SOME RESULTS OF DEVELOPMENTS IN THE STUDY OF ELECTROCHEMICAL REACTION MECHANISMS IN THE LAST FIVE YEARS*

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In my report I would like to characterize some results of developments in electrochemical kinetics since the third conference and this should promote their further thorough discussion. The immense expansion of work in this field during the last few years makes it impossible for me to examine it all and so I must limit myself to a consideration of the simplest electrochemical reactions. As the program of the conference includes reports which reflect the results of various approaches, I will therefore describe in greater detail the results of investigations carried out in the electrochemistry section of the Institute of Physical Chemistry, Academy of Sciences USSR and in the Department of Electrochemistry of the Lomonosov State University of Moscow.

These past years have been an important stage in the development of electrochemical kinetics: they may be characterized as a period during which the theoretical basis of the subject has been strengthened. Only comparatively recently, an exposition of electrochemical kinetics consisted mainly of a survey of a series of competing theories on hydrogen overvoltage. Now quite a large amount of factual material has been collected in this field of knowledge and has appeared in the form of a series of systematic reports and monographs.

METHODICAL BASES OF ELECTROCHEMICAL KINETICS

The consolidation of the foundations of electrochemical kinetics has promoted an expansion of kinetic investigations to cover a considerably wider area of electrochemical processes. Thus, in the last few years the kinetics of the exchange between amalgams and metal ions and the reduction of a series of simple and complex ions have been studied and though insufficiently complete, extremely numerous data have been obtained on the electrochemistry of organic compounds. In this, the use of a convenient and readily reproducible form of electrode, such as the dropping-mercury electrode proposed by Heyrovsky, has played an important part.

The development of methods making it possible to remove diffusion limitations to a certain extent has been of particular value in extending the range of reactions which come within the scope of electrochemical kinetics. If the rate of a strictly electrochemical process considerably exceeds the diffusion rate, then the kinetics of the over-all process are largely determined by the diffusion stage. I will not dwell on the results of studying the so-called purely diffusion kinetics, which are observed in these cases and which are often of decisive importance in practical electrolysis processes, as the review of V. G. Levich will be devoted to this. Naturally the observation of an electrochemical process under these conditions, generally speaking, cannot provide a basis for elucidating the mechanism of the reaction itself.

The problem of removing diffusion limitations has recently been solved mainly by carrying out processes under nonstationary conditions. On applying a current for short intervals of time, the diffusion front is unable to move an appreciable distance from the electrode surface, making it possible to pass a considerably greater current through the cell than under the stationary conditions with normal mixing. This also makes it possible to demonstrate the kinetic stages of the process.

The first example of the use of measurements under nonstationary conditions for the quantitative investigation of the kinetics of electrode processes was given in the work by P. I. Dolin and B. V. Ershler [1], who determined the kinetics of hydrogen-ion discharge on platinum by the conductivity of the electrode in relation to

*Introductory report to the First Plenary Meeting of the Conference, which took place October 1, 1956.

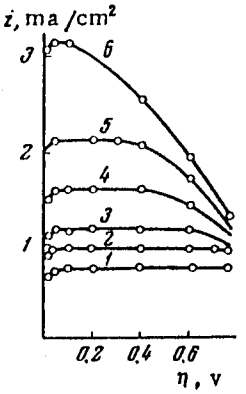

Fig. 1. i,η-Curves of hydrogen ionization at a smooth platinum electrode in 1 N H_2SO_4. 1) 120 rev/min; 2) 200 rev/min; 3) 330 rev/min; 4) 600 rev/min; 5) 960 rev/min; 6) 2400 rev/min.

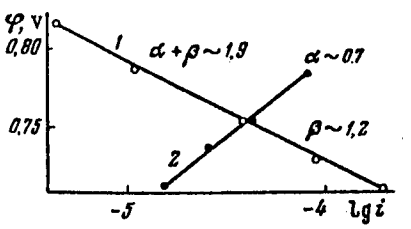

Fig. 2. Anode (1) and cathode (2), φ, log i-curves in the 0.3% Zn amalgam, 0.1 N $ZnSO_4$ system in the presence of $(C_4H_9)_4N^+$. The densities of the anode and cathode currents were determined by the rate of transfer of labeled zinc from one phase to another.

an alternating current. The application of the alternating-current method to the investigation of electrode process kinetics has been widely developed since the war in the theoretical and experimental work of B. V. Ershler [2], Randles [3], Gerischer [4], Grahame [5] and Bokris [6]. Other promising methods of investigating the kinetics of electrode processes are: a method based on determining the time dependence of the electrode potential during the passage of a current at constant strength, which was first applied by V. A. Roiter, V. A. Yusa and E. S. Poluyan [7], and the method of determining the time dependence of the current during the application of defr inite polarization. These methods have recently been developed and widely used by Delahay [8], Gierst [9], Lorenz [10] and Gerischer [11]. Oscillographic polarography of Heyrovsky [12] belongs to this group of methods. At the present time it is hardly possible to give a comparative evaluation of the efficiency of the methods listed; undoubtedly one or another method is preferable for solving certain problems. Thus, alternating current measurements are especially convenient for detecting the reversible stages of a process and measurements at constant current density for detecting slow chemical reactions preceeding the strictly electrochemical stage. The mathematical treatment of these methods, based on a solution of the differential equations of diffusion under limiting conditions, determined by the rules of the electrochemical process itself, is frequently extremely complex, especially where a dropping electrode is used. The fact that the results of these calculations for a series of electrochemical processes were completely confirmed by experiment is a particularly convincing demonstration of the accuracy of the basic phenomenological premises of electrochemical kinetics. The first example of a sufficiently accurate treatment of this type of problem and an experimental test of the deductions obtained from it was given in the work of N. N. Meiman, V. G. Levich and V. S. Bagotskii [13], who solved the problem of the course of the irreversible electrode process at a dropping electrode in the presence of concentration polarization.

