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IRREVERSIBLE POLAROGRAPHIC WAVES

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I. INTRODUCTION

The fundamental basis of classical polarographic theory[1-4], which has contributed to the wide and varied use of the polarographic method, is the hypothesis that the magnitude of the current is determined only by the rate of diffusion of the reacting substances, and the electrochemical reaction proceeds sufficiently quickly for electrochemical equilibrium to be attained at the electrodes. For many so-called "reversible" polarographic waves, these assumptions are quite justified. In the interpretation of such waves by means of the Nernst equation[5], the standard electrode potential φ^0, and hence also the half-wave potential $\varphi_{\frac{1}{2}}$, depend simply on the standard free energy $\Delta G^0 (-\Delta G^0 = nF\varphi^0)$[6,7].

For a series of inorganic, and the majority of organic, compounds the rate of electrode reaction is less than, or about the same as, the rate of supply of the depolariser to the electrode surface. During the passage of current the electrochemical equilibrium is disturbed. Polarographic waves obtained under these conditions are termed irreversible. Until recently, irreversible polarographic waves could be handled only by means of empirical expressions,

but lately there has been great interest in developing a more general theory of irreversible polarographic waves[8-22], embracing also the familiar relations of reversible waves as a particular case. Conclusions based on the theory of irreversible waves can provide information concerning the mechanism of electrode processes and concerning certain properties of materials.

The approach of different authors to the study of irreversible electrode processes varies, but they all appear to start from the premiss that irreversible waves are determined by the rate of electrode reactions as well as by concentration polarisation. For the interpretation of irreversible polarographic waves, the equations of the delayed discharge theory are usually employed[23-26]. The substances at the surface of the electrode which determine the concentration potential can limit the electrode process not only by hindering diffusion[8-21], but also as a consequence of kinetic limitations, *i.e.* retardation of chemical reactions which precede the electrochemical stage of the process (kinetic currents)[27-37], and also because of the presence of an adsorbed film[38-41].

The present article examines only those irreversible polarographic waves for which the concentrations of the reactants at the electrode surface are determined solely by the diffusion rate. Certain earlier theories of irreversible polarographic waves are considered briefly. The analyses of the waves made by Eyring *et al.*[9] and by Tanaka and Tamamushi[42,43] were based on the Nernst hypothesis concerning the diffusion layer. According to Nernst[44] a layer of liquid of thickness δ close to the surface of the electrode is stationary. From this assumption and also from the condition for constant transfer of material through this layer it follows that the concentration of the reacting substance inside the diffusion layer changes linearly with distance.

Let the following reaction take place at the electrode:

$$O + ne \underset{k_2}{\overset{k_1}{\rightleftarrows}} R, \qquad (1)$$

where O and R are the oxidised and reduced forms of the depolariser, and k_1 and k_2 are the rate constants for the direct and reverse electrochemical reactions. The following general assumptions, which are known to apply approximately under the conditions of ordinary polarography, were made for the derivation: the migration of the reacting ions can be neglected in considering the presence of an excess of inert electrolyte in the solution, provided this is not agitated; adsorption effects at the electrode surface are also absent; the diffusion coefficient is independent of the distance from the electrode surface; the reactants and reaction products are soluble in the solution or in the electrode material; the difference between activities and concentrations can be neglected; apart from the delayed reactions considered there are no other stages which could limit the course of the whole process. Under the specified conditions Fick's first law enables us to write for the current, for the reduction of substance O:

$$i = \frac{D_O}{\delta_O l}(c_O^0 - c_O)\frac{nF}{N}, \qquad (2)$$

where D_O is the diffusion coefficient of substance O, δ_O the thickness of its diffusion layer, l the thickness of a monomolecular layer, c_O^0 and c_O the concentrations of substance O in the bulk of the solution and at the surface of the mercury drop, n the number of electrons taking part in the reaction, F the Faraday number, and N the Avogadro number.

On the other hand, the general expression for current can be presented in the following form[45-47]:

$$i = \frac{nFs}{N}[c_O(0)\,k_1 e^{\alpha n\varphi F/RT} - c_R(0)\,k_2 e^{-(1-\alpha)nF\varphi/RT}], \qquad (3)$$

where s is the sum of the transport numbers of all the ions except those discharging, $k_i = (KT/h)\exp(-\Delta G_i/RT)$, $c_R(0)$ is the concentration of substance R at the surface of the electrode, α the transport coefficient, φ the electrode potential, R the gas constant, and T the absolute temperature. The value of the concentration is designated by $c(0)$ and not $c(0t)$ since it is assumed that the transfer of substance remains constant.

From Eqns.(2) and (3) and the assumption that $D_R = D_O = D$ and $\delta_0 = \delta_O = \delta$, we obtain the general equation[9]:

$$i = \frac{c_O^0 - c_R(0)\,e^{-nF(\varphi-\varphi^0)/RT}\frac{nF}{N}}{\frac{s\delta l}{D} + \frac{1}{k_1}e^{-\alpha nF\varphi/RT}\frac{1}{N}}, \qquad (4)$$

where φ^0 is the standard electrode potential, δ_R the thickness of the diffusion layer for substance R, and D_R the diffusion coefficient for substance R.

If the rate-determining stage in the electrode process is diffusion, then

$$\frac{s\delta l}{D} \gg \frac{1}{k_1}e^{-\alpha nF\varphi/RT}$$

and the second term in the denominator of Eqn.(4) can be disregarded. Eqn.(4) then takes the form:

$$i = \frac{D}{s\delta l}[c_O^0 - c_R(0)\,e^{-nF(\varphi-\varphi^0)/RT}]\frac{nF}{N}. \qquad (5)$$

In the more general case when $(1/k_1)\exp(-\alpha nF\varphi/RT) < s\delta l/D$ but cannot be disregarded, Eqn.(4) can be written in the form:

$$i = \left\{\frac{D}{s\delta l}[c_O^0 - c_R(0)\,e^{-nF(\varphi-\varphi_0)/RT}]\frac{nF}{N}\right\}\left[1 + \frac{D}{s\delta l k_1}e^{-\alpha nF\varphi/RT}\right]^{-1}.$$

Since the first term (within braces) is identical with Eqn.(5) for the reverse current wave (i_{rev}), then:

$$i = i_{rev}\left[1 + \frac{D}{s\delta l}\frac{1}{k_1}e^{-\alpha nF\varphi/RT}\right]^{-1}. \qquad (6)$$

According to Eqn.(6), at the potential corresponding to the limiting current, $i \simeq I_{lim} \simeq i_{rev}$, that is, the limiting current I_{lim} is independent of the rate of electrochemical reaction. Along the polarographic wave, $i < i_{rev}$. From Eqn.(6) it also follows that the half-wave potential is independent of the concentration of the reacting substances. For larger values of overvoltage ($\eta > 0.1$ V) the second part of Eqn.(3) can be neglected – this is the case of completely irreversible waves. Starting from Eqns.(2) and (3), k can be determined, and therefore also the free energy of activation.

Results obtained on the basis of the assumptions concerning the diffusion layer are only approximate. It has been shown that the assumptions concerning the properties of the diffusion layer are not sufficiently strict and do not always agree with the experimental data[48-49]. The dependence of the layer thickness δ on the diffusion coefficient is more complex than that assumed when employing δ in Eqn.(2).[50-51] Also, in the theory stated above, the influence of the growth of the mercury drop on the diffusion process has not been considered. A study of electrode processes taking account of the diffusion layer is of great interest in the case of agitated liquids, where it is difficult to carry out more accurate calculations[52].

