, the relation for the self-dissolution rate

$$i_c = k_1[H^+]^{\frac{\beta_2}{\alpha_1+\beta_2}}. \qquad (290)$$

It is evident from Eq. (289) that the stationary potential for a metal, for which the rates of ionization and discharge of the metal ions at the equilibrium potential are small and comparable with the rate of discharge of the hydrogen ions, should vary with variation of the hydrogen ion concentration in the solution in the same manner as the potential of the reversible hydrogen electrode. The coefficient in front of the logarithm of the hydrogen ion concentration is of course not equal to the coefficient in the equation for the reversible hydrogen electrode because the sum ($\alpha_1 + \beta_2$) may differ from unity.* However, as α_1 and β_2 are proper fractions close to 1/2, this difference is not very great and the trend of the relationship between φ_s and $[H^+]$ is generally the same as with the hydrogen electrode [10, 12]. Figure 128 is an example, giving data which characterize the dependence of the stationary potential of the iron electrode on the pH of the solution [18].

The rate of self-dissolution increases with increase in the hydrogen ion concentration. The relation expressed in Eq. (290) is a consequence of the superposition of two factors. On the one hand, the rate of hydrogen separation increases proportionally with increasing hydrogen ion concentration; on the other hand the increase in the rate of the ionization reaction of the iron, which is connected with this, shifts the electrode potential to the positive side and thus slows down somewhat the hydrogen separation. In consequence of this the rate of self-dissolution is proportional to a certain fractional power of the hydrogen ion concentration. The relation expressed by Eq. (290) at moderately high acid concentration is well confirmed by experiment: this is evident, for example, from Fig. 129, in which the dependence of the rate of dissolution of steel (0.18% C) is given as a function of the mean activity of the sulfuric acid ions [19].

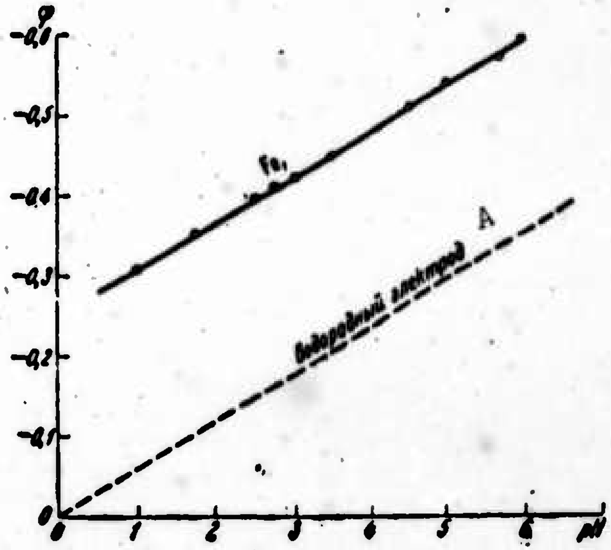

Fig. 128. Stationary potential of the iron electrode as a function of the pH in the Na_2SO_4 – containing buffer solutions. A) Hydrogen electrode.

The examples of the dissolution of lead and iron in acids considered in the foregoing correspond to two extreme cases. In the first case the process of hydrogen separation affects the relation between the rates of ionization of the metal and the discharge of its ions only very slightly, so that the stationary potential is close to the equilibrium potential for a solution with the same metal ion concentration.

In the second case the shift of the stationary potential to the positive side compared with the equilibrium potential, caused by the discharge of the hydrogen ions, is so large that the rate of discharge of the metal ions at the stationary potential can be neglected compared with the ionization rate.

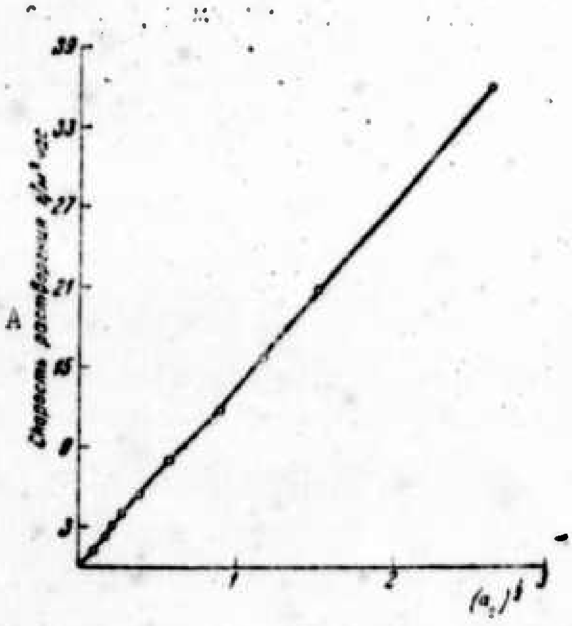

Fig. 129. Rate of dissolution of steel in sulfuric acid as a function of the mean activity $a_{\pm}$ of the sulfuric acid ions. A) Rate of dissolution g/m^2 hour.

Cases are often observed corresponding to intermediate conditions, where the reaction of hydrogen separation causes a marked shift of the stationary potential but where the reactions of ionization and discharge of the metal ions nonetheless remain comparable. To these belongs the self-dissolution of iron in alkaline solutions. In consequence of the low solubility of the ferrous hydroxide $Fe(OH)_2$ formed under these conditions the solution can always be considered to be saturated with respect to this compound. The equilibrium potential of the Fe electrode in an NaOH solution, saturated with $Fe(OH)_2$ (Fig. 130, ordinate a) is -0.075 v relative to the reversible hydrogen electrode in the same solution. The stationary potential of unpassivated iron in the same solution, determined by the intersection of the polarization curves of hydrogen separation 1 and the anodic dissolution of iron 2, is strongly shifted to the positive side and is situated at −0.045 v (point *A*). This potential has long been regarded as the equilibrium potential of this system until comparison of the exchange current for iron and the rate of hydrogen separation showed that we are dealing here merely with a stationary and not with an equilibrium value [20].

The above-described ideas on the kinetics of the dissolution of metals are not valid if passivating layers form on their surfaces which is possible during the dissolution of lead in sulfuric acid as well during the dissolution of iron in alkali (see Chapter 7).

In the foregoing we have examined the dependence of the dissolution kinetics on the exchange current of the metal. The hydrogen overvoltage is also of great importance in this connection, however. With a given polarization characteristic of the anodic process, the rate of self-dissolution will evidently be greater if the hydrogen separation overvoltage is less. The self-dissolution reaction in acid solution, however, cannot be accelerated indefinitely because the rate of hydrogen separation limits the rate of diffusion of the hydrogen ions towards the electrode surface.

In cases where separation of hydrogen from alkaline solutions is not possible on the metal surface and the rate of discharge of the hydrogen ions from acid solutions is fairly large, the rate of the self-dissolution is determined by diffusion of hydrogen ions towards the metal surface. These conditions are particularly frequently realized during the dissolution of technical, fairly electronegative metals, for example, zinc, containing impurities which lower the hydrogen overvoltage. In such cases the rate of dissolution depends on all factors which determine the magnitude of the limit diffusion current, such as, for example, the rate of mixing and the viscosity of the solvent (see Chapter 1).* This conclusion is fully confirmed by experiment. The existence of an approximately inverse proportionality between the rate of dissolution of the metals and the viscosity of the solution, which must be expected in this case, has already been observed by Kayander in 1881 [1].

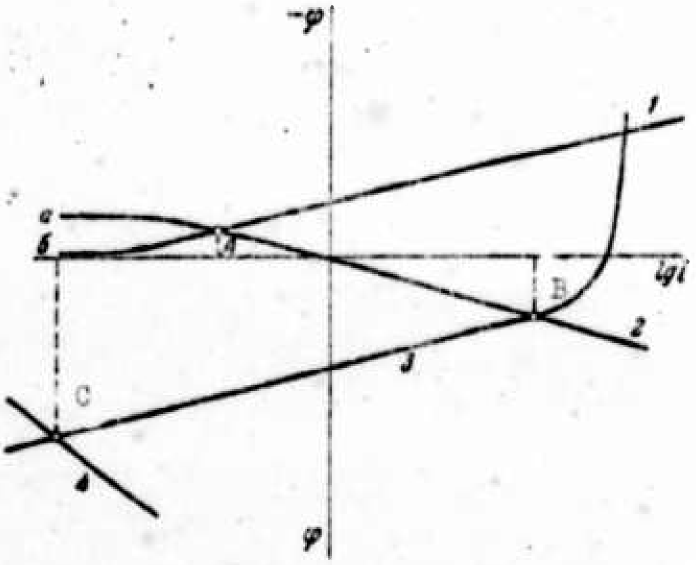

Fig. 130. Effect of oxygen on the rate of self-dissolution of iron in alkaline solution: 1) Cathodic curve of hydrogen separation; 2) anodic curve of the dissolution of the active iron electrode; 3) cathodic curve of oxygen reduction; 4) anodic curve of the passive iron electrode. The abscissae of the points A, B and C express, respectively, the corrosion rate of the active iron electrode with hydrogen separation, of the active electrode with reduction of oxygen, and of the passivated electrode. The ordinate of the point *a* is the equilibrium potential of iron in the same solution. The potentials are related to the reversible hydrogen potential in the same solution.