Particular difficulties are presented by the treatment of irreversible processes involving H^+ ions at a dropping electrode in unbuffered solutions. In the presence of catalysis by the reaction products as, for example, in the case of reduction of nitrate ion or hydroxylamine on a lanthanium base, jumps in the current density and hysteresis phenomena are observed. Although a strict mathematical solution of this problem could not be achieved, a semiquantitative examination of it, carried out together with S. I. Zhdanov [14], shows, in my opinion, that these phenomena also are covered by the equations of electrochemical kinetics and the theory of diffusion and that their explanation does not require such additional assumptions as, for example, the hypothesis on the effect of macroscopic nonuniformity of the electric field at the surface of a spherical drop on the movement of ions.

This valid approach, which has led to the investigation of electrochemical processes under nonstationary conditions, has led to underevaluation of the possibilities of the classical methods of plotting stationary polarization curves under conditions of vigorous mixing. As an example of a disclosure of the rules characterizing a strictly electrochemical process as the intensity of mixing increases, I present Fig. 1, which gives the dependence of the current density $\underline{i}$ on the overvoltage η at different rates of rotation for the oxidation of molecular hydrogen at a rotating platinum disc electrode in 1 N sulfuric acid [15]. At a low rotation rate, within the range of potentials examined, only the limiting current determined by the diffusion rate was observed and this increased as the rotation rate increased; at a rotation rate exceeding 2400 rev/min, the effect of diffusion practically

disappeared and a further increase in the rotation rate had no further effect on the form of the curve, the unusual character of which was connected with passivation of platinum by adsorbed anions with increasing anode polarization. By increasing the mixing to 10-20,000 rev/min and especially by the use of turbulent conditions, it is possible to investigate reactions with rate constants of the order of several tenths of a $cm \cdot sec^{-1}$, which corresponds to current densities of up to approximately 100 a/cm^2 at a reagent concentration of 1 N (B. N. Kabanov [16], Bockris and Azzam [17] and É. A. Aikazyan [15] and approaches the limit of application of alternating-current measurements. Measurements with vigorous mixing, however, have only found application in electrochemical kinetics up to now for the reactions of hydrogen ionization and evolution, though they probably merit wider use.

Together with the removal of diffusion difficulties, an essential procedural problem is the determination of the ohmic fall in the solution. A valuable contribution to this section of electrochemistry was made by Piontelli [18], who determined the optimal conditions for using a Luggin capillary.*

The use of tracers has made it possible to extend the investigation of electrochemical kinetics in other directions. In certain cases, the use of tracers makes it possible to choose between different reaction routes; thus, interesting results were provided by the use of O^{18} in investigating the mechanism of oxidation processes (V. I. Veselovskii and K. I. Rozental' [19] and M. A. Gerovich and R. I. Kaganovich [20]). Of special interest in electrochemical kinetics is the use of tracers in measuring the rate of an electrode process when the reverse process proceeds at a comparable or even greater rate (Audubert [21] and V. V. Losev [22]), which makes it possible to find directly from experimental data the potential dependence of the ratio of the rates of the forward and reverse processes, an important criterion of the mechanism of an electrochemical reaction. The first step in this direction consisted of determining the exchange currents at equilibrium potential. This problem was considered at the third conference in the report of Viktor Arturovich Pleskov [23], who died prematurely. In recent years V. V. Losev has been able to use tracers to plot full polarization diagrams over a quite wide range of potentials φ. Figure 2 shows the data of V. V. Losev [22], referring to the 0.3% Zn amalgam, 0.1 N $ZnSO_4$ system in the presence of a suppressing agent, namely, tetrabutylammonium sulfate. They made it possible to check the important conclusion from the equations of electrochemical kinetics on the relation between the constants α and β, characterizing the anode and cathode processes, whose sum in this case (a process involving two electrons) must equal 2.* *

For developing the study of an electrochemical process, it is of great importance to determine the dependence of the reaction rate on a series of parameters, namely, the concentration of the reagents, temperature and the intensity of external energy effects. In earlier work we showed that the evolution of hydrogen on mercury from acid solutions both with and without excess of a foreign electrolyte is a reaction of the first order with respect to the hydrogen ion in the double layer covering; this conclusion was a convincing argument in favor of the hypothesis that the rate of hydrogen evolution on mercury is determined by the hydrogen-ion discharge stage. An equally convincing demonstration of the fact that hydrogen evolution on mercury in alkaline solutions is determined by the kinetics of the discharge, not of hydrogen ions, but of water molecules, was obtained by Z. A. Iofa and É. A. Maznichenko [24], who showed that the rate of hydrogen evolution from a solution containing tetramethylammonium cations was completely independent of solution pH in the range from 10-11 to 13.

Together with the direct determination of the concentration dependence of the current density at constant potential, other methods of determining the order of the reaction have been used. Thus, the latter may be found from the dependence of the current strength at a rotating disc electrode on the rotation rate at the transition from the diffusion to the kinetic region [15]. The use of this method led to the unexpected

*I would like to take this opportunity to draw attention to the following situation. Exaggerated surmises frequently appear in the literature on the possible value of the ohmic fall in the diffusion layer in the case of electrolysis of a binary electrolyte, arising as a result of impoverishment of this layer in solute. In actual fact, in electrolysis under stationary conditions and in the absence of convection, this ohmic fall is a value of the same order as the concentration polarization, to which it is related in a simple way, and at current densities appreciably less than the limiting diffusion current, it can be neglected.

**Here it is assumed that the rates of the cathode and anode processes are proportional to $\exp\left(-\frac{\alpha\varphi F}{RT}\right)$ and $\exp\left(\frac{\beta\varphi F}{RT}\right)$, respectively. If, as is often done, the expression in brackets is multiplied by the number of electrons n participating in the over-all process, then at any value of n the equation $\alpha + \beta = 1$ holds.

