

Ionic transport by diffusion and migration is analyzed theoretically for reduction of cations occurring in parallel with the reduction of molecular oxygen while allowing for the recombination of  $\text{OH}^-$  and  $\text{H}^+$  ions in the diffusion layer. It is shown that qualitatively different types of behavior of the system being discussed are possible depending on the relative concentrations of the cations undergoing discharge and of the  $\text{H}^+$  ions in the solution. It was discovered that under certain conditions the cations may exhibit an unusual limiting diffusion and migration current because their concentration has fallen to zero inside the diffusion layer.

An effect of migration current exaltation can be observed when cations and a neutral substance are reduced in parallel; then the limiting current of the first process increases with increasing current of the second process [1-3]. The theory of this effect was developed in [4-6]. A physically related effect of increasing limiting currents is observed when cations of two or more different kinds are reduced in parallel; this has become known as correlational exaltation of migration currents [5, 7].

It has been assumed in [4] when developing a theory for the effect of migration current exaltation that the reduction products of the neutral substance are not present in the bulk solution. In oxygen reduction according to the scheme of



these products are the  $\text{OH}^-$  ions. In [8] a theory of migration current exaltation was developed where it was taken into account that owing to water dissociation in the solution a very small but finite concentration of  $\text{H}^+$  ions is present and that these ions can recombine with the  $\text{OH}^-$  ions as the products of oxygen reduction.

It was the aim of the present work to theoretically analyze cation reduction and reduction of oxygen dissolved in water as processes occurring in parallel at arbitrary values of solution pH. The  $\text{OH}^-$  ions produced by  $\text{O}_2$  reduction then should recombine with the  $\text{H}^+$  ions in the diffusion layer. At low  $\text{H}^+$  ion concentrations in the solution the resulting process is expected to be very similar to that observed in migration current exaltation. In the other limiting case where the  $\text{H}^+$  ion concentration in the solution is high one can expect that practically all  $\text{OH}^-$  ions will react with  $\text{H}^+$  directly at the electrode surface, so that the resulting oxygen reduction reaction will be



Then we have the parallel reduction of solution cations and  $\text{H}^+$  ions which is described by the theory of correlational migration current exaltation. At intermediate  $\text{H}^+$  ion concentrations in the solution one expects a changeover from the situation described by the effect of migration current exaltation to that described by correlational migration current exaltation.

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The system of electrodiffusion equations describing the reduction of cations  $A^+$  according to



and parallel reduction of oxygen according to reaction (1) with subsequent recombination of the  $OH^-$  with  $H^+$  within the Nernst diffusion layer, is given by

$$\frac{dc_1}{dx} - c_1 \mathcal{E} = \frac{I_1 L}{ED_1 c^0} = j_{1x} \quad (4)$$

$$\frac{dc_2}{dx} + c_2 \mathcal{E} = 0, \quad (5)$$

$$\frac{d^2 c_3}{dx^2} + \frac{d}{dx} (c_3 \mathcal{E}) = \frac{L^2 c^0 K}{D_3} (c_3 c_4 - K_0), \quad (6)$$

$$\frac{d^2 c_4}{dx^2} - \frac{d}{dx} (c_4 \mathcal{E}) = \frac{L^2 c^0 K}{D_4} (c_3 c_4 - K_0), \quad (7)$$

$$c_2 + c_3 = c_1 + c_4. \quad (8)$$

Here  $c_1, c_2, c_3, c_4$  are the concentrations of cations  $A^+$ , anions,  $OH^-$  ions, and  $H^+$  ions made dimensionless through the  $A^+$  ion concentration  $c^0$  in the bulk solution (we assume, for the sake of simplicity, that the ions present in the system are univalent),  $\mathcal{E} = -d\Psi/dx = -F/RT \cdot dE/dx$  is the dimensionless electric field,  $x$  is the dimensionless coordinate ( $0 \leq x \leq 1$ ),  $L$  is the thickness of the Nernst diffusion layer,  $D_i$  are the diffusion coefficients of the corresponding components,  $I_1$  is the current of cation discharge,  $F$  is the Faraday constant,  $K$  is the rate constant of recombination of the  $H^+$  and  $OH^-$  ions, and  $K_0$  is the equilibrium constant of water dissociation made dimensionless through  $(c^0)^2$ . Equation (8) is a statement of the condition of local electroneutrality.

