

The theory of hidden diffusion limiting currents

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Abstract

The theoretical analysis of parallel electrode processes under conditions when the product of one of the reactions is involved in a homogeneous reaction with a reactant of the other is presented. As a result the limiting current of the second reaction depends on the current of the first: an effect which was called "hidden limiting current" by Kemula and Grabowski. The analytical and numerical calculations performed cover a wide range of parameters of the problem. The results of Kemula and Grabowski are used in the particular case of the limit of an infinitely high rate constant for the homogeneous reaction.

1. INTRODUCTION

The phenomenon of hidden limiting currents was first discovered by Kemula and Michalski [1] nearly fifty years ago. Its first theoretical analysis was made in ref. 2. This phenomenon is observed in systems with parallel electrode processes, in which the product of one of the electrode process enters a homogeneous reaction with the reactant in the other parallel electrode process.

Let, for example, the solution contain substances A and B which are reduced at the electrode. For clarity we shall suppose that B is reduced at more negative potentials:



Here n_i , $i = 1, 2$ is the number of electrons transferred in the i th reaction, n_i are stoichiometric coefficients for electrode reactions.

If the reaction



proceeds in the diffusion layer, then, with the terminology of ref. 2, a hidden limiting current of the first kind is observed in the system. This current is defined as

a difference of limiting currents i_2 in the absence of a secondary reaction (3) and i_2' in the presence of a secondary reaction:

$$\Delta i_2 = i_2 - i_2' \quad (4)$$

If, however, the reaction



proceeds in the solution, then a hidden limiting current of the second kind $\Delta i_1 = i_1 - i_1'$ is observed.

Hidden diffusion limiting currents were analysed in ref. 2 with the assumption, that the homogeneous reaction rate is infinitely high.

A special case of a reaction inhibiting an electrode process has been analyzed in ref. 3. In this process the electrode reaction product interacts with the initial substrate, and hidden currents of the third kind can be observed. The experimental studies of hidden diffusion limiting currents have been described [3,4].

This paper develops a theory of hidden diffusion limiting currents for arbitrary values of the homogeneous reaction rate constant.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

We shall consider here hidden limiting currents of the first kind only (the problem of hidden limiting currents of the second kind can be solved in a similar manner) and for simplicity we shall assume all stoichiometric coefficients to be equal to unity: $\nu_i = 1$, $n_i = 1$, $n^1 = 1$. On the assumption that all the processes under consideration proceed in an excess of the background electrolyte, so that the electromigration effects are negligible, the equations governing the distribution of substance B and reaction (1) product A* concentrations in a diffusion layer, can be written as

$$D_{1*} \frac{d^2 c_{1*}}{d\xi^2} - k_1 c_{1*} c_2 = 0 \quad (6)$$

$$D_2 \frac{d^2 c_2}{d\xi^2} - k_1 c_{1*} c_2 = 0 \quad (7)$$

Here D_{1*} and D_2 are diffusion coefficients of the corresponding substances, k_1 is the rate constant of reaction (3), ξ is the coordinate perpendicular to the electrode surface.

The boundary conditions are assumed to be specified by concentration c_2 in the bulk of solution

$$c_2(L) = c^0$$

and by zero concentration of substance A*:

$$c_{1*}(L) = 0$$

Here \mathbf{L} is the diffusion layer thickness, which is supposed to be approximately the same for substances \mathbf{A}^* and B. We shall seek the solution under the condition $c_2(0) = 0$ which corresponds to achieving a limiting current in substance B.

To obtain the last boundary condition, one must find the solution of the diffusion equation for substance \mathbf{A} , which does not participate in homogeneous reaction (3):

$$D_1 \frac{d^2 c_1}{d\xi^2} = 0 \quad (8)$$

with the boundary condition at $\xi = \mathbf{L}$: $c_1(\mathbf{L}) = c_1^0$ and the condition of limiting current in substance \mathbf{A} : $c_1(0) = 0$. Integrating (8) twice, one obtains a linear profile for c_1 : $c_1 = c_1^0 \xi / \mathbf{L}$. Since the stoichiometry of reaction (1) shows that the fluxes of substances \mathbf{A} and \mathbf{A}^* near the electrode are equal and opposite in direction, the last boundary condition for c_{1^*} can be written in the form

$$D_{1^*} \left. \frac{dc_{1^*}}{d\xi} \right|_{\xi \rightarrow 0} = -D_1 \left. \frac{dc_1}{d\xi} \right|_{\xi \rightarrow 0} \equiv -D_1 \frac{c_1^0}{\mathbf{L}} \quad (9)$$