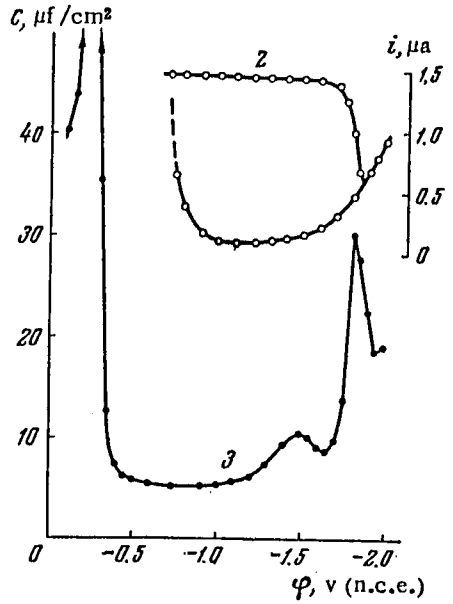

Fig. 3. Dependence of current strength i on potential: 1) during the reduction of 10^{-3} N $K_2S_2O_8$; 2) the same in the presence of 10^{-5} N $[(C_4H_9)_4N]_2SO_4$; 3) dependence of differential capacity of mercury in 10^{-2} N Na_2SO_4 + 10^{-5} N $[(C_4H_9)_4N]_2SO_4$ on potential.

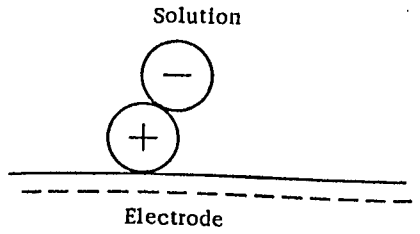

Fig. 4. Scheme of cation-bridge formation.

conclusion that the ionization of molecular hydrogen on active platinum was a zero-order reaction. Gerischer and Vetter [25] widely applied the determination of the composition of discharging complexes from the dependence of the exchange current on the reagent concentration.

Investigation of the temperature dependence of the reaction rate had been used little (in comparison with other fields of chemical kinetics) in the kinetics of electrode processes and the frequently applied comparison of current density values observed at various temperatures and constant potential, measured against a standard electrode at constant temperature (instead of comparing them at constant overvoltage) carries an element of uncertainty in the interpretation of the activation energies calculated from the temperature coefficient of the current density, as was shown by M. I. Temkin [26] and Agar [27]. This deficiency was avoided in the earlier work on the temperature coefficient of hydrogen overvoltage of Z. A. Iofa and K. M. Mikulin [28], Post and Hiskey [29] and also V. A. Pleskov [23] and Randles [3], who found the activation energy from the temperature dependence of the exchange current. A large amount of data on the activation energies of electrochemical reactions was obtained by S. V. Gorbachev and his co-workers [30], however, without consideration of the difficulties arising under conditions when the current densities were compared at different overvoltages.

In the literature one frequently encounters the statement that low activation energies (for example, of the order of 3-4 calories) characterize the diffusion kinetics of an electrochemical process and that higher values indicate the presence of a rate determining, slow chemical or electrochemical stage. Actually, a fall in the activation energy, connected with an increase in polarization, moves electrode processes from the kinetic to the diffusion region in many cases. However, this conclusion cannot be generalized for all reactions. As was shown by N. V. Nikolaeva [31], in the case of reduction of persulfate anion on a mercury electrode, the apparent activation energy of the process is close to zero at potentials at which the rate of the process is considerably less than the limiting rate of the diffusion stage and when the process proceeds in a cesium base, the apparent activation energy may even have a negative value.*

Up to now, the action of light on electrode processes has only been studied on a small number of examples. V. I. Veselovskii and his co-workers [33], who investigated the action of light on anode-polarized electrodes, obtained results showing the semiconductor nature of oxide surfaces. The application to electrochemical processes of short-period, intense irradiations, similar to those used at the present time in studying the kinetics of gas reactions, could be promising.

The problem of the use of atomic energy necessitates an investigation of the action of hard radiation on electrochemical processes. It is very probable that these problems will occupy one of the central positions in our subsequent conferences.

KINETICS OF ELECTRODE PROCESSES AND THE STRUCTURE OF THE METAL–SOLUTION BOUNDARY

A prerequisite for understanding the mechanism of electrochemical processes is a knowledge of the

*According to V. I. Zykov and S. I. Zhdanov [32], a negative temperature coefficient is also observed in the case of BrO_3^- reduction in the presence of alkali metal cations at pH > 4.

topography of that part of space in which they occur, i.e., the metal–solution boundary, and, in the first instance, the structure of the electrical double layer at this boundary. At the present time we have a quite full picture of the distribution of charges at a mercury–solution boundary. A valuable contribution to the theory of the double layer at this boundary has been made by Grahame [34] over the last few years.

A large amount of material on the mechanism of the adsorption of organic compounds on mercury and on their effect on the kinetics of electrode processes has been accumulated in the work of Soviet authors (V. I. Melik-Gaikazyan [35], M. A. Loshkarev and A. A. Kryukova [36], T. A. Kryukova [37], A. G. Stromberg [38], N. V. Nikolaeva [39], V. V. Losev [40], T. V. Kalish [41] and others) and also of Kolthoff [42], Heyrovsky [43], Brdicka [44], Lorenz [45], Tamamushi [46] and others; the authors made an attempt to classify the results obtained [47]. As an example of the way in which the use of adsorption data makes it possible to analyze processes occurring even under complex conditions, I present the polarization curves of electroreduction of the persulfate anion at the negatively charged surface of a dropping-mercury electrode, obtained by N. V. Nikolaeva and B. B. Damaskin [31] (Fig. 3). On the curve showing the dependence of the current strength $\underline{i}$ on the potential φ during the reduction of 10^{-3} N $K_2S_2O_8$ there is a drop in current caused by repulsion of the anion by the negative charges of the surface. This is a typical φ_1-effect (according to the terminology of Gierst [9]), which is connected with the sign and value of the φ_1-potential, i.e., the potential at distances from the electrode determined by the dimensions of the particles reacting at the electrode. As can be seen from Fig. 3 (upper curve) small amounts of the surface-active cation tetrabutylammonium change the sign of the φ_1-potential and remove the repulsion effect; the current increases to the value of the limiting diffusion current. However, the question arises as to why the action of the cation ceases at more negative potentials. An answer to this question is provided by measurements of the differential capacity of the mercury C in solutions containing the tetrasalt in the presence of an indifferent electrolyte. The right peak on the curve of the potential dependen· of the differential capacity shows that desorption of the organic cation from the mercury surface occurs during the transition to more negative potentials. The desorption is produced by the fact that during the increase in the charge on the surface, the filling of the double layer by large organic cations, lowering the capacity, is made energetically unprofitable and they are displaced by the smaller alkali metal ions and water molecules. In this respect, the behavior of the tetrabutylammonium cation is analogous to that of neutral organic molecules. The potential of the desorption peak coincides with the break on the polarization curve, indicating that the action of the additive ceased. Figure 3 also illustrates the fact that in interpreting the action of surface-active organic compounds it is necessary to pay attention not only to the change in the structure of the double layer, but also the capacity of these compounds to fill the surface of the electrode. The latter conclusion may also be extended to other manifestations of the action of such substances. However, the importance of the first factor should not be underestimated. The addition of the cation $(C_4H_9)_4N^+$, which, as was shown, accelerates the discharge of the anion $S_2O_8^{2-}$, suppresses the discharge of the cations Zn^{2+} and Cd^{2+} by a factor of hundreds [22, 23].

