DEVELOPMENTS IN CORROSION AND ELECTROCHEMICAL RESEARCH AT THE L. Ya. KARPOV INSTITUTE OF PHYSICAL CHEMISTRY (IN COMMEMORATION OF THE FIFTIETH ANNIVERSARY OF THE INSTITUTE)

Ya. M. Kolotyrkin, V. M. Novakovskii, and G. M. Florianovich

UDC 620.193.01

The state of science is always a state of motion and development. In order to size it up correctly, it is necessary to know not only the state of affairs at a given moment, but also the basic trends and mutual relationships of scientific theories under formation; thus it is possible to estimate, even if only for the immediate future, the prospects of their development. At the same time, the historical profundity offering a clear picture of the development process of the field of knowledge dealt with is absent, as a rule, from ordinary reviews. The readers may therefore be evidently interested, side by side with reviews of the traditional type, in the essay type of reviews devoted to the work of various scientific teams and presenting information on the history, essence, and dynamics of the complex development of theories which at present constitute the features of one or another scientific school. And the present essay is related to this category, featuring a description of corrosion and electrochemical research at the Karpov Institute of Physical Chemistry, and written in commemoration of the 50th anniversary of the institute.

The work conducted at the Karpov Institute has played an important part in the development of metallic corrosion studies. This scientific trend was born at the institute in the years preceding the Great Patriotic War, and was stimulated by an increased interest in corrosion science on the part of the developing industries which needed reliable and effective methods of protection against corrosion.

On the other hand, the formulation of corrosion problems as being essentially of an electrochemical nature was also due to the logic of development of the institute itself, since a progressive electrochemical school headed by A. N. Frumkin which had played an important part in establishing and developing present-day electrochemistry was formed just here already before the war. This school contributed decisively to the solution of such fundamental problems as the mechanism of the potential difference occuring at the boundary between a metal and an electrolyte solution, the structure of the electrical double layer formed at such a boundary, and its effect on the kinetics of electrode reactions. This resulted in laying grounds for the foremost section of current theoretical electrochemistry, i.e., the studies on the kinetics of electrode processes. According to this concept, the specific character of the electrochemical stage of an electrode reaction is represented not only by the dependence of the reaction rate on ordinary variables of chemical kinetics, i. e., concentration and temperature, but also by its dependence on the potential difference at the metal–solution partition boundary which affects the activation energy of this stage as well as the effective concentration of reacting particles.

Thanks to the accomplished successes, it has been possible to approach, in an entirely new way, the interpretation of the mechanism of an electrochemical corrosion process such as, e.g.,

$$Me + nH_3O^+ \rightarrow Me^{n+} + \frac{n}{2}H_2 + nH_2O,$$

divided into two electrode reactions, i. e.,

$$Me \rightarrow Me^{n+} + ne, \quad (1)$$

$$nH_3O^+ + ne \rightarrow \frac{n}{2}H_2 + nH_2O \quad (2)$$

L. Ya. Karpov Scientific Research Institute of Physical Chemistry. Translated from Zashchita Metallov, Vol. 4, No. 6, pp. 619-636, November-December, 1968.

The artificial but, at that time, generally acceptable postulate of the theory of local elements stating that a stationary spatial distribution is binding upon all anodic and cathodic processes was abandoned in favor of a more general idea suggesting that, independently of the presence or absence of any microheterogeneities, the corroding surface may be regarded as a single electrode on which, from the standpoint of statistics, reactions (1) and (2) are taking place simultaneously and independently of each other. According to laws of electrochemical kinetics, the rates of these reactions are determined by the properties of the electrode surface, the electrode potential, the composition of the solution, and the conditions of diffusion exchange between the solution bulk and the layer adjacent to the electrode; the interdependence of these parameters is due to the existence of a common electrode potential exerting an influence on each of them, expressed by the fact that the metal loses or gains electrons. During spontaneous solution of the metal in the electrolyte, the rate (i_c) of the corrosion process and the potential (φ_c) of the corroding metal are determined by the condition of stationary behavior which comes to an equality of the rates of reactions (1) and (2). The specific form of expressions obtained depends on actual conditions of the corrosion process (nature of the metal, composition and concentration of the electrolyte, diffusion conditions, and temperature); a change in these conditions may bring about a change in the degree of reversibility of reactions (1) and (2), their limiting stages, and other kinetic peculiarities. When the metal ionization reaction and hydrogen evolution are limited by the electrochemical stages in states far removed from equilibrium, then their rates (i_1 and i_2, respectively) for a general case can be expressed by the following relations:

$$i_1 = k_1 \exp\left(\frac{\beta n F}{RT}\varphi\right), \tag{3}$$

$$i_2 = k_2 C_{H_3O^+} \exp\left(-\frac{\alpha F}{RT}\varphi\right). \tag{4}$$

Here φ is the electrode potential, $C_{H_3O^+}$ is the concentration of H_3O^+ ions, T is absolute temperature, α and β are transfer coefficients, and k is a constant. On the condition that $i_1 = i_2 = i_c$ (where i_c is the corrosion rate), Eqs. (3) and (4) yield expressions for i_c and for the corrosion potential φ_c:

$$i_c = k_3 C_{H_3O^+}^{\beta n/(\alpha+\beta n)}, \tag{5}$$

$$\varphi_c = k_4 + \frac{RT}{(\alpha+\beta n)F}\ln C_{H_3O^+}. \tag{6}$$

The presence of chemical or structural heterogeneities on the metallic surface may bring about a partial localization of reactions (1) and (2) to those sections where the corresponding limiting stage meets the least hindrances. In such a case, reactions (1) and (2) may proceed at different rates on different surface sections. However, owing to the microscopic size of the heterogeneities, this in practice does not disturb the equipotentiality of the surface and does not exclude the possibility of applying the laws of electrochemical kinetics to both the various electrode reactions and the corrosion process as a whole.

The first qualitative interpretation of experimental relationships based on the described notions is due to Frumkin [1] who analyzed data obtained by Brönsted and Kane [2] in a study on dissolving sodium amalgam in alkali. The proportionality between sodium dissolving rate and the square root of its concentration in the amalgam as found by [2] allowed for a satisfactory explanation based on the assumption that the evolution of hydrogen which accompanies the transfer of sodium ions into the solution can be described by the same equations of electrochemical kinetics as that occuring on a pure mercury electrode; since the overvoltage of this reaction is much higher than that pertaining to the processes of formation and discharge of sodium ions, the potential of the amalgam is near to the reversible potential of the reaction $Na \rightarrow Na^+ + e$. Analogous results were obtained several years later by German researchers Wagner and Traud [3] in a study on zinc amalgam solution in sulfuric acid.