II. EQUATION FOR CURRENT, TAKING ACCOUNT OF THE GROWTH OF THE MERCURY DROP

Meiman[8] put forward a more rigorous approach to the study of irreversible polarographic waves. During the electrolysis, the concentration of the reacting particles is a function of the duration of the electrolysis and the distance from the electrode, *i.e.* $c(x,t)$. The current flowing through the electrode depends on the concentration of the reacting substances at the surface of the electrode. This concentration differs from that in the body of the solution and cannot be determined experimentally: in this lies the difficulty of obtaining an expression for the current. If the concentration at the electrode surface is determined only by the diffusion, then $c(x,t)$ can be found by solution of the appropriate differential equation of diffusion and use of the initial and boundary conditions of electrolysis. The solution of a diffusion problem gives a value of $c(x,t)$ expressed in terms of the known concentration in the bulk of the solution, c^0. For the simplest case, linear diffusion, Fick's second law is the diffusion equation. The equation for symmetrical spherical diffusion comes closest to the conditions existing in polarography:

$$\frac{\partial c(\rho, t)}{\partial t} = D\left[\frac{\partial^2 c(\rho, t)}{\partial \rho^2} + \frac{2}{\rho}\left(\frac{\partial c(\rho, t)}{\partial \rho}\right)\right], \qquad (7)$$

where ρ is the radius of the sphere. Angular co-ordinates are not introduced here since it is assumed that the diffusion field is symmetrical. However, in the case of the mercury dropping electrode, owing to the radial growth of the drop, the area of the diffusion field is continually changing throughout the drop life and the solution moves in a direction opposite to the diffusion direction. Ilkovič[2-3] solved the problem of diffusion towards the mercury dropping electrode; the same expression was derived in another way by MacGillavry and Rideal[4]. In order to apply Eqn. (7) to diffusion at the dropping mercury electrode the fixed co-ordinate ρ must be replaced by a moving co-ordinate r to take into account the increase in area of the diffusion field during the growth of the mercury drop. The differential equation for diffusion towards the dropping electrode then takes the form[4]:

$$\frac{\partial c(r, t)}{\partial t} = \frac{D\rho^4}{r^5}\left[r\frac{\partial^2 c(r, t)}{\partial r^2} + 2\,\frac{(r^3 - \gamma t)}{r^3 + \gamma t}\cdot\frac{\partial c(r, t)}{\partial r}\right],$$

where $\gamma = 3m/4\pi d$, m being the mass of mercury flowing from the capillary per second, and d the density of mercury. The solution of this equation is:

$$c(r, t) = \frac{2c^0}{\sqrt{\pi}}\int_0^b e^{-z^2}dz, \qquad (8)$$

where

$$b = \frac{1}{6}\sqrt{\frac{7\gamma}{3D}}\cdot\frac{r^3}{(\gamma t)^{7/6}}.$$

Eqn. (8) enables us to obtain an expression for the mean limiting diffusion current (the Ilkovič equation):

$$I_d = \frac{6}{7}\cdot 4\left(\frac{7\pi}{3}\right)^{1/2}\left(\frac{3}{4\pi d}\right)^{2/3} nFD^{1/2}m^{2/3}\cdot\tau^{1/6}c^0. \qquad (9)$$

In the derivation of this expression the following initial and boundary conditions have been assumed: at the initial moment of time ($t = 0$) the concentration of the solution is constant and equal to the concentration in the bulk of the solution, that is, $c(x,t) = c^0$; the drop potential during the period of polarography is held constant, that is $\varphi = \text{const.}$; at $t > 0$, $c(0,t) \ll c^0$ or $c(0,t) = 0$, that is, the concentration at the electrode surface during the lifetime of an individual drop is constant; at $x \to \infty$, $c(x,t) \to c^0$; the current density is inversely proportional to the square root of the time measured from the start of the formation of the drop, $i = \text{const.} \times t^{-\frac{1}{2}}$. The combination of these conditions is practicable only in the case of a reversible electrochemical reaction, in which the electrode potential depends only on the concentration of the reacting substances, with $c = \text{const.} \times \exp(nF\Delta\varphi/RT)$, and the constancy of the potential denotes a constancy of the electrode surface potential.

In the case of irreversible electrode reactions both the potential and the concentration depend on the current density, and obviously on the rate of electrochemical reaction, $i = f(c, \varphi)$. Because of this, the boundary conditions for irreversible electrode reactions will not be those for reversible ones. For irreversible electrode reactions of the first order the boundary and initial conditions were formulated by Meiman, who was the first to solve the differential equation for diffusion towards the dropping electrode for an irreversible reaction[8]. This solution will be outlined.

We will consider a reaction of the first order, Eqn. (1), and assume that the rate of the reverse reaction can be neglected ($k_2 = 0$). The concentrations of the reacting substances at the surface of the electrode during the irreversible reaction will depend on both the potential and the current density:

$$c(0, t) = \vartheta i, \qquad (10)$$

where ϑ is a coefficient dependent upon the electrode potential. Since i is proportional to the concentration gradient:

$$i = nFD\left(\frac{\partial c}{\partial r}\right),$$

the concentration at the electrode surface is

$$c(r, t) = nFD\vartheta\left(\frac{\partial c}{\partial r}\right). \qquad (11)$$

Eqn. (10) is the boundary condition which must be used for an irreversible electrode reaction instead of the corresponding condition for a reversible reaction. The conditions:

$$c(x, t) = c^0 \quad \text{at} \quad t = 0 \qquad (12)$$

and

$$c(x, t) = c^0 \quad \text{at} \quad x \to \infty \qquad (13)$$

are independent of the nature of the electrochemical reaction and can therefore be used for both reversible and irreversible electrode reactions.

After substitution of variables, the equation for diffusion towards the surface of a dropping electrode becomes[49]:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial z^2}. \qquad (14)$$

In this the boundary conditions (11), (12), and (13) become:

$$\vartheta p\tau^{2/7}\frac{\partial c}{\partial z} = c \quad \text{at} \quad z = 0, \qquad (15)$$

where

$$p = nFD\left(\frac{7}{3D}\right)^{2/7},$$

$$c \to c^0 \quad \text{at} \quad z \to \infty \qquad (16)$$

$$c \to c^0 \quad \text{at} \quad \tau = 0. \qquad (17)$$

Calculating the current in the case of an irreversible reaction consists in solving Eqn. (14) at boundary conditions (15)–(17).

In solving Eqn. (14) it is first necessary to convert it into

an equation in complete differentials. A solution must be sought in the form:

$$c(\tau, z) = c^0 + \tau^{\nu} f_{\nu}(\eta),$$

where f_ν is some function of argument η,

$$\eta = \frac{z}{\sqrt{\tau}}, \qquad (18)$$

and the index can take a series of positive values. Let the solution $c(\tau, z)$ be presented in the form of a convergent series:

$$c(\tau, z) = c^0 + \sum_{\nu} \tau^{\nu} f_{\nu}(\eta). \qquad (19)$$

Taking condition (14) into account, we can write the equation:

$$c^0 + \sum \tau^{\nu} f_{\nu}(0) = \vartheta p \sum_{\nu} \tau^{\nu - \frac{3}{14}} f'_{\nu}(0).$$

Comparing coefficients for identical powers of τ, we obtain a set of equations which are true only if ν is a multiple of 3/14, *i.e.* $\nu = 3/14n$ ($n = 1, 2, 3 \ldots$). The resulting Eqn.(19) allows Eqn.(14) to be transformed into an expression in complete differentials:

$$\frac{d^2 f_{\nu}}{d\eta^2} + \frac{\eta}{2}\frac{df_{\nu}}{d\eta} - \nu f_{\nu} = 0 \quad . \qquad (20)$$

This equation must be satisfied by a function f_ν. The solution of Eqn.(20) is obtained by using a Laplace transform in the form of the contour integral:

$$f_{\nu}(\eta) = \int_{ku} l^{-\frac{1}{4}\eta^2 u} P_{\nu}(u)\, du,$$

and then

$$\frac{d^2 f_{\nu}}{d\eta} + \frac{\eta}{2}\frac{df_{\nu}}{d\eta} - \nu f_{\nu} = \int_{ku} \left[\left(\frac{1}{2}u + \nu\right) - \frac{1}{4}\eta^2 (u-1)u\right] P_{\nu}(u)\, du.$$

Transforming to the variable ξ, where $u = 1/(1 - \xi)$, and carrying out a series of transformations, we obtain:

$$c(\tau, z) =$$

$$= c^0 \left\{1 - \frac{1}{\Gamma\left(\frac{1}{2}\right)} \int_0^{t} (1-\xi)^{-1/2} e^{-\frac{\eta}{4(1-\xi)}} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{\Gamma\left(\frac{3}{14}+\frac{1}{2}\right)\Gamma\left(\frac{3}{14}\cdot 2+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}+1\right)\Gamma\left(\frac{3}{14}\cdot 2+1\right)} \cdots \right.$$

$$\left. \cdots \frac{\Gamma\left[\frac{3}{14}(n-1)+\frac{1}{2}\right]}{\Gamma\left[\frac{3}{14}(n-1)+1\right]} \xi^{\frac{3}{14}\cdot n - \frac{1}{2}} \mu^n d\xi \right\}, \qquad (21)$$

where μ is a dimensionless quantity:

$$\mu = \frac{\tau^{3/14}}{\vartheta p} = \left(\frac{3}{7}\right)^{1/2} \frac{t^{1/2}}{D^{1/2}\vartheta}, \qquad (22)$$

and Γ denotes a gamma function of the corresponding argument. At large values of η,

$$\frac{\Gamma\left(\frac{3}{14}n+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}n+1\right)} \simeq \frac{1}{\sqrt{\frac{3}{14}n+1}}.$$

Therefore series (21) is convergent for all values of μ and positive values of η. Expression (21) is the required solution of Eqn.(13). It permits determination of the concentration of the reacting substances at the electrode surface:

$$c(\tau, 0) = c^0 \theta(\mu), \qquad (23)$$

where

$$\theta(\mu) = 1 - \frac{\Gamma\left(\frac{3}{14}+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}+1\right)}\mu + \frac{\Gamma\left(\frac{3}{14}+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}+1\right)} \cdot \frac{\Gamma\left(\frac{3}{14}\cdot 2+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}\cdot 2+1\right)}\mu^2 \cdots (24)$$