Let c_1 and c_2 be the dimensionless concentrations of substances \mathbf{A}^* and B, respectively,

$$c_1 = c_{1^*} D_{1^*} / c^0 D_2 \quad c_2 = c_2 / c^0 \quad (10)$$

$x = \xi / \mathbf{L}$ is the dimensionless coordinate ($0 \leq x \leq 1$), κ is the dimensionless reaction rate, j is the dimensionless flux of substance \mathbf{A} :

$$\kappa = k_1 \mathbf{L}^2 c^0 / D_{1^*} \quad j_1 = D_1 c_1^0 / D_2 c^0 \quad (11)$$

Then the system of equations (6) and (7) and the boundary conditions can be written as:

$$\frac{d^2 c_1}{dx^2} = \kappa c_1 c_2 \quad (12)$$

$$\frac{d^2 c_2}{dx^2} = \kappa c_1 c_2 \quad (13)$$

$$c_2(0) = 0 \quad c_2(1) = 1 \quad (14)$$

$$\left. \frac{dc_1}{dx} \right|_{x=0} = -j_1 \quad c_1(1) = 0 \quad (15)$$

We set out to find the relation between

$$j_2 = dc_2 / dx |_{x=0} \quad (16)$$

the dimensionless limiting flux of substance B and j_1 — the dimensionless limiting flux of substance \mathbf{A} for different values of κ .

The above set of equations can be reduced to a single differential equation. Subtraction of equation (13) from (12), twice integrating the result by use of the

boundary conditions (14) and (15) and substitution into (16) gives the linear relation between c_1 , and c_2

$$c_1 - c_2 = (j_1 + j_2)(x - 1) - 1 \quad (17)$$

By substitution of (17) into (12), the system (12) and (13) reduces to a single equation.

The set of equations (12) to (15) has no analytical solution in the general form. To study some limiting cases, when either κ or j_1 is small or large, we can use the method of asymptotic expansion in a small parameter while retaining, as a rule, the zero and first terms of the expansion only. In this case the variables X , Y , Z used below, designate functions having a scale of the order of unity.

3. THE CASE OF LOW REACTION RATES, $\kappa \ll 1$

In this case the solution for c_1, c_2 can be sought in the form of an expansion over small parameter κ :

$$c_1 = X + \kappa Y \quad (18)$$

$$c_2 = Z + \kappa U \quad (19)$$

Substitution of (18) and (19) into (12) and (13), respectively, to an accuracy of terms of the first order of smallness, gives

$$\frac{d^2 X}{dx^2} + \kappa \frac{d^2 Y}{dx^2} = \kappa XZ \quad (20)$$

$$\frac{d^2 Z}{dx^2} + \kappa \frac{d^2 U}{dx^2} = \kappa XZ \quad (21)$$

Thus retaining in these equations the terms of zero order of smallness only,

$$\frac{d^2 X}{dx^2} = 0 \quad \frac{d^2 Z}{dx^2} = 0 \quad (22)$$

Twice integrating these equations with the boundary conditions (14) and (15) gives

$$X = j_1(1 - x) \quad Z = x \quad (23)$$

Substituting (23) into (20) and (21) gives

$$\frac{d^2 Y}{dx^2} = j_1 x(1 - x) \quad \frac{d^2 U}{dx^2} = j_1 x(1 - x) \quad (24)$$