Studies on the relationships governing the solution of lead and nickel in acids [4, 5] represent an important stage in the development of these notions. A qualitative agreement was found between actual corrosion rates determined by the volume of evolved hydrogen and those calculated on the basis of electrochemical measurements. In addition, special tests [6] conducted with nickel revealed that such a coincidence is preserved even after coating a part of the metallic surface by platinum. The same publication was the first to point out that not only amalgams but also solid metals including those with surfaces deliberately prepared so as to expose chemical heterogeneities dissolve in a manner corresponding completely to the laws of electrochemical kinetics. Having obtained this fundamental result, the authors used the

same metals to investigate in detail the relation of the corrosion behavior of a metal to the kinetics of reactions (1) and (2). This study showed that, for metals of the nickel type where these reactions proceed irreversibly and are limited by electrochemical stages, the observed dependence of corrosion rate and potential on the pH of the solution is in full agreement with Eqs. (5) and (6). The picture is different for metals of the lead type where only reaction (2) proceeds irreversibly while reaction (1) is near to equilibrium. Here the electrode potential of the corroding metal is determined fully by the concentration of its ions in the vicinity of the metallic surface, and the corrosion rate is given by the conditions of diffusion of its ions into the solution bulk.

The experimental substantiation of applicability of the laws of electrochemical kinetics to corrosion processes marked the beginning of a wide and fruitful utilization of electrochemical methods in studies on kinetics and mechanisms of these processes as well as in preliminary evaluation of corrosion stability of metallic materials under various conditions; this, in turn, stimulated further development of studies on metallic corrosion and methods of protection against corrosion. In particular, the new notions represented the most important part of the theory pertaining to individual variants of the method of electrochemical protection which now came to be widely used in practice.

As one of the results of the accumulation of experimental material and more profound theoretical studies, the teaching on corrosion of new systems came into existence, contributing also to theoretical electrochemistry. For instance, it was known from practice that the corrosion rate of many metals in acidic solutions depends not only on pH but also on the nature of the acid. The cause of this relationship remained unknown for a long time, since most researchers assumed that simple metallic ions are formed in the elementary act of anodic solution, and that the participation of the components of the solution, including anions of the electrolyte, comes to their subsequent reaction with these simple ions. It was shown later on, however, that such a notion is not correct. As a result, systematic investigations succeeded in proving that, in most cases, the anodic solution proceeds indirectly in the way of forming a complex of the metal with the anions and other components of the solution in the electrochemical stage

$$Me + mA^- \rightarrow (MeA_m)^{+(n-m)} + ne$$

and, correspondingly, the rate of solution is expressed by the equation

$$i = KC_A^m \exp\left(\frac{Fn\varphi}{RT}\right). \quad (7)$$

As an example, a curve is shown in Fig. 1 which represents the relationship between the dissolving rate of indium amalgam and the concentrations of NaBr (1) and NaI (2) in acidic perchlorate solutions at a constant potential of −0.275 V [7]. It is apparent from this figure that, starting at a certain halogenide concentration, a distinct exponential relationship exists between the rate of the process and this concentration in correspondence with Eq. (7).

Studies carried out at the Karpov Institute represented an important contribution to the development of theories on the participation of anions in the processes of solution of metals. Following an investigation on dissolving platinum in acids, Érshler [8] brought to attention the systematic increase in the dissolving rate upon raising the chloride concentration in the solution, and was the first to suggest that complex formation is the mechanism of this process. Further on, Chemodanov [9] compared the electrochemical and the radiochemical methods and confirmed this result on a more extensive experimental material. Medvedeva [10] found that the solution of cadmium in acidic iodide solutions is based on the mechanism of complex formation. Analogous results for indium amalgam in halogenide and sulfate solutions were obtained by Losev and Molodov [7].

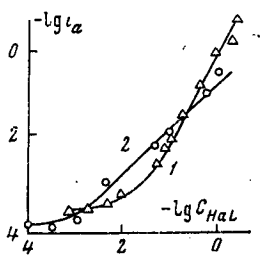

Fig. 1. Dependence of the rate of solution of indium amalgam (at a constant potential) in 0.01 N $In(ClO_4)^+$ + 0.01 N $HClO_4$ + NaHal on the concentration of NaHal. Curve 1) NaBr; 2) NaI.

It must be emphasized that a similar anode reaction mechanism is not necessarily restricted to cases where the final products of the anode reaction are present in the solution in a complex form. The participation of anions in the electrochemical stage of the process may come to a formation of an only intermediate complex subject to later decomposition, so that simple ions or products of their hydrolysis are present in the solution. In this case, the anions do not take part

in stoichiometric equations of the overall process, and their interaction mechanism is determined solely by their effect on the rate of the anodic process or the density of the respective exchange current.

Dissolving bismuth amalgam in acid perchlorate solutions containing chloride, bromide, or iodide additions represents an example of a reaction proceeding according to such a catalytic mechanism. Upon comparing electrochemical and radiochemical methods, Losev and Gorodetskii [11, 12] found that the introduction of said additions does not change the amalgam equilibrium potential, i.e., that it is not accompanied by formation of complexes in the solution. At the same time, such an introduction accelerates both the anodic solution and the cathodic deposition of bismuth, as is apparent from a simultaneous displacement of the corresponding polarization curves and an increase in exchange current.

The conclusion that components of the solution (anions in particular) can take part in the reaction of anodically dissolving a metal is of a fundamental importance for corrosion problems in agressive media. Hence, it follows that neither a reliable evaluation of the corrosion rate is possible nor a correct structural material in designing the equipment for technological processes can be selected unless the anionic composition of the corrosion environment is taken into account. This lends a particular importance to the work carried out at the institute on determining the dependence of the described effect on the nature of the metal as well as the nature and concentration of the anion. It was shown that an anion introduced into a solution does not exert an accelerating effect at all its concentrations in such solutions, i.e., upon reaching a certain critical concentration C_{crit} which depends on the nature of both the metal and the anion. Thus, according to data by Losev and co-workers [7, 11], the value of C_{crit} in dissolving amalgams in halogenide-containing solutions is by three to six orders of magnitude lower for bismuth than for indium, and increases in the order of J^-, Br^-, and Cl^- for each of these metals (see Table 1). The accelerating effect of the sulfate on the ionization of bismuth from its amalgam in acidic perchlorate solutions is apparent at even higher critical concentrations. Analogous, although in some cases qualitatively different results were also obtained for a number of structural materials (iron, nickel, and chromium alloys). This has revealed still another extraordinarily important detail: the accelerating effect of anions is generally independent of pH, the influence of which is usually tied up with the accelerating effect of the hydroxyl group. This in particular has been confirmed by data obtained by Sokolov [13], according to which (Fig. 2) the rate of anodic solution of iron at a constant potential increases linearly upon both raising the pH of the solution (at a constant sulfate activity) and increasing the logarithm of sulfate activity (at a constant pH). The sulfate ions are evidently taking part in the anodic reaction of dissolving iron.

