

CONCERNING THE THEORY OF LATENT LIMITING DIFFUSION CURRENTS

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The paper theoretically examines parallel electrode processes occurring under conditions when the product of one of them is involved in a homogeneous reaction with a reactant of the other. As a result the limiting current of the second reaction depends on the current of the first, and an effect is seen which was called a "latent limiting current" by Kemula and Grabowski. The analytical and numerical calculations performed cover a wide range of parameters of the problem, and include the results of Kemula and Grabowski as a particular case for the limit of an infinitely high rate constant of the homogeneous reaction.

The phenomenon of latent limiting currents which is very common in voltammetry arises from the special features exhibited by parallel electrochemical reactions when the product of one of them irreversibly interacts with a reactant of the other reaction [1-3]. As a result of this interaction, the diffusional flux of the reactant in the second reaction depends on the rate of the first reaction, ie, the processes no longer are independent.

Suppose, for instance, that two substances A and B are present in the solution which are reduced at the electrode. We shall assume, to be specific, that B is reduced at more negative potentials:



In the terminology of [1], a latent limiting current of the first kind is observed for substance B when the reaction



occurs in the solution. This current is defined as the difference between the limiting currents observed in the absence (i_B) and presence (i_B') of substance A:

$$\Delta i = i_B - i_B'. \quad (4)$$

But a latent limiting current of the second kind, $\Delta i = i_A - i_A'$, is observed when the reaction



occurs in the solution.

The theoretical analysis of latent limiting currents performed in [1, 2] was concerned with the case where reactions (3) or (5) occur infinitely fast as compared to the rate of diffusional transport of the reactants and reaction products. In the present work a theory of latent diffusion currents is developed which does not employ the above assumption.

We restrict the discussion to latent limiting currents of the first kind (the problem of latent limiting currents of the second kind can be solved analogously), and shall in addition assume, for the sake of simplicity, that $p = q = 1$. Assuming that the processes to be discussed occur under conditions of excess base electrolyte when migration effects are unimportant* we can write the equations describing the concentration distributions of substance B and of the product A^* of reaction (1) in the diffusion layer as

$$D_{A^*} \frac{d^2 c_{A^*}}{d\xi^2} - K c_{A^*} c_B = 0, \quad (6)$$

$$D_B \frac{d^2 c}{d\xi^2} - K c_{A^*} c_B = 0. \quad (7)$$

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

One can assume for the boundary conditions that in the bulk solution the concentration of B:

$$c_B(\delta) = c_0, \quad (8)$$

and zero concentration of substance A^* :

$$c_{A^*}(\delta) = 0, \quad (9)$$

are given. Here δ is the diffusion-layer thickness, which is regarded as approximately the same for substances A^* and B. The condition of $c_B(0) = 0$ is fulfilled when the limiting current of substance B is attained. Moreover, at the electrode the value of $j_{A^*} = -j_A$ is given, where j_A is the flux of substance A, ie,

$$D_{A^*} \frac{dc_{A^*}}{d\xi} \Big|_{\xi=0} = -j_A \quad (10)$$

We change to dimensionless variables:

$$X = c_{A^*} D_{A^*} / c_0 D_B, \quad Y = c_B / c_0; \\ t = \xi / \delta; \quad \beta = K \delta^2 c_0 / D_{A^*}; \quad \kappa = j_A \delta / D_B c_0. \quad (11)$$

Then the system of Eqs. (6), (7) and the boundary conditions for them can be written as

$$\frac{d^2 X}{dt^2} = \beta X Y, \quad (12)$$

$$\frac{d^2 Y}{dt^2} = \beta X Y, \quad (13)$$

$$\frac{dX}{dt} \Big|_{t=0} = \dot{X}(0) = -\kappa, \quad X(1) = 0, \quad (14)$$

$$Y(0) = 0, \quad (15)$$

$$Y(1) = 1. \quad (16)$$

It will be our aim to find the relation between $\dot{Y}(0) = dY/dt \Big|_{t=0}$, which is the dimensionless limiting current of substance B, and κ , which is the dimensionless limiting current of substance A, for different values of the parameter β .

System (12) to (16) has no analytic solution in the general case. Below we shall present results obtained when investigating a number of limiting cases for which one can obtain approximate solutions of the problem (see Table 1), and also the results of a numerical calculation obtained by computer.