§5. DISSOLUTION OF METALS IN PRESENCE OF OXYGEN AND OTHER OXIDANTS

In the preceding sections we have considered the process of self-dissolution of metals in electrolyte solutions accompanied by discharge of hydrogen ions and the separation of gaseous hydrogen. As pointed out earlier, the reaction of self-dissolution of a metal can also take place by different pathways: if the solution contains substances capable of electrochemical reduction at the metal surface (for example, dissolved atmospheric oxygen, nitric acid, iodine or other oxidants), the reaction of ionization of the metal can be compensated by the reaction of reduction of these substances and not by the reaction of hydrogen ion discharge.

Of great practical importance are the processes of metal dissolution accompanied by reduction of dissolved oxygen (so-called metal dissolution with "oxygen depolarization").* The latter have been studied in detail by N.D. Tomashov [21]. The reduction of oxygen takes place on most metals at potentials which are slightly more positive than the reaction of hydrogen separation. In consequence of this, when the solutions are saturated with atmospheric oxygen, the dissolution of the metals is accelerated if the surface is maintained in an active state.

Figure 130 gives the curves of the ionization rate of iron (curve 1) and also of hydrogen separation (curve 2) and the reduction of oxygen (curve 3) as a function of the potential of the active iron electrode (for alkaline solutions). The point A corresponds to the stationary state established in the absence of atmospheric oxygen (for example, in solutions saturated with hydrogen or nitrogen) while the point B represents the stationary state of the electrode in a solution in contact with air. In the presence of air, as the figure shows, the rate of self-dissolution increases.

In consequence of the low solubility of oxygen in electrolyte solutions (in moderately concentrated solutions which are saturated with air, the concentration of dissolved oxygen amounts approximately to $2.5 \cdot 10^{-4}$ moles per liter), the reaction rate of the cathodic reduction of oxygen is limited by the diffusion of oxygen towards the electrode surface and cannot exceed the values corresponding to the limit diffusion current of oxygen as is evident from the polarization curve of oxygen reduction (curve 3, Fig. 130). The section of the latter with the steep rise corresponds to the limit diffusion current of oxygen.

Three cases must be distinguished in the corrosion of metals in the presence of oxygen.

While the position of the curve which expresses the potential of the metal as a function of the anodic process corresponds to the case 1' in Fig. 131, the point of its intersection with the curve, which expresses the rate of the cathodic process lies in the range of the limit oxygen current (point B). In this case it is said that the self-dissolution potential lies in the oxygen diffusion range. The abscissa of the intersection point which defines the self-dissolution current in this case remains almost constant during variation of the position of the curve 1'; in other words, the corrosion rate, determined by the diffusion of oxygen to its surface, is independent of the nature of the metal but depends on the mixing rate, the viscosity of the solution, etc., as has been explained earlier during the examination of the dissolution of metals in acids. The situation is different in the case 1, corresponding to a lower rate of the anodic process at the same potential. At the self-dissolution potential we are in the kinetic oxygen range. The density of the self-dissolution current in this case is considerably less than the density of the diffusion current and depends greatly on the nature of the metal.

If the curve of the anodic process is situated at more negative potentials than the curve 1' (curve 1"), the separation of hydrogen is also possible at a high rate at the stationary potential of self-dissolution in the presence of oxygen. Hence during the dissolution in an oxygen atmosphere of metals which have a strongly negative potential (for example, sodium amalgams), an intense hydrogen evolution can take place simultaneously with the reduction of the oxygen. In this case the shift of the stationary potential and the increase in the dissolution rate upon transition from a hydrogen to an oxygen atmosphere is relatively slight.

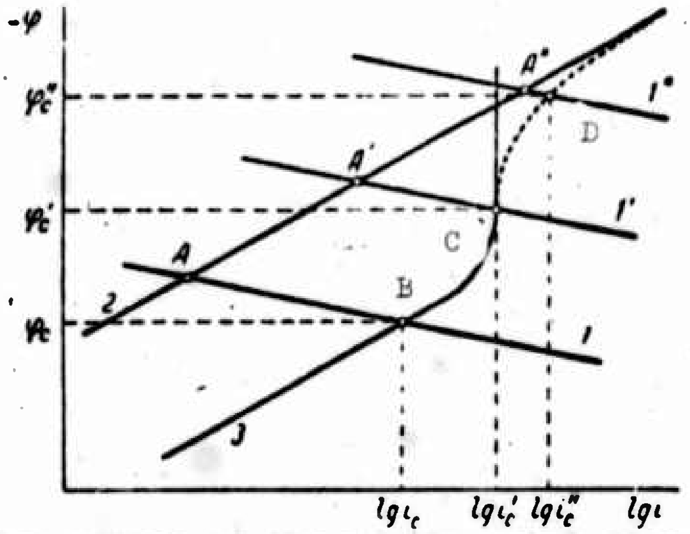

Fig. 131. Polarization curves of the anodic metal dissolution (1, 1', 1"), of hydrogen separation (2) and oxygen reduction (3) in acid solutions. The summary rate of the processes of hydrogen separation and oxygen reduction is represented by the dotted line. The ordinates of the points A, A' and A" represent the self-dissolution potentials in the absence of oxygen, the ordinates of the points B, C and D, in the presence of oxygen.

It has been shown in Chapter 4 that on some metals the cathodic reduction of oxygen leads to the formation of hydrogen peroxide while on other metals oxygen is reduced straight to water [22]. The formation of hydrogen peroxide during the corrosion of many metals in air in the presence of water can be readily shown experimentally, particularly if the ability of the hydrogen peroxide vapor to cause darkening of a photographic plate is utilized. The conclusions given here on the kinetics of metal dissolution in presence of oxygen can be particularly easily confirmed by using as an example the dissolution of mercury and amalgam because in this case all complications due to the formation of passivating films and surface heterogeneity are absent [23].

During the oxidation of mercury by atmospheric oxygen in a solution of sulfuric acid, mercury ions are formed; because the mercury exchange current is large compared with the rate of reduction of the oxygen on the mercury cathode, the mercury electrode assumes an equilibrium potential corresponding to the concentration of the mercury ions which is established in the solution at the given mixing conditions, and the rate of dissolution of the mercury is determined by the rate of the electrolytic reduction of the oxygen at this potential. Because the reduction of oxygen at the potentials of mercury in solutions containing mercury ions can proceed only to hydrogen peroxide, hydrogen peroxide accumulates in the solution in a quantity equivalent to the quantity of mercury ions which have passed into solution. If the potential of the mercury electrode is shifted strongly to the negative side, by introducing into the solution instead of H_2SO_4 an electrolyte, whose anions bind the mercury ions by complex formation, for example, KCN, the rate of oxygen reduction at the stationary potential increases* and we come close to the conditions corresponding to curve 1' in Fig. 131; the rate of dissolution is then basically determined by the diffusion of oxygen towards the electrode surface.

Analogous relationships are observed during the dissolution of the amalgams of metals such as cadmium or thallium in presence of oxygen. In this case the ions of the electronegative metal pass into solution at a rate which is equal to the rate of the oxygen reduction. If the concentration of the amalgam is low, the rate of oxygen reduction, as in the case of pure mercury, is determined by the electrode potential (kinetic oxygen range); at higher metal concentrations in the amalgam, however, an oxygen limit current is attained which no longer depends either on the potential or the nature of the metal (diffusion range).

The presence of other oxidants in the solution, in addition to atmospheric oxygen, as a rule also causes an increase in the rate of self-dissolution of metals. However, exceptions are observed in individual cases due to changes of the surface state. Thus, for example, addition of $Cr_2O_7^{--}$ ions (or CrO_4^-) to the solution, which have a strong oxidizing effect and, consequently, are readily reduced, intensifies the self-diffusion of some metals. Under different conditions, the same ions exert an inhibiting effect on the self-dissolution process because a thin passivated layer is formed on the metal surface under their influence which alters the kinetics of the electrode reactions and partially protects the electrode. For this reason chromates are often added to electrolyte solutions with the aim of reducing the corrosion of the metals [24].