TABLE 1. Dependence of C_{crit} on the Nature of the Anion in the Solution and the Metal in the Amalgam, g-eq/liter

Halogen ion	Amalgam	
	indium	bismuth
Cl^-	0,02	$3{,}5\cdot10^{-5}$
Br^-	$5\cdot10^{-3}$	$5\cdot10^{-7}$
I^-	$2\cdot10^{-3}$	$5\cdot10^{-9}$

Various points of view were presented in interpreting the mechanism of the dissolving effect of anions. Studying the solution of platinum in chloride solutions, Érshler [8] suggested that a decelerated stage of this process is represented by a "discharge" of chloride ions

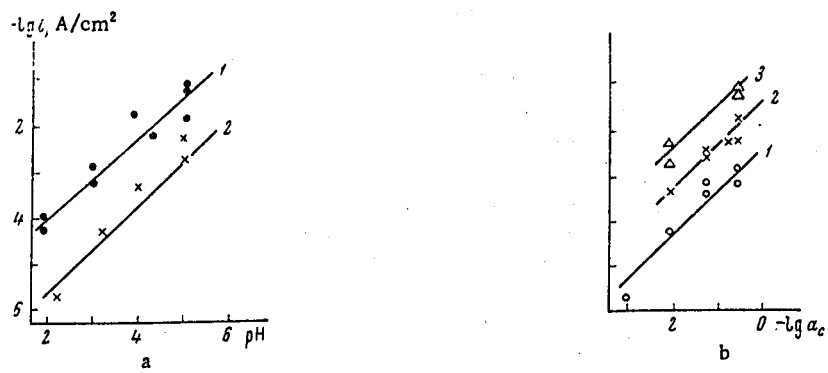

Fig. 2. Dependence of the rate of dissolving iron at a potential of −0.35 V (standard hydrogen scale) in solutions of $H_2SO_4 + Na_2SO_4$. a) On pH at a constant sulfate activity a_c: 1) $a_c = 1$ N; 2) $a_c = 0.1$ N; b) on a_c at a constant pH: 1) pH 8; 2) pH 4; 3) pH 5.

at the electrode surface. According to his view, such a "discharge" is accompanied by a transfer of platinum ions from the metallic lattice into the solution.

Another view was expressed by Kolotyrkin and co-workers [10, 14] who concluded that the solution of metals with the participation of anions proceeds in two stages, the first of which is a specific adsorption of anions on the metal resulting in a formation of a surface complex:

$$Me + mA^- \rightarrow (Me\,..\,A_m)^{-m}.$$

The second, electrochemical stage controlling the overall process rate consists in a transfer of this complex into the solution:

$$(Me\,..\,A_m)^{-m} \rightarrow (MeA_m)^{+(n-m)} + ne.$$

Such a mechanism is in good agreement with both the results of kinetic measurements and the data on anion adsorption as obtained for various metals. Medvedeva [15] showed that the adsorption of iodide ions on silver in solutions of H_2SO_4 + KI starts at potentials more negative than those at which dissolving of silver in iodide solutions begins at a noticeable rate. Simultaneously, it was also found that the potential affects not only the degree of metallic surface packing by adsorbed ions but also the strength of their bond with the surface atoms of the metal.

These and other analogous tests contributed to a more definite picture of anodic solution of metals with the participation of anions; according to this view as expressed in [14], the specific adsorption of an anion at sufficiently negative potentials is to be considered the beginning of the formation of the corresponding salt. However, the form of chemical bond at these potentials differs considerably from that in the molecule which is capable of existing independently outside the surface. The bond strength increases upon shifting the potential to more positive values, and when, at a certain potential, this bond strength coincides with that of the independent compound, the metal starts dissolving as an anionic complex.

Taking into account concurrent adsorption, these notions make it possible to determine both the stimulating and the inhibiting effects of various solution components on the process of anodic solution of metals. The inhibiting effect of KI additions on the process of anodically dissolving nickel in acidic sulfate solutions studied by Lopovko and Medvedeva [16] represent one of interesting examples of this type. A combination of electrochemical and radiochemical methods made it possible to find that, in pure sulfate solutions of pH > 2, the anodic solution of nickel at a constant potential proceeds in conformity with a certain law and its rate decreases very sharply with decreasing solution acidity. This result can be understood and accounted for if it is assumed that OH^- ions formed on account of dissociation-type adsorption of water at the nickel surface according to the scheme

$$Ni + mH_2O \rightarrow Ni\,..\,(OH)_m^{-m} + mH^+,$$

take a direct part in the reaction and that the solution of the metal proceeds mainly by means of transfer of surface complexes into the solution; these complexes are formed, as a result of this adsorption, according to reaction

$$Ni\,..(OH)_m^{-m} \rightarrow [Ni(OH)_m]^{+(n-m)} + ne.$$

In correspondence with values of the exponent of OH^- ion concentration in Eq. (7) as obtained for this case, the mean value of m is near 1.5. Further on, the kinetic and adsorption measurements showed that the impeding effect of KI additions on this process is connected with an adsorption of I^- ions on the nickel surface and an inhibition of the stimulating effect of OH^- ions. Simultaneously, the sensitivity of the process to pH changes is decreased and, consequently, the value of m in Eq. (7) falls to 0.4.

Analogous views were also applied to explain the inhibiting effect of halogen ions on anodic solution of iron and steels in sulfuric acid [17].

The notions about the adsorption-chemical interaction of solution components with surface atoms of the metal evidently make it possible to account for the phenomenon of anomalous solution of a number of structural materials; this phenomenon discovered at the institute did not fit in the framework of the classical electrochemical corrosion mechanism. Essentially, this phenomenon consists in that, under certain conditions, the dissolving rate of a metal in its active state does not depend on potential. As a rule, this takes place in acidic solutions (particularly at elevated temperatures) at potentials more negative than the stationary potential. However, for some metals, e.g., chromium, such an independence is also retained

within a certain interval of potentials more positive than the stationary potential; then the rate of the process is appreciably higher than the value equivalent to the actual anodic current.

This phenomenon was first observed by Knyazheva [18] in investigating active solution of chromium in sulfuric acid during cathodic polarization. Later on, it was studied systematically by the authors of this article [19, 20] who found that iron and Fe – Cr alloys are also subject to anomalous dissolving in acidic solutions. Analogous results were obtained by Agladze [21] for manganese.

These investigations showed that an increase in process rate related to the decrease in solution pH is one of the characteristic features of anomalous solution. This is exactly why this phenomenon is more distinct in strongly acidic solutions.

It could be assumed that the phenomenon studied which, as a rule, was observed in the region of cathodic polarization, is related to a disintegration of the metal by the generated hydrogen. Up to the present, however, tests conducted with a cathodically polarized iron membrane did not establish any connection of the effects observed with either hydrogen diffusion into the metallic bulk or its evolution from the metal [22].

An analysis of all these results allowed for the conclusion that, in principle, metals can dissolve in acidic environments not only according to the electrochemical mechanism described above but also according to a chemical mechanism, i.e., on the basis of a simultaneous interaction of the surface atoms of the metal with the oxidizing component of the solution, owing to a spontaneous electron transfer from the reacting atom to a particle of the oxidizer which can be described as

$$Me + Ox^{+m} \rightarrow Me^{n+} + Red^{+(m-n)},$$

where Red is the reduction product of oxidizer Ox. Analogous notions about amalgam decomposition in alkaline solutions were developed by Frumkin and co-workers [23].