The boundary conditions for  $x = 1$  (the boundary between the diffusion layer and the bulk solution) are

$$c_1(1) = 1, \quad c_2(1) = 1 + k, \quad c_3(1) = 0, \quad c_4(1) = k. \quad (9)$$

Combining (6) and (7) one can obtain

$$D_3 \left( \frac{dc_3}{dx} + c_3 \mathcal{E} \right) - D_4 \left( \frac{dc_4}{dx} - c_4 \mathcal{E} \right) = - \frac{I_2 L}{F c^0} \quad (10)$$

Here  $I_2$  is the current of oxygen reduction.

We now take into account that the rate constant of recombination of the  $H^+$  and  $OH^-$  ions is extremely high, so that at any point of the diffusion layer one can assume equilibrium with respect to the dissociation and recombination of water:

$$c_3 c_4 = K_0. \quad (11)$$

We shall assume in addition that the equilibrium constant itself when made dimensionless through  $(c^0)^2$  is much smaller than unity. For instance for  $c^0 = 0.1$  M the value of  $K_0 = 10^{-12}$ . Hence instead of relation (11) one can highly accurately use the equality of  $c_3 c_4 \approx 0$ . In the region to the left of  $x = \theta$  (the "point" of recombination of the  $H^+$  and  $OH^-$  ions) one then has  $c_3 > 0$  and  $c_4 \approx 0$  while in the region to the right of  $x = \theta$  one can assume that  $c_4 > 0$  and  $c_3 \approx 0$ . Using these approximations one can change from Eqs. (10) and (11) to the two equations

$$\frac{dc_3}{dx} + c_3 \mathcal{E} = - \frac{I_2 L}{F D_3 c^0} = - j_2, \quad 0 < x < \theta, \quad (12)$$

$$\frac{dc_4}{dx} - c_4 \mathcal{E} = \frac{I_2 L}{F D_4 c^0} = j_2 \nu, \quad \theta < x < 1, \quad (13)$$

where  $\nu = D_3/D_4$ . We mention that the dimensionless fluxes  $j_1$  and  $j_2$  introduced in (4) and (12) are positive.

Thus, the original system of electrodiffusion equations (4) to (8) has been resolved into two simpler systems of first-order equations. In the region of  $0 < x < \theta$  the system of equations is given by relations (4), (5), (12), and (8), and coincides with the system used to describe the effect of migration current exaltation. In the region of  $\theta < x < 1$  the system of equations is given by relations (4), (5), (13), and (8) and coincides with the system used to describe the effect

of correlational migration current exaltation.

In the point of  $x = \theta$  all concentrations  $\mathbf{c}_i$  should be continuous. The point  $\theta$  itself can be found simultaneously with the solution of the system of electrodiffusion equations. According to what has been said above, its position should depend, both on the values of currents  $\mathbf{I}_1$  and  $\mathbf{I}_2$  and on the parameters  $\nu$  and  $k$ , ie, on the  $\text{H}^+$  ion concentration in the solution. As the latter is raised the point  $x = \theta$  should move closer to the electrode, and at sufficiently high  $\text{H}^+$  concentrations when reaction (1) is replaced by reaction (2)  $\theta$  should become zero.

We start our inquiry with the case where the point  $x = \theta$  is located in the interval  $(0, 1)$ . We shall find the concentration distributions  $\mathbf{c}_1(x)$ ,  $\mathbf{c}_2(x)$ ,  $\mathbf{c}_3(x)$ , and  $\mathbf{c}_4(x)$  in the two regions  $0 < x < \theta$  and  $\theta < x < 1$ .

The concentration distribution  $\mathbf{c}_2(x)$  in region  $\theta < x < 1$  is readily obtained by addition and subsequent integration of Eqs. (4), (5), and (8) while allowing for boundary conditions (9):

$$\mathbf{c}_2 = (j_1 + \nu j_2)(x-1)/2 + 1 + k. \quad (14)$$

Using (14) we find from Eq. (5)

$$\mathcal{E} = - \frac{j_1 + \nu j_2}{2(1+k) + (j_1 + \nu j_2)(x-1)}. \quad (15)$$

Substituting (15) into (4) and integrating the resulting linear equation while allowing for (9) we obtain the cation distribution  $\mathbf{c}_1(x)$  in the region of  $\theta < x < 1$ :

$$\mathbf{c}_1 = \frac{1 - j_1(1+k)/(j_1 + \nu j_2)}{(x-1)(j_1 + \nu j_2)/(1+k) + 2 + 1} + \frac{j_1(1+k)}{j_1 + \nu j_2} \left[ (x-1) \frac{j_1 + \nu j_2}{2(1+k)} + 1 \right]. \quad (16)$$

The concentration distribution  $\mathbf{c}_4(x)$  in the same region follows from the electroneutrality condition (8) and the condition of  $\mathbf{c}_3(x > \theta) = 0$ . For  $x = \theta$  the values of concentrations  $\mathbf{c}_1$  and  $\mathbf{c}_2$  given by relations (14) and (16) assume identical values of

$$\mathbf{c}_1(\theta) = G, \quad \mathbf{c}_2(\theta) = G \quad (17)$$

because of the condition of  $\mathbf{c}_3(\theta) = \mathbf{c}_4(\theta)$  mentioned above.