The concentration at the electrode surface is a function of the dimensionless parameter μ, in which, in addition to time, there appear the diffusion coefficient of the reactants and the coefficient, $1/\vartheta$, *cf.* Eqn.(22). If the diffusion coefficient falls or if the rate of electrochemical reaction increases, then the depolariser concentration at the electrode surface falls, since under these conditions, μ increases at a constant value of τ. Knowing $c(\tau, 0)$, on the basis of Eqn.(9), it is possible to write an expression for current density:

$$i = \frac{c(\tau, 0)}{\vartheta} = \frac{c^0}{\vartheta}\theta(\mu). \qquad (25)$$

If the reaction rate is quite small, then $\vartheta \to \infty$, and $\mu \to 0$, so that in the limit we obtain:

$$c(\tau, 0) = c^0, \; i = 0 \; .$$

Since the series determining $\theta(\mu)$ at $\mu \gg 1$ converges extremely slowly it is necessary to give an asymmetric expression for $\mu \to \infty$. Introducing a new function $v(\mu, \eta)$ and changing the boundary conditions (15–17), after transformation the asymmetric representation can be written in the form:

$$\theta(\mu) = \left\{ \frac{\mu^{-1}}{\Gamma\left(\frac{1}{2}\right)} - \frac{\mu^2}{\Gamma\left(\frac{1}{2}\right)} \frac{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)}{\Gamma\left(1-\frac{3}{14}\right)} + \ldots \right\}. \qquad (26)$$

The current density is expressed thus:

$$i = \frac{c(\tau, 0)}{\vartheta} = \frac{c^0}{\vartheta}\left\{ \frac{\mu^{-1}}{\sqrt{\pi}} - \frac{\mu^2}{\sqrt{\pi}} \frac{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)}{\Gamma\left(1-\frac{3}{14}\right)} + \ldots \right\}. \qquad (27)$$

It follows from Eqns.(26) and (27) that at high reaction velocities $\vartheta \to 0$, and μ^{-1} at all terminal values tends to zero, so that $c(\tau, 0) \simeq c^0/\mu\sqrt{\pi}$ and for the limiting current density i_d we obtain

$$i_d = \frac{c^0}{\Gamma\left(\frac{1}{2}\right)} \lim_{\vartheta \to 0} \frac{\sqrt{\frac{7}{3}}\, nFD^{1/2}\vartheta}{\vartheta t^{1/2}} = \frac{c^0}{\sqrt{\pi}}\sqrt{\frac{7}{3}}\, nFD^{1/2}t^{-1/2},$$

that is, the Ilkovič equation is applicable under these conditions.

Thus, to calculate the concentration at the electrode surface and the current density it is sufficient to determine function $\theta(\mu)$, for which it is necessary to use Eqn.(24) at $\mu \leqslant 1$, and Eqn.(26) at $\mu \gg 1$.

Table 1 gives values of the function $\theta(\mu)$ for different values of the argument μ.[8] The values of $\theta(\mu)$ for $\mu < 1.2$ were calculated from Eqn.(24) and those for $\mu > 2.5$ by use

TABLE 1. Dependence of $\theta(\mu)$ on the parameter μ.

μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$	μ	$\theta(\mu)$
0.00	1.0000	0.2	0.7753	1.0	0.3881	1.8	0.252	2.8	0.1758	5.0	0.1040
0.01	0.9862	0.4	0.6263	1.2	0.3431	2.0	0.232	3.2	0.1565	10.0	0.0543
0.04	0.9467	0.6	0.5221	1.4	0.306	2.2	0.214	3.6	0.1410	40.0	0.0140
0.1	0.8754	0.8	0.4456	1.6	0.276	2.5	0.1936	4.0	0.1282	100.0	0.0056
											0.0000

of the asymmetric expansion (26). In the interval $1.2 < \mu < 2.5$, values of the function $\theta(\mu)$ are obtained by graphical integration. The function $\theta(\mu)$ decreases monotonically as μ increases (Fig. 1).[8]

The total current I is connected with the current density by the following expression:

$$I = 4\pi\rho^2 i = \frac{4\pi\gamma}{\vartheta} t^{2/3} c^0 \theta(\mu). \qquad (28)$$

For calculations it is usual to employ the reduced current $\tilde{I}$:

$$\tilde{I} = \frac{I}{I_d} = \frac{7\sqrt{\pi}}{6} \frac{\mu^{1/6}}{\mu_0^{1/6}} \theta(\mu), \qquad (29)$$

where I_d is given by Eqn. (9).

The mean value of the reduced current for the lifetime of an individual drop, $\bar{\tilde{I}}$, is:

$$\bar{\tilde{I}} = \frac{1}{t}\int_0^t \tilde{I}\,dt = \frac{7\sqrt{\pi}}{6}\int_0^t \mu^{1/6}\theta(\mu)\,dt = \frac{7\sqrt{\pi}}{3}\frac{1}{\mu_0^{7/6}}\int_0^{\mu_0} \mu^{1/6}\theta(\mu)\,d(\mu), \qquad (30)$$

i.e. the mean reduced current is a function only of the parameter μ_0. Substituting in Eqn. (30) the series expansion of the function $\theta(\mu)$, we obtain an expansion for $\bar{\tilde{I}}$ in powers of μ_0. For values $\mu_0 \geqslant 1$, from Eqns. (24) and (30) we obtain:

$$\bar{\tilde{I}} = 7\sqrt{\pi}\left\{\frac{1}{10}\mu_0 - \frac{1}{13}\frac{\Gamma\left(\frac{3}{14}+\frac{1}{2}\right)}{\Gamma\left(\frac{3}{14}+1\right)}\mu_0^2 + \ldots\right\} =$$

$$= 1.241\mu_0 - 1.332\mu_0^2 + 1.278\mu_0^3 \ldots . \qquad (31)$$

At $\mu \geqslant 10$, using Eqns. (26) and (30), the mean reduced current is:

$$\bar{\tilde{I}} = 1 - \frac{7}{4}\frac{\Gamma\left(1-\frac{3}{14}\right)}{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)}\mu_0^{-1} + 7\frac{\Gamma\left(1-\frac{3}{14}\right)\cdot\Gamma\left(1-2\cdot\frac{3}{14}\right)}{\Gamma\left(\frac{1}{2}-\frac{3}{14}\right)\cdot\Gamma\left(\frac{1}{2}-2\cdot\frac{3}{14}\right)}\mu_0^{-2} - \ldots =$$

$$= 1 - 0.656\mu_0^{-1} + 0.303\mu_0^{-2}. \qquad (32)$$

Hence, as the parameter μ_0 increases, the mean reduced current tends to unity, *i.e.* at $\mu \gg 1$, the current of the irreversible polarographic wave agrees with the current calculated by the Ilkovič equation. Fig. 2 shows the dependence of the mean reduced current on $\log \mu_0$; it is the universal reduced curve of the concentration polarisation at the dropping mercury electrode during an irreversible electrochemical reaction of the first order.

It is possible to obtain information on the kinetics of an electrochemical reaction from experimental data on the irreversible polarographic curve using the dependence of $\bar{\tilde{I}}$ on μ_0 (Eqns. 30–32), since μ_0 is connected by a definite relation – Eqn. (22) – with the coefficient $1/\vartheta$, which characterises the reaction rate and is in general dependent on the electrode potential. Alternatively, if the kinetics of the electrochemical reaction is known then the current *vs.* potential curve can be calculated.

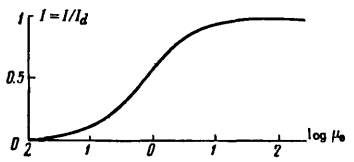


Fig. 2. Dependence of I on $\log \mu_\theta$.

The dependence of the reduced current on the parameter μ was verified experimentally by Bagotskii[53], who studied the evolution of hydrogen at the mercury dropping electrode in hydrochloric acid solutions.

The dependence of current on potential can be calculated by use of Eqns. (30)–(32) and (22), taking into account the overvoltage[24] and the coefficient ϑ[54]. A comparison of these calculations with experimental results for a solution 3.9×10^{-4} *N* HCl + 0.33 *N* KCl is shown in Fig. 3.[53] The continuous line denotes a curve calculated from the equation for reduced current, Eqn. (30), the circles represent the experimental results; they are in good agreement. For comparison, Fig. 3 also includes a broken I *vs.* φ curve calculated assuming a constant concentration of reacting substances at the surface of the mercury drop throughout its life. This curve is displaced towards the side of more negative potentials. The greatest separation between the curves corresponds to a certain negative half-wave potential. The curve calculated for reversible processes (broken line in Fig. 3) coincides with a curve calculated for the case of irreversible reactions only for limiting values of μ, namely $\mu \to 0$ and $\mu \to \infty$. The theory advanced for irreversible electrode reactions[8] is thus more general and includes reversible reactions as a particular case.