In the light of above reasoning, the chemical solution mechanism is possible on the condition that the adsorption of an oxidizing component on a surface atom of the metal results in a chemical bond between these two which will make it easier to exchange electrons simultaneously.

The work carried out indicated that, in principle, all the metals studied dissolve chemically and electrochemically at the same time; however, the ratio of the two process rates may change considerably depending upon conditions in effect. It follows from the above reasoning as well as the known laws of electrochemical kinetics that the specific weight dissolved electrochemically increases for any metal with an increase in anodic potential and solution pH.

The chemical solution mechanism which is manifested and assumes a dominating part at potentials more negative than the stationary potential may decrease sharply the effectiveness of cathodic protection of metals from corrosion in agressive, low-pH environments. Therefore, the search and development of methods to inhibit the processes of chemical dissolving are very important. In this connection, the conclusion as to the partial inhibition of the anomalous solution of alloys based on Fe – Cr upon introducing Ni into the alloy [24] is of an interest as well as the possibility (recently discovered at the institute by Raskin) of this effect as displayed on chromium and chromium steels being inhibited by adding some oxidizers (nitrates, hydrogen peroxide, chromates) to the agressive medium; the effect of these oxidizers may be connected with a formation of some oxide-type protective layers on the metal.

Studies on the mechanism of these reactions carried out by Losev and co-workers assumed an important part in the development of the theory of active electrochemical solution of metals. The studies were conducted on amalgams of a number of metals (indium, bismuth, zinc, copper, etc.) which, when compared with solid metals, offered a number of advantages connected primarily with their surface homogeneity, absence of additional reactions, the possibility of changing the concentration of the studied metal in the amalgam, etc. Original radiochemical methods of direct determination of the exchange current in metal – metallic ion systems as well as the apparent dissolving and deposition rates of metals polarized by an applied current were worked out [25-27]. Using these methods, it has been succeded in answering the question of whether the formation and the deposition of polyvalent cations take place at one electrochemical stage or during several consecutive stages.

Phasic development criteria [26, 28, 29] were formulated on the basis of an analysis of the kinetic laws of the stage mechanism. A comparison of the slopes of apparent anodic and cathodic curves for zinc

and indium amalgams made it possible to show that the separation of the last electron is the limiting stage of the electrode process [29]. By combining radiochemical and electrochemical measurements, Losev and Gorodetskii [30, 31] were able to detect abrupt slope changes and two linear parts of different slopes on the apparent anodic curve for bismuth amalgam and to obtain a number of other unequivocal proofs to the effect that a process where the rates of consecutive electrochemical stages are comparable proceeds in stages. An analogous conclusion was drawn on the basis of polarization measurements on copper amalgam [32].

The construction of an apparatus for automatic recording of the rapidly changing solution radioactivity [27] allowed for the development of a method of radiochemical measurements and, in particular, for determining the exchange current on solid electrodes [33]. The application of radiochemical methods in combination with electrochemical measurements made it possible to confirm that unstable particles of univalent indium and bismuth are formed in the process of anodically dissolving their amalgams and also solid indium [34-36]. Chemical and electrochemical reactions with the participation of these intermediate particles [34-37] were studied by means of special indicator electrodes. These results confirmed unequivocally the theory of phasic development and allowed for an interpretation of a number of experimental relationships. For instance, Losev and Pchel'nikov [34] proved that it is exactly the initial formation of univalent indium ions and their subsequent oxidation by hydrogen ions in the bulk of the solution which account for the negative differential effect observed in experimental anodic solution of indium.

The most important direction of corrosion-electrochemical investigations conducted at the institute was represented by studies on the relationships and mechanisms of various cases of inhibiting the anodic reaction dissolving a metal, particularly the passivation mechanism and disruptions of the passive state. The wide-scale development of these studies was rendered possible by the application of the potentiostatic method of polarizing the electrode studied; the Karpov Institute played a leading part in the country in application, improvement, and promotion of this method [38]. It was this method which made it possible to determine fully the part of potential in corrosion-electrochemical behavior of metals and to accumulate a large amount of experimental data which reveal the features of this behavior. It has been confirmed that the dependence of the dissolving rate on potential is the most important characteristic of the corrosion behavior of a metal [39]. It was found that this dependence can be employed in both predicting the corrosion stability of a metal in various environments and selecting appropriate protection methods, particularly anodic protection [40], to prevent corrosion at given conditions. In addition, this dependence shows optimum alloying in the development of new alloys.

In order to allow for selecting materials resisting corrosion under one or another set of conditions, it was important to have a description available as to the characteristics of basic metallic structural materials. The institute initiated the accumulation of such information. Systematic data were obtained here which made it possible to draw conclusions on the relations between the nature of the metal and the composition and structure of alloys on the one hand, and their susceptibility to passivation and ability to preserve the passive state on the other hand. The electrochemical behavior of chromium [41, 42], nickel [41, 43], and steels [44-46] was analyzed in detail in the very first years of development of the potentiostatic methods, and conclusions were drawn as to the part of individual alloying elements in the corrosion behavior of alloys.

The potentiostatic method made it possible to undertake once again an investigation into intercrystalline corrosion of stainless steels [47-49]. The method was applied in studying the effect of stabilizing additions (Ti, Nb), carbon content, and heat treatment on the susceptibility of steels to this kind of defect. Upon combining corrosion-electrochemical measurements with potentiostatic etching, a dependence of the intensity of intercrystalline corrosion on potential was found which, in complete agreement with the work of other researchers, allowed to formulate the optimum service conditions for steels exposed to the corrosion type in question. A course was also laid down for setting up new methods of testing the susceptibility of steels to intercrystalline corrosion.

As the data on corrosion-electrochemical behavior of metallic materials were being accumulated, their generalization and the development of common views of the true nature of corrosion stability of metals, the mechanism of its improvement by various alloying components, the possible mechanisms of disruption corrosion stability, and the specific part played in this process by various solution components were becoming more and more urgent.

Regardless of the extreme variety of metallurgical and metal physics factors which affect corrosion stability, it can be stated that, upon establishing a contact with agressive electrolytic media, all these

factors are manifested essentially through the instrumentality of some common electrochemical relationships which, allowing for some or other variations, can be tracked down for both an overwhelming majority of corrosion-resisting alloys and most of their alloying components. Among these relationships, the decisive part is assumed by those which govern passivation and disruption of the passive state.

Notions representing passivation as a phenomenon which comes to a simple covering of the metallic surface by a complete layer of oxidation products difficult to dissolve came to represent the dominant attitude in the studies conducted at the institute. According to the theory based on these notions, such a layer which separates the metal from the electrolyte results in a discontinuation of the process of electrochemically dissolving the metal and, from this moment on, the anodic current can only be consumed in forming new portions of the passivating substance; even that can only take place to the extent to which the preceding portions are dissolved. And inasmuch as this solution was regarded to be a purely chemical process, it was considered possible to describe the stationary behavior of the passivated metal as a whole by classical equations of chemical kinetics which did not include the electrode potential.