*The interaction of two kinetically unrelated electrode processes on account of migrational ion transport leads to the effect of migration-current exaltation; a theory of this effect was presented in [4-7].

TABLE 1. Approximate Analytic Relations for the Flux of Substance B, $Y(0)$, as a Function of κ

Parameter κ	Parameter β		
	$\ll 1$	~ 1	$\gg 1$
$\ll 1$	(21)	(27)	(28)
~ 1	(21)	numerical computer solutions	$\kappa \leq 1$ (29), (32) $\kappa \geq 1$ (36)
$\gg 1$	(20)	(24) $\kappa^2 \gg \beta > 1$	(24) $\kappa^2 \ll \beta$

Note. An arrow shows that the corresponding relation can be obtained as a particular limiting case of a more general relation.

1. The case of low reaction rates ($\beta \ll 1$). We shall assume that flux κ is sufficiently large ($\kappa \gg 1$) so that $\kappa\beta \sim 1$. Here function X has a characteristic scale of $X \sim \kappa$ while function $Y \sim 1$. Hence one can seek the solution of the problem in the form of an expansion in terms of parameter $1/\kappa$ where the first terms are $X = \kappa X_0 + X_1$ and $Y = Y_0 + Y_1$ and X_0, X_1, Y_0, Y_1 are functions having a scale of the order of unity.

Using boundary conditions (14) and (15) one can obtain a linear relation between X and Y from (12), (13):

$$X = Y + (\kappa + \dot{Y}(0))(1-t) - 1. \quad (17)$$

Substituting X and Y written in terms of X_0, X_1, Y_0, Y_1 and considering terms of the order of κ we obtain $X_0 = 1 - t$. Using (20) to (22) we can reduce Eq. (7) to the form of

$$\frac{d^2 Y_1}{dt^2} = \beta \kappa (1-t) Y_1. \quad (18)$$

A linear combination of Airy functions can be used as the solution of this equation:

$$Y_1 = S_1 \text{Ai}[q(1-t)] + S_2 \text{Bi}[q(1-t)], \quad (19)$$

where $q = \sqrt[3]{\beta \kappa}$, while S_1 and S_2 are constants. After determining S_1 and S_2 from boundary conditions (15), (16) and differentiating (19) we obtain the desired expression for the limiting current of substance B:

$$\dot{Y}(0) = - \frac{q}{\text{Ai}(0)} \frac{\text{Bi}(q) \text{Ai}'(q) - \text{Ai}(q) \text{Bi}'(q)}{\text{Bi}(q) - \text{Ai}(q) \sqrt{3}} \quad (20)$$

In the case of sufficiently small β when $q \ll 1$ one can employ the leading terms of asymptotic expansions of the Airy functions [8]. As a result, (20) can be reduced to

$$\dot{Y}(0) = 1 - \beta \kappa / 12. \quad (21)$$

Relation (21) can also be obtained directly from the original system (12) to (15) by writing the solution as an expansion in terms of the small parameter β : $X = X_0 + \beta X_1$ and $Y = Y_0 + \beta Y_1$ where X_0, X_1, Y_0, Y_1 are functions of the order of unity, and by assuming that $\beta \kappa \ll 1$. The behavior of $X(t)$ and $Y(t)$ defined by (19) and (17) is shown in Fig. 1. Thus, expression (20) is applicable at any κ and $\beta \ll 1$.

2. **The case of large fluxes of substance A*** ($\kappa \gg 1$). In the case of low reaction rates $\beta \ll 1$ and $\beta \kappa \sim 1$ functions $X(t)$ and $Y(t)$ vary smoothly throughout the range of $0 \leq t \leq 1$, but when $\beta \geq 1$ and $\beta \kappa \gg 1$ function $Y(t)$ varies very abruptly when $t \approx 1$, and throughout the remaining interval it varies smoothly and assumes values close to zero. In other words, at the boundary $t = 1$ of the diffusion layer a boundary layer is formed.