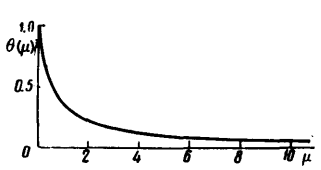


Fig. 1. Dependence of $\theta(\mu)$ on μ.

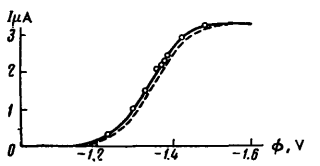


Fig. 3. Concentration polarisation in the solution 3.9×10^{-4} *N* HCl + 0.33 *N* KCl. Full curve: calculated by Eqn. (30); broken curve: calculated for $c(\tau, 0) = \text{const.}$; circles: experimental data.

If in the reaction represented by Eqn. (1) $k_2 \neq 0$, then in order to obtain equations for the current at a growing droplet it is necessary to solve a system of differential equations:

$$\left.\begin{aligned}\frac{\partial c_O}{\partial t} &= D_1 \frac{\partial^2 c_O}{\partial x^2} + \frac{2x}{3t}\frac{\partial c_O}{\partial x}\\ \frac{\partial c_R}{\partial t} &= D_2 \frac{\partial^2 c_R}{\partial x^2} + \frac{2x}{3t}\frac{\partial c_R}{\partial x}\end{aligned}\right\} \quad (33)$$

with the following initial and boundary conditions:

$$t = 0,\ x > 0:\ c_O = c_O^0;\ x \geqslant 0,\ c_R = c_R^0 \quad (34)$$

$$x = 0,\ t > 0:\ D_1\frac{\partial c_O}{\partial x} \pm D_2\frac{\partial c_R}{\partial x} = 0;\ -D_1\frac{\partial c_O}{\partial x} = k_2 c_R - k_1 c_O \quad (35)$$

$$x \to +\infty,\ t > 0:\ c \to c^0;\ x \to \pm\infty;\ c_R \to c_R^0. \quad (36)$$

In conditions (35) and (36) the plus sign refers to the case when the product of the electrochemical reaction (R) is soluble in the solution; if R is soluble in the electrode, the sign will be negative. In both cases the symmetry of the diffusion processes leads to identical expressions for the current.

Koutecký[17,55] solved Eqns. (33)–(36) by a method similar to that used by Meiman[8]. The expression obtained for instantaneous current is:

$$i = -nFq\sqrt{\frac{7D_O}{12t}}\left(\frac{\partial c}{\partial s_1}\right)_{s_1=0},$$

where

$$\left(\frac{\partial c}{\partial s_1}\right)_{s_1=0} = \frac{1}{\sqrt{D_O}}\frac{k_1 c_O^0 - k_2 c_R^0}{\frac{k_1}{\sqrt{D_O}} + \frac{k_2}{\sqrt{D_R}}}\sum_{i=1}\nu_i \kappa^i,$$

$$\nu_1 = 1,\ \frac{\nu_{i+1}}{\nu_i} = -\frac{1}{\rho_{\frac{3}{7}i}},\ \kappa = \left(\frac{k_1}{\sqrt{D_O}} + \frac{k_2}{\sqrt{D_R}}\right)\sqrt{\frac{12t}{7}}. \quad (37)$$

The results can be simplified if we put:

$$i_\infty = -nFq\frac{2}{\sqrt{\pi}}\sqrt{\frac{7D_O}{12t}}\frac{1}{\sqrt{D_O}}\frac{k_1 c_O^0 - k_2 c_R^0}{\frac{k_1}{\sqrt{D_O}} + \frac{k_2}{\sqrt{D_R}}},$$

where i_∞ is the current for an electrode reaction for which these conditions are maintained on the electrode surface:

$$\kappa = 0,\quad t > 0:\quad c_O = \frac{k_2}{k_1} c_R.$$

The solution can be written in the form:

$$\frac{i}{i_\infty} = F(\kappa), \quad (38)$$

where

$$F(\kappa) = \frac{\sqrt{\pi}}{2}\sum_{i=1}^{\infty}\nu_i \kappa.$$

This solution is applicable for values of κ not greatly exceeding unity. For $\kappa \gg 1$, an asymmetric solution is used, in which we obtain

$$F(\kappa) = \sum_{i=0}^{\infty} v_i \left(\frac{1}{\kappa}\right)^i,$$

where

$$v_0 = 1,\ \frac{v_{+1}}{v_i} = -p_{-\frac{3}{7}(i+1)}.$$

The dependence of the function $F(\kappa)$ on the argument is shown in Table 2.[17]

In the derived equations, as in Eqns. (25) and (28), the current is proportional to some function which can be presented in the form of two different series corresponding to values of the argument near to unity and much greater than unity.

TABLE 2. Dependence of $F(\kappa)$ on the parameter κ.

κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$	κ	$F(\kappa)$
0.1	0.0828	0.6	0.369	1.2	0.555	2.5	0.740	5	0.858	10	0.927
0.2	0.155	0.7	0.409	1.4	0.597	3.0	0.777	6	0.880	12	0.939
0.3	0.219	0.8	0.444	1.6	0.623	3.5	0.803	7	0.895	14	0.946
0.4	0.275	0.9	0.476	1.8	0.662	4.0	0.827	8	0.909	16	0.953
0.5	0.325	1.0	0.505	2.0	0.690	4.5	0.844	9	0.919	18	0.958
										20	0.963

For the mean polarographic currents, Eqn. (38) takes on the form:

$$\frac{\bar{i}}{i_\infty} = \frac{7}{3}\kappa_1^{-\frac{7}{3}}\int_0^{\kappa_1} F(\kappa)\cdot\kappa^{\frac{4}{3}}d\kappa = \bar{F}(\kappa_1). \quad (39)$$

For small values of κ_1:

$$F(\kappa_1) = \sum_{i=1}^{\infty} m_i \kappa_1^i, \text{where } m_i = \frac{\nu_i}{1+\frac{3}{7}i}. \quad (40)$$

Function $F(\kappa_1)$ has an approximate form for $\kappa_1 > 3$:

$$F(\kappa_1) = \sum_{i=0}^{5} n_i \kappa^{-i} - 0.01\left(\frac{3}{\kappa_1}\right)^{\frac{7}{3}},\quad n_i = \frac{v_i}{1-\frac{3}{7}i}.$$

The mean polarographic current is given sufficiently accurately by the equation:

$$\frac{\bar{i}}{i_\infty} = \frac{0.87\left(\frac{k_1}{\sqrt{D_O}} + \frac{k_2}{\sqrt{D_R}}\right)\sqrt{t_1}}{1 + 0.87\left(\frac{k_1}{\sqrt{D_O}} + \frac{k_2}{\sqrt{D_R}}\right)\sqrt{t_1}} \quad (41)$$

III. EQUATION FOR LINEAR DIFFUSION AND THE DROPPING ELECTRODE

Expressions for the current at the mercury dropping electrode can also be obtained by transformation of equations derived for an irreversible electrode reaction in the case of linear diffusion. However, it must be noted that such a procedure[13,14,56] leads to less accurate results than the direct solution of diffusion problems taking into account the growing surface of the mercury drop[8,17,55].

The expression for the current dependent on reaction (1) taking place was obtained for linear diffusion by various authors[11,14,57]:

$$i = nFqc_O k_1 \exp(Q^2 t)\operatorname{erfc}(Qt^{1/2}), \quad (42)$$

$$Q = \frac{k_1}{D_O^{1/2}} + \frac{k_2}{D_R^{1/2}},\quad \operatorname{erf}(a) = \frac{2}{\sqrt{\pi}}\int_0^a \exp(-z^2)\,dz,$$

$$\operatorname{erfc}(a) = 1 - \operatorname{erf}(a).$$

The dependence of function $\exp(Q^2t).\operatorname{erfc}(Qt^{\frac{1}{2}})$ on the argument $Qt^{\frac{1}{2}}$, is analogous to the dependence of function $\theta(\mu)$ on the argument μ.[8] It follows from this equation that the current is proportional to the product $\exp(Q^2t).\operatorname{erfc}(Qt^{\frac{1}{2}})$. Hence, just like this product, the current falls with increasing time (the argument).