This hypothetic picture which rendered a false impression of simplicity and self-evidence of the passivating mechanism and thence came to be called the phase layer theory was seriously shaken for the first time by Érshler [8, 50] whose work was published in the early 1940's. Using an oscillographic method, he found that the rate of anodically dissolving platinum in hydrochloric acid can be slowed down by an order of magnitude when very small amounts of oxygen corresponding to no more than several percent of the adsorption monolayer are introduced to the platinum surface. Upon increasing the amount of the passivating oxygen, the dissolving rate falls not linearly (as could be expected if the surface were covered mechanically) but exponentially. A hypothesis was expressed describing a so-called electrochemical or adsorption mechanism of passivation where the solution of the passive metal retains its electrochemical character, and where the adsorbed oxygen either changes the potential jump distribution over the metal– solution boundary or in some other way increases the overvoltage of the process.

At the beginning, this hypothesis was acknowledged only a narrow application range limited to the described behavior of platinum. Later on, it has been applied in interpreting the passivation of iron in alkaline solutions [51].

Wide-scale experimental grounds for the notions about the electrochemical nature of dissolving passive metals, their extension to the most different cases of passive behavior of metallic materials, and their gradual development into an organic, generalized passivation theory were laid already in the middle of the 1950's, owing to potentiostatic studies on chromium and nickel passivity carried out by Kolotyrkin and Knyazheva [41, 42].

They were the first to express and substantiate the idea that the degree of passivation which characterizes the stationary behavior of chromium in the region of the positive critical passivation potential is not constant but is rather a function of potential, increasing upon a potential shift towards positive values up to the beginning of passivation.

It was found that the dependence of the stationary, metal-dissolving current density on potential can be regarded as exponential even after the passivation has begun; in these conditions, however, the denominator of the exponent which was positive for the curve corresponding to active dissolving (Fig. 3, AB [42]), becomes first negative (passivation part, BC, of the curve) and later zero (part CD corresponding to constant dissolving rate). In contrast to the stationary current density which retains its constant value over a wide range of potentials corresponding to the passive state, the current density recorded at the moment

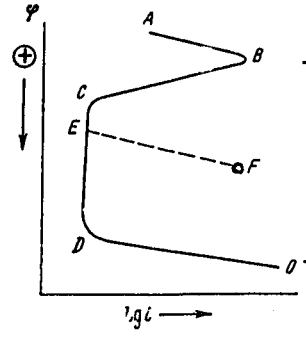

Fig. 3. Schematic dependence of the stationary rate of dissolving chromium in a sulfuric acid solution on the potential. AB is active solution, BC is passivation, CD is the passive state, DO is transpassivation. Point F is the result of rapid potential displacement from E.

of a sudden increase in applied potential (Fig. 3, point F) is always described by the exponential equation of electrochemical kinetics, i.e.,

$$i_2 = i_1 e^{(\varphi_2 - \varphi_1)/b},$$

with an ordinary Tafel coefficient b in the denominator of the exponent (Fig. 3, EF).

Studies on the behavior of metals in the presence of oxidizers were of importance in the development of these notions. Buné and Kolotyrkin [53] showed that the rate of stationary solution of nickel along all the three characteristic parts of its polarization curve is a simple function of potential, regardless of whether this potential was achieved by applied anodic polarization or by introducing a number of suitable redox systems into the solution. In addition to the correctness of measurement and the high information value of potentiostatic studies in investigating and establishing models of existing corrosion processes, these results testified to the effect that, in anodic and chemical passivation of nickel in electrolytic solutions, a single electrochemical passivation process exists, supplied from a single source of passivating oxygen, i.e., water. This principal conclusion was given the most brilliant confirmation in later investigations by Kossyi [52] who studied the behavior of chromium in acidic water – methanol solutions and showed unequivocally the direct participation of water in the process of anodic passivation of chromium.

Analyzing the relationships relating to the effect of potential on stationary and momentary changes in current density as described above, Kolotyrkin [54] concluded that the solution of all passivated metals studied is of an electrochemical nature and that the passivation is connected with comparatively slight changes in the surface characteristics of the electrode. According to the theoretical interpretation submitted by Kolotyrkin, these surface processes affect the current density by changing the value of multiplication factor $k(\varphi)$ in the electrochemical kinetics equation which, correspondingly, assumes the form

$$i = k(\varphi) e^{\varphi/b}. \tag{8}$$

If it is assumed, on the basis of some general considerations, that the stationary value of $k(\varphi)$ becomes an exponentially decreasing function of potential, i.e., $k(\varphi) = e^{-\varphi/b_1}$, then equation (8) corresponds to a negative slope of the straight line expressed by $\log i = f(\varphi)$ for $b > b_1$, and to a zero slope for $b = b_1$. In this sense, passivation which results in a decrease of $k(\varphi)$ (i.e., in an increase of constant a in the logarithmic Tafel equation) is formally analogous to electrode poisoning which increases anodic overvoltage.

Taking into account the data by Érshler noted above, it was natural to assume as well that as far as the degree of packing of the metallic surface is concerned, the passivating oxygen also acts in a way similar to those of catalytic poisons, i.e., it forms a more or less filled monolayer. However, it was shown later on that this assumption is not valid.

Novakovskii [55] noted that also the relationships of electrochemically dissolving conductive metallic oxides come to Eq. (8); these oxides were studied a short time before in Germany by Engell [56] who noticed that the transfer of the cation from the oxidic lattice into the solution is an ordinary anodic act. Thence, it logically followed that the postulate stating that the solution of a passive metal is of an electrochemical nature as well as Eq. (8) suggested by Kolotyrkin ought to be right, regardless of whether the metal is passivated by a monolayer of adsorbed oxygen or by a considerably thicker layer of an electrically conductive oxide. Then $k(\varphi)$ must change with potential since, according to laws of equilibrium applicable to a homogeneous, crystalline phase, any increase in the chemical potential of oxygen in the surface layer of the oxide brought about by an increase in anodic potential results in a decrease in the chemical potential of metallic atoms of the same oxide.

A direct confirmation of the electrochemical mechanism of dissolving cations from the surface of a variety of passive metals was obtained when it was succeeded in determining the true dissolving rate over sufficiently short periods of time following sudden potential jumps in the region of a constant stationary dissolving rate (Fig. 3, part CD).

In full agreement with the theory under development and in direct contradiction to the classical phase layer theory according to which the electrode potential under such conditions could not affect at all the rate of cation transfer into the solution, it was found that, at the moment when the potential is changed, this rate always changes in correspondence with ordinary laws of electrochemical kinetics. Only gradually, just as the applied current density, the dissolving rate returns again to its stationary value which is independent of potential. Indeed, the electrode balance of transition processes shows here an undisputable causal relationship between passivity itself and the oxide layer present at the surface; the degree of metal passivation is subject to change upon changing the thickness of this layer.

