

REVIEW OF THE LATEST THEORETICAL WORK OF THE PRAGUE SCHOOL OF POLAROGRAPHY

J. Koutecký

Institute of Physical Chemistry, Czechoslovakia Academy of Sciences, Prague

This review includes only that new work of Czech scientists on theoretical polarography which is devoted to the discovery of quantitative rules on the basis of the main ideas on the mechanism of the phenomenon studied. Most of the purely theoretical work of Czech scientists is largely concerned with the transfer of material reacting at a given electrode from the solution to the electrode. The electrode reaction is considered as known and is included in the original formula of the problem. The specific conditions in the electrical double layer are not considered. We have not undertaken theoretical work on the mechanism whereby polarographic maxima arise. Thus, Czech work is normally devoted to the determination of the polarographic current on the basis of a given depolarization scheme, with conditions within the solution the determining factors for the transfer of the depolarizer, while the conditions directly at the electrode are included in the formulation of the problem as limiting conditions. For maximum simplification of the allowance for the natural transfer of electrical charge between a depolarizer and the mercury electrode and to avoid a description of this process, the nature of which has not been investigated sufficiently, in most cases only the limiting polarographic currents are considered. In the same way that the measurement of the limiting currents is used in quantitative analysis of electrolytes, here the limiting current is used as a means of studying phenomena accompanying the electrode reaction and, in the first instance, homogeneous reactions at the electrode occurring during depolarization.

This field, in which investigators have mainly been concerned with so-called kinetic polarographic currents, obviously has given many interesting results. However, it cannot be denied that even at the present time investigators have found need for a more thorough study of conditions close to the electrode and the nature of the true electrode reaction. This undoubtedly requires, for example, an investigation of the relation between polarographic curves and the parameters of the included chemical reactions. Therefore, a more thorough study of calculation and theoretical work on this problem, which we have studied insufficiently, would be of very great benefit to Czech scientists. On the other hand, for an accurate investigation of electrode reactions it is necessary to use polarographic investigations, which have been developed by Czech scientists, for, as has been explained, most electrode processes are complicated by homogeneous reactions in solution.

Two main methods have been developed for determining polarographic kinetic currents. In the so-called accurate method [1-3] of determining polarographic kinetic currents, the starting differential equations are transformed by the introduction of new independent variables which are dimensionless parameters. This method has been found extremely convenient, as the course of an electrode process, together with diffusion, is determined by the chemical reaction in the solution. M. Meiman [4] arrived at the same formulation in 1948 by a somewhat different route in solving the problem of an irreversible electrode reaction. This work remained unknown to us, however, as its name did not indicate that it was devoted to an investigation of a slow electrode reaction. I arrived at this method independently by calculating corrections for the Il'kovich equation; subsequently it was mainly used for kinetic polarographic currents.

After the solution of the problem with the very fast chemical reaction [5], preceding the electrode process,



* ecr -- electrochemical reaction. In all the equations the starting materials in solution are given on the left-hand side.

the problem of the regeneration of the depolarizer by a reversible monomolecular reaction [6],



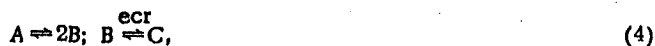
and the problem of partial regeneration of the depolarizer [7],



the results of the work were extended to systems including any number of substances reacting by very fast monomolecular reactions, while the electrode reactions encountered in the depolarization scheme could have been slow [8]. Finally, in view of the fact that very fast reactions were examined, a limitation was introduced, and this consisted of the fact that substances interacting by the monomolecular reaction preceding the electrode process have approximately identical diffusion coefficients [9]. In all cases there was complete agreement between theory and experiment. This was the position at the end of 1953.

In 1954 we turned to bimolecular reactions included in depolarization schemes. After the development of a general method which could be used in the case of slow bimolecular reactions in the depolarization schemes and a method of calculation for fast reactions [2], these methods were applied in the following cases:

Preceding reversible monomerization [10],



subsequent rapid irreversible deactivation of the depolarization product by dimerization [10],



regeneration of the depolarizer by disproportionation of the depolarization product [11],



a preceding chemical reaction of a monomolecular nature, whose constant is linearly related to the concentration of a substance arising as a side product in the electrode reaction [12],



$$k = k_0 + k_1 [D]; k' = k'_0 + k'_1 [D]; \frac{k}{k_1} = K_1; \quad (7)$$

and, finally, the case of bimolecular regeneration of the depolarizer from the depolarization product [13],



Experimental data obtained by Čermak [14] in polarographic investigations of dithionate, $S_2O_4^{2-}$, in an alkaline medium confirmed the results of the solution of the first of the schemes presented. The disproportionation of pentavalent uranium, partially regenerating hexavalent uranium as a starting depolarizer, is an example of a slow chemical reaction. The kinetic constants calculated by means of the equations obtained from the polarographic data presented in the work of Koryta and Koutecký [15] correspond to values determined by other methods.