When finding the concentration distributions  $\mathbf{c}_i(x)$  in the region of  $0 < x < \theta$  we shall use the continuity relations

$$\mathbf{c}_1(\theta-0) = \mathbf{c}_1(\theta+0) = G, \quad \mathbf{c}_2(\theta-0) = \mathbf{c}_2(\theta+0) = G \quad (18)$$

as boundary conditions at  $x = \theta$ . The two conditions (17) represent a system of equations from which one can determine the unknown quantities  $\theta$  and  $G$ :

$$G = \sqrt{(1+k)(1-j_1 k/\nu j_2)}, \quad (19)$$

$$\theta = 1 - 2(1+k) \left[ 1 - \sqrt{(1-j_1 k/\nu j_2)/(1+k)} \right] / (j_1 + \nu j_2). \quad (20)$$

The solution of the system of Eqs. (4), (5), (8), and (12) with boundary conditions (18) in region  $0 < x < \theta$  can be found by a method similar to that used in [4], and is given by the relations

$$\mathbf{c}_1 = (j_1 - j_2)(x-\theta)/2 + G, \quad (21)$$

$$\mathcal{E} = - \frac{j_1 + j_2}{(j_1 - j_2)(x-\theta) + 2G}, \quad (22)$$

$$\mathbf{c}_2 = G \left[ (j_1 - j_2)(x-\theta)/2G + 1 \right]^{(j_1 + j_2)/(j_1 - j_2)}. \quad (23)$$

The distributions of all component concentrations and of potential in the full coordinate region of  $0 \leq x \leq 1$  are given by relations (14) to (16), (18) to (23), and (8) when

$$\nu j_2 \geq k j_1, \quad (24)$$

and

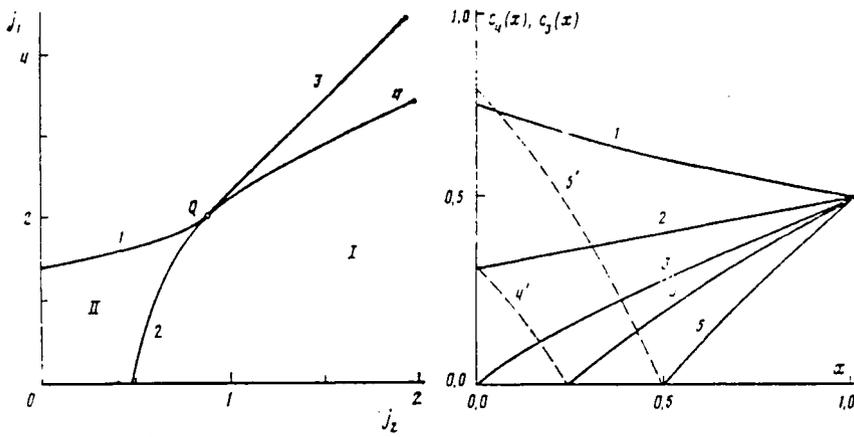


Fig. 1

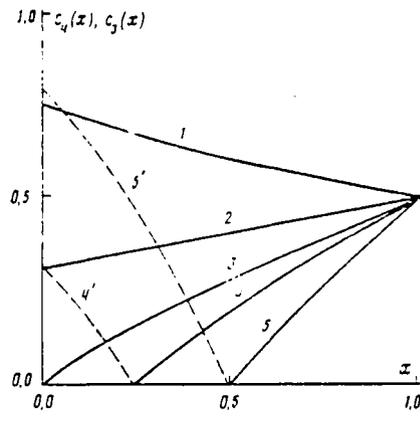


Fig. 2

Fig. 1. The regions of different behavior of the system in the plane of  $j_1$  and  $j_2$  for  $k < \nu$ : 1) the curve of  $j_1^{\ell}(j_2)$  defined by relation (28); 2) the curve for  $\theta = 0$  defined by relation (27); 3) the straight line for  $G = 0$  defined by relation (31); and 4) the curve of  $j_1^{\ell 0}(j_2)$  defined by relation (30).