Since X and Z have already satisfied the inhomogeneous boundary conditions (14) and (15), Y and U should satisfy the homogeneous boundary conditions

$$\left. \frac{dY}{dx} \right|_{x=0} = 0 \quad Y(1) = 0 \quad (25)$$

Twice integrating (24) in terms of (25), gives the first terms of the expansion of (18) and (19):

$$Y = j_1(2x^3 - x^4 - 1)/12 \quad U = j_1(2x^3 - x^4 - x)/12$$

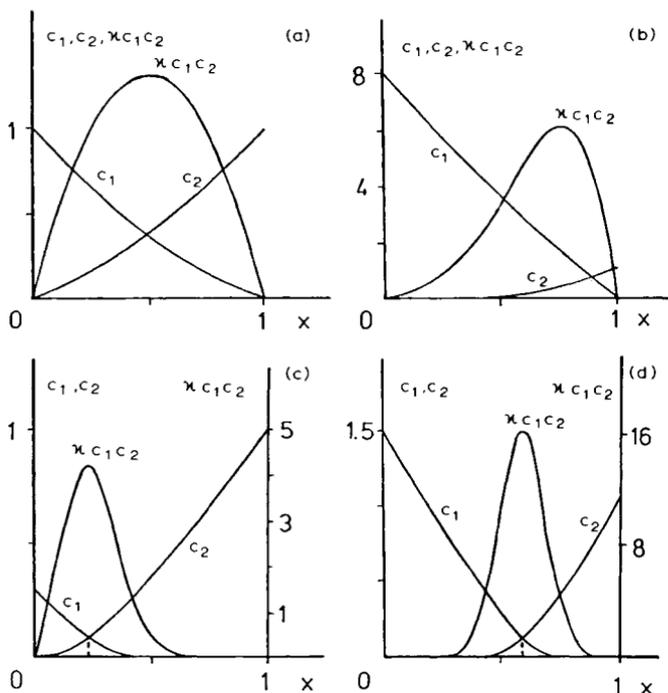


Fig. 1. The distribution of concentrations c_1 and c_2 and of homogeneous chemical reaction rate $\kappa c_1 c_2$ in the diffusion layer for the following values of dimensionless parameters: (a) $c_1(0)=1$, $\kappa=10$, (b) $c_1(0)=8$, $\kappa=10$, (c) $c_1(0)=0.3$, $\kappa=1000$, ($j_1 < 1$), (d) $c_1(0)=1.5$, $\kappa=1000$, ($j_1 > 1$).

The distribution of the concentrations c_1 and c_2 , which illustrate this solution, are shown in Fig. 1a.

Solving and differentiating (19), gives the unknown relation between fluxes j_1 and j_2 :

$$j_2 = 1 - \kappa j_1 / 12 \quad (26)$$

Expression (26) is applicable for $\kappa j_1 \ll 1$ only, i.e. for sufficiently small fluxes j_1 . For $\kappa j_1 \sim 1$ a different method of solution is required.

4. THE CASE OF LOW REACTION RATE $\kappa \ll 1$ AND HIGH FLUX VALUE $j_1 \gg 1$

The parameters κ and j_1 should satisfy the condition $\kappa j_1 \sim 1$. In this case function c_1 has a characteristic scale $c_1 \sim j_1$, and function $c_2 \sim 1$. This permits the problem to be solved as an expansion in terms of $1/j$ whose initial terms are $c_1 = j_1 X + Y$, $c_2 = Z$ where X , Y , Z are functions with the scale of the order of unity.

Substituting c_1 and c_2 as functions of X , Y , and Z into (12) and (13) and regarding the terms of the order of j_1 , one obtains $X = 1 - x$. Substituting the

solution found for X into equation (13), the latter reduces to

$$\frac{d^2 Z}{dx^2} = \kappa j_1 (1 - x) Z \quad (27)$$

The solution of this equation is a linear combination of Airy's functions:

$$Z = s_1 Ai[q(1 - x)] + s_2 Bi[q(1 - x)] \quad (28)$$

where $q = \sqrt[3]{\kappa j_1}$ and s_1, s_2 are constants. Determining s_1 and s_2 from the boundary conditions (15) and (16) and differentiating (28), one obtains the expression for the limiting flux of substance B:

$$j_2 = \left. \frac{dc_2}{dx} \right|_{x=0} = - \frac{q}{Ai(0)} \frac{Bi(q)Ai'(q) - Ai(q)Bi'(q)}{Bi(q) - Ai(q)\sqrt{3}} \quad (29)$$

In the case of sufficiently small κ values, when $q \ll 1$ expression (29) can be simplified by retaining the leading terms of the asymptotic expansions of the Airy functions only [5]. Thus equation (29) is reduced to formula (26). Thus, expression (29) is applicable for $J \ll 1$ and for any κ value.