It is possible to present many examples of agreement between the results of kinetic and adsorption investigations. However, despite the undoubted successes achieved by studying the adsorption of ions and molecules on a mercury surface, our theoretical ideas in this field require further refinement. This is evident from the example of the adsorption of anions. As was shown by N. V. Nikolaeva and B. B. Damaskin [31], Zezula [48] and V. I. Zykov and S. I. Zhdanov [49], the rate of electroreduction of the anions $S_2O_8^{2-}$, $S_4O_6^{2-}$, BrO_3^- at a negatively charged mercury surface in the presence of the singly charged cations Li^+, Na^+, K^+, Rb^+, Cs^+ changed over a wide range in relation to the radius of the cation. This phenomenon indicates facilitation of the approach of the anion to the electrode surface due to the formation of cation bridges, illustrated schematically in Fig. 4, which leads to the reduction of the absolute value of the negative φ_1-potential. The formation of these bridges, like adsorption of the cation in the electrical double layer, apparently involves partial destruction of the hydration envelope of the cation and this is easier in the case of cesium than, for example, lithium.* To explain the possibility of formation of such bridges it is necessary to consider the nonuniformity

*This idea has a general similarity to the explanation of the effect of the cation charge on the reduction of anions of the NO_3^- type through the formation of ion pairs, put forward by Heyrovsky [50]; however, at the same time it differs from the latter in many ways. The polarization of the anion by the cation, which, according to Heyrovsky, is of fundamental importance as a factor facilitating the reduction of the anion, evidently cannot explain the great rate of the process in the presence of cations with a large radius, as observed experimentally. Then, according to Heyrovsky, the role of the ion pairs formed in the [footnote continued on next page]

of the potential distribution in the double layer parallel to the electrode surface, which has been demonstrated by our work [51] and by O. A. Esin [52] and B. V. Érshler [53] but which is not considered in the generally accepted theory of the double layer. Undoubtedly the concentration of anions in the double layer is low at a sufficiently high negative surface charge and the detection of their presence by measurements concerned with the equilibrium properties of the double layer is difficult, though not completely impossible, as shown by the report of N. V. Nikolaeva. The low value of this concentration, however, does not detract from the importance of solving this problem from the point of view of electrochemical kinetics.

A problem which naturally arises in evaluating the significance of contemporary theory of the double layer in electrochemical kinetics is the question of the extent to which this theory, which is based on data obtained with mercury electrodes, may be applied to solid metals. It must be acknowledged that the experimental material on this problem is as yet insufficient, on the whole. There are more numerous data on the dependence of the position of the zero-charge point on the nature of the metal, but I will not dwell on this as many recent reviews have been devoted to this problem.

More detailed information on the structure of the double layer at the surface of solids may be obtained by measuring the differential capacity and, partly, by directly determining the adsorption of ions. The differential-capacity method was used by T. I. Borisova and B. V. Érshler [54], É. Ayazyan [55], V. L. Kheifets and B. S. Krasikov [56] and D. I. Leikis and B. N. Kabanov [47].

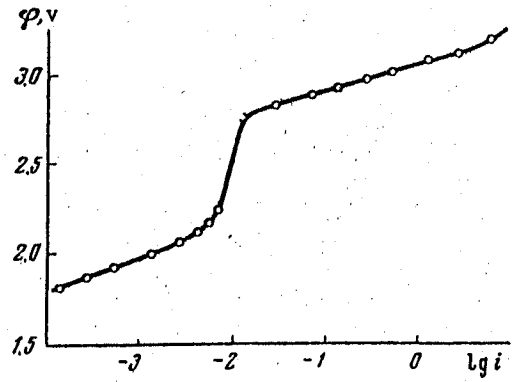

Fig. 5. Dependence of potential on logarithm of current density during the evolution of oxygen from a 40% solution of $HClO_4$ at a platinum anode (according to R. I. Kaganovich, M. A. Gerovich and É. Kh. Enikeev). The current density is expressed in a/cm^2.

From the data obtained it follows that such characteristic traits of the structure of the double layer on mercury as the dependence of the degree of diffusion on concentration, the specific adsorption of anions and the effect of the double layer field on the adsorption of neutral molecules are retained at the surface of a solid body.

We should note some peculiarities of the differential capacity of the double layer at the surface of solid metals, which have not been fully interpreted as yet. Thus, the minimum close to the zero charge point in a series of experiments with solid electrodes was also observed at such high concentrations that it could not be explained by a change in the degree of diffusion. At solid surfaces, dispersion of capacity is observed, indicating the slowness with which equilibrium in the double layer is established. In the case of lead, this effect disappears when the surface is smooth.

The most essential difference in the properties of the double layer at the surface of solid metals and mercury, from the point of view of kinetics, is the change in the character of the interaction of anions, for example halogen anions, with the metal. In all cases, the specific adsorption of halides reflects the presence of some chemical interaction of the anion with the metal surface. However, we should not overestimate the role of this chemical interaction in the case of the adsorption of chlorine or bromine ions on mercury, at least if it is assumed that electrocapillary measurements give an exhaustive representation of this adsorption. B. S. Gurenkov [57] compared the dependence of the shift in the potential maximum on the electrocapillary curve in

*[footnote continued from previous page] volume of the solution consists of facilitating the attraction of the anion into the range of the double layer during electrolysis, while according to the scheme proposed, in the double layer with a negative charge at the surface there is some equilibrium in the anion concentration with respect to the volume of the solution. At the present time it would be premature to decide whether direct contact is established between the anion and the cation during the formation of cation bridges, as is shown in Fig. 4, or whether they retain an interlayer of water molecules. It is also not quite clear whether some specific adsorbability should be ascribed to a cation with a large radius.

concentrated solutions of H_2SO_4, HCl and HBr on the logarithm of the average activity of the ions with the analogous dependence for the adsorption potential at the solution – air boundary, measured by Kendrick's method. It was found that although the surface activity at the mercury boundary exceeded that at the air boundary, the difference was small. In quite concentrated solutions, the adsorption potentials at the air boundary also reached high values.