If the conditions for the formation of a passivating film are favorable, it is possible that even in the presence of oxygen a decrease instead of an increase of the metal self-dissolution takes place. These relationships are well illustrated by the behavior of the iron electrode in caustic solution (Fig. 130). As pointed out previously, the smooth iron electrode, whose surface is free of an oxide film, assumes a potential in an oxygen-free solution, which is 0.045 v more negative than that of the reversible hydrogen electrode in the same solution (point *A*) and whose value is determined by the equality of the rates of the process of the anodic dissolution of iron with formation of $Fe(OH)_2$ (curve 2) and the hydrogen separation (curve 1).

If a caustic solution is saturated with oxygen, the cathodic process of hydrogen separation is replaced by the process of oxygen reduction, characterized by the polarization curve 3; this process, if the comparison is made at the same potential, is faster than that of the hydrogen separation. This results in an intensification of the flow of positive charges towards the electrode which causes a shift of the stationary electrode potential to the positive side (point *B*) and, consequently, an increase in the rate of the anodic process as long as the surface properties remain unchanged.

After some time, however, a passivating layer appears on the iron at this more positive potential, which, as is obvious from the position of the polarization curve 4, slows down the rate of the anodic process at this potential considerably. Hence, the rate of the cathodic process of oxygen reduction, which is equal to it under stationary conditions, should also decrease greatly, which is possible only if the stationary potential subsequently shifts even more to the positive side; the latter attains values which are 0.7-0.8 v more positive than the reversible hydrogen potential in the same solution (point *C*). This shift, caused by the alteration of the nature of the anodic process and which corresponds to the decrease in the rate of the cathodic process, in contrast to the initial shift, in which the nature of the cathodic process was altered and the rate of the anodic process increased correspondingly, is accompanied not by an increase but by a decrease in the corrosion rate. At the same time the chemical nature of the corrosion products changes in consequence of the appearance of trivalent iron in them.

In all cases in which several electrochemical reactions proceed simultaneously on the surface of a metallic electrode, the stationarity conditions, as pointed out earlier, are determined by the equality of the summary rate of all anodic and all cathodic reactions. If the form of the kinetic equations of the individual reactions is known, the value of the stationary potential and the rate of self-dissolution can be determined exactly in the same manner as in the above-considered case of the dissolution reactions which involve hydrogen separation.

It must be pointed out that frequently on electrodes which we consider to be in equilibrium many electrochemical reactions actually take place simultaneously. Thus on a platinum electrode in a hydrogen atmosphere, on which the basic reactions are the discharge and ionization of hydrogen, numerous other reactions are possible involving the oxidation or reduction of impurities which are always present in the solution such as, for example, reactions of the reduction of traces of oxygen which has remained in the solution. The rates of these reactions depend on the experimental conditions and on the degree of purity of the solution and, at least theoretically, they must be taken into account in the over-all balance of the electric charges. Practically, however, their rates are usually so small compared with the rates of the main reaction that they can be completely neglected; for this reason such electrodes can be regarded as being in equilibrium with a sufficient degree of approximation. In some cases, however, the relations between the rates of the main and side reactions change. For example, in the presence of small traces of arsenic compounds the rates of the reactions of the ionization and discharge of hydrogen on platinum are greatly decreased; in this case the rates of the side reactions become comparable with the rate of the main reaction, the equilibrium on the electrode surface is upset and its potential is shifted to the positive side (poisoning of the platinum electrode).

§6. SELF-DISSOLUTION AND ANODIC DISSOLUTION OF METALS

Up to now we have considered the behavior of isolated metal electrodes, which are not connected with an external electric circuit, in electrolyte solutions.

The passage of electric current through the electrode and the polarization of the electrodes connected with it affects the rate of all the electrochemical reactions taking place on the metal surface, including the rate of dissolution of the metal. Polarization upsets the above-described equality of the rates of dissolution of the metal and the hydrogen separation (Eq. 273). The density of the external current is naturally equal to the difference between the densities of the hy-

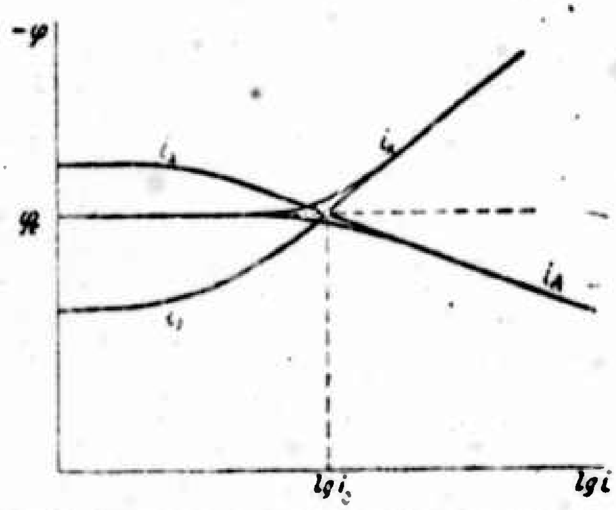

Fig. 132. Cathodic and anodic polarization of a metallic electrode, which dissolves with separation of hydrogen, by an external current: i_1) curve of hydrogen separation; i_2) curve of anodic dissolution of the metal; i_K) curve of cathodic polarization; i_A) anodic polarization curve of a metal electrode in an acid solution.

drogen discharge and metal ionization currents

$$i_K = i_1 - i_2 = \overrightarrow{i}_1 - \overleftarrow{i}_1 - (\overleftarrow{i}_2 - \overrightarrow{i}_2), \tag{291}$$

while the external anodic current is equal to the excess of the metal ionization current over the hydrogen discharge current

$$i_A = i_2 - i_1 = \overleftarrow{i}_2 - \overrightarrow{i}_2 - (\overrightarrow{i}_1 - \overleftarrow{i}_1). \tag{292}$$

If we polarize, for example, an iron electrode in an acid solution with small currents (i.e., with currents which are small compared with the self-dissolution current in the absence of external polarization), the stationary state is almost undisturbed and the potential shift of the electrode is slight. This is evident from the fact that the curves of dissolution of the iron and of the hydrogen separation at small current densities in semilogarithmic coordinates approach a horizontal line, whose ordinate corresponds to the stationary potential of self-dissolution of the metal. It is easy to show that the potential shift caused by the action of an external polarizing current is less when the self-dissolution current is large. The stationary dissolution potential of iron φ_s in acid can be determined (neglecting the rates of the two other electrochemical reactions) by the equality of the rates of the processes of hydrogen ion discharge and ionization of the iron

$$k_1[\mathrm{H}^+]\,e^{-\frac{\alpha_1 \varphi_c F}{RT}} = k_2 e^{\frac{\beta_2 \varphi_c F}{RT}} = i_c, \qquad (293)$$

where i_s is the density of the self-dissolution current. At small deviations $\Delta\varphi$ of the potential from the stationary value the intensity of the cathodic polarization current is

$$i_K = k_1[\mathrm{H}^+]\,e^{-\frac{\alpha_1 F(\varphi_c+\Delta\varphi)}{RT}} - k_2 e^{\frac{\beta_2 F(\varphi_c+\Delta\varphi)}{RT}} \approx -i_c \frac{(\alpha_1+\beta_2)F}{RT}\cdot\Delta\varphi, \qquad (294)$$

hence

$$\Delta\varphi \approx -\frac{RT}{(\alpha_1+\beta_2)F}\,\frac{i_K}{i_c}. \qquad (295)$$

Equation (295) is analogous to Eq. (145a) obtained in Chapter 3 for the potential shift of the equilibrium hydrogen electrode at low densities of the polarizing current but instead of the exchange current it contains the self-dissolution current i_s.

If a large cathodic current is passed through the electrode, the rate of ionization of the iron in the acid solution is greatly lowered and the points of the cathodic polarization curve i_K fall practically on the hydrogen separation curve $i_1 = \vec{i}_1$. An analogous relation obtains when a large anodic current is passed through: the rate of hydrogen separation is greatly reduced in consequence of which the anodic polarization curve i_A practically coincides with the metal dissolution curve $i_2 = \vec{i}_2$.

As can be seen in Fig. 132, the polarization curves of the self-dissolving iron electrode are connected with the curves of the anodic dissolution of the metal and the cathodic separation of hydrogen in the same way as, for example, the polarization curves of the hydrogen electrode are connected with the curves of the discharge and ionization of hydrogen (compare Fig. 72 and 73). The principal difference, however, consists in the fact that in the latter case the discharge and ionization curves relate to individual electrochemical reactions while the curves of metal dissolution and hydrogen separation for iron express each the difference in the rates of two reactions (the cathodic and anodic).