5. THE CASE OF LARGE REACTANT FLUXES $J, \gg 1$

The case of larger fluxes j_1 has been studied already in Section 4 under the extra condition $\kappa \ll 1$. In this section κ is assumed to be of the order of unity.

Unlike the case considered in Section 4, where functions $c_1(x), c_2(x)$ varied smoothly throughout the $0 \leq x \leq 1$ interval, in the case of $\kappa \geq 1$ and $\kappa j_1 \gg 1$ function $c_2(x)$ changes sharply for values x near 1, but throughout the remaining interval it varies smoothly, taking the values close to zero. In other words, the boundary layer is formed near the diffusion layer boundary at $x = 1$.

Since in the case under consideration $dc_2(0)/dx = \delta \ll 1$ the relation between c_1 and c_2 (17) can be written as:

$$c_1 \approx c_2 + j_1(1 - x) = c_2 + j_1(x^* - x) \quad (30)$$

where $x^* = 1 - 1/j_1$.

Outside the narrow region near $x = 1$, where $1 - x \gg 1/j_1$, the first term in (30) can be neglected. In this case (13) transforms into the equation

$$\frac{d^2 c_2}{dx^2} = \kappa j_1 (x^* - x) c_2$$

The solution of this equation is a linear combination of Airy functions

$$c_2 = s_3 Ai[q(x^* - x)] + s_4 Bi[q(x^* - x)]$$

Determining s_3 and s_4 coefficients from the boundary conditions (15), taking into account that $(x^* - 1)q = \sqrt[3]{\kappa/j_1^2} \gg 1$ and $qx^* = \sqrt[3]{j_1 \kappa} \gg 1$ and using the leading

terms of the asymptotic expansions for Airy functions at large and small values of the arguments [5], one obtains the expression for a limiting flux of substance B:

$$j_2 = \left. \frac{dc_2}{dx} \right|_{x=0} = \frac{-\sqrt[3]{\kappa j_1}}{Ai(0)} Ai'(\sqrt[3]{\kappa j_1}) = \frac{\sqrt[3]{\kappa j_1}}{\pi Ai(0) Bi(\sqrt[3]{\kappa j_1})} \quad (31)$$

Note that formula (31) is a particular case of (29) where $q \gg 1$. In deriving (31) only the condition $j_1^2 \gg \kappa > 1$ was used, therefore, relation (31) is valid for $j_1 \gg 1$, $\kappa \gg 1$ and $j_1^2 \gg \kappa$ as well. Thus, one can conclude that formula (29) is applicable not only for $\kappa \ll 1$ and any j_1 , but also for $j_1 \gg 1$ and (not only small) κ values satisfying the $\kappa \ll j_1^2$ condition.

The behaviour of $c_1(x)$, $c_2(x)$ functions for $j_1 \gg 1$ and $\kappa \sim 1$ is shown in Fig. 1b.

6. THE CASE OF SMALL FLUXES OF SUBSTANCE A ($j_1 \ll 1$)

For $j_1 \ll 1$ and sufficiently small κ values, so that $j_1 \kappa \ll 1$, the flux of substance B is given by formula (26). Below we consider the cases with $\kappa \sim 1$ and $j_1 \kappa \gg 1$.

Since the characteristic scale of variation of function $c_1(x)$ is $\sim j_1 \ll 1$, we shall find c_1 , c_2 as expansions in j_1 , whose initial terms are:

$$c_1 = j_1 X \quad c_2 = Y + j_1 Z \quad (32)$$

where X , Y , Z are functions with the scale of variation of the order of unity. Substitution of (32) into (13), in the zero approximation and taking into account the boundary conditions, gives $Y = x$. In this case equation (12) becomes $d^2 X/dx^2 = j_1 x X$. Its solution, which satisfies (15), is a linear combination of Airy functions

$$c_1 = -\kappa^{-1/3} \frac{Bi(\sqrt[3]{\kappa}) Ai(\sqrt[3]{\kappa} x) - Ai(\sqrt[3]{\kappa}) Bi(\sqrt[3]{\kappa} x)}{Bi(\sqrt[3]{\kappa}) Ai'(0) - Ai(\sqrt[3]{\kappa}) Bi'(0)} \quad (33)$$