In order that Eqn. (42), developed for linear diffusion, can be applied to the mercury dropping electrode it is necessary to express the electrode surface q in terms of the capillary characteristics m and t and to multiply the right-hand side of the equation by the Ilkovič coefficient[14], $(7/3)^{\frac{1}{2}}$. After transformation, we obtain an equation for the instantaneous current during the life of a drop for any point along the wave:

$$i = 1255\, nm^{2/3}t^{2/3}c_O^0 k_1 \exp(Q^2 t)\, \mathrm{erfc}\,(Q^2 t)^{1/2}, \qquad (43)$$

in which i is expressed in mA, m in mg sec^{-1}, t in sec, c_O^0 in mM, and k_1 and k_2 in cm sec^{-1}. Eqn. (43) is a general expression for polarographic currents (reversible and irreversible waves), determined by diffusion and electrode reactions. The Ilkovič equation is a particular case of Eqn. (43), in which the rate constant is very large ($k_1 \to \infty$).

If the reverse reaction is negligible, *i.e.* if $k \ll k_1$, then in Eqn. (43) Q takes the value $k_1/D_O^{\frac{1}{2}}$ and the wave will be irreversible. The effect of the reverse process cannot be taken into account for those portions of the wave in which the overvoltage exceeds 0.1 V. This condition is easily verified by taking oscillograms[58,59] or by comparing the cathodic and anodic polarographic waves. If the electrode process is accompanied by subsidiary chemical reactions, the comparison may indicate an irreversible electrode process although it is actually reversible. From Eqn. (43) the following condition of reducibility[14] is deduced:

$$k_s > \sim 2\times10^{-2}\ \mathrm{cm\ sec^{-1}} \qquad (44)$$

where $k_s = k_1 = k_2$.

If k_s for a certain electrode process is less than $\sim 2 \times 10^{-2}$ cm sec^{-1}, then the wave obtained acquires an irreversible character, shifts to more negative potentials and becomes more sloping. The smaller the value of constant k_s, the greater the displacement. If $k_s \leq 3 \times 10^{-5}$ cm sec^{-1}, then the overvoltage exceeds $2 \times 2.3\ (RT/nF)$ by ~ 0.12 mV, since the influence of the reverse reaction can be neglected, *i.e.* the waves at such an overvoltage are almost completely irreversible. Condition (44) can be expressed in terms of the free energy of activation. The rate constant k_s (puting $n = n_a$, where n_a is the number of electrons in the activation phase) is equal to[60]:

$$k_s = \frac{kT}{h}\rho \exp\left[\alpha \Delta G^0 - \Delta G_1^*/RT\right]$$

and condition (44) is expressed (with $\rho \simeq 10^{-6}$ cm, $T = 298°$):

$$\Delta G_1^* \leqslant 11.5 + \alpha \Delta G^0.$$

Analysis of Eqn. (43) shows that in the lower part of the irreversible wave the current is independent of the height of the mercury column (h_{Hg}), since in this equation m and t are raised to the same power (2/3) and it is known that m is directly proportional to h_{Hg} and t is inversely proportional to h_{Hg}. In the expressions for the currents in the upper part of the wave, where $i \to i_d$, we have $m^{2/3}$ and $t^{1/6}$, so that the current is proportional to the square root of the height of the mercury column[13,61]. The dependence of the current on the height of the mercury column can be used as a criterion of reversibility, since in the case of a reversible polarographic wave, the current at any point along the wave is proportional to the square root of the height of the mercury column[61,62].

Kuta and Smoler[22] recently showed that for reversible oxidation–reduction systems the dependence of the exponent of the $i = kt^{\kappa}$ curve on the potential varies according as to whether the reaction product is soluble or insoluble in the mercury: in the first case the exponent is independent of the potential, in the second it increases with increasing potential up to a constant value at the potential of the limiting current. For irreversible processes, this dependence is determined by the magnitude of the overvoltage. At low overvoltages the dependence of the exponent of the i *vs.* t curves on the potential exhibits a maximum, and at greater values of η the value of the exponent changes monotonically along the wave from 1/6 to 2/3.

The expressions for the current of irreversible electrode processes enable us to determine the rate constant of the electrochemical reaction. From the dependence of the reaction rate constant on the potential it is possible to obtain the value of the free energy of activation ΔG^0 and the product αn_a. In order to find the reaction rate constant it is necessary to measure experimentally the ratio of the current along the irreversible polarographic wave to that determined only by the diffusion rate[62].

For irreversible processes where the rate of the rereverse reaction can be neglected, in the case of linear diffusion this ratio is found by comparison of Eqn. (42) with the equation for the diffusion current; it is equal to:

$$\frac{i}{i_d} = \pi^{1/2}\lambda \exp(\lambda^2)\, \mathrm{erfc}\,(\lambda),$$

where

$$\lambda = k_1 t^{1/2}/D_O^{1/2}. \qquad (45)$$

The value of k_1 is found from the dependence of i/i_d upon λ. When determining the reaction constant for the case of the mercury dropping electrode Eqns. (38) and (41) are used for the instantaneous and mean polarographic currents respectively[17]. The parameter κ is given by Eqns. (37) and (39). Table 2[17] gives the dependence of $F(\kappa)$ on the parameter κ. In practice the current is limited by diffusion when λ or κ exceed 15, which occurs when the reaction rate constant is sufficiently large.

The reaction rate constant can also be determined graphically[13,56,63]. The mean value of the current obtained from Eqn. (43) can be expressed:

$$i_{mean} = 1255\, nm^{2/3}\tau^{2/3}c^0 k_1 z, \qquad (46)$$

where

$$z = \gamma\, \mathrm{erfc}\,(k_1 t^{1/2} D^{-1/2}) \exp(k_1^2 t D^{-1}). \qquad (47)$$

The value of γ (the ratios of the mean current to the maximum current) is found from Fig. 4, which gives the variation of γ with mercury drop time for different values of

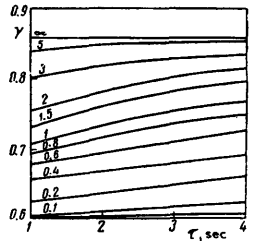


Fig. 4. Dependence of γ on τ for different values of $kD^{-\frac{1}{2}}$.

$kD^{-\frac{1}{2}}$. Values of z for different values of $kD^{-\frac{1}{2}}$ are calculated by use of Eqn.(47) and Fig.4. Fig.5 gives the variation of $zkD^{-\frac{1}{2}}$ with mercury drop time.

In order to determine the reaction rate constant, zk is calculated by Eqn.(46) and then the product $zkD^{-\frac{1}{2}}$ is obtained. A point is found on Fig.5 with abcissa of τ (drop time) and ordinate $zkD^{-\frac{1}{2}}$ and the value of $kD^{-\frac{1}{2}}$ for the curve passing through the point is obtained by interpolation. k is calculated from this value of $kD^{-\frac{1}{2}}$.

Fig.4 shows that $\gamma \simeq 0.60$ when $kD^{-\frac{1}{2}} < 0.05$. The magnitude of the current is then determined by the rate of reaction. When $kD^{-\frac{1}{2}} > 5$, then $\gamma = 0.857$, or 6/7, *i.e.* the value found from the Ilkovič equation. When $kD^{-\frac{1}{2}} < 0.05$, the rate constant can be calculated directly from the value of the limiting current by Eqn.(46), in which z is put equal to 0.60.

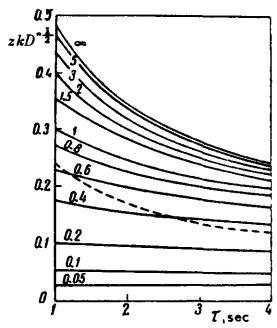


Fig.5. Dependence of $zkD^{-\frac{1}{2}}$ on τ. Figures on the curves give values of $kD^{-\frac{1}{2}}$ in $sec^{-\frac{1}{2}}$.

The dependence of the reaction rate constant on the overvoltage (η) can be expressed by the equation:

$$k = \frac{kT}{h}\delta \exp\frac{-\Delta G^0 + \alpha n_a F\eta}{RT}, \qquad (48)$$

where k is the Boltzmann constant, and h the Planck constant. From this formula it follows that finding the dependence of the logarithm of the reaction rate constant on the overvoltage makes it possible to determine αn_a and the free energy ΔG^0. [13] The slope of the log k *vs.* η curve is proportional to αn_a. The value of log k at $\eta = 0$ characterises the speed of the electrode process. This quantity is a linear function of the free energy of activation ΔG^0. By determining the values of k and ΔG^0 at various temperatures, the entropy of activation can be calculated from the equation $\Delta G = \Delta H - T\Delta S$. These data are very important in studying the mechanism of electrochemical reactions.

IV. SUCCESSIVE ELECTROCHEMICAL REACTIONS

In considering irreversible polarographic waves above it was assumed that the rate of reduction of the substance was determined by the kinetics of only one electrochemical step. If this step did not include all the number of electrons necessary for the reduction of substance O to R, then it was proposed that an intermediate substance Z is formed, having a high rate of reduction and no effect on the form of the wave. In the more general case it is necessary to calculate the influence of the successive individual electrochemical steps [16,64].