The first studies of this kind were carried out by Novakovskii and Kikhachev [57] who combined a potentiostatic polarization method using an automatic recording of anodic current passing after changing the potential (excess current) with a radiometric determination of the true dissolving rate of passive iron marked by a Fe^{59} isotope. They showed that, in acidic solutions, a great part of the aforementioned excess current is due to actual changes in the rate of iron transfer into the solution. The remaining part of this current which corresponds to deposition at positive shifts of potential and to removing additional amounts of passivating oxygen at negative shifts is in good agreement with the independently measured thicknesses of oxide layers on iron known from the literature. Analogous results were obtained later on for titanium and zirconium in acidic solutions [58, 59].

Direct proofs were obtained of the fact that the stationary thickness of the passivating layer decreases upon decreasing the pH simultaneously with an increase in the stationary dissolving rate of passive iron [60]. It can also be confirmed that, at identical electrolyte compositions and potentials, the stationary rates of electrochemical solution of cations from a passive iron surface and a magnetite electrode surface were found to be the same.

It follows from the results obtained [58, 59] that the electrochemical processes of passivating oxide formation and of dissolving cations of the passive metal proceed parallel to each other [as it has to be in the sense of Eq. (8)] and that they are subject to inhibition by the same factor connected with the increase in the oxide layer thickness.

It should be added that recent tests by Kossyi [61] showed that, in strongly acidic solutions containing HF, the growth of the passivating layer on titanium comes to an end even before the rate of anodic oxide formation becomes zero. In such a case, the abatement of the excess current is also held up at an early stage while the stationary current of metal solution may exceed many times the equivalent current of the parallel chemical removal of its passivating oxide on account of an interaction with HF molecules.

In all the studies described, the increase in passivation of the metallic electrode was due to an anodic transfer of oxygen from water molecules or hydroxyl ions to the electrolyte surface while a reduced passivation was due to the same reaction proceeding in reverse direction. This is in full agreement with the already emphasized special part which water assumes in passivation processes. This does not mean, however, that water is the only passivating agent possible.

Some oxidizers containing oxygen and giving it up more readily than water or hydroxyl ions may evidently act as direct donors of passivating oxygen. This is confirmed by data obtained at the institute on the anomalous stimulation of anodic passivation of iron by hydrogen peroxide (to a degree not corresponding to the cathode current of peroxide reduction) [55, 62], on the inhibition of electrochemical solution of chromium by the same agent at potentials more negative than the critical passivation potential, and also by data on the increase in the passive state stability of stainless steel (at a constant potential) in the presence of a chlorate [63].

Moreover, as is well known, oxygen certainly is not the only agent which, interacting with the surface layers of the metallic lattice, may bring about a sharp decrease in chemical potential of the surface atoms (or in electrochemical potential of the cations) which, as has already been noted, constitutes the basis of the passivating action. An analogous effect may also be excercised by other anions, first of all by those which form strong and difficult-to-dissolve compounds with the metal. This is confirmed by the fact that the formation of a protective phosphate layer on iron in neutral solutions [64] and of a sulfate layer in concentrated sulfuric acid [65] is accompanied by the occurence of such passivation parts on the polarization curve as are observed in the "deposition" of passivating oxygen.

In a manner similar to that of oxygen, some particles which form ionic or covalent bonds with the surface atoms of the metal can simultaneously inhibit its anodic solution even when their number at the surface constitutes but a fraction of the adsorption monolayer. For instance, a nickel electrode may be affected this way by iodine anions [66], molecular carbon dioxide [67-69], and also by elemental hydrogen [70]. These components often begin to manifest their passivating action at less positive potentials than oxygen, and in that case a mutual competition and replacement of one type of particles by another may substantially modify the character of the relation between dissolving rate and potential. The behavior of nickel in acidic solutions containing I^- or CO which are adsorbed by nickel and inhibit its solution already at low anodic potentials may serve as an example. In this case, the passivation due to oxygen which is accompanied by a removal of these ions from the surface proceeds at appreciably more positive potentials than

passivation in pure solutions of acids, and the replacement itself of one type of passivating particles by another may be accompanied by electrode activation and marked by the occurence of a narrow current maximum at the polarization curve. It is possible that this exactly is connected with the increase in dissolving current prior to the final oxidic passivation of iron in neutral phosphate solutions, observed when the iron surface succeeded in becoming passivated at a slightly more negative potential, owing to the phosphate ions [62]. However, the mutual replacement of the passivating particles constitutes only a part of the activation mechanism. A subsequent spontaneous increase in current is related to the development of a solution front along certain crystallographic directions and depends on the purity and structure of the metal.

The competition between solution components capable of taking part in the electrode process may, under different conditions and upon increasing the anodic potential, also bring about a reverse result, i.e., to replace the passivating, oxygen-containing particles at the electrode surface by activating anions. Such a mechanism was accepted as accounting for the activation of nickel in sulfuric acid* as discovered by Buné [71] as well as the activation of iron in neutral solutions containing anions of some strong acids (perchlorate, sulfate) as studied by Freiman [72-75]. The investigations showed that the passivation of metals which, in these cases, has started upon displacing the potential to more positive values and is related to the "deposition" of oxygen, is followed by a breakthrough at a part of the surface and a stable passivation takes place only upon increasing further the potential. As a result, two maxima of dissolving rate are found on the polarization curve, corresponding to two passivation processes. As was shown by Freiman, here the iron potential at which a stable passive state is reached differs substantially from the Flade potential predicted by Franck's equation [76]. Moreover, the former potential is not a function of the solution pH but of the anion activity and, evidently, the activity of water.

The discoveries of similar phenomena break down the opinion formed of Franck's equation as of an universal relationship sufficient to evaluate the potentials of stable passive state or iron in a medium of given pH. It vividly shows how important the part of the anionic composition of a solution may be in passivation processes.

The competition of the passivating and the activating components of a solution occurs in the region of pitting corrosion which develops most often in the presence of halogenides. In contrast to activation processes described earlier, the pitting corrosion due to halogenides is peculiar in that the active nidi once formed do not become passivated but grow upon increasing further the potential. The studies carried out at the institute largely contributed to the clarification of the mechanism of this highly dangerous type of corrosion damage inflicted to metals. Contrary to existing views regarding such corrosion as a purely chemical process, these studies established unequivocally its electrochemical nature [77]. In the first place, this is confirmed by the fact that pitting develops at a precisely determined potential which, for any given metal, decreases roughly linearly with the increase of the logarithm of halogen ion concentration and increases from Cl^- to Br^- and I^-. It is highly important that these potentials are always more positive than the passivation potential of the corresponding metal in solutions of the same pH. Thence it follows that a higher affinity of the metal to oxygen than to the activating anion is a necessary condition of pitting development. Investigations showed that a clear-cut localization of the process characteristic for this corrosion type is connected primarily with the fact that the state when passivating oxygen was removed is stable only at those parts of the surface where the concentration of activating ions has reached a certain critical value. However, inasmuch as the accumulation of anions near the surface occurs on account of anion transfer due to the current which, owing to an initial heterogeneity of the solid metal, is always distributed irregularly over the surface, the critical anion concentration is reached first in the vicinity of particles dissolving at the highest rate. This concept formed on the basis of an analysis of experimental results made it possible to clarify both the localization of the corrosion process and the stable existence of pitting [78].