Now, taking into account the linear relation between c_1 and c_2 (17), the flux j_2 can be found:

$$j_2 = \left. \frac{dc_2}{dx} \right|_{x=0} = 1 - j_1 + c_1(0) = 1 - j_1(1 - X(0)) \\ = 1 - j_1 \left[1 + \kappa^{-1/3} \frac{Ai(0)(Bi(\sqrt[3]{\kappa}) - \sqrt{3} Ai(\sqrt[3]{\kappa}))}{Ai'(0)(Bi(\sqrt[3]{\kappa}) + \sqrt{3} Ai(\sqrt[3]{\kappa}))} \right] \quad (34)$$

Using the leading terms of asymptotic expansions of the Airy functions one can see that (34) transforms into (26) for $\kappa \ll 1$. For high reaction rates, $\kappa \gg 1$, the solution of the problem corresponds to the existence of a boundary layer near $x = 0$. In this case $dc_1(1)/dx \ll 1$, and the solution is found by use of the method that is

described above for the case of the boundary layer at $x = 1$. The result here coincides with the expression for flux j_2 derived from (34) at $j_1 \gg 1$.

$$j_2 = 1 - j_1 \left[1 + \kappa^{-1/3} \text{Ai}(0) / \text{Ai}'(0) \right] \quad (35)$$

Thus, formula (34) is valid for $j_1 \ll 1$ and for any value of κ .

7. HIGH REACTION RATES ($\kappa \gg 1$)

In considering this case we shall distinguish two situations: $j_1 < 1$ and $j_1 > 1$.

Let $j_1 < 1$. At high reaction rates substance A^* has time enough to react almost completely with substance B near the electrode. The boundary layer is formed near the electrode surface, where $c_1 \cdot c_2$ has a sharp maximum, since $c_2(0) = 0$, and then, after the maximum, $c_1(x)$ decreases exponentially, since all substance A^* reacts near the electrode. It is this limiting case, which corresponds to hidden limiting currents considered in ref. 2, where the flux of substance B to the electrode in the limit of $k = \infty$ was supposed to be equal to $(1 - j_1)$.

We shall assume that for $\kappa \gg 1$ the flux of substance B to an electrode differs from $(1 - j_1)$ by a small value δ :

$$j_2 = 1 - \kappa + \delta \quad (36)$$

Then, taking into account (15), the relation between c_1 and c_2 becomes

$$c_2 = c_1 + (1 + \delta)(x - x_0) \quad (37)$$

where $x_0 = \delta / (1 + \delta) \approx \delta$. In the limit of $\kappa \rightarrow \infty$, $\delta = 0$, $c_2(x) = x$, $c_1(x) = 0$.

The solutions will be sought in the form of

$$c_1 = X^-, \quad c_2 = Y^- \quad \text{for } 0 < x \leq x_0$$

$$c_1 = X^+, \quad c_2 = Y^+ \quad \text{for } x_0 \leq x < 1$$

For $x \gg x_0$ one can neglect c_1 in (30) and obtain the equation for X^+ :

$$\frac{d^2 X^+}{dx^2} = \kappa(x - x_0) X^+$$

whose solution, satisfying (15), is given by the expression:

$$X^+ = s_1 \left[\text{Ai} \left(\sqrt[3]{\kappa} (x - x_0) \right) - \text{Bi} \left(\sqrt[3]{\kappa} (x - x_0) \right) \cdot \text{Ai} \left(\sqrt[3]{\kappa} \right) / \text{Bi} \left(\sqrt[3]{\kappa} \right) \right]$$

Note that at $x \approx x_0$ the second term in the expression for X^+ is exponentially small compared to the first one and can thus be neglected. Function Y^+ corresponding to X^+ , is found from (37):

$$Y^+ = (1 + \delta)(x - x_0) + s_1 \text{Ai} \left(\sqrt[3]{\kappa} (x - x_0) \right)$$

In the $x \leq x_0$ region $c_2 \sim x$, and $s_1 \sim \delta \approx x_0$. Therefore, neglecting c_1 compared to the second term in (37), one arrives at the following equation for Y^- :

$$\frac{d^2 Y^-}{dx^2} = \kappa(x_0 - x) Y^-$$

The solution of this equation is a linear combination of Airy functions:

$$X^+ = s_5 \text{Ai}(\sqrt[3]{\kappa}(x_0 - x)) - s_6 \text{Bi}(\sqrt[3]{\kappa}(x_0 - x)) \quad (38)$$