The problem of the variation of the rate of self-dissolution during the polarization of a metal by an external current source often arises during the solution of practical problems. Figure 133 illustrates the relations observed in such a case. The curves 1 and 2 represent the rates of ionization of the metal and the separation of hydrogen as a function of the potential. To the intersection point of these curves (point *A*) on the abscissa axis corresponds the logarithm of the rate of self-dissolution of the metal. Anodic polarization shifts the electrode potential to the positive side, for example to the value φ_a and in consequence of this the rate of hydrogen separation is greatly reduced (point *B*).

Thus the rate of dissolution of the metal (i.e., dissolution with evolution of hydrogen) is greatly reduced during anodic polarization of the metal. This phenomenon is commonly termed positive difference effect in the corrosion literature.

The difference effect can be expressed to a varying degree in different cases. In the case of the reaction of dissolution of sodium amalgam we had an example of a very weak difference effect: as pointed out in the foregoing, at moderate anodic (and also cathodic) current intensities, in consequence of the large exchange current of sodium, the potential of the amalgam electrode varies only very slightly and the rate of self-dissolution of the electrode under an external current differs little from the rate of self-dissolution of the unpolarized electrode."

A positive difference effect corresponds to normal conditions on a metal surface. In some cases, however, phenomena are observed during the polarization of an electrode which are opposite to those described just now and which consist in an increase in the rate of self-dissolution of the metal during anodic polarization (negative difference effect). These phenomena serve as an example of the complications due to variation of the surface state by the simultaneous occurrence of several electrochemical processes. The negative difference effect may be connected with the fact that the nature of the oxide film is modified by the anodic polarization. If the formation of the oxide film on the surface requires time, then it cannot always be renewed during strong anodic dissolution of the metal and the surface is less protected. The rate of hydrogen separation can also increase under the influence of this alteration; if the increase in the rate of hydrogen separation due

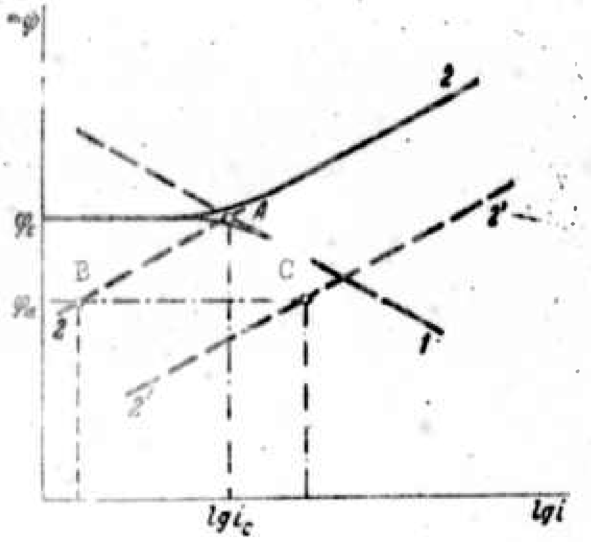

Fig. 133. Positive and negative difference effects: A) Stationary state of the unpolarized metal; φ_a) potential during anodic polarization; B) self-dissolution of the metal with positive difference effect, and C) self-dissolution of the metal with negative difference effect.

to a change of the surface state more than compensates for the decrease in the rate of this process which is caused by the potential shift to the positive side, the self-dissolution of the metal is intensified. Thus, if curve 2 (Fig. 133) is shifted to the side of more positive potentials (curve 2') during anodic polarization in consequence of a transition of the electrode to a different state, the rate of self-dissolution at the potential φ_a may prove to be greater than in the initial state (point *C*) although the potential is more positive. Such phenomena can be observed, for example, during the anodic polarization of magnesium in an alkaline solution in presence of chlorine ions.

In analogy to the slowing down of the discharge of hydrogen ions during anodic polarization under normal conditions, the cathodic polarization slows down the reaction of ionization of the metal and, consequently, reduces the rate at which it goes into solution. This last phenomenon is termed protection effect in the corrosion literature [6, 21]. The protection method of corrosion prevention which is widely used in practice is based on it. Thus, for example, if an iron surface in sea water is to be protected against corrosion, it is polarized cathodically by being brought into contact with zinc electrodes. Cathodic polarization can also be achieved by means of an external current source. Owing to the negative potential shift caused by the cathodic polarization the corrosion rate of the iron is greatly reduced. In this case exceptions can be likewise observed for passivating metals because the reduction of the oxide film during the cathodic polarization can lead to accelerated self-dissolution of a metal. Thus when aluminum is subjected to cathodic polarization in solutions of LiOH and NaOH with large current densities, rapid self-dissolution takes place [29].

§7. LOCAL ELEMENTS

Up to now we have considered the dissolution of a metal from a homogeneous surface, i.e., we have assumed that the rate of electrochemical reactions taking place on the surface is the same at all points and that all points of the surface have the same potential (i.e., that the surface is strictly an equipotential one). This assumption is completely justified for a liquid metal, for example, for the surface of mercury or an amalgam electrode, which can serve as an example of a homogeneous surface. When we pass on to a solid metal this assumption can only be a certain approximation. Even if the solid metal is chemically quite homogeneous, different regions on its surface cannot be considered to be completely homogeneous in a physical sense. As discussed already in Chapter 6, different points of the surface which differ by their position in the lattice of the individual crystallites have different energies and different properties which is reflected in the electrochemical reactions taking place at these points. A particularly marked deviation from the simplified picture used by us occurs when the metal contains foreign inclusions and when, in consequence of this, its surface is divided into regions with different physical and chemical properties. Hence the problem arises under what conditions the concepts developed in the foregoing can be applied to a real solid metal and to what degree the influence of the surface heterogeneity must be taken into account in different partial cases.

Let us consider first the extreme case of the presence on the surface of a pure dissolving metal (which we shall arbitrarily term the base metal in the following) of foreign inclusions with physical and chemical properties, which differ markedly from the properties of the base metal. To be more specific, let us assume that the hydrogen separation overvoltage on these inclusions is greatly lowered and that these inclusions do not dissolve in the electrolyte solution or dissolve very slowly. The stationary potential of these inclusions is obviously more positive than the potential of the base metal because otherwise the inclusion on which the hydrogen separation is disinhibited would be subjected to rapid self-dissolution.

As has been pointed out in §1, the inclusions and base metal on a metal surface form a large number of galvanic elements of microscopic dimensions. The internal resistance of these microelements is mainly determined by the dimensions and shape of the inclusions and the electrical conductivity of the solution; the resistance of the metal between the inclusions and the surface of the pure metal is very small and can be practically neglected compared with the resistance of the solution.

As will be shown further on, the total resistance of the microelements in solutions with fairly good electrical conductivity is low. For this reason the latter often cause the appearance of large local electric currents. The currents flow in the metal from the more positive regions of the inclusions to the more negative regions of the surface of the base metal. In the solution the direction of the current in these short-circuited elements is the opposite. In consequence of the passage of current the reaction of anodic metal dissolution takes place mainly on the surface of the base metal while the reaction of cathodic hydrogen separation takes place at the inclusions.

The effect of the inclusion can be also explained in the following way. In the balance of inclusions a stationary potential would be established on the base metal at which the cathodic process of ion discharge and the anodic process of ionization would proceed at the same rate. The presence of inclusions on which the hydrogen ion discharge is disinhibited causes a shift of the potential of the base metal to the positive side. Because of this the anodic process of metal dissolution is accelerated on the base metal and the cathodic process of hydrogen separation is slowed down. In other words, the anodic process now predominates on the base metal and the cathodic on the inclusions, i.e., a spatial separation of the electrochemical reactions has taken place. Because the rate of hydrogen ion discharge (see Chapter 3) depends greatly on the nature of the metal, the presence of inclusions with lower overvoltage can cause a strong increase in the rate of self-dissolution of a metal with large overvoltage in acids. Inclusions of iron in zinc or antimony in lead, for example, have such an effect.

The cathodic and anodic surface regions are polarized during the passage of current. The current intensity in the local elements can be calculated if the polarization characteristics of the cathodic and anodic regions and the ohmic resistance between them are known.