We will consider two particular cases of successive electrochemical reactions, examined by Delahay [64]. In the first case, the effect of the reverse reaction is neglected for both electrochemical stages, *i.e.*

$$O \xrightarrow[n_1 e]{k_I} Z \xrightarrow[n_2 e]{k_{II}} R. \qquad 49)$$

The boundary conditions are obtained from the balance for substance Z at the electrode surface:

$$c^0 k_I \exp(k_I^2 t D_O^{-1})\,\mathrm{erfc}\,(k_I t^{1/2} D_O^{-1/2}) - k_{II} c_Z(0,t) + D_Z\,[\partial c_Z(x,t)/\partial x]_{x=0} = 0. \quad (50)$$

The first term of Eqn.(50) gives the rate of reduction O → Z, the second Z → R, and the third term expresses the rate of diffusion of substance Z from the surface of the electrode into the solution. The initial conditions have the normal form: $c_Z(x,0) = 0$; $c_Z(x,t) \to 0$ at $x \to \infty$. The current for reaction (49) is the sum of those for the reductions O → Z and Z → R. For stage O → Z, the current is given by Eqn.(42) for a single-stage irreversible reaction.

To find the current for stage Z → R, our knowledge of the concentration $c_Z(0,t)$ is used. This concentration is found by solving, for the cited conditions, the differential equation expressing Fick's second law. Using the conditions for linear diffusion the total current of reaction (49) is:

$$i = n_1 F q c_O k_I \exp(k_I^2 t D_O^{-1})\,\mathrm{erfc}\,(k_I t^{1/2} D_O^{-1/2}) + \\ + n_2 F q c^0 \frac{k_{II}}{(D_Z/D_I)^{1/2} - \frac{k_{II}}{k_I}} \left\{ \begin{array}{ll} \exp(k_{II} t D_Z^{-1}) & \mathrm{erfc}\,(k_{II}\, t^{1/2} D_Z^{-1/2}) \\ -\exp(k_I^2 t D_O^{-1})\,\mathrm{erfc}\,(k_I t^{1/2} D_O^{-1/2}) & \end{array} \right\}. \quad (51)$$

If the surface of the electrode is expressed in terms of the capillary characteristics m and τ, and a correction coefficient [2,3] of $(7/3)^{\frac{1}{2}}$ is introduced, then Eqn.(51) can be applied approximately to the mercury dropping electrode. Fig.6 depicts the dependence of the average current on the potential calculated by Eqn.(51) for the following conditions: $\tau = 3$ sec, $m = 10^{-3}$ g sec^{-1}, $c^0 = 10^{-6}$ mole cm^{-3}, $n_1 = n_2 = 1$, $D_O = D_Z = 10^{-5}$ cm^2 sec^{-1}, $k^0 = 10^{-6}$ cm sec^{-1}, with k_0 determined by the expression $k = k_0 \exp(-\alpha n_a F\varphi/RT)$. In the calculations it was found that the products αn_a for the successive stages of reaction (49) were identical. In this case the ratio of rate constants k_I/k_{II} is independent of the potential and this makes it possible to construct polarographic waves for different k_I/k_{II} ratios. From Eqn.(51) and Fig.6 it is seen that separation into two waves is noticeable at ratios $k_I/k_{II} > 100$. If the rate constant of the second stage is significantly greater than that of the first, the wave has practically the same form as in the case of a single-stage process. If k_{II} is appreciably less than k_I then the lower part of the wave is determined mainly by the kinetics of the first stage (curves *4* and *5*). If $k_{II} \to \infty$, Eqn.(51) takes the form of Eqn.(42), with n_1 replaced by the total $n_1 + n_2$. If $k_I \to \infty$ and $k_{II} \to \infty$, then Eqn.(51) will become identical with the equation for current determined only by diffusion.

In order to find out whether the electrode process takes place in a single stage or several successive stages, it is

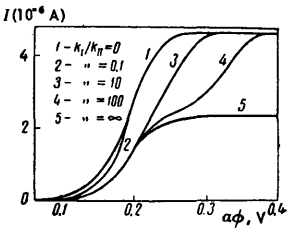


Fig. 6. Dependence of the average current on the product $\alpha\varphi$, calculated from Eqn. (51).

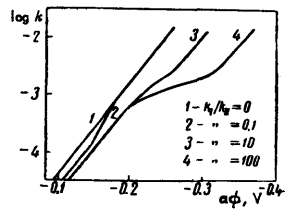


Fig. 7. Dependence of log k on $\alpha\varphi$ for the curves of Fig. 6.

necessary to look at the polarographic wave plotted on co-ordinates log k *vs.* φ. The polarographic waves presented in Fig. 6 have been plotted on these co-ordinates in Fig. 7, from which it is evident that the existence of successive stages of the reaction can be detected even within the limits of one wave from the presence of separate parts of different slope in the log k *vs.* φ curve. If the values of n_1 and n_2 are known, then the kinetics of each stage can be determined separately. In the analysis of the lower part of the wave it is necessary to calculate only the diffusion current (i'_d) which depends on the n_1 part of the electrons, that is, $i'_d = i_d n_1/(n_1 + n_2)$; for the upper part, the diffusion current (i''_d) corresponding to the transfer of n_2 electrons, $i''_d = i_d n_2/(n_1 + n_2)$.

Waves for the reduction of chromium and certain polyphosphate complexes[64-66] are examples of electrode processes proceeding in successive electrochemical stages. The process depends on the temperature and pH of the electrolyte. The slope of the lower part of the log k *vs.* φ curve for the $Cr^{VI}-Cr^{III}$ wave is approximately twice the slope of the upper portion, and since the total number of electrons is equal to three then the first stage we can take $n_1 = 2$, and for the second $n_2 = 1$. This provides a basis for the hypothesis that Cr^{IV} is the intermediate product in the reduction of Cr^{VI}. This assumption is confirmed by studying the potential *vs.* time curves at constant current[67]. For studying unstable intermediate products of electrochemical reactions rotating electrodes have recently been used [68,69].

In the second case two successive electrochemical reactions are assumed; that between the substances O and Z is determined by electrochemical equilibrium but the second stage is completely irreversible and its reverse reaction can be neglected:

$$O \underset{n_1 e}{\overset{\text{equilibrium}}{\rightleftharpoons}} Z \xrightarrow[n_2 e]{k} R. \qquad (52)$$

For this process:

$$i = n_1 F q D_O [\partial c_O(x, t)/\partial x]_{x=0} + n_2 F q c_Z(0, t).$$

The terms $[\partial c_O(x,t)/\partial x]_x = 0$ and $c_Z(0,t)$ are the solution of a system of two differential equations with corresponding boundary and initial conditions. Use of a Laplace transform leads finally to the expression:

$$\frac{i}{nFq} = \frac{c^0}{\theta + (D_Z/D_O)^{1/2}} \left[\left(\frac{D_Z}{\pi t}\right)^{1/2} + \frac{k[2\theta + (D_Z/D_O)^{1/2}]}{\theta + (D_Z/D_O)^{1/2}} \exp(a^2 t)\, \mathrm{erfc}\,(at^{1/2}) \right], \qquad (53)$$

where

$$a = k/(\theta D_O^{1/2} + D_Z^{1/2}), \quad n_1 = n_2 = n.$$

The condition that the slope of the straight line log $[(i_d - i)/i]$ *vs.* φ is 2.3 RT/nF does not hold for processes with successive electrochemical stages.

For electrochemical processes conforming to schemes (49) or (52), the half-wave potential does not have a simple physical significance. In general, the half-wave potential for irreversible polarographic waves has no special significance, unlike that for reversible waves. In the case of irreversible waves the half-wave potential depends on the concentration of the reacting substances, the diffusion coefficient, the product αn_a, and the drop time of the mercury[14,56,61,70]. Actually, by defining as $\lambda_{\frac{1}{2}}$ the value of $kt^{\frac{1}{2}}D^{\frac{1}{2}}$ at half-wave potential we obtain for an irreversible wave with one retarded stage [62]:

$$\varphi_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k_\eta}{\lambda_{1/2} D_O^{1/2}} + \frac{RT}{2\alpha n_a F} \ln t. \qquad (54)$$

The variations in half-wave potential with the drop time are insignificant. Thus the half-wave potential for the reduction of Ni^{2+} changes from -0.959 V to -1.016 V when the drop time changes from 7.66 sec to 2.09 sec[61]; in the case of the reduction of weak acids the shift in half-wave potential when t is changed from 2 to 4 sec amounts to 0.0083 V. The changes are more noticeable for $t < 3$ sec[56].