The relation between s_5 and s_6 is found by using the boundary conditions (15) and conditions of matching the solutions. The matching conditions for Y^- and Y^+ are as follows:

$$Y^- \Big|_{x=x_0} = Y^+ \Big|_{x=x_0} \quad \frac{dY^-}{dx} \Big|_{x=x_0} = \frac{dY^+}{dx} \Big|_{x=x_0}$$

Upon determining coefficients s, s_5, s_6 from (36) and (38), one obtains the equation for δ :

$$2\pi \text{Ai}'(0) \text{Bi}(\sqrt[3]{\kappa} \delta) = [1 + \delta - j_1]^{-1} \quad (39)$$

The value of δ , determined by equation (39), has the order of $\kappa^{-1/3}$ for values of j_1 not close to unity. When $j_1 \ll 1$ formula (35) can be obtained from (39) and (36).

It can be readily seen that for $1 - j \ll 1$ and $\sqrt[3]{\kappa} \delta \gg 1, j_2 = 1 - j_1 \ll 1$. Thus, equation (36) given an accurate solution for small fluxes of reactant A $j_1 \ll 1$ and for all values $j_1 < 1$ and $\kappa \gg 1$.

Now we shall turn to the situation where $\kappa \gg 1, j_1 > 1$. In contrast to the case of $j_1 \gg 1$ considered above, the boundary layer arises here at some intermediate point θ inside the $0 < x < 1$ region, rather than at the right-hand boundary $x = 1$.

We shall seek the solution of the problem in the form of first terms of the expansion in a small parameter κ^{-1} :

$$c_1 = X + \kappa^{-1}Y, \quad c_2 = Z + \kappa^{-1}U \quad (40)$$

where $X, Y, Z, U = 1$. In the zero approximation, $X \cdot Z = 0$ except in the vicinity of the point $\delta = 1 - 1/j_1$; then the equation and boundary conditions are satisfied by the functions

$$\begin{aligned} X = j_1(\theta - x) \quad Z = 0 \quad \text{for } x \leq \theta \\ X = 0, \quad Z = j_1(x - \theta) \quad \text{for } x \geq \theta \end{aligned} \quad (41)$$

In the vicinity of $x = \theta$ the reaction zone is concentrated, localized to where substance B enters the reaction with substance A*. Only a small portion of substance B reaches the electrode: $j_2 = \delta \ll 1$. To find θ we shall seek the solution in the form that follows from (40) and (41):

$$\begin{aligned} c_2 = Y^- \quad c_1 = X^- = Y^- + j_1(\theta - x) \quad \text{for } x \leq \theta \\ c_1 = X^+ \quad c_2 = Y + j_1(x - \theta) \quad \text{for } x \geq \theta \end{aligned} \quad (42)$$

where $Y^-, X^+ - j_1^{-1} \ll 1$. The algorithm for finding the solution is analogous to that described above. If sufficiently far removed from point $x = \theta, Y^-$ or X^+ in (37) can be neglected, to give Airy equations in each of two regions and so the coefficients in the linear combination of Airy functions from the boundary conditions and from

conditions of matching of Y^- and Y^+ functions and of their derivatives at $x=0$ can be found. As a result, one obtains:

$$j_2 = \delta = j_1 \text{Ai}' \left[\sqrt[3]{\kappa j_1} (1 - 1/j_1) \right] / \text{Ai}(0) \quad (43)$$

In obtaining (43) it was assumed that $(j_1 - 1)\kappa \gg 1$, $j_1 \ll \kappa$, i.e. that the point θ is not too close to the ends of the interval $\theta \gg \delta$, $1 - \theta \gg \delta$. If one assumes, however, that $1 - \theta \ll \delta$, then j_2 is given by formula (31). When $\theta \ll 1$ the flux $j_2 = 0$.

The profiles of the concentrations $c_1(x)$, $c_2(x)$ when $\kappa \gg 1$, $j_1 = 1$ are shown in Fig. 1c,d.