The graphic method of calculating the current intensity in the local elements by means of the polarization curves of the anodic and cathodic regions (the so-called method of polarization diagrams) [6, 25] is widespread in the corrosion literature. An example of such a diagram is given in Fig. 134. Curve 1 corresponds to the anodic polarization curve of the base metal and curve 2 to the polarization of the inclusions during the separation of hydrogen on them. In contrast to the earlier used graphic method, the logarithm of the current intensity in the local element is plotted on the abscissa axis in Fig. 134 instead of the logarithm of the current density. In consequence of the fact that the cathodic and anodic processes take place at different regions of the surface which differ in size, and that the total intensity of the cathodic current should equal the total intensity of the anodic current, the current densities at the cathodic and anodic regions during the course of the corrosion process are not equal; for this reason it is more convenient to use the polarization curves which are related to the current intensity. It is logical that with this method of representation the position of the polarization curve depends not only on the nature of the metal and solution but also on the size of the corresponding regions.

Furthermore it must be emphasized that the abscissa in Fig. 134 does not express the rates of the individual reactions but the total intensity of the anodic current, on the one hand, and the cathodic, on the other, i.e., that they correspond to the curves i_A and i_K in Fig. 132. Instead of the logarithm, current intensity itself is often plotted on the abscissa axis of such diagrams in the corrosion literature.

During the stationary state of the operation of the microelement the base metal is anodically polarized and the inclusions cathodically and the potential difference established between these regions is less than the initial difference (more correctly, less than the potential difference between the base metal and the inclusion material if insulated from each other in the same electrolyte). This potential difference corresponds to the ohmic potential difference in the solution between the anodic and cathodic regions.

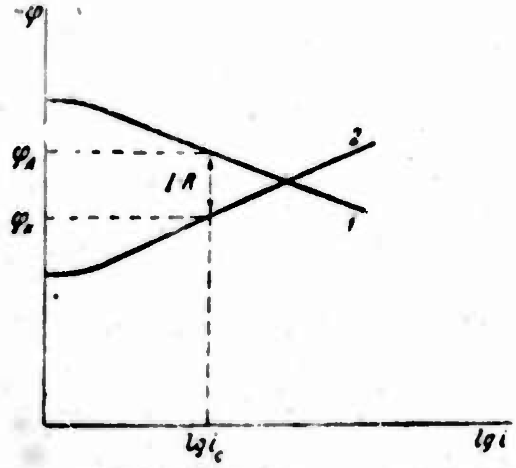

Fig. 134. Polarization curves of a local element: 1) Curve of the anodic polarization of the base metal; 2) curve of the cathodic polarization of the inclusion.

If the internal resistance of the microelement is known, the corrosion current can be readily found by means of the polarization curves of Fig. 134. For this purpose one must select a current intensity I at which the potential difference between the anodic and cathodic regions is precisely equal to the ohmic potential drop IR. In the most general form the corrosion current I can be found as the solution of the equation

$$I = \frac{\varphi_K - \varphi_A}{R}, \tag{296}$$

where φ_K and φ_A are also functions of I. Strictly speaking, the quantity R also depends on I because the passage of current causes a change in concentration and, consequently, of the electrical conductivity of the solution.

It must be emphasized, however, that Eq. (296) which has been widely used in corrosion literature in different forms, does not give a correct idea of the difficulties encountered in the calculation of the operation of the microelements. This equation is entirely applicable to a normal galvanic element with spatial separation of cathode and anode because the resistances along the path of the current in the electrolyte between different points of the cathode and anode differ little from each other. The situation is different in the case of the microelement in which the cathode and anode are in contact with each other along a certain perimeter. The quantity R in this case varies considerably from point to point and vanishes when the point under consideration is in the direct vicinity of the interface between the cathodic and anodic regions. Hence to get an idea of the operation of microelements it is essential to determine the full pattern of the distribution of the current density and potential on the metal surface. This calculation can be carried out, however, only for certain partial cases, for example, for inclusions with disc shape which are at large distances (relative to the disc diameter) from each other and even then only under certain assumptions (absence of polarization of the anodic regions and approximate constancy of the current density at different points of the inclusion) [26]. This problem is reduced to the solution of the Laplace differential equation under certain limit conditions:

$$\frac{\partial^2 \varphi}{\partial x^2}+\frac{\partial^2 \varphi}{\partial y^2}+\frac{\partial^2 \varphi}{\partial z^2}=0, \qquad (297)$$

which expresses the potential distribution in the electrolyte in the absence of free space charges. If the axes x and y are placed on a plane in the metal with the coordinate origin at the center of the inclusion,* and the positive direction of the z axis extends in the direction of the electrolyte, Eq. (297) should be fulfilled at $z > 0$. The limit conditions for our partial case are easily formulated on the basis of the physical assumptions made. Because we consider the base metal to be unpolarized, the potential at its surface has a constant value, i.e.,

$$\text{at } z=0 \text{ and } r>r_0 \ \varphi=\text{const} \qquad (298)$$

(where r is the distance from the coordinate origin and r_0 the radius of the disc).

At the surface of the inclusion the cathodic current density i_K is constant, and, consequently,

$$\text{at } z=0 \text{ and } r<r_0,\ i_K=\varkappa\frac{\partial\varphi}{\partial z}=\text{const}, \qquad (299)$$

where κ is the specific electrical conductivity of the solution.

Equation (297) under these boundary conditions can be integrated and thus the potential and current density distribution in the electrolyte can be found. From this it is then not difficult to find the magnitude of the resistance R along the current paths. It is found that the resistance between the anodic part surrounding the disc and a point at a distance r from the center of the disc is

$$R=\frac{2r}{\pi\kappa}\sqrt{1-\left(\frac{r}{r_0}\right)^2}. \tag{300}$$

The maximum value of the resistance R_m corresponds to the position of the point at the center of the disc:

$$R_m=\frac{2r_0}{\pi\kappa}. \tag{300a}$$

For the maximum potential difference between the base metal and the center of the inclusion we obtain

$$\Delta\varphi=\frac{2r_0 i_K}{\pi\kappa}. \tag{301}$$

The potential difference between the anodic and cathodic regions, like the resistance, will be consequently less if the dimensions of the inclusion are less and the electrical conductivity of the solution is greater. Let us assume that the dissolution of the metal takes place in a normal electrolyte solution ($\kappa \sim 0.1$) and that $r_0 \sim 10^{-4}$ cm. Then it follows even at a very high current density of 1 amp/cm^2 from formula (301) that $\Delta\varphi \sim 0.001$ v.* Thus, although the metal surface is not strictly an equipotential surface in presence of inclusions, the deviation from equipotentiality is slight. Because the potential difference between the base metal and the center of the inclusion is small, the potential at different points of the inclusion is almost constant (i.e., the potential variations are small compared with RT/F), consequently the density of the cathodic current should also be approximately constant which justifies the assumption made by us in the formulation of the boundary conditions. The distribution of the current density at the surface of the metal in presence of a disc-shaped inclusion is shown in Fig. 135.

Equation (300) has been derived for the partial case of a disc-shaped inclusion. The result thus obtained remains valid, however, with regard to order of magnitude even for inclusions with a more complex

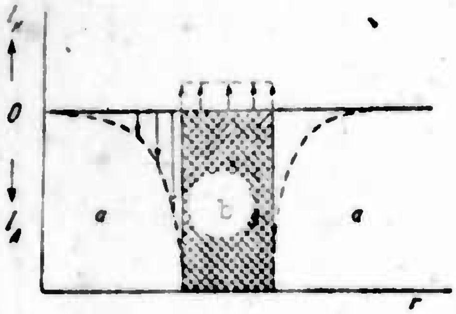

Fig. 135. Current density distribution on the surface of a metal near a disc-shaped cathodic inclusion: a) Base metal; b) inclusion.

shape. Hence it can be inferred that the surface of a corroding metal remains approximately equipotential even in presence of heterogeneities provided that the dimensions of the inclusions are small and that the electrical conductivity of the electrolyte is fairly high. This conclusion is confirmed by the measurements of G.V. Akimov and A.I. Golubev [27, 28]. By moving the orifice of a thin capillary, filled with electrolyte and connected with an auxiliary electrode, along the surface of a corroding metal by means of a micromanipulator, they measured the potential variation during the transition from one structural component of the alloy to another and gave a pattern of the potential distribution along the surface of the corroding metal. The results of such measurements for the case of zinc with an iron content of 1.5% are represented in Fig. 136. The anode in this case is zinc, the cathode the intermetallic compound $FeZn_7$. It can be seen that the potential varies considerably when going from one component to the other but the absolute variation is not very large. This permits us in cases in which we are interested only in the total corrosion and not in its distribution over the surface (for example, during the determination of the self-discharge of a current source electrode) to treat a surface known to be heterogeneous as a homogeneous surface with certain intermediate values of its parameters, for example, the hydrogen overvoltage.

In the calculation of the rate of self-dissolution of metals containing inclusions one has to take into account that during prolonged dissolution of the metals an ever increasing number of particles of the inclusion material will accumulate at the surface (if the inclusions are not soluble) and the relation and arrangement of the areas of the cathodic and anodic regions varies continuously. This often leads to a gradual acceleration of the dissolution of metals which were initially not very strongly contaminated with foreign inclusions.