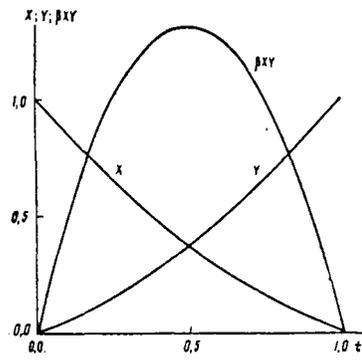


Fig. 1

Fig. 1. Functions $X(t)$, $Y(t)$, and $\beta X(t)Y(t)$ for $X(0) = 1$ and $\beta = 10$.

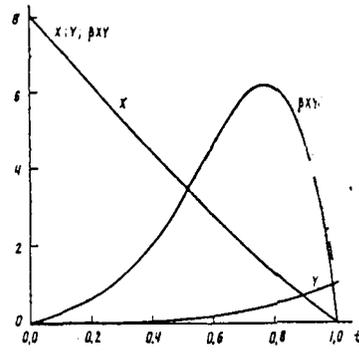


Fig. 2

Fig. 2. Functions $X(t)$, $Y(t)$, and $\beta X(t)Y(t)$ for $X(0) = 8$ and $\beta = 10$.

The relation between X and Y (17) can be written in the form of

$$X = Y + \kappa(1-t) - 1 = Y + \kappa(t^* - t), \quad (22)$$

where $t^* = 1 - 1/\kappa$, since in the case being discussed one has $\dot{Y}(0) = \varepsilon \ll 1$. Outside the narrow region close to $t = 1$ where $1 - t \gg 1/\kappa$ one can neglect the first term in (22). Then (13) changes to the equation

$$\frac{d^2 Y}{dt^2} = \beta \kappa (t^* - t) Y. \quad (23)$$

The linear combination of Airy functions

$$Y = S_1 \text{Ai}(q(t^* - t)) + S_2 \text{Bi}(q(t^* - t))$$

where $q = \sqrt[3]{\beta \kappa}$ serves as the solution of this equation.

After determining coefficients S_1 and S_2 from boundary conditions (15), taking into account that $(1 - t^*)q = \sqrt[3]{\beta/\kappa^2} \ll 1$ and $qt^* \approx \sqrt[3]{\beta \kappa} \gg 1$, and using the leading terms of asymptotic expansions of the Airy functions at high and low values of the argument [8] we obtain an expression for the limiting flux of substance B:

$$\dot{Y}(0) = -\frac{\dot{\sqrt[3]{\beta \kappa}}}{\text{Ai}(0)} \text{Ai}'(\dot{\sqrt[3]{\beta \kappa}}) = \frac{\dot{\sqrt[3]{\beta \kappa}}}{\pi \text{Ai}(0) \text{Bi}(\dot{\sqrt[3]{\beta \kappa}})}. \quad (24)$$

We point out that relation (24) is the particular case of (20) when $q \gg 1$. In deriving (24) we only employed the condition of $k^2 \gg \beta > 1$, hence (24) is fulfilled also for $\kappa \gg 1, \beta \gg 1, k^2 \gg \beta$. One can conclude, therefore, that relation (20) can be used, not only under conditions where $\beta \ll 1$ (and any κ) but also under conditions where $k \gg 1$ and the values of β are not low although they satisfy the condition of $\beta \ll k^2$.

The behavior of functions $X(t)$ and $Y(t)$ is shown in Fig. 2 for parameter values $\kappa \gg 1$ and $\beta \sim 1$.

3. The case of small fluxes of substance A* ($\kappa \ll 1$). For $\kappa \ll 1$ and values of β sufficiently low so that $\beta \kappa \ll 1$ the flux of substance B is given by relation (21). Below we shall discuss the cases of $\beta \sim 1$ and $\beta \gg 1$. Since the characteristic scale of change of function $X(t) \sim \kappa \ll 1$ we shall seek X and Y in the form of expansions in terms of the parameter κ where the first terms are of the form of

$$X = \kappa X_1, \quad Y = Y_0 + \kappa Y_1, \quad (25)$$

and X_1, Y_0, Y_1 are functions with a scale of change of the order of unity. Substituting (25) into (13) and allowing for the boundary conditions we obtain $Y_0 = t$. Then Eq. (12) becomes $d^2 X_1 / dt^2 = \beta t X_1$. The linear combination of Airy functions