8. NUMERICAL SOLUTION OF THE PROBLEM

To describe completely the behaviour of a limiting flux of substance B for arbitrary values of κ and j_1 the set of equations (12)–(15) was solved numerically.

The solution was found as follows: It follows from relation (17) at $x=0$, that

$$c_1(0) = c_2(0) + j_1 - 1 \quad (44)$$

Substituting (44) into (17):

$$c_2 = c_1 + c_1(0)(x - 1) + x \quad (45)$$

Using (45), equation (12) is transformed to:

$$\frac{d^2 c_1}{dx^2} = \kappa c_1 [c_1 + c_1(0)(x - 1) + x] \quad (46)$$

Equation (46) with boundary conditions $c_1(1) = 0$, $c_1(0) = \tau$ was solved numerically by the method of linearization and sweep.

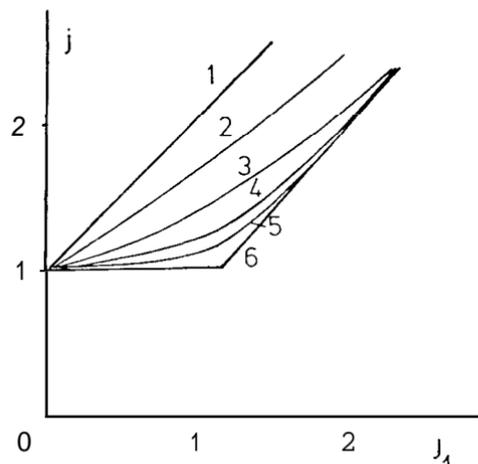


Fig. 2. Dependence of the dimensionless total flux on the dimensionless flux j_1 , for values of κ : (1) $\kappa = 0$, (2) $\kappa = 1$, (3) $\kappa = 10$, (4) $\kappa = 100$, (5) $\kappa = 1000$, (6) $\kappa = \infty$.

TABLE 1

Approximate analytical formulae^a for the dependence of flux j_2 on j_1 for different ranges of j_1 and values of κ

j_1	κ		
	$\ll 1$	~ 1	$\gg 1$
$\ll 1$	(26)	(34)	(35)
~ 1	(26)	Computer numerical solutions	$j_1 \leq 1$ (36),(39) $j_1 \geq 1$ (43)
$\gg 1$	(24)	(31) $j_1^2 \gg \kappa > 1$	(43) $j_1 \ll \kappa$ (31) $j_1^2 \ll \kappa$

^a An arrow indicates that the corresponding formula can be obtained as a particular limiting case from the more general formula.

From the solution the values of $j_1 = dc_1/dx|_{x=0}$ and j_2 (the limiting flux of substance) B as functions of τ were found; therefore, the unknown dependence $j_2(j_1, \kappa)$ was found in the parametric form. The calculated values of the total flux $J = j_1 + j_2$ of substances A and B to the electrode are presented in Fig. 2 for some values of κ . The family of curves j_1 shows the degree to which the reaction rate κ influences the resulting kinetics of the process. The $\kappa = \infty$ limit, considered previously [2], corresponds to $j = 1$ for $j_1 < 1$ and to $J = j_1$ for $j_1 > 1$. This means that the asymptotes found for the solution represent the straight lines corresponding to the approximate Kemula and Grabowski theory. The hidden limiting current of substance B, which is difference in the current at $\kappa = 0$ and that at $\kappa > 0$, is given by $\Delta j = 1 - j_2$.

The analytical calculations obtained for different values of κ and j_1 are listed in Table 1.

9. CONCLUSIONS

The dependence of hidden limiting currents on j_1 , which was determined for a wide range of κ values (see Fig. 2), makes it possible to estimate the value of homogeneous reaction rate constant k , from the relevant experimental relationships. To find this value one should compare the experimental curve of the dependence of limiting current on current j_1 , i.e. on the composition of a solution with calculated curves and choose a value of κ that corresponds to the theoretical curve, which describes experimental data with the greatest accuracy.

Note that the asymptotes, which the calculated $j(j_1)$ relationships approach, are determined by the stoichiometry of processes (1) and (2). Thus, in analogy with the formulae described in ref. 2, the theory developed permits the stoichiometry of processes under consideration to be derived and allows the rate of a homogeneous reaction conjugating two parallel electrode processes to be found simultaneously.

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