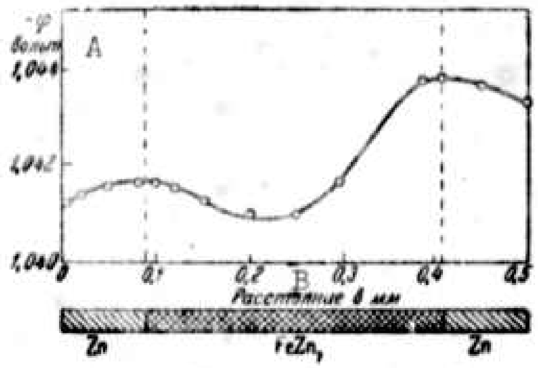

Fig. 136. Measurement of the potential along the surface of corroding zinc containing inclusions ($FeZn_7$). A) Volt; B) distance in mm.

Of considerable interest is the case in which the rate of the cathodic proce... on the whole electrode surface is not determined by the reaction itself but by the diffusion of the reacting substance. Such conditions are often encountered, for example, in the corrosion of metals in presence of dissolved oxygen. In this case the summary rate of the corrosion process is obviously independent of the size and nature of the surface heterogeneities but depends only on the geometrical dimensions of the surface and the conditions under which the oxygen diffuses towards it. In this case there is no need either that the regions on which the rate of reduction of the oxygen attains the value of the limit diffusion current, should occupy the entire electrode surface; it is sufficient if the distances between them are small compared with the thickness of the diffusion layer [21]. However, if the rate of reduction of the oxygen or other oxidant at the surface of the base metal is so small that it does not attain the value corresponding to the limit diffusion current, the presence of foreign inclusions or other heterogeneities can increase the corrosion rate even in an oxidizing medium, as has been indeed observed in many experimental cases [39].

It must be kept in mind, however, that in the case of a metal with heterogeneous surface the summary rate of the corrosion process in most cases does not by any means determine the magnitude and degree of the risk of corrosion damage. This follows already from an examination of the current distribution on the metal surface using as an example the simplest model of a local element, given in the foregoing. As is evident from Fig. 135, the rate of the anodic process increases rapidly with approximation to the edge of the cathodic inclusion. Consequently, the corrosion of the metal takes place nonuniformly; in this case it is concentrated mainly near the inclusion.

We encounter such a nonuniform distribution of the anodic process very frequently in the corrosion of solid metals accompanied by hydrogen evolution or the reduction of some oxidant. The degree of nonuniformity can vary very greatly; in some cases, for example, in the corrosion of a partly protected metal, a strong localization of the corrosion process is observed resulting in the formation of deep pits on the metal surface ("pitting"); this form of corrosion is a great danger because it can occasion the appearance of open channels in the walls of chemical apparatus. Another dangerous form of corrosion is the so-called intergranular corrosion taking place predominantly between the faces of the individual crystallites of which the metal consists, resulting in a loss of the bond between them and a lowering of the mechanical strength. Thus the corrosion process is characterized generally not only by the total corrosion but also by the "structure" of the corrosion which takes place; this term has been proposed by G.V. Akimov [30].

Great attention is given in the corrosion literature to the problem of the distribution of the disintegration process; considerable successes in this direction have been obtained by Soviet researchers.

In the foregoing we have examined the simplest model of a local element. Under real conditions, however, we encounter diverse and often much more complex relations between the cathodic and anodic regions on the surface of a metal. Thus, in the technically important alloys we are often dealing not with two but three or more types of regions; in many cases one must also take into account the differences between the normal surface of the grains of the individual components and the boundary regions, in which, for example, an accumulation of some impurity can take place during the freezing of the alloy. Methods for calculating these "multielectrode" systems on the basis of the polarization characteristics which replace in the more complex cases the polarization diagram shown in Fig. 134, have been given by G.V. Akimov and coworkers [31]; they also worked out a method for determining the polarization characteristics of the individual components of real alloys.

To determine by calculation the spatial distribution of the current density and potential in the manner done for the simplest model, shown in Fig. 135, is not possible in the case of more complex systems, with the exception, naturally, of the simplest case in which the ohmic potential drop need not be taken into account and where the current density on all points of the surface which have the same physicochemical properties, is assumed to be constant.

The heterogeneity of a metal surface can be due to the presence of a protective film with pores. If such a metal is subjected to corrosion in presence of oxygen, and if the substance of the film possesses electronic conductivity, the reduction of the oxygen can take place over the whole surface, i.e., the sites covered by the film and those free of it, although the rates of reduction may be different in these two cases. The anodic process of ionization of the metal, however, can take place only in the unprotected pores of the film; thus the surface of the film is the cathodic and the surface of the metal in the pores is the anodic region of the electrochemical system.

In this chapter we have considered mainly two extremes of the mechanism of self-dissolution of metals: the uniform dissolution of homogeneous regions and the dissolution in consequence of the operation of local elements with spatial separation of the cathodic and anodic processes.

In order to explain their interrelation, let us examine the behavior of an individual homogeneous part of the surface of a dissolving metal. By the homogeneous part of a surface, which is on the whole heterogeneous, we intend the sum of all points with the same physical and chemical properties independently of whether they are geometrically grouped into separate relatively large regions or scattered over the whole metal surface.

On the uniform region of the surface of the base metal, if it were isolated from its other regions, the anodic process of ionization of the metal and the cathodic reaction of hydrogen separation (or other cathodic reactions) would proceed, as on any other homogeneous metal electrode, at a certain constant rate. As a result of the compensation of these conjugated processes a certain stationary potential would be established on this region of the surface. If other regions with different physical and chemical properties, on which the cathodic process is disinhibited, are close to this region of the surface, the entire surface region under consideration would be anodically polarized under the influence of the current of the local element. The over-all rate of dissolution of the metal is composed of the rate of "self-dissolution" on this region of the surface and the rate of anodic dissolution as a result of the "external" polarization. Depending on the difference in properties between the cathodic and anodic sections, the "external" polarization causes a varying positive potential shift. The phenomena observed in this are analogous to the phenomena occurring during the anodic polarization of a homogeneous self-dissolving electrode (see §6). If a positive difference effect is observed on a given metal this means that under the influence of the anodic polarization its self-dissolution (i.e., dissolution accompanied by hydrogen evolution or other cathodic reaction) is reduced. A strong potential shift reduces the self-dissolution potential so strongly that it can be neglected compared with the dissolution under the action of the current of the local elements.

The degree of the spatial separation of the anodic and cathodic processes thus depends on the rate of the conjugated reactions on the anodic regions and on the anodic polarization of these regions under the influence of the neighboring cathodic regions. As is evident from the foregoing, we must generally always consider the possibility that cathodic reactions take place on the anodic regions in addition to the basic anodic processes. On the other hand the application of a similar argument to the cathodic regions shows that anodic processes can also take place on them at a lower rate.

Of great importance for the course of the corrosion processes are not only the microscopic heterogeneities which cause the appearance of local elements on the metal surface but also the macroscopic differences in the electrochemical properties of different parts of any metallic system. Thus, for example, a chemical apparatus may contain parts made of different metals which are in contact with the same electrolyte solution. If a current-conducting contact exists between them, electrical currents arise in the system which can cause severe damage to the parts of the surface on which the anodic processes take place. Such a spatial separation of the cathodic regions can also arise because of differences in the composition of the solution. Assuming, for example, that the concentration of atmospheric oxygen is greater in some part of a neutral solution in which an iron structure is immersed, compared with its other parts (so-called difference or differential aeration). At first sight it would seem that the corrosion of the iron in this part should be intensified. Actually, however, this is not the case. The electrolytic reduction of oxygen causes the appearance of hydroxyl ions and, consequently, an alkalinization of the solution which promotes the formation of insoluble corrosion products and protective films which slow down the anodic process. The rate of dissolution of the iron may thus be greater at the points which are more remote from the point with intensified access of oxygen; under these conditions, the more strongly aerated regions are the cathodes on which reduction of oxygen predominates, and the weakly aerated ones are the anodes on which dissolution of the iron predominates.