$$X = -\beta^{-1/2} \frac{\text{Bi}(\sqrt[3]{\beta}) \text{Ai}(\sqrt[3]{\beta} t) - \text{Ai}(\sqrt[3]{\beta}) \text{Bi}(\sqrt[3]{\beta} t)}{\text{Bi}(\sqrt[3]{\beta}) \text{Ai}'(0) - \text{Ai}(\sqrt[3]{\beta}) \text{Bi}'(0)} \quad (26)$$

serves as its solution; it satisfies (15). Using now the linear relation (17) between X and Y we can find the flux of B:

$$\begin{aligned} \dot{Y}(0) &= 1 - \kappa + X(0) = 1 - \kappa (1 - X_1(0)) = \\ &= 1 - \kappa \left[1 + \beta^{-1/2} \frac{\text{Ai}(0)}{\text{Ai}'(0)} \frac{\text{Bi}(\sqrt[3]{\beta}) - \sqrt[3]{\beta} \text{Ai}(\sqrt[3]{\beta})}{\text{Bi}(\sqrt[3]{\beta}) + \sqrt[3]{\beta} \text{Ai}(\sqrt[3]{\beta})} \right]. \end{aligned} \quad (27)$$

Using the leading terms of asymptotic expansions of the Airy functions we can see that for $\beta \ll 1$ (27) changes into (21).

At high reaction rates $\beta \gg 1$ the solution of the problem implies that a boundary layer exists near $t = 0$. Then $X(1) \ll 1$ and the solution of the problem can be found via a scheme analogous to that described above for the boundary-layer case involving $t = 1$. The result obtained coincides with the expression following for the flux of substance B from (27) when $\beta \gg 1$:

$$\dot{Y}(0) = 1 - \kappa (1 + \beta^{-1/2} \text{Ai}(0) / \text{Ai}'(0)). \quad (28)$$

Thus, relation (27) is valid for $\kappa \ll 1$ and any values of β .

4. **High reaction rates** ($\beta \gg 1$). When discussing this case we shall distinguish the two situations of $\kappa < 1$ and $\kappa > 1$. Suppose that $\kappa < 1$. At high reaction rates ($\beta \gg 1$) practically all of substance A* can react with substance B near the electrode. At the electrode surface a boundary layer is formed where $Y(t)$ has a sharp maximum since $Y(0) = 0$, while beyond the maximum $Y(t)$ drops off exponentially since all of substance A* has reacted near the electrode. It is precisely this limiting case which corresponds to the discussion of latent limiting currents in [1] where it was assumed that in the limit of $\beta = \infty$ the flux of substance B at the electrode is given by $1 - \kappa$.

We shall assume that at $\beta \gg 1$ the flux of substance B to the electrode differs from $1 - \kappa$ by the small quantity ε :

$$\dot{Y}(0) = 1 + \varepsilon - \kappa. \quad (29)$$

Then the relation between X and Y is given (with (15)) by the expression

$$Y = X + (1 + \varepsilon) (t - t_*), \quad (30)$$

where $t_* = \varepsilon / (1 + \varepsilon) \approx \varepsilon$. In the limit of $\beta \rightarrow \infty$ one has $\varepsilon = 0$, $Y(t) = t$, and $X(t) = 0$.

We shall seek the solution in the form of

$$\begin{aligned} X &= X_-, \quad Y = Y_- \quad \text{for } 0 < t \leq t_*, \\ X &= X_+, \quad Y = Y_+ \quad \text{for } t_* \leq t < 1. \end{aligned}$$

At $t \gg t_*$ one can neglect X in (30), and obtain an equation for X_+ :

$$\frac{d^2 X_+}{dt^2} = \beta (t - t_*) X_+,$$

which has a solution satisfying (15) that is given by the expression

$$X_+ = S_1 \left[\text{Ai}(\sqrt[3]{\beta} (t - t_*)) - \text{Bi}(\sqrt[3]{\beta} (t - t_*)) \frac{\text{Ai}(\sqrt[3]{\beta})}{\text{Bi}(\sqrt[3]{\beta})} \right]$$

We point out that for $t \approx t_*$ the second term in the expression for X_+ is exponentially small as compared to the first, and can be neglected. The function Y_+ that corresponds to X_+ can be found from (30), and is given by

$$Y_+ = (1 + \varepsilon) (t - t_*) + S_1 \text{Ai}(\sqrt[3]{\beta} (t - t_*)).$$