A comprehensive verification and confirmation of the initial notions about pitting made it possible to lay grounds for further, more detailed studies on the kinetics and mechanism of processes fundamental for the phenomenon as a whole. Simultaneously with studying the nucleation kinetics of actual pitting on the passive surface of zirconium [79] and steels [80], models were also formed simulating the individual stages of the process by means of microelectrodes [81-83].

The results obtained showed clearly that the apparent potential of pitting formation is near to the metal–solution potential difference at which the dissolving current density pertaining to the metal in an

* According to latest data [84], this effect may also be of a different nature.

active nidus becomes equal to the limiting current density of cation removal. The saturated, and possibly even supersaturated, electrode-adjacent solution layer of anode metal chlorides shields the surface from the passivating action of water, never stopping the dissolving action itself. The halogen ions which evidently possess the optimum properties for forming such layers are also the most active pitting-formers. Nevertheless, other anions may also exhibit such properties to some or other degree.

In full correspondence with the picture of working pitting described here, the rate of its development in the early stages is determined by the rate of setting up and extending the shielding, electrode-adjacent layers of the concentrated chloride solution. Thus, the initial rate of increase of the dissolving current at a suddenly activated microelectrode in relatively dilute electrolytes is proportional to the current itself. Upon actual pitting nucleation, this is expressed as an exponential dependence of the activation rate on potential.

In the light of the obtained results, it became evident that, together with alloying components increasing the affinity of the alloy to oxygen generated from water (e.g., Cr), the susceptibility of an alloy to pitting should be decreased by such components which reduce the rate of its active solution (Ni, Mo, etc.). The results of the described potentiostatic studies on pitting can be successfully applied in solving practical problems of pitting corrosion due to the effect of oxidizers. However, it is necessary to consider that, as has been stated in an aforementioned study [63], some oxidizers which are not capable of being reduced at the passive surface of the metal (e.g., ClO_3^-) are easily reduced in the active nidi. Pitting can be extraordinarily interesting in concentrated solutions of such oxidizers, owing to the fact that the corrosion nidus acts simultaneously as a local anode and a local cathode. It should be also noted that a definite resemblance exists between the fundamental electrochemical relationships of pitting and corrosion cracking of austenitic steels in chloride-containing solutions [83]. The difference between these two is connected with the fact that the dissolving action may begin at slightly less positive potentials along dislocation line outlets.

Concluding the review, we consider it necessary to emphasize once again that it aimed neither at proclaiming in declarative form the notions described nor at negating or making light of the significance of theoretical and experimental work carried out, and being carried out, by other Soviet and foreign corrosion schools. Its basic objective was to present a sketch of successive developments of a definite system of views which at present characterizes the corrosion and electrochemical school of Karpov Institute.

This system is far from complete. Its development continues and, moreover, it inevitably carries along some elements open to discussion and, at other times, also mutually competing elements of standpoints being developed by various representants of the school. To be sure, the origination and development of these views was always affected, to some or other extent, also by the work of other schools and researchers. However, it is simply impossible to track down all these effects within the scope of one article. Therefore, we are only able to present here the most cardinal and permanent facts of this kind.

LITERATURE CITED

1. A. N. Frumkin, Z. Phys. Chem., 160, 116 (1932).
2. J. Brönsted and N. Kane, J. Amer. Chem. Soc., 53, 3624 (1931).
3. C. Wagner and W. Traud, Z. Electrochem., 44, 391 (1938).
4. Ya. M. Kolotyrkin and A. N. Frumkin, Zh. Fiz. Khim., 15, 346 (1941).
5. Ya. M. Kolotyrkin and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 33, 446 (1941).
6. Ya. M. Kolotyrkin and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 33, 451 (1941).
7. V. V. Losev and A. I. Molodov, Dokl. Akad. Nauk SSSR, 130, 111 (1960).
8. B. V. Érshler, Dokl. Akad. Nauk SSSR, 37, 258 (1942).
9. Ya. M. Kolotyrkin, A. N. Chemodanov, and M. A. Dembrovskii, Élektrokhimiya, 5 (1969) (in press).
10. Ya. M. Kolotyrkin and L. A. Medvedeva, Zh. Fiz. Khim., 29, 1477 (1955).
11. V. V. Gorodetskii and V. V. Losev, Élektrokhimiya, 2, 656 (1966).
12. V. V. Gorodetskii and V. V. Losev, Élektrokhimiya, 2, 664 (1966).
13. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Élektrokhimiya, 3, 1359 (1967).
14. Ya. M. Kolotyrkin, Uspekhi Khimii, 31, 322 (1962).
15. Ya. M. Kolotyrkin and L. A. Medvedeva, Dokl. Akad. Nauk SSSR, 140, 168 (1961).
16. Ya. M. Kolotyrkin, L. A. Medvedeva, and G. G. Lopovok, Zashchita Metal., 5 (1969) (in press).
17. G. V. Golovina, G. M. Florianovich, and Ya. M. Kolotyrkin, Zashchita Metal., 2, 41 (1966).