The same methods can be applied to the calculation of the operation of these "macroelements" as those described in this section in connection with the discussion of the theory of the microelements, for example, the method of polarization diagrams and the method of calculation of multi-electrode systems. Experiments with normal galvanic couples and more complex systems are often used in corrosion research for the modeling of the processes which take place in the microelements. It must be remembered, however, that in proportion to the increase in the geometrical dimensions of a system, the ohmic potential drops increase which has the consequence that the behavior of the macro and micro systems is not quite comparable. To model a microelement correctly by means of a normal galvanic couple it would be necessary, as follows, for example, from Eq. (301), to increase the electrical conductivity of the solution when going over from the first to the second in the same ratio in which the geometrical dimensions of the system increase, while leaving the polarization characteristics of the cathode and anode unchanged.

Within the framework of the present book we can give only a general idea of the electrochemical theory of corrosion which plays an important part in the selection of corrosion-resistant materials and in the working out of anticorrosion measures; a more detailed presentation of this important problem can be found in the corresponding special literature.

§8. USE OF INHIBITORS DURING THE DISSOLUTION OF METALS IN ACIDS

Let us consider the question of the effect of additions to the electrolyte which affect the process of dissolution of metals. This kind of effect on the rate of dissolution is of great practical importance because this can cause a strong reduction in the rate of self-dissolution, i.e., it can be used to reduce metal corrosion.

When considering the mechanism of these processes, attention must be paid to the following circumstance. If we are dealing with a system in a state of thermodynamic equilibrium, a change in the rate of one of the reactions which are possible in this system, automatically involves a change in the rate of the corresponding reverse reaction. Let us take the silver electrode in $AgNO_3$ solution as an example. The equilibrium potential of this system depends on the thermodynamic properties of the metal and solution (in particular, on the concentration of the silver ions in the solution) and is established as a result of the compensation of the reactions of ionization of metallic silver and discharge of silver ions. In the equilibrium state the electrode potential is independent of the partial rates of these processes provided that these rates are equal: $\overrightarrow{i}_2 = \overleftarrow{i}_2$. Any variation of the rate of one of these reactions, if it is not to disturb the equilibrium, must be accompanied by a variation of the rate of the reverse reaction so that the equivalence is preserved and the potential remains unchanged. The same applies to other equilibrium electrodes.

In the case of the processes of metal dissolution in acids considered in this chapter the situation is different. Because the dissolving metal is in a state differing from the state of thermodynamic equilibrium, the rate of one reaction can be affected without affecting the other, or its rate can be affected differently than the rate of the other.

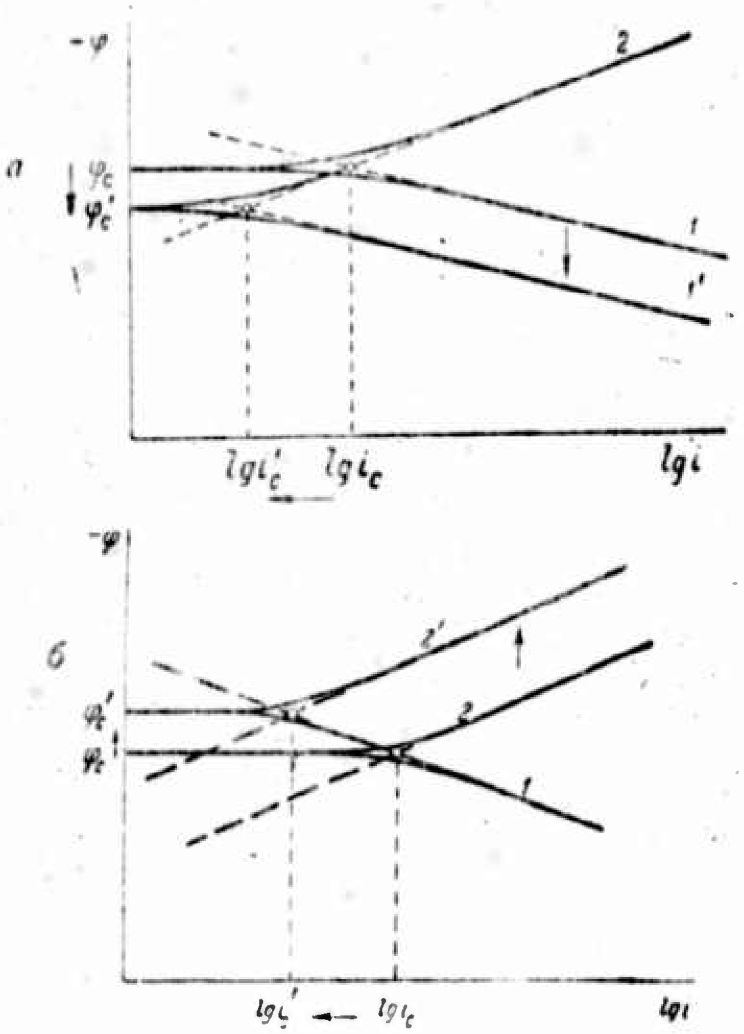

Fig. 137. Polarization curves of a metal electrode in the presence of an inhibitor: a) Inhibition of the cathodic process (1 anodic curve; 2 cathodic curve; i_s rate of self-dissolution in the absence of an inhibitor; correspondingly 1', 2' and i_s' are the same in presence of an inhibitor).

A large number of different additives (agents) have been proposed and used to date which lower the rate of self-dissolution of metals in acids [32]. These substances which are termed corrosion inhibitors consist of various organic compounds and their mixtures, often with addition of inorganic electrolytes.

The inhibitory effect of these additives (i.e., the effect of lowering the rate of self-dissolution of the metal) can be due to an effect of these substances on the anodic reaction of ionization of the metal as well as on the cathodic reaction of hydrogen separation.

Generally, a change in the rate of one or both of these reactions, in addition to causing a variation of the rate of self-dissolution of the metal, also alters its stationary potential.

Figure 137a shows the pattern of action of an inhibitor which inhibits the anodic process of metal dissolution. The polarization curve of this process is shifted to the positive side in presence of such a substance (increase in the overvoltage of the anodic process). As the diagram shows, the point of intersection of the anodic and cathodic polarization curves, which characterizes the stationary state of the metal, is shifted in presence of this inhibitor in the direction of lower current densities and of more positive potentials. In presence of a substance, which inhibits the cathodic process, the self-dissolution current also decreases but the stationary potential is then shifted to the negative side, as can be seen in Fig. 137b.

Finally, addition of an inhibitor can also vary the rate of both processes although the effect on each of the processes under consideration may not be the same; this pattern of action of an inhibitor is the most common. Figure 138 shows the case in which the inhibitor decreases the rate of both processes but with a stronger effect on the anodic process (effect of tetradecyl tetrahydropyridine bromide on the iron

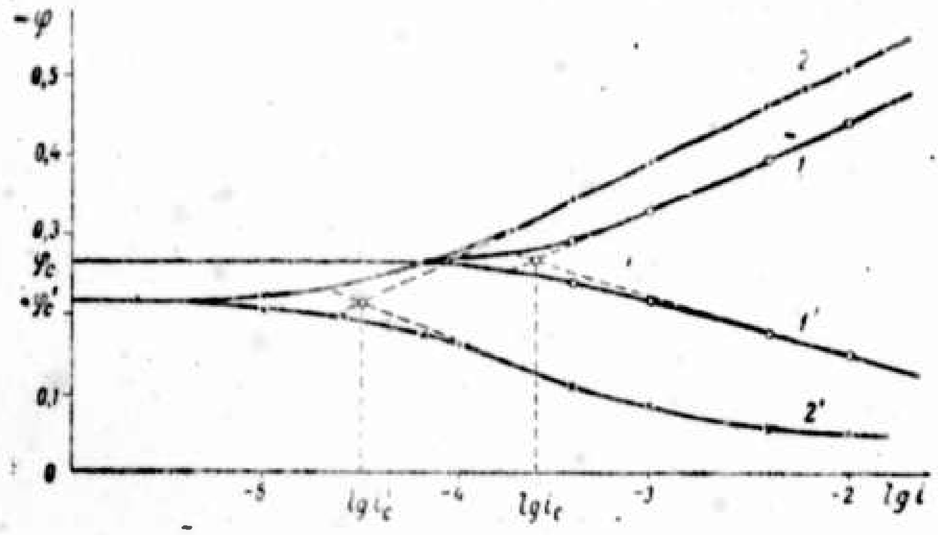

Fig. 138. Cathodic and anodic polarization curves of an iron electrode in a pure solution of 1 N HCl (curves 1 and 1') and in presence of $5\cdot10^{-5}$ equivalents/liter of n-$C_{14}H_{29}NC_5H_9Br$ (curves 2 and 2'); i_s and i'_s are the currents of self-dissolution in the first and second solution. The potential was measured relative to the hydrogen electrode in the same solution.

electrode in 1 N HCl). In this case the effect of the inhibitor on the rate of self-dissolution is naturally greater than when it acts only on one of the electrochemical processes. Because in this case the effect of the inhibitor on the anodic process is greater, the stationary potential (Ψ_s) is shifted to the anodic side (Ψ'_s). The shift is obviously greater if the difference in the effect of the inhibitor on the two processes is greater.