A depolarization scheme in which the depolarizer is formed as a result of a fast chemical reaction from an electrically inactive substance, catalyzed by a by-product of the electrode process, is encountered in the electrolysis of formaldehyde in inadequately buffered solutions. The solution of the problems [12] makes it possible to calculate the absolute values of the limiting currents by means of kinetic reaction constants of depolarizer formation, which were obtained from the limiting currents of formaldehyde in a buffer medium. The experimental results of Brdička [16] agreed completely with theoretical conclusions.

Reactions which result in the regeneration of the depolarizer from the depolarization product normally are not monomolecular; their pseudomonomolecular nature is produced by an excess of one of the reagents. Therefore, an examination was made of a bimolecular regeneration reaction in which one of the agents was the depolarization product and the other an electrically inactive substance, previously present in the solution in a concentration comparable with that of the depolarizer. The solution of this problem, in which the chemical reaction mentioned was assumed to be very fast, was used by Matyska [17] in an investigation of the system iron complexonate -- hydrogen peroxide; good agreement was found between theory and experiment.

It should be noted that in all the cases which have been solved theoretically up to now the simplest case, i.e., subsequent fast dimerization, has not been applied to experimental data. This serves as an illustration of the statement given at the beginning of our communication. In all the other cases it is possible to confine oneself to limiting currents, and only in the latter reactions is it necessary to use the form and position of the whole polarographic curve to apply the theory.

After 1953 four more cases of a monomolecular reaction in the depolarization scheme were investigated. The subsequent, very fast chemical reaction deactivating the depolarization product:

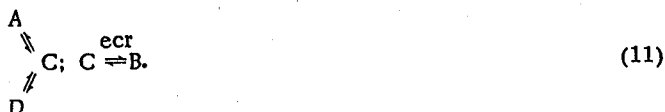


was discussed in detail and the results were applied to polarographic curves of ascorbic acid [18]. It was shown that in accordance with experiment, the equation of the ascorbic acid wave has a reversible character; we determined the position and height of the wave of dihydroascorbic acid, which according to Heyrovsky, is the final inactive product of ascorbic acid oxidation. The polarographic current was then calculated for the depolarization scheme consisting of a slow electrode reaction with preceding and subsequent fast chemical reactions [19]:



As far as I know, this scheme has not yet been applied; it provides an answer to the comment of Hans that the given case has not yet been solved [20].

Finally, in the work of Paldus and Koutecký [21], a depolarization scheme was developed in which the depolarizer arises in parallel from two electrically inactive substances in very fast, reversible monomolecular reactions:



This work, which gives an accurate solution to this problem, shows that the approximate solution of Los, Simpson and Wiesner [22] generally leads to accurate results. It is important for the study of the reduction of some aldoses. Koryta [23] showed that it is possible to apply the calculation of kinetic currents to the determination of coordination numbers of complexes which are discharged directly on the electrode.

Another group of works consists of the two papers of Čížek and Koutecký [24, 25], in which polarographic currents were determined for cases with a preceding very fast monomolecular chemical reaction and a reaction which completely regenerates the depolarizer from the depolarization products, allowing for the sphericity of diffusion at the dropping electrode. The corrections, which are obtained by the same method as in the calculation of corrections for the sphericity of diffusion in the case of currents limited solely by diffusion (Il'kovich equation), are worthy of attention. The same corrections must be considered in the case of slow electrode processes.