18. V. M. Knyazheva, Electrochemical Behavior of Chromium [in Russian], Candidate's Dissertation, Moscow (1958).
19. G. M. Florianovich and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 157, 422 (1964).
20. Ya. M. Kolotyrkin and G. M. Florianovich, Zashchita Metal., 1, 7 (1965).
21. Ya. M. Kolotyrkin and T. R. Agladze, Zashchita Metal., 3, 413 (1967).
22. G. M. Florianovich, Ya. M. Kolotyrkin and L. A. Sokolova, Proc. of 3rd Congress on Metallic Corrosion, 1966 [in Russian], Moscow (1968) (in press).
23. A. N. Frumkin, V. N. Korshunov, and Z. A. Iofa, Dokl. Akad. Nauk SSSR, 141, 143 (1961).
24. N. V. Andrushova, V. M. Knyazheva, Ya. M. Kolotyrkin, A. A. Babakov, and M. Yu. Ustimenko, Zashchita Metal., 3, 536 (1967).
25. V. V. Losev, Dokl. Akad. Nauk SSSR, 100, 111 (1955).
26. V. V. Losev and A. M. Kholin, Proc. of 4th Conference on Electrochemistry [in Russian], Moscow (1959), p. 116.
27. V. V. Losev, M. A. Dombrovskii, and A. I. Molodov, Probl. Fiz. Khim., 37, 1904 (1963).
28. G. M. Budov and V. V. Losev, Zh. Fiz. Khim., 37, 578, 1023, 1230, 1461 (1963).
29. V. V. Losev and V. V. Gorodetskii, Élektrokhimiya, 3, 1061 (1967).
30. V. V. Gorodetskii and V. V. Losev, Dokl. Akad. Nauk SSSR, 37, 842 (1963); Élektrokhimiya, 3, 1192 (1967).
31. V. V. Gorodetskii, K. A. Mishenina, V. V. Losev, A. M. Grimberg, and G. M. Ostrovskii, Élektrokhimiya, 4, 46 (1968).
32. V. V. Losev, L. E. Sribnyi, and A. I. Molodov, Élektrokhimiya, 2, 1431 (1966).
33. A. P. Pchel'nikov and V. V. Losev, Élektrokhimiya, 1, 1058 (1965).
34. A. P. Pchel'nikov and V. V. Losev, Zashchita Metal., 1, 482 (1965).
35. V. V. Gorodetskii, L. I. Fedortsov, and V. V. Losev, Élektrokhimiya, 4, 967 (1968).
36. V. V. Losev, A. I. Molodov, G. N. Markos'yan, and L. P. Pchel'nikov, Élektrokhimiya, 5 (1969) (in press).
37. A. P. Pchel'nikov and V. V. Losev, Zh. Fiz. Khim., 41, 971 (1967).
38. Ya. M. Kolotyrkin, I. E. Bryksin, G. M. Florianovich, and A. N. Chemodanov, Probl. Fiz. Khim., No. 3, 14 (1963).
39. Ya. M. Kolotyrkin, Probl. Fiz. Khim., No. 1, 81 (1958).
40. Ya. M. Kolotyrkin and V. M. Knyazheva, Khim. Prom-st', 81, No. 2, 40 (1963).
41. Ya. M. Kolotyrkin and V. M. Knyazheva, Zh. Fiz. Khim., 30, 1990 (1956).
42. V. M. Knyazheva and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 114, 1265 (1957).
43. Ya. M. Kolotyrkin, V. M. Knyazheva, and N. Ya. Buné, Proc. 4th Conference on Electrochemistry [in Russian] (1956), p. 594.
44. G. M. Florianovich and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 130, 585 (1960).
45. N. Ya. Buné and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 111, 1050 (1956).
46. G. M. Florianovich, Ya. M. Kolotyrkin, and N. K. Smirnova, Dokl. Akad. Nauk SSSR, 120, 845 (1958).
47. V. M. Knyazheva, Ya. M. Kolotyrkin, M. A. Vedeneeva, and R. S. Ramazanova, Khim. Prom-st', No. 5, 381 (1964).
48. V. M. Knyazheva, M. A. Vedeneeva, Said Esel'din Khamil', and Ya. M. Kolotyrkin, Zashchita Metal., 1, 465 (1965).
49. V. M. Knyazheva, I. S. Sumakova, Ya. M. Kolotyrkin, and A. A. Kruzhkovskaya, Zashchita Metal., 2, 628 (1966).
50. B. V. Érshler, Zh. Fiz. Khim., 14, 357 (1940).
51. B. N. Kabanov and D. I. Leikis, Zh. Fiz. Khim., 20, 995 (1946).
52. Ya. M. Kolotyrkin and G. G. Kossyi, Zashchita Metal., 1, 272 (1965).
53. N. Ya. Buné and Ya. M. Kolotyrkin, Zh. Fiz. Khim., 35, 1544 (1961).
54. Ya. M. Kolotyrkin, Zh. Fiz. Khim., 62, 6444 (1958).
55. V. M. Novakovskii, Electrochim. Acta, 10, 353 (1965).
56. H. J. Engell, Z. Phys. Chem., 7, 158 (1956).
57. V. M. Novakovskii and Yu. A. Likhachev, Zashchita Metal., 1, 13 (1965).
58. V. M. Novakovskii and V. I. Ovcharenko, Zashchita Metal., 4, 656 (1968).
59. T. P. Bondareva, Zashchita Metal., 5 (1969) (in press).
60. Yu. A. Likhachev and V. M. Novakovskii, Zashchita Metal., 5 (1969) (in press).
61. G. G. Kossyi, V. M. Novakovskii, and Ya. M. Kolotyrkin, Zashchita Metal., 5 (1969) (in press).

62. M. D. Kononova, G. M. Florianovich, and Ya. M. Kolotyrkin, Zashchita Metal., 4, 315 (1968).
63. V. A. Levin, L. D. Ryzhova, A. E. Romanushkina, and V. M. Novakovskii, Zashchita Metal., 4, 437 (1968).
64. Ya. M. Kolotyrkin, M. D. Kononova, and G. M. Florianovich, Zashchita Metal., 2, 609 (1966).
65. V. M. Novakovskii and L. L. Faingol'd, Zashchita Metal., 2, 300 (1966).
66. G. G. Lopovok, Ya. M. Kolotyrkin, and L. A. Medvedeva, Zashchita Metal., 2, 527 (1966).
67. A. T. Sklyarov and Ya. M. Kolotyrkin, Élektrokhimiya, 1, 360 (1965).
68. A. T. Sklyarov and Ya. M. Kolotyrkin, Zashchita Metal., 1, 585 (1965).
69. A. T. Sklyarov and Ya. M. Kolotyrkin, Élektrokhimiya, 2, 1073 (1966).
70. G. N. Trusov, M. F. Fandeeva, and V. M. Novakovskii, Zashchita Metal., 5 (1969) (in press).
71. N. Ya. Buné, Zashchita Metal., 1, 168 (1965).
72. L. I. Freiman and Ya. M. Kolotyrkin, Zashchita Metal., 1, 161 (1965).
73. L. I. Freiman, Ya. M. Kolotyrkin, and A. Ya. Givental', Zashchita Metal., 1, 286 (1965).
74. L. I. Freiman and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 171, 1138 (1966).
75. L. I. Freiman and Ya. M. Kolotyrkin, Zashchita Metal., 5 (1969) (in press).
76. U. F. Franck, Z. Naturforschung, 4a, 378 (1949).
77. Ya. M. Kolotyrkin, Khim. Prom-st', No. 9, 38 (1963).
78. Ya. M. Kolotyrkin and V. A. Gil'man, Dokl. Akad. Nauk SSSR, 137, 642 (1961).
79. V. A. Gil'man and Ya. M. Kolotyrkin, Dokl. Akad. Nauk SSSR, 143, 640 (1962).
80. G. V. Golovina, G. M. Florianovich, and Ya. M. Kolotyrkin, Élektrokhimiya, 1, 12 (1965).
81. V. M. Novakovskii and A. N. Sorokina, Corrosion Sci., 6, 227 (1966).
82. V. M. Novakovskii and A. N. Sorokina, Zashchita Metal., 2, 416 (1966).
83. V. M. Novakovskii and A. N. Sorokina, Zashchita Metal., 5 (1969) (in press).
84. G. N. Trusov, E. P. Gochalieva, and V. M. Novakovskii, Élektrokhimiya, 4, 366 (1968).