The adsorption of halogen ions on mercury affects the kinetics of electrode processes, accelerating the discharge of cations and, in particular, the hydrogen ion [58]. According to Ya. M. Kolotyrkin, a fall in the hydrogen overvoltage is also observed in the case of anion adsorption on cadmium and thallium [59]. These effects may be interpreted qualitatively by considering the change in the φ_1-potential produced by the adsorption of anions. A large amount of material illustrating the accelerating action of adsorbed anions on the discharge of cations was collected by L. I. Antropov [60]. However, as Ya. M. Kolotyrkin and L. A. Medvedeva [59] showed, in the case of lead, the action of the adsorbed layers of halides clearly cannot be reduced to a change in the φ_1-potential, since the adsorption of an iodine ion on lead over a certain concentration range does not accelerate, but retards the discharge of a hydrogen ion. The latter effect indicates a reduction in the adsorption energy of hydrogen as a result of saturation of the surface valences of the metal by chemosorption of iodine.

On discussing such metals as iron, nickel and platinum, the importance of the formation of chemosorbed layers becomes even greater. In recent years, Soviet investigators have obtained a considerable amount of material on the electrochemical and chemical properties of both oxygen layers and layers formed by other negatively charged atoms on these metals. Various methods were used for this: measurement of the differential capacity and charging curves, determination of the adsorption by means of radioactive tracers, measurement of the adsorption potentials and the photogalvanic effect and determination of the effect of these layers on the kinetics of electrode processes.

Since the bond between the metals and the adsorbed atoms has a dipole character, the formation of atomic layers leads to destruction of the structure of the electrical double layer right up to a change in the sign of the φ_1-potential [61]. New data on this problem, obtained by means of tracers, are presented in the report of N. A. Balashova. Another characteristic is a strong fall in the capacity of the double layer caused by the formation of these layers [62].

The presence of atomic layers not only complicates the structure of the ionic envelope of the electrical double layer, but to some extent hinders its investigation, for example, the determination of the change in diffusion with concentration from measurements of the differential capacity. Therefore, the interpretation of the results of such measurements in the case of platinum in dilute solutions of electrolytes is still not completely unequivocal.

In contrast to layers of the ionic type formed by halogens on mercury, as Z. A. Iofa [63] showed, atomic layers of halogens on iron retard the discharge of hydrogen ions and also the formation of iron cations. The ionization of molecular hydrogen on platinum is especially sharply retarded by adsorbed layers of halogens, oxygen and a series of anionic groups (Wicke and Weblus [64] and E. A. Aikazyan [15]). In interpreting the mechanism of the latter phenomenon, it is necessary to consider the nonuniformity of the electrode surface. As was shown by direct determinations of the shift in the potential of an isolated electrode during the adsorption of anions, carried out by A. D. Obrucheva [65], the process of adsorption on a large part of a platinum surface requires a few minutes, while the poisoning of the active centers on which the ionization of molecular hydrogen depends, continues to increase for a period of several hours [15]. It has already been noted above that the ionization of molecular hydrogen is a zero-order reaction. This indicates saturation of the active centers by hydrogen at potentials somewhat more positive than reversible, while for the electrode as a whole, in this region of potentials a logarithmic adsorption isotherm is observed, as shown by the charging curves. The nonuniformity of the electrode surface undoubtedly plays a great, but as yet insufficiently studied role in the case of reactions proceeding on electrodes of the platinum and iron group of metals. The report of A. T. Vagramyan sheds light on the important problem of the role of surface nonuniformity in electrodeposition reactions.

Retardation of the reaction produced by the formation of oxide layers on platinum, leading to a fall in current with an increase in anode polarization, is observed not only in the oxidation of H_2, but also in a large number of other anode processes: evolution of Cl_2 [66], oxidation of alcohols [67], SO_2, NH_3, thiosulfates [68],

nitrates [69], aniline [70], etc. Apparently, this retardation cannot be explained by a change in the potential distribution in the electrical double layer. It is sooner connected with saturation of the surface valences of platinum, leading to a fall in the adsorption energy of intermediate reaction products, for example, Cl atoms arising from Cl^- ions or H atoms, formed from H_2 molecules.

The atoms and groups of atoms forming the chemosorbed layers may also play an active part in the electrode process. An example of such participation of adsorbed atoms is the electrochemical desorption of hydrogen in which the H_2 molecule arises due to combination of an adsorbed hydrogen atom with a hydrogen ion and an electron. The importance of the active role of chemosorbed oxygen in anode processes was recently especially emphasized by the work of V. I. Veselovskii and his co-workers [19], who were able to confirm the participation of the oxygen of surface platinum oxides in the formation of O_2 molecules, which indicates the analogy of the mechanism of this process to the mechanism of the electrochemical desorption of H_2. In the case of oxygen evolution from H_2SO_4 and $HClO_4$ solutions on platinum, at definite current density values, sudden increases in the anode potential were observed and these were first described by N. A. Izgaryshev and E. A. Efimov [71] (Fig. 5). A series of authors explained this phenomenon by a change in the state of the oxide film [72]. M. A. Gerovich and R. I. Kaganovich [20], who carried out experiments with solutions of perchloric acid labeled with O^{18}, were able to show that while the whole of the oxygen was liberated from water at polarizations corresponding to the lower branch of the curve, at potentials of the upper branch, part of the oxygen was formed from the ClO_4^- anion, especially at high perchloric acid concentrations. This result indicates that the change in the state of the surface oxide on going from the lower to the upper branches of the curve is accompanied by adsorption of anions.