The method of dimensionless parameters has also been applied to direct-current electrolysis with planar and spherical stationary electrodes [26]. The same calculations had been carried out for all the depolarization schemes which were developed previously for electrolysis with a constant potential applied to the electrode. In this work Koutecký and Čížek used a simpler method to solve not only the cases which were solved previously by Delahay by means of the Laplace transformation [27], but also other cases and the interrelation of these solutions was demonstrated. The interrelation of the methods of dimensionless parameters and the Laplace transformation in the general form was pointed out by Smutek [28], who, together with Pliva, used the Laplace transformation to investigate for

a planar electrode the case of a slow electrode reaction with a preceding monomolecular chemical reaction without limitations with respect to the rate of this chemical reaction [29]. The work of Smutek [28] on the interrelation of the methods of the Laplace transformation and dimensionless parameters is particularly important at the present moment because work of Japanese authors [30] has recently appeared in which known polarographic kinetic problems were solved by means of the Laplace transformation. These authors were apparently unaware of the work of Smutek and other Czech scientists.

The Laplace transformation has been applied to the investigation of polarographic currents corresponding to the reversible electrode reaction on the surface of a growing dropping electrode [31] with an applied periodic voltage. The results of this work, like the work of Kambara [32] (planar stationary electrode), are being tested experimentally at the present time. Micka [33] attempted to allow for the capacity currents on oscillographic polarographic curves. For the capacity currents he proposed an approximate expression which explains experimental oscillographic curves.

In concluding the section devoted to this method, I should point out the problems which remain unsolved in the accurate elucidation of transfer phenomena in electrolysis on a dropping electrode; we will not consider hydrodynamic problems. The first of these is the determination of polarographic currents in the case when any of the participating substances are adsorbed on the surface of a dropping electrode. The second problem is that of asymptotic approximation and, though it is formal, it is of very great importance in the solution of the problem of adsorption currents, where it is probably of the greatest importance.

The second method of determining polarographic kinetic currents is the so-called approximate method developed by Wiesner and Brdička [3, 34, 35]. The value of this method lies in its original simple form; however, it is only applicable to fast reactions [35]. In recent years this method has been used to examine some depolarization schemes with bimolecular chemical reactions; inactivation of the electrode reaction product by dimerization [5] and decomposition of the inactive dimer to an electrically active monomer [4] were determined simultaneously by the approximate and accurate methods in the work of Koutecký and Hanuš [10]. By using the approximate method Brdička [36] solved the depolarization scheme in which an electrically active substance is formed from an inactive substance as a result of a fast reaction catalyzed by a by-product of the electrode reaction [7]. As has already been mentioned, this scheme, which is encountered in the reduction of formaldehyde in an unbuffered medium, has also been solved by the accurate method. In some work the approximate method has also been used to investigate bimolecular oxidation of the depolarizer [37, 38]. In addition, Hanuš used this method to solve the case of reversible dissociation of an inactive substance, prior to the electrode reaction, to electrically active and electrically inactive substances [39]:



which is encountered in the liberation of hydrogen from weak acids [40], and then the case of intramolecular disproportionation, preceding the true electrode process, in which a substance with reduced and oxidized forms arises from an electrically inactive substance [39]. Finally, Hanuš investigated the case of fast formation of the depolarizer prior to the electrode process [37]:



By using these conclusions it is possible to explain experimental data on kinetic currents in the system hemin- peroxide [38].

As was shown by a comparison with the results of the accurate method of determining polarographic currents, the approximate method gives the correct form to the dimensionless parameters of which the kinetic polarographic current is a function; in addition the form of these functions is very similar to the corresponding functions obtained by the accurate method. However, rate constants determined by means of the approximate method may contain a large error. Our work showed that in some cases the rate constants of a reaction have extremely high values -- of the order of 10^{13} and above. This rate constant value corresponds to a kinetic layer with a thickness of 10^{-8} cm. With such small thicknesses it is impossible to use the normal macroscopic ideas on diffusion. It seems interesting to develop a theory for diffusion under these conditions. A second interesting problem is the possibility of the appearance of maxima on polarographic curves, produced not by movement of the mercury surface, but by the kinetic course of the reaction.

In the present review I have mentioned the main theoretical work of Czech scientists. I have omitted some work of a nonquantitative character, such as the work of Vleck on the relation between the electronic structure of complexes and the half-wave potentials of these substances.

The review presented shows the limited nature of the field covered by the work, as was mentioned at the beginning of this communication.

In conclusion it should be noted that by combination of different fields of theoretical polarography it may be possible to use polarography to a much greater extent as a method for obtaining valuable data on phenomena observed both in solution and on the surface of a mercury electrode.

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