Fig. 2. Concentration distributions  $c_4(x)$  (curves 1 to 5) and  $c_3(x)$  (curves 4' and 5'). Curves 1 and 2 correspond to region II, curves 4, 4', 5, and 5' correspond to region I, and curve 3 corresponds to the condition of  $\theta = 0$ .

$$0 \leq \theta \leq 1, \quad (25)$$

$$c_i(x) \geq 0 \text{ for } 0 \leq x \leq 1. \quad (26)$$

We point out that inequality (24) must be fulfilled, both for the existence of  $G$  (see (19)) and for the existence of  $\theta$  (see (20)). It is readily seen that the condition of  $\theta \leq 1$  imposes no additional limitations upon the parameters  $\nu$ ,  $k$ ,  $j_1$ ,  $j_2$ . At fixed  $j_2$ , the value of  $\theta$  defined by relation (20) generally will decrease with increasing  $j_1$ . The condition of  $\theta = 0$  leads to the following relation between  $j_1$  and  $j_2$ :

$$j_1 = \nu j_2 (1 - (1+k)(2k/\nu j_2 - 1)^2) / k. \quad (27)$$

Allowing for inequality (24) has the effect that  $j_1$  in (27) can vary within the limits of  $0 \leq j_1 \leq 2$ . Quantity  $\nu j_2$  in (27) then changes from the value of  $\nu j_2 = 2\sqrt{1+k}(\sqrt{1+k} - 1)$  which is found for  $j_1 = 0$  to the value of  $\nu j_2 = 2k$  when  $j_1 = 2$ . In the plane of  $(j_2, j_1)$ , the condition of  $0 < \theta \leq 1$  corresponds to region I in Fig. 1 which is located to the right of the curve  $j_1(j_2)$  defined by relation (27).

Consider now in more detail the situation when oxygen reduction follows the scheme (2), and  $\text{OH}^-$  ions are not present in the diffusion layer. Then the distributions of  $c_1$ ,  $c_2$ ,  $c_4$ , and  $\mathcal{E}$  throughout the region of  $0 \leq x \leq 1$  are described by Eqs. (4), (5), (13), and (8) and boundary conditions (9), the solutions of which are given by relations (14), (16), and (8). The values of surface concentrations  $c_1(0)$  and  $c_4(0)$  depend, both on parameters  $\nu$  and  $k$  and on the values of currents  $j_1$  and  $j_2$ . One can assume, in accordance with the generally adopted definition of limiting currents, that the limiting current,  $j_1^{\ell}$ , of cation reduction corresponds to the condition of  $c_1(0) = 0$ . This current depends on current  $j_2$  of parallel oxygen reduction. The dependence of  $j_1^{\ell}$  on  $j_2$  follows from (16) and the condition of  $c_1(0) = 0$ , and is given by the relation [7]:

$$j_1^{\ell} = \frac{2(1+k)}{1 + \nu j_2 / j_1} \left( 1 - \sqrt{\frac{k - \nu j_2 / j_1^{\ell}}{1+k}} \right) \quad (28)$$

shown in Fig. 1. At  $j_2 = 0$ , the curve of  $j_1^{\ell}(j_2)$  issues from the point of