A deeper investigation of the chemical and physicochemical properties of surface compounds, arising on electrodes, is a prerequisite of further successful development of electrochemistry.

ELECTROCHEMICAL AND CHEMICAL STAGES IN ELECTRODE PROCESSES

As kinetic investigation shows, the actual electrochemical processes may be divided into a series of stages. As an example, I give a scheme for the reduction of oxygen to hydrogen peroxide, investigated in our laboratory by Z. A. Iofa et al., [73] and V. S. Bagotskii and I. E. Yablokova [74], and also a scheme for the reduction of quinone to hydroquinone in acid solutions according to Vetter [75]:

$$O_2 \xrightarrow{e} O_2^- \xrightarrow{H^+} HO_2 \xrightarrow{e} HO_2^- \xrightarrow{H^+} H_2O_2;$$

$$Q \xrightarrow{H^+} QH^+ \xrightarrow{e} QH \xrightarrow{H^+} QH_2^+ \xrightarrow{e} QH_2$$

where Q is quinone.*

The individual stages in each case may be reduced to the addition of electrons or protons; we should recognize, however, that such a differentiation, even for comparatively well-studied reactions, cannot always be established unequivocally and, for example, the possibility of the addition of a proton and an electron in one elementary act has not yet been determined.

A consideration of the rates of the stages leading to the addition or elimination of an electron by the reacting particles and the changes in the degree of solvation accompanying them has played an important role in the history of electrode process kinetics. For a long time the arguments put forward as proof of the possible irreversibility of electrochemical stages ("the theory of retarded discharge," according to accepted terminology) were based predominantly on a study of hydrogen-evolution processes. Thus, it is of primary importance that the kinetic investigations carried out lately, particulary the work by Gerischer, Vetter, Randles and Audubert and a series of works carried out in the USSR, have demonstrated the irreversibility of other electrochemical processes, in particular, processes which could not be said to have slow, purely chemical stages. As an example we can quote the reduction of Fe^{3+} to Fe^{2+} and Eu^{3+} to Eu^{2+} (Gerischer [4], Lewartowicz [76] and Randles and Somerton [3]) and the exchange reaction between thallium amalgam and thallium salt solutions (V. A. Pleskov and N. B. Miller [77] and M. A. Loshkarev and A. A. Kryukova [78]), in which the number of charges changes

* The method used for outlining these schemes is incomplete as it does not reflect changes in the degree of hydration of the reacting particles when their charges change.

by one unit on the reacting particles without subsequent chemical conversions of the reaction products. Proof of the existence of various electrochemical processes whose rate is determined by the discharge stage has deprived the discussion on the nature of hydrogen overvoltage of its determining role in electrochemical kinetics as a whole; nevertheless, the widespread reactions of hydrogen evolution, which are of practical importance and possess a series of interesting characteristics, continue to attract attention and I shall describe the results of work in this field.

The idea first put forward by Erdéy-Gruz and Volmer [79] that the rate of hydrogen evolution from acid solutions on mercury is determined by the rate of the hydrogen-ion discharge stage has been substantiated by investigations in the USSR on the dependence of the rate of this process on solution composition and the structure of the double layer [80] and has been confirmed repeatedly in recent years by the work of Bockris et al., [81], Bethune [82], Gerischer [83], Tamamushi [84] and others. Eyring [85], who held a different opinion for a number of years, has agreed with this concept. Although some scientists continue to question the theory of the retarded discharge of hydrogen ions on mercury (Knta [86], Horiuti [87], N. I. Kobozev [88] and O. M. Poltorak [89]) presumably it may be considered as accepted by a considerable majority of electrochemists.

A more complicated situation exists for metals with low or average hydrogen overvoltage, particularly those belonging to the platinum and iron groups. In spite of the large number of papers, on the whole, no unequivocal results have been obtained as yet. Thus, the extensive use of measurements of the impedance and charging curves for investigating processes occurring during hydrogen evolution and its ionization on metals of the platinum group and on gold, Knorr et al. [90], in agreement with the results obtained by P. I. Dolin and B. V. Érshler [1], concluded that the discharge of hydrogen ions proceeds at a finite and measurable rate; at the same time one must also consider the slowness with which equilibrium is established between hydrogen molecules and atoms and the slowness of diffusion processes, with the relation of the rates of these stages changing with the state of the surface. From an investigation of the kinetics of molecular hydrogen ionization on a rotating, active platinum electrode, the author and É. A. Aikazyan [15] concluded that on the greater part of the surface, the limiting stage is the conversion of H_2 molecules into adsorbed atoms, and at active centers, where this reaction proceeds unhindered, a subsequent reaction occurs (either ionization or surface diffusion).

According to Bockris [91], the rate of hydrogen evolution on nickel is determined by the stage of electron addition to a hydrogen ion or a water molecule. According to Knorr [90], hydrogen evolution on nickel from an acid solution follows the equations of the theory of retarded discharge; however, it was also necessary to consider retarded recombination on some samples of electrodes. By the method of measuring the potential fall after switching off the polarizing current, V. É. Past and Z. A. Iofa [92] could detect only a very small amount of "excess" adsorbed hydrogen on nickel at considerable overvoltages, especially in the case of acid solutions, when the presence of the hydrogen would have indicated deceleration of the elimination processes, while in alkaline solutions the concentration of excess hydrogen on iron was quite considerable. The use of such a criterion as the determination of the relation of the cathode potential to alkali concentration in the case of hydrogen evolution on nickel gives variable results, which depend on the preliminary processing of the electrode, according to the latest experiments of S. D. Levina.