In the case of an equal effect of the inhibitor on both processes the stationary potential may not change although the rate of self-dissolution is greatly decreased.

Some additions accelerate one of the electrochemical reactions; such additions are termed stimulators. The stimulators (for example, H_2S) naturally increase the rate of self-dissolution and shift the stationary potential to the side opposite to the shift caused by an inhibitor which affects the same electrode reaction [33].

The inhibitor can exert its effect on the kinetics of electrode processes only if it adsorbed on the surface of the metal electrode, hence the action of an inhibitor depends primarily on its adsorption. If the potential at which the dissolution of the metal takes place is far from the zero point of this metal, an inhibitor, which is capable of being adsorbed under other conditions on this metal, may be completely displaced from the surface by water molecules; in this case its inhibitory effect will not be manifest. Hence it is essential for the adsorption of the inhibitor present in the solution in the form of molecules that the surface charge of the metal in this medium is not too high. If the inhibitor is adsorbed in the form of ions, its adsorption is promoted by the charge on the metal surface if its sign is opposite to the sign of this ion. Nitrogen-containing organic compounds which form surface-active cations in acid solutions are often used in practice as inhibitors; such inhibitors will obviously be well adsorbed on negatively charged surfaces, while they may be totally ineffective on a positively charged metal surface [34].

In many technological cases one uses mixtures of two or more substances as inhibitors. The combined effect of several inhibitors is often stronger than the effect of each component separately; this intensification of the inhibitor effect may be due, in particular, to the fact that the presence of one of these substances promotes the adsorption of the other. Thus, the inhibitory effect of organic bases is greatly intensified by the presence of adsorbed anions, for example, bromine or iodine. As pointed out previously, the latter form adsorbed dipole layers on the surface of iron, the negative end of the dipole being directed towards the solution, which should promote the adsorption of cations [35, 36].

Inhibitors are widely used in technology for reducing the rate of dissolution of parts, for example, of iron and steel during etching, i.e., during their cleaning with strong acids from rust and scale. In etching baths the effect of the inhibitors is due to the fact that without exerting an influence on the dissolution of oxides in acids, they lower the rate of dissolution of the base metal considerably.

The great importance of the inhibitors consists also in the fact that in some cases they prevent the hydrogen embrittlement which occurs when technical acids act on iron. The reduction in the hydrogen embrittlement in presence of various inhibitors is due to the decrease in the diffusion of atomic hydrogen into the interior of the metal [37].

It is obvious that the inhibition of the anodic process, which causes a shift of the self-dissolution potential to the positive side without affecting the mechanism of the cathodic process, should result in a decrease in the rate of penetration of hydrogen into the interior of the metal in the same way as it leads to a decrease in the rate of its separation. The hypothesis has often been advanced, based on the ideas of the desorption theories, that the inhibition of the cathodic process, i.e., the increase in the hydrogen overvoltage must necessarily entrain an intensification of the penetration of hydrogen into the metal. In actual fact the inhibitors can also increase the hydrogen overvoltage through an inhibition of the discharge state without causing an increase in the proportion of the hydrogen which goes into the interior of the metal or even reducing it (§12, Chapter 3).

We have dwelt here only on the mechanism of action of corrosion inhibitors in acid medium, accompanied by hydrogen separation. The effect of the inhibitors used for corrosion protection in neutral media in presence of oxygen (chromates, silicates, phosphates) is based on other principles. Under these conditions an adsorbed or phase oxide film is always present on the iron surface, and the corrosion-inhibiting effect is produced by substances which intensify its protective properties.

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Manuscript Page No.	[Footnotes]
480	Under the action of gases containing water vapor, metal corrosion takes place with participation of an adsorbed film of water and, as in aqueous electrolyte solutions, it takes place according to an electrochemical mechanism. The dissolution of metals in poorly conducting nonaqueous solutions also takes place in some cases via an electrochemical mechanism.
484	For the sake of simplification we shall everywhere in this chapter, unless the reverse is specially indicated, consider the quantity ψ_1 constant by way of a first crude approximation (i.e., relate all equations to solutions with the same total electrolyte concentration).
491	For the same reasons (the existence of a large exchange current for the reaction of discharge and ionization of the alkali metals) the potential varies little even during the cathodic polarization of the amalgam. This circumstance is of great importance in the determination of the optimum working conditions of the mercury bath for chlorine electrolysis. Because the potential of the mercury electrode varies little

with the density of the external current. increase of the latter entrains mainly an increase in the rate of sodium separation while the rate of the hydrogen separation remains almost unchanged. On the other hand, the rate of chlorine separation at the anode of the bath is proportional to the current density. Hence to avoid the formation of an explosive mixture of chlorine and hydrogen in the bath, the electrolytic formation of amalgam should be carried out at fairly high current densities.

492 The amalgams of the alkali metals even at low concentrations of the alkali metal show large deviations from the laws of ideal solutions. Hence if the concentration of sodium in the mercury is not too low, the value for the concentration of [Na] in Eq. (278) should be replaced by the activity, which leads to more complex kinetic relations.

500 In the case considered previously (Chapter 3), when we compared the rate of discharge and ionization of the hydrogen, the sum of these constants was equal to unity for thermodynamic reasons. Here, however, we have two different processes, there is no connection between the quantities α_1 and β_2 and their sum may differ from unity.

504 The rate of dissolution of a metal in acid under certain conditions may depend on the intensity of mixing even at current densities which are considerably lower than the limit diffusion current of the hydrogen ions. Let us visualize, for example, a lead electrode washed by a stream of hydrogen chloride which does not contain any lead ions. The concentration of the lead ions at the electrode surface in this case at a given rate of dissolution obviously depends on the velocity of the flow which removes the ions from the electrode. Because, on the other hand, the concentration of the lead ions determines the electrode potential and, consequently, also the rate of hydrogen separation, equal to the rate of dissolution of the metal, the latter in turn should depend on the intensity of mixing. Calculation shows, however, that in this case this relationship is incomparably less pronounced as in the case considered in the text [12].

505 The origin of this term which is widely used in corrosion literature is connected with the distribution of the earlier incorrect view concerning the role of oxygen in the dissolution of a metal, according to which the oxygen oxidizes the separated hydrogen and lowers the polarization of the electrode due to the appearance of hydrogen on the metal surface. In actual fact the electrolytic reduction of oxygen is an independent reaction which takes place independently of the hydrogen separation.

508 As has been shown in Chapter 4, the reduction of oxygen on the mercury electrode at constant potential is inhibited when surface-active anions, among which belongs also the ion CN^-, are added to the solution. However, the shift of the anodic curve of the dissolution of mercury and in consequence of this also of the stationary self-dissolution potential in the

direction of negative values is so great that the rate of reduction of oxygen at the stationary potential and, consequently, also the rate of self-dissolution of the mercury, do not decrease but increase strongly.

522 Because, according to the hypothesis, the distances between the individual inclusions are large compared with the radius of the inclusions, we can consider each of them to be isolated from the others.

523 Let us carry out a calculation of the effect of the inclusions in the case of practical interest of the dissolution of lead, containing metallic antimony, in the sulfuric acid of a lead battery. The self-dissolution potential of lead in 8 N H_2SO_4 is −0.37 v. The hydrogen overvoltage on pure antimony in H_2SO_4 of this concentration is expressed by the formula $\eta = 0.71 + 0.12 \log i$.

Thus, at $\varphi = -0.37$ v, $\log i = -2.9$ and because $\kappa = 0.74$, we obtain from Eq. (301) at $r_0 = 10^{-4}$ cm $\Delta\varphi = 10^{-7}$ v, and at $r_0 = 10^{-1}$ cm $\Delta\varphi = 0.0001$ v. Hence we can neglect the potential drop between the base metal and the inclusions in this case even if the latter have relatively large dimensions.

In other cases the same calculation gives greater values of $\Delta\varphi$. For example, the potential difference between Ni inclusions in Zn and the base metal during its dissolution in 1 N H_2SO_4 at $r_0 = 10^{-4}$ cm, according to Eq. (301), is $\Delta\varphi = 0.013$ v, if it is assumed that the hydrogen overvoltage on the inclusions is the same as on pure Ni.

Manuscript Page No.	[Transliterated Symbols]
484	p = r = ravnovesnyy = equilibrium
485	c = s = samorastvoreniye = selfdissolution
488	c = s = statsionarnyy = stationary

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

rot	curl
lg	log