In the region of $t \leq t_0$ one has $Y \sim t$ but $X \sim \varepsilon \approx t_0$. Hence when neglecting Y in (3) relative to the second term we arrive at the following equation for Y_- :

$$\frac{d^2 Y_-}{dt^2} = \beta(t-t_0) Y_-.$$

The linear combination of Airy functions

$$Y_- = S_3 \text{Ai}(\sqrt[3]{\beta}(t-t_0)) + S_4 \text{Bi}(\sqrt[3]{\beta}(t-t_0)) \quad (31)$$

serves as the solution of this equation. The relation between S_3 and S_4 can be found with the aid of boundary conditions (15) and the matching conditions for the solutions. The matching condition for Y_- and Y_+ is of the form of

$$Y_-|_{t=t_0} = Y_+|_{t=t_0}, \quad \frac{dY_-}{dt}|_{t=t_0} = \frac{dY_+}{dt}|_{t=t_0}.$$

After determining the coefficients $S_1, S_3,$ and S_4 from (29) and (31) we obtain the equation for ε :

$$\frac{1}{2\pi \text{Ai}'(0) \text{Bi}(\sqrt[3]{\beta\varepsilon})} = 1 + \varepsilon^{-\kappa}. \quad (32)$$

For values of κ not close to unity, the value of ε which is determined by Eq. (32) is of the order of $\beta^{-1/3}$. In the particular case of $\kappa \ll 1$ one can obtain relation (28) from (32) and (29). One can readily see that for $1 - \kappa \ll 1$ one has $\sqrt{\beta\varepsilon} \gg 1$ $Y(0) = 1 - \kappa \ll 1$. Thus, (29) yields the correct solution for small fluxes of substance A^* when $\kappa \ll 1$, and at all values of $\kappa < 1$ when $\beta \gg 1$.

We shall now turn to the situation where $\beta \gg 1$ and $\kappa > 1$. In contrast to the case of $\kappa \gg 1$ considered above, the boundary layer here does not arise at the right-hand boundary $t = 1$ of the region but at some intermediate point t_0 within the region $0 < t < 1$.

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

$$X = X_0 + \beta^{-1} X_1, \quad Y = Y_0 + \beta^{-1} Y_1, \quad (33)$$

where $X_0, X_1, Y_0, Y_1 \sim 1$. In the zeroth approximation we have $X_0 Y_0 = 0$ everywhere except in the vicinity of point $t_0 = 1 - 1/\kappa$, hence the equation and the boundary conditions are satisfied by the function

$$\begin{aligned} X_0 &= \kappa(t_0 - t); \quad Y_0 = 0 \quad \text{for } t \leq t_0, \\ X_0 &= 0; \quad Y_0 = \kappa(t - t_0) \quad \text{for } t \geq t_0. \end{aligned} \quad (34)$$

The reaction zone where substance B reacts with substance A^* is centered around $t = t_0$. Only a small part of substance B reaches the electrode: $Y(0) = \varepsilon \ll 1$. To find ε we shall seek the solution in the form that follows from (33) and (34):

$$\begin{aligned} Y &= Y_-; \quad X = X_- = Y_- + \kappa(t_0 - t) \quad \text{for } t \leq t_0; \\ X &= X_+; \quad Y = Y_+ = X_+ + \kappa(t - t_0) \quad \text{for } t \geq t_0, \end{aligned} \quad (35)$$

where $Y_-, X_+ \sim \beta^{-1} \ll 1$. The scheme to be used for finding the solution is entirely analogous to that described above. Sufficiently far from the point $t = t_0$ one can neglect Y_- or X_+ in (30), obtain the Airy equation in each of the two regions, and find the coefficients in the linear combination of Airy functions from the boundary conditions and the conditions for matching of functions Y_- and Y_+ as well as of the derivatives of these functions for $t = t_0$. As a result we obtain

$$Y(0) = \varepsilon = \frac{\chi}{\text{Ai}'(0)} \text{Ai}'(\sqrt[3]{\beta\kappa}(1 - 1/\kappa)). \quad (36)$$