This forced us to search for a criterion which would allow us to determine the mechanism of hydrogen evolution on this group of electrodes more unequivocally and at least qualitatively. Evidently, we may consider the displacement of the potential of the polarized cathode when further amounts of atomic hydrogen are introduced onto its surface from a foreign source as such a criterion. This introduction may be carried out by two methods: in the variant developed by S. D. Levina and T. V. Kalish, free hydrogen atoms diffuse through a thin liquid film and in the variant of I. A. Bagotskaya, diffusion through metal is used and these are described in detail in the appropriate reports. These experiments showed that the magnitude and sign of the changes in potential depend on the nature of the cathode and the value of the overvoltage. In the case of a number of cathodes, in particular, nickel in acid solutions, with an increase in the atomic-hydrogen concentration due to its diffusion through the metal, there is a shift in potential towards the negative side at low overvoltages and to the positive side at high overvoltages. It can be shown readily that with a recombination mechanism for the evolution, an increase in the atomic hydrogen concentration should always lead to a shift in potential towards the negative side and this would disappear if the equilibrium between the adsorbed hydrogen and the gas phase were established infinitely rapidly. A shift in the potential to the positive side would be possible by eliminating the adsorbed hydrogen from the surface by an electrochemical desorption mechanism:

$$H_{ads} + H^+ + e \rightarrow H_2, \quad (1)$$

as in the case the increase in atomic-hydrogen concentration facilitates electron capture.*

Calculations have led to the following expressions for the magnitudes of the changes in overvoltage [95]:

$$\left(\frac{\partial \eta}{\partial i'}\right)_i = \frac{RT}{4F}\left(\frac{1}{i_{0II}} - \frac{1}{i_{0I}}\right),$$

at high overvoltages

$$\left(\frac{\partial \eta}{\partial i'}\right)_i = \frac{RT}{\alpha F i}\,\frac{k_1^0 - k_3^0}{k_1^0 + k_3^0},$$

where η is the overvoltage; i the polarizing current density; i' the diffusion current of additional atomic hydrogen in electrical units; i_{0I} the exchange current of the discharge stage; i_{0II} the exchange current of the electrochemical desorption stage; k_1^0 the rate constant of the discharge reaction on free sections; k_3^0 the rate constant of electrochemical desorption from occupied sections.

It follows from the above that the phenomenon observed, for example, on nickel in an acid medium at high overvoltages, indicates hydrogen elimination by an electrochemical desorption mechanism with a retarded discharge stage ($k_1^0 < k_3^0$) and at low overvoltages a choice remains between the concepts of electrochemical desorption with reverse relation between the rates of the discharge and desorption stages ($i_{0I} < i_{0II}$) and of a recombination mechanism of elimination with a finite recombination rate.

On examining the kinetics of the electron-transfer stage, a number of essential problem arise. In the paper by Horiuti and Polanyi [94] it was shown that the activation energy of the discharge stage on a free surface must decrease with an increase in the adsorption energy of the reaction product on the surface, i.e., in the strength of the bond arising as a result of the reaction. From their approximate calculations it follows that the relation

$$\eta = \text{const} - \frac{q_{ads}}{F}. \quad (2)$$

exists between the overvoltage η, measured at constant current density, and the energy of adsorption of a hydrogen atom on a metal surface q_{ads}. An analogous relation based on different theoretical concepts was put forward previously by N. I. Kobozev and N. I. Nekrasov [95]. The conclusion of Horiuti and Polanyi contains a large number of simplifications so that it can only be considered to have a semiquantitative value. Attempts were later made to make it more accurate. Thus, according to Rüetschi and Delahay [96], the coefficient for q_{ads} should be increased by a ratio of approximately $\frac{1}{\alpha}$; however, an examination of this conclusion by

* In the original variant of Heyrovsky [93] this reaction is resolved into the following stages:

$$H_{ads} + e \rightarrow H^-_{ads};$$
$$H^-_{ads} + H^+ \rightarrow H_2.$$

According to Horiuti [87] the molecular hydrogen ion H^{2+} is formed first:

$$H_{ads} + H^+ \rightarrow H_2^+{}_{ads};$$
$$H_2^+{}_{ads} + e \rightarrow H_2.$$

According to Gerischer [83], reaction (1) proceeds in one elementary act. The problem of how this reaction should be resolved into the various stages should be considered unanswered as yet.

M. I. Temkin and the author [97] has raised doubts on the basic premises of this correction. In spite of the semi-quantitative character of the relation between η and q_{ads}, it has a considerable value as it shows what must determine the dependence of the overvoltage on the electrode material if the rate of the process is determined by the discharge stage.

Some authors, for example, O. M. Poltorak [89], consider that from the theory of retarded discharge it follows that the right section of the last equation should include the electron work function of the metal in vacuum in addition to the adsorption energy. A detailed examination of the conditions for the derivation of this equation, which I cannot describe in detail here, showed the error of this idea [98]; the electron work function has no place here and, obviously, neither does another value, which is to a certain degree related to the work function, namely the potential of the zero-charge point, which is also contrary to what has sometimes been stated in the literature [99]. We should, however, bear in mind that in deriving the last equation, the actual structure of the electrical double layer was not considered. If this omission is corrected then it is necessary to include in the ratio determining the value of the overvoltage the value of the φ_1-potential as an additional term. The latter value at a given overvoltage or electrode potential depends on the position of the zero charge point, which in this way may have an effect on the kinetics of the process. In the case of hydrogen evolution at sufficiently great concentrations and in the absence of adsorbed anions, the φ_1 effects are comparatively small and they may be neglected in comparing overvoltages on different cathodes. However, the situation is different in other reactions, particularly in the case of the electroreduction of anions. Due to the electrostatic repulsion between the anions and the electrode surface, the rate of these processes depends to a considerable degree on the value of the φ_1-potential and, consequently, on the position of the zero-charge point. On the other hand, in the case of reduction of the persulfate anion with a negative charge on the electrode surface, for example, the reaction product, namely sulfate ion, is not adsorbed specifically so that the relation of the energy of adsorption on the electrode material does not enter the calculations. Thus, in the case of hydrogen evolution, the disposition of the current–potential curves for various cathodes with high overvoltages is determined by the order of the adsorption energies, while in the case of reduction of the $S_2O_8^{2-}$ ion at a moderate base concentration, it is determined by the position of the zero-charge points [47].

One should remember that the effects related to the distribution of potential within the limits of the electrical double layer (φ_1 effects) in the presence of ions and especially anions that are adsorbable and also atomic chemisorbed layers maintain their value when the over-all concentration of the solution is raised, which agrees with the picture of the double layer structure developed by Grahame.

As with the reaction of anions with the electrode metal, the reaction of anions with particles, if it has an attractive nature, generally speaking cannot be reduced to purely electrostatic effects; it is necessary to consider the possibility of all types of chemical bonds forming in the surface layer, as in the formation of complexes in the volume of the solution.