V. IRREVERSIBLE WAVES AND EXCHANGE CURRENT DENSITY

With the presence of both the oxidised and reduced forms of the depolariser at the beginning of electrolysis, polarography enables the cathodic and anodic processes to be studied simultaneously. Both forms of the depolariser may be in the solution being examined, or one of them may be in the solution and the other in the amalgam. In the case of reversible systems a general anodic-cathodic reversible wave is obtained. Irreversible oxidation-reduction systems give branched anodic and cathodic waves [11,12,18,71-73].

In studying irreversible electrode processes of oxidation-reduction systems, Smutek[11,15] and Tockstein[12] used methods previously examined by us[8,17]. We will deal with the approach of Stromberg[18,19], which is based on the theory of retarded discharge and employs ideas concerning

current exchange. The rate of discharge ($\vec{i}$) of ions from solution and the rate of ionisation ($\overleftarrow{i}$) of atoms from the amalgam at potential φ can be expressed[74]:

$$\vec{i} = k_1 c_O \exp(-\alpha nF/RT)\varphi,$$

$$\overleftarrow{i} = k_2 c_R \exp(\beta nF/RT)\varphi,$$

where k_1 and k_2 are rate constants for the discharge and ionisation processes, and α and β are the coefficients for the theory of retarded discharge ($\alpha + \beta = 1$). At the equilibrium potential (φ_{eq}), $\vec{i} = \overleftarrow{i}$ and these equal the exchange current (i_0):

$$i_0 = \vec{i} = \overleftarrow{i} = k_1 c_O^0 \exp(-\alpha nF/RT)\varphi_{eq} = k_2 c_R^0 \exp(\beta nF/RT)\varphi_{eq}.$$

Expressing the constants k_1 and k_2 in terms of the exchange current and the concentrations of O and R in terms of the current, we obtain the fundamental equation of the irreversible electrode process of oxidation-reduction systems[18]:

$$\frac{i}{i_0} = \frac{I_k - i}{I_k}\exp(\alpha nF/RT)\eta - \frac{I_a + i}{I_a}\exp(-\beta nF/RT)\eta, \quad (55)$$

where I_k and I_a are the cathodic and anodic limiting currents.

When $i_0 \to \infty$, Eqn. (55) is transformed into the equation for the reversible overall anodic-cathodic wave:

$$\varphi = \varphi_{1/2\,rev} - \frac{2.3RT}{nF}\log\frac{I_a + i}{I_k - i},$$

and

$$\text{and } \varphi_{1/2\,rev} = \varphi_{eq} - \frac{2.3RT}{nF}\log\frac{I_k}{I_a}, \quad (56)$$

where $\varphi_{\frac{1}{2}rev}$ is the reversible half-wave potential of the anodic-cathodic wave (Fig. 8, curve *1*). It follows from this equation that the reversible cathodic wave ($I_a = 0$) and the reversible anodic wave ($I_k = 0$) have half-wave potentials and slopes identical with those of the reversible anodic-cathodic wave.

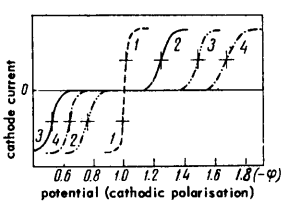


Fig. 8. Dependence of the current on the potential calculated by Eqn. (55) for different values of i_0 α and β : $Ik = I\alpha = I$; $t = 25°$; $n = 2$. Curve *1*) reversible anodic-cathodic wave ($i_0 \to \infty$); *2*) $i_0 = 10^{-4}I$, $\alpha = \beta = 0.5$; *3*) $i_0 = 10^{-6}I$, $\alpha = \beta = 0.5$; *4*) $i_0 = 10^{-6}I$, $\alpha = 0.35$, $\beta = 0.65$; φ_0 conditionally taken as 1.0 V. In the case taken $\varphi_0 = \varphi_{\frac{1}{2}\,rev}$.

When the exchange current is sufficiently small and the polarisation sufficiently high, then one of the terms in the right-hand side of Eqn. (55) can be neglected, and we can write the following expressions for the cathodic and anodic waves:

$$\left.\begin{aligned}\varphi_{1/2k} &= \varphi_{eq} - \frac{2.3RT}{\alpha nF}\log\frac{I_k}{i_0}\\ \varphi_{1/2a} &= \varphi_{eq} + \frac{2.3RT}{\beta nF}\log\frac{I_a}{i_0}\end{aligned}\right\}, \quad (57)$$

where $\varphi_{\frac{1}{2}a}$ and $\varphi_{\frac{1}{2}k}$ are the cathodic and anodic half-wave potentials.

It follows from Eqns. (56) and (57) that:

$$\left.\begin{aligned}\Delta\varphi_{1/2k} &= \varphi_{1/2\,rev} - \varphi_{1/2\,k} = \frac{2.3RT}{\alpha nF}\log\frac{I_k}{i_0} + \frac{2.3RT}{nF}\log\frac{I_a}{I_k}\\ \Delta\varphi_{1/2a} &= \varphi_{1/2a} - \varphi_{1/2\,rev} = \frac{2.3RT}{\beta nF}\log\frac{I_a}{i_0} + \frac{2.3RT}{nF}\log\frac{I_k}{I_a}\end{aligned}\right\}. \quad (58)$$

Eqn. (58) shows that in the case of irreversible electrode processes in oxidation-reduction systems, not one but two waves appear on the polarogram: the cathodic, shifted to negative voltages, and the anodic shifted to positive voltages by comparison with the half-wave potential of the reversible anodic-cathodic wave. On the basis of Eqn. (58) we can write:

$$\left.\begin{aligned}\Delta\varphi_{1/2\,ak} &= \varphi_{1/2\,a} - \varphi_{1/2\,k} = \Delta\varphi_{1/2\,k}\,\Delta\varphi_{1/2\,a} = \frac{-2.3RT}{\alpha\beta nF}\lg\frac{i_0}{I_k^{\beta} I_a^{\alpha}}\\ \alpha\varphi_{1/2\,k} &+ \beta\varphi_{1/2\,a} = \varphi_{1/2\,rev} \quad \text{and} \quad \frac{\Delta\varphi_{1/2\,k}}{\Delta\varphi_{1/2\,a}} = \frac{\beta}{\alpha}\end{aligned}\right\}. \quad (59)$$

It follows from these expressions that the difference between the half-wave potentials of the anodic and cathodic waves increases as the exchange current (expressed in terms of the limiting current) decreases (Fig. 8, curves *2* and *3*). In addition, the displacement of the wave from the reversible curve is directly proportional to the slope of the wave.

If $\alpha = \beta$, then the maximum deformation of the wave occurs at the half-wave potential of the equilibrium curve, the anodic and cathodic branches being symmetric relative to this point. If $\alpha > \beta$, the maximum deformation is transferred to a more positive (if $\alpha < \beta$ to a more negative) potential, the anodic and cathodic branches then being unsymmetrical (Fig. 8, curves *2* – *4*).[18] Smutek[11] reached this conclusion in another way.

The magnitude of the exchange current is characteristic of the degree of reversibility of the electrode process. Introducing the conception of reduced exchange current (i_0^0):

$$i_0^0 = \frac{i_0}{I_k^{\beta} I_a^{\alpha}},$$

we obtain a simple relation between the departure from reversibility $\Delta\eta$ ($\Delta\eta = \eta - \eta_{rev}$) and the exchange current. A plot of $\log i_0^0$ against $\log \Delta\eta$ shows that with an increase in the departure from reversibility by more than 0.1 V there is an appreciable reduction in the reduced exchange current (Fig. 9).[19]

As is evident from Eqn. (55), a plot of $\log[(I_a + i)/(I_k - i)]$ *vs.* η can serve as an indication and measure of polarographic reversibility; it is generally non-linear; only for a reversible wave is the dependence expressed by a straight line with slope $2.3\,RT/nF$. When $\eta \gg 0$, the slope of the curve tends to the value $2.3\,RT/\alpha nF$, and at $\eta \ll 0$ to $2.3\,RT/\beta nF$. These conclusions are analogous to those of Tockstein[12]. The departure from the equilibrium curve increases with reduction in drop time of the mercury or

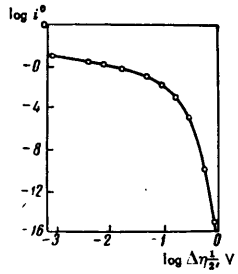


Fig. 9. Theoretical form of the relation between the reduced exchange current and the departure from reversibility in logarithmic co-ordinates. I_k-I_a-I; i=½I; α=β=0.5; n=2. [19]

amalgam, the rate constant of the electrode process, and the coefficients α and β.

The effect of the drop time on the half-wave potential for oxidation-reduction systems can be represented by the expression:

$$-\varphi_{1/2} = A + B\log\tau, \qquad (60)$$

where

$$B = \frac{2.3\,RT}{2\alpha nF}, \quad A = -(\varphi_{1/2})_{\tau=1} = -\varphi^0 - \frac{2.3\,RT}{\alpha nF}\log 0.0051\, j_0 k_{dif}.$$

(where $j_0 = k_1^{\alpha} k_2^{\beta}$).