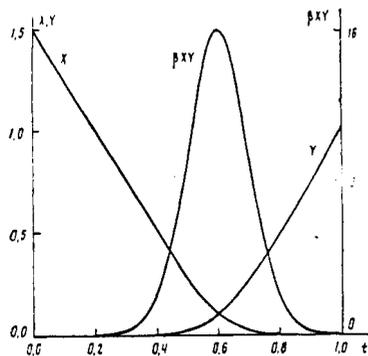


Fig. 3

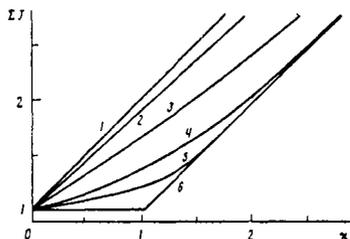


Fig. 4

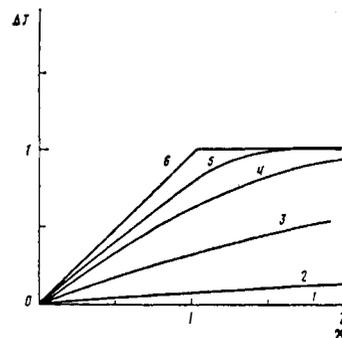


Fig. 5

Fig. 3. Functions $X(t)$, $Y(t)$, and $\beta X(t)Y(t)$ for $X(0) = 1.5$ and $\beta = 1000$.

Fig. 4. ΣI as a function of n for values of parameter β of: 1) 0, 2) 1, 3) 10, 4) 100, 5) 1000, and 6) ∞ .

Fig. 5. Latent limiting currents as functions of κ for values of parameter β of: 1) 0, 2) 1, 3) 10, 4) 100, 5) 1000, and 6) ∞ .

It was assumed when obtaining (36) that $(\kappa - 1)\beta \gg 1$ and $\kappa \ll \beta$, ie, that point t_0 is located not too close to the ends of the interval of $t_0 \gg \varepsilon$ and $1 - t_0 \gg \varepsilon$. But if it is assumed that $1 - t_0 \ll \varepsilon$ one can see that $Y(0)$ is given by relation (24). In the case of $t_0 \ll 1$ one has $Y(0) \approx 0$.

The concentration profiles $X(t)$ and $Y(t)$ for the case of $\beta \gg 1$ and $\kappa \sim 1$ are shown in Fig. 3.

5. Numerical solution of the problem. The system (12) to (15) was solved numerically in order to obtain the full picture of behavior of the limiting flux of substance B at arbitrary values of parameters β and n . The solution scheme was set up as follows. It follows from relation (17) for $t = 0$ that

$$X(0) = Y(0) + \kappa - 1. \quad (37)$$

Substituting (37) into (17) we have

$$Y = X + X(0) (t-1) + t. \quad (38)$$

Using (38), we can transform (12) to read

$$d^2 X / dt^2 = \beta X (X + X(0) (t-1) + t). \quad (39)$$

Equation (39) with boundary conditions $X(1) = 0$ and $X(0) = \gamma$ was solved numerically by the method of linearization and sweep [9, 10]. From the solution we found the values of $X(0) = -\gamma$ and $Y(0)$, ie, the limiting flux of substance B, which were functions of γ , hence we found the desired function $Y(0) (n, \beta)$ in parametric form. The calculated functions of total flux $\Sigma I = n + Y(0)$ of substances A and B to the electrode are presented in Fig. 4 for a number of values of the parameter β . The family of curves ΣI shows the degree of influence exerted by the reaction rates β on the resulting reaction kinetics. The limit of $\beta = \infty$ discussed in [1-3] corresponds to $\Sigma I = 1$ when $\kappa < 1$ and to κ when $\kappa > 1$. The latent limiting current of substance B which is the difference between the currents at $\beta = 0$ and $\beta \neq 0$ is given by the relation $\Delta I = 1 - Y(0)$ and shown as a function of n in Fig. 5.

6. Conclusion. The above calculations of the latent limiting currents as functions of parameter κ which were performed for a wide range of values of β make it possible to estimate homogeneous rate constant K from the corresponding experimental functions. To find this constant one must compare the experimental plot of overall current against solution composition with the calculated curves, and select the value of β which corresponds to the theoretical curve that most accurately describes the experimental data.

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