From the viewpoint of electrochemical kinetics and general kinetics of ion reactions in solution, there is great interest in the possibility of tunnel electron transfer, – the occurrence of an elementary electrochemical act at a distance from the electrode surface, as first proposed by Gurney [100] for hydrogen ion discharge. The inapplicability of this concept to the phenomenon of hydrogen overvoltage was established some time ago, however, it seemed to us that in the case of anion electroreduction, when electrostatic repulsion makes reaction at a distance from the surface more favorable energetically, tunnel transfers became more probable. At one time it seemed that the hypothesis on a tunnel mechanism for the electroreduction of anions was confirmed by the low value of the temperature coefficient of the rate of these reactions, but the dependence of the rate of these processes and of the apparent activation energy on the radius of the base cations found later [31] compels one to assume the formation of cation bridges, facilitating the approach of the anion to the cathode. If tunnel transfers at distances comparable to the thickness of the ionic atmosphere were quite probable, then the formation of such bridges could not affect the kinetics of the process. However, the possibility of tunnel transfers at smaller distances is not excluded. These conclusions can presumably also cover the volume reactions of electron exchange between anions of different charges, which have recently been studied thoroughly by tracer methods [101]. *

* This conclusion was confirmed by the paper by Sheppard and Wahl on the exchange between MnO_4^- and MnO_4^{2-} J. Am. Chem. Soc., 79, 1020 (1957). (Note added during correction.)

Among the chemical stages which are steps in electrochemical processes, there is particular interest in reactions involving H^+ and OH^- ions, which determine the relation of the kinetics of the over-all process to the pH of the solution. Even quite recently it was considered that in the layer adjacent to the electrode an acid-base equilibrium was established at a rate which was great in comparison with the rate of the over-all process. A series of papers from the Prague school, mainly associated with the names of Brdicka and Koutecky, showed, however, that the processes of elimination and addition of a hydrogen ion in the volume of the solution may limit the rate of the electrode process as a whole and this results in the appearance of limiting kinetic currents that are independent of the potential. The development of an accurate mathematical theory of the processes on a dropping electrode, taking into account the superposition of volume reactions and diffusion, has not only made it possible to analyze the mechanism and explain quantitatively the rules governing numerous electrochemical reactions, but also has made electrochemical measurements a valuable tool in the study of the kinetics of rapid volume reactions in solution. I will not dwell in detail on this important group of works as Koutecky's report is devoted to it; I will only mention that by using these methods, Weisner [102] was able to confirm by direct experiments the applicability to proton elimination reactions by weak acids of Brönsted's equation, which establishes a relation between the activation energies and the reaction energies, i.e., he was able to test experimentally the relation on which the theory of retarded discharge is based.

A series ofother chemical stages of electrochemical processes, proceeding both on the electrode surfaces and in the volume of the solution, are also of considerable interest.

The alternating-current measurements carried out by Gerischer by different methods [4, 103] showed that in a number of cases, complexes are electroreduced which have a smaller number of groups in the coordination sphere than that corresponding to the composition of the dominating components in the solution. Therefore, volume reactions of the type

$$Cd(CN)_4^{2-} \rightarrow Cd(CN)_3^- + CN^-,$$

should precede the electrochemical process itself.

Even before the war, O. A. Esin put forward the hypothesis that the decomposition of complexes may act as reactions limiting electrode processes [104]. Such a possibility has been examined in the literature several times recently [105], but evidently no definite conclusions may be drawn on this subject as yet.

Of the chemical stages proceeding on the electrode surface, we should first of all note the electroreduction reactions involving adsorbed atomic hydrogen, which must be taken into account with the reactions proceeding by the proton–electron mechanism discussed above, in the case of the Pt group of metals as cathodes, as follows particularly from the paper by A. I. Shlygin,et al. [106].

As M. A. Loshkarev showed [36], the transfer of reacting particles from the volume of the solution into an adsorbed layer of an organic substance should be considered among the nonelectrochemical stages determining the kinetics of the process as a whole in certain cases.

Among the surface chemical stages, of particular interest are dimerization processes arising as a result of a single electron transfer of unsaturated particles, radicals, accompanied by doubling of the molecular weight. The simplest example of such a reaction is the recombination of hydrogen atoms into molecules which, as has been established reliably, may act under certain conditions as a determining factor in the over-all rate of the stage on platinum and gold electrodes. Unfortunately, the kinetics of dimerization of more complex radicals or radical-ions, which result in the formation of chain products in a number of cases, have been studied little; some ideas on this subject have been put forward by L. I. Antropov [107]. In the case of more complex organic compounds, the stabilization of the radicals formed as a result of a single electron transfer may cause the dimerization reaction to affect the over-all kinetics of the reduction process on a mercury cathode, as S. G. Mairanovskii showed in his report, i.e., a partial recombination mechanism occurs which had been looked for most thoroughly in the case of molecular-hydrogen evolution on mercury.

In this report I have tried to show from a few examples that despite a series of gaps, electrochemical kinetics may now be used with sufficient reliability for analyzing the mechanism of many reactions. Up to now the efforts of electrochemists have been mainly directed to a selective study of separate reactions, which

which were examined as typical examples of electrochemical processes, proceeding by a definite mechanism. It seems to me that in time ever-greater attention will be paid to a wide, systematic investigation of reactions involving various classes of chemical compounds. The results from such an investigation will make it possible for us to delve into the problems of the relation between electronic structure and the reactivity of a substance and may have a determining effect on the development of solution kinetics as a whole. Attempts have already been made to systematize the data on the kinetics of electrode processes, but these works are based on insufficient data that have not been exhaustively analyzed kinetically, and so these works should be considered as only the beginning.

Development of electrochemical kinetics and improvement of the experimental methods have made possible a much wider application of this group of ideas in various branches of applied electrochemistry, the development of technical electrolysis processes and the solution of problems on the efficient conversion of chemical energy into electrical energy. This involves the second line of development in our field. As I see it, the main purpose of this conference, in helping to complete the examination of as yet unsolved problems relating to the bases of electrochemical kinetics, is to stimulate its development in the given directions.

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