This equation differs from Eqn. (54) in its first term. Eqn. (60) shows that with an increase in the drop time the half-wave potential must be displaced in the direction of more positive potentials; the plot of $\varphi_{\frac{1}{2}}$ *vs.* log τ must be linear with a slope equal to half that of the wave. An analysis of the irreversible wave for manganese confirms the correctness of Eqn. (60). [75]

Surface-active substances affect the degree of reversibility of electrode processes significantly. Their influences on polarographic curves are diverse: displacement of the wave towards the side of more negative values of the potential, reduction of the limiting current, the appearance of a second wave, branching of the anodic-cathodic wave, and variation in the slope of the wave [38-41,58,76-86].

The theories advanced to explain the influence of surface-active substances on the electrode process are varied; they consider the influence of the adsorbed film on the migration of the depolariser, or on its discharge, or on the conjugate chemical reaction [38-40,58,76-88].

A study of the dependence of current on time at various potentials along the wave [85,86,89,90] helps to explain the mechanism of the action of surface-active substances on polarographic curves. Schmid and Reilley [89] considered three limiting types of *i vs. t* curves in relation to what determines the growth of the adsorption film. Quantitative evaluation of the first type, determined by the rate of diffusion of the surface-active substance (electrically inactive), is expressed by the following equation [86,90]:

$$\frac{i_{ads}}{i} = 1 - \frac{k^0 - k_1}{k^0}\left(\frac{t}{t'}\right)^{1/2}, \qquad (61)$$

where k^0, k_1 are rate constants for the electrode reaction on the free surface and surface occupied by the adsorbed substance respectively, and t' is the time necessary for complete coverage of the electrode surface. The experimental i *vs.* t curve shows good agreement with Eqn. (61) only for surface-active substances of the molecular type. The marked discrepancies which are observed in the presence of surface-active cations can be explained by supposing that their specific adsorption on the mercury cathode is followed by potential changes in the electrical double layer. In the presence of surface-active substances the change in the ψ_1-potential can become significant [74]. Eqn. (55) for calculating the ψ_1-potential takes the form [18]:

$$\frac{i}{i_0}\exp\left\{\frac{\beta nF}{RT}(\psi_{1eq} - \psi_1)\right\} = \frac{I_k - i}{I_k}\exp\frac{\alpha nF\eta}{RT} - \frac{I_a + i}{I_a}\exp -\frac{\beta nF}{RT}\eta,$$

where $\psi_{1\,eq}$ is the value of the potential ψ_1 at equilibrium potential. This dependence has been confirmed experimentally.

Measurements of the capacity of the electrode can be used to evaluate the coverage on it [85].

The i *vs.* t curves and the effect of potential on the rate constant of the electrode reaction on the coated part of the electrode surface (k_1) provide an explanation for the anomalous course of the polarographic wave in the presence of an adsorbed substance [86]. If the reaction rate constant is zero on the occupied surface, then in the presence of surface-active substances the limiting current of reversible waves is reduced, and in the case of irreversible waves the wave is shifted towards the side of negative potentials as well as being diminished in height. When k_1 on the rising part of the wave is greater than zero and changes with potential, then there is a displacement of the wave and a change in its steepness. A second wave is formed if, at the potential of limiting current, the value of k_1 grows with rising potential.

The value of the coefficient α is reduced in the presence of a surface-active substance; this can be explained by assuming that polarisation of the depolariser is the determining factor for an irreversible electrode process [91].

VI. CONCLUSION

Electrode processes in agitated solutions have been studied less [49,92]. Expressions for non-stationary irreversible electrode processes have been obtained only for linear diffusion [52], and then – because of the difficulties in solving the differential equations for convection-diffusion with laminar flow – starting from the equations:

$$\left.\begin{aligned}\frac{\partial c_O}{\partial t} &= D_O\frac{\partial^2 c_O}{\partial x^2}, \quad O \leqslant x \leqslant \delta_O\\ \frac{\partial c_R}{\partial t} &= D_R\frac{\partial^2 c_R}{\partial x^2}, \quad R \leqslant x \leqslant \delta_R\end{aligned}\right\}, \qquad (62)$$

the convective transfer of the reacting substances is calculated with the quantities δ_O and δ_R in the boundary conditions $c_O(\delta_O, t) = c_O^0$ and $c_R(\delta_R, t) = 0$. δ is the thickness of the pre-electrode layer in which the change in concentration of substances O and R takes place. In the case of non-stationary processes δ will be equal to the distance between the electrode surface and the moving boundary of the solution of changing concentration. This distance, the so-called distance to the diffusion front, is a variable dependent on the duration of electrolysis, the rate of electrode reaction, and hence also on the electrode potential.

The expression for the current, obtained for small values of t (or large values of δ) agrees with Eqn.(42), obtained for stationary solutions[11,14,57] under conditions when the effect of agitation can be neglected. For large values of t (or small values of δ), the current density is expressed as follows:

$$i = nFkc_O^0\left[\frac{1}{1+\frac{Q\delta_O}{D_O^{1/3}}} + H\exp\left(-\frac{\gamma^2 D_O}{\delta_O^2}t\right)\right],$$

where $H = \sin 2\gamma/[\frac{1}{2}(\sin 2\gamma) - \gamma]$; γ is a quantity appearing in the solution of Eqn.(62) and taking values between $\pi/2$ and π ($\pi/2 \leqslant \gamma \leqslant \pi$) for different values of the ratio $Q\delta_O/D_O^{\frac{1}{3}}$. Unlike the stationary solutions, the value of i does not tend to zero as t tends to infinity, but takes the value:

$$i_{t\to\infty} = nFk_0c_O^0\frac{1}{1+\frac{Q\delta_O}{D^{1/3}}} . \qquad (63)$$

The solution of the differential equations for convective diffusion for the particular case of the stationary state gives an expression identical with Eqn.(63) when $i \to \infty$.[49,52]

In the cases analysed above, when considering irreversible electrode processes it was supposed that the concentration of the potential-determining substances at the electrode surface is determined only by their diffusion rate. However, this concentration can be limited also by so-called kinetic hindrances.

Kinetic polarographic waves began to be studied much later than diffusion waves. Initially, the concept of the pre-electrode reaction layer[93-95] was used to calculate the kinetic component of the limiting current, and this idea has been criticised[17,96]. A firmer basis for the study of kinetic currents was provided by the method used in the analysis on irreversible polarographic waves. By suitable substitution of variables, problems of kinetic currents can be changed into problems of irreversible electrode processes for which the concentration of reacting substances at the electrode surface is determined by diffusion. In both cases the solution is similar in form. Thus the expression for instantaneous kinetic currents can be presented as a relationship analogous to Eqn.(38), except that the values of κ and i are different. The expression for mean polarographic kinetic currents is analogous to Eqn.(39) but with different values of κ_1.

Surveys of the work on kinetic currents with various depolarisers have been made by Delahay[62], Brdička and Koutecký[97-99], Koryta[100], and Hans[101]. In particular, a solution has been found for the case where the reacting electrochemical substance is partially regenerated as a result of a chemical process with part of the product of the electrochemical reaction (catalytic wave). Several papers[102-115] contain interesting material on kinetic and catalytic currents. Kinetic hindrance affects the height of the limiting current but not the slope of the wave, which remains at the theoretical value for diffusion waves, nor does it cause branching of the wave in oxidation-reduction systems. The study of kinetic and catalytic currents began with irreversible electrochemical reactions[116-119]. Solutions were obtained for the problems of slow electrode reactions with a previous unimolecular chemical reaction of any speed[117] and also with previous and subsequent chemical reactions[118].

More recently it has been shown that the rotating disc electrode[120] can be used successfully in the study of kinetic and catalytic currents. The conditions for the supply of a substance to any point on the surface of such an electrode are identical if boundary effects are neglected. On the rotating disc electrode, reversible electrode reactions with quasi-unimolecular and bimolecular rapid chemical reactions have been examined.[120-121]. This method of solving problems is also used for other types of process with other systems of differential equations for diffusion and boundary conditions. On the rotating disc electrode, as opposed to the dropping electrode, processes take place under steady state conditions, which simplifies calculations. This extends the range of processes which can be studied, and in particular, the range of irreversible electrochemical reactions.

The theory of irreversible polarographic waves is still being developed. It does not provide a general approach to the solution of various depolarisation schemes and it cannot always be used in cases where different irreversible processes are taking place simultaneously in a system. However, even in this the theory has already enabled wider use to be made of the polarographic method and a nearer approach to the study of electrode processes.

The theory of irreversible polarographic waves has made it more possible to study the kinetics of electrode processes where slow electrode reactions are concerned. In this respect, the polarographic method and the method of superimposed alternating current[122] are complementary.

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