$$j_1^{\ell} = 2(1+k) (1 - \sqrt{1 - 1/(1+k)}),$$

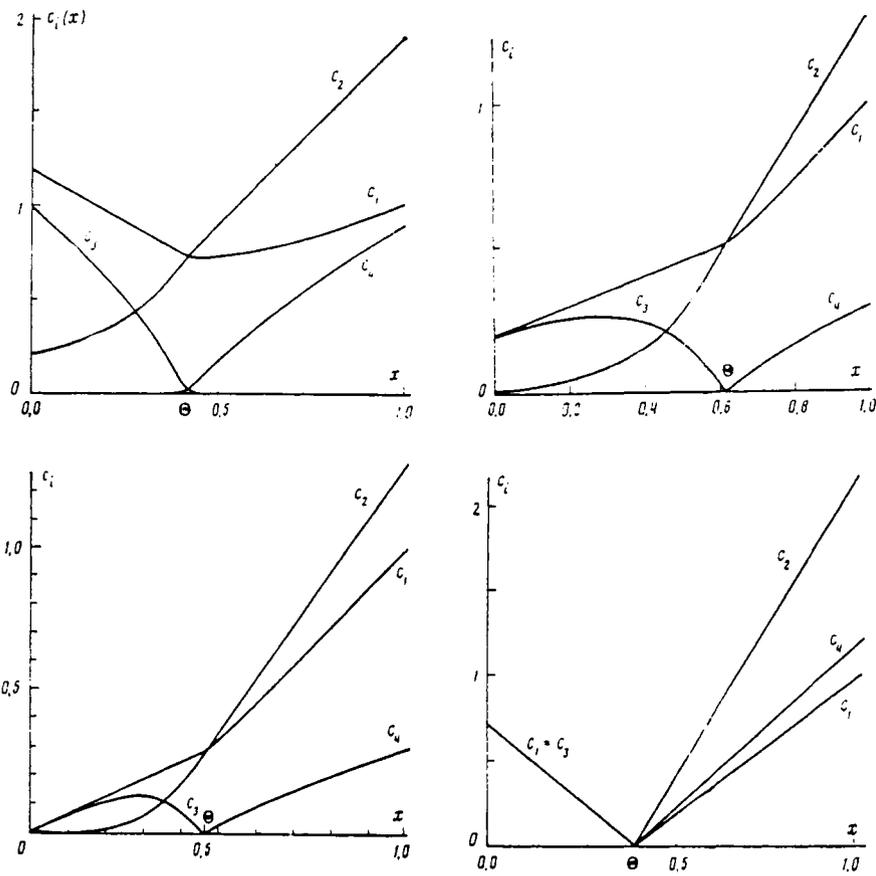


Fig. 3. Different types of distribution of the ionic component concentrations corresponding to region I in Fig. 1: a) current  $j_1$  lower than the limiting value and  $c_1(0) > G$ ; b) current  $j_1$  lower than the limiting value and  $c_1(0) < G$ ; c) current  $j_1$  equal to the limiting value while  $c_1(0) = 0$ ; and d) current  $j_1$  equal to the limiting value while  $c_1(\theta) = 0$ .

which corresponds to Eucken's relation [9], and when  $\nu j_2/k = 2$  goes through the point Q where  $j_1^L = 2$  and where it links up with the curve (27) and the straight line of  $j_1 = \nu j_2/k$ . For  $j_1 < j_1^L$  and  $c_4(0) > 0$  the system's behavior corresponds to region II in the plane of  $j_1$  and  $j_2$  in Fig. 1. Concentration  $c_4(0)$  decreases with increasing current  $j_2$  when current  $j_1$  is constant (see Fig. 2, curves 1 and 2). When the condition of  $c_4(0) = 0$  is fulfilled, which is readily seen to coincide with the condition of  $\theta = 0$  (curve 3 of Fig. 2), we reach the right-hand boundary of region II that is described by relation (27). We stress that  $c_4(0)$  becoming zero does not imply the onset of a limiting current of oxygen reduction but corresponds to a change in mechanism of the electrode reaction from scheme (2) to scheme (1) turning on the generation of  $\text{OH}^-$  ions and the ensuing homogeneous recombination of  $\text{OH}^-$  and  $\text{H}^+$ . Upon further increase in  $j_2$  in region I, the point of  $x = \theta$  which is determined by relation (20) moves to the right (curves 4 and 5 in Fig. 2) while the  $\text{OH}^-$  ions generated at the electrode are distributed over the region of  $0 < x < \theta$ .

We now shall examine region I in Fig. 1, and analyze the changes in cation concentration  $c_1(x)$  which occur at fixed current  $j_2$  when their reduction current  $j_1$  changes.

For  $j_1 = 0$  concentration  $c_1(x)$  decreases linearly with increasing  $x$  in the region of  $0 < x \leq \theta$  and it continues to decrease in the region of  $\theta \leq x \leq 1$ . As current  $j_1$  increases concentration  $c_1(x)$  in region  $0 < x \leq \theta$  varies linearly as before, and both  $c_1(0)$  and  $c_1(\theta) = G$  decrease with increasing  $j_1$ . At sufficiently high values of  $j_1 > \nu j_2/(1 + 2k)$  a minimum appears in the function  $c_1(x)$  in the region of  $\theta \leq x \leq 1$  (at  $x = \theta^*$ ) which is determined by the relation

$$\theta^* = 1 - 2(1+k) [1 - \sqrt{(vj_2 - j_1 k) / (j_1(1+k))}] / (j_1 + \nu j_2). \quad (29)$$

As  $j_1$  increases further the situation can arise (for  $j_1 > j_2$ ) where  $c_1(0)$  becomes smaller than  $G$  (see Fig. 3b). The condition of  $c_1(0) = 0$  where  $c_1$  is given by relation (21) corresponds to the generally adopted definition of limiting currents,  $j_1^{L0}$ , of cation discharge and leads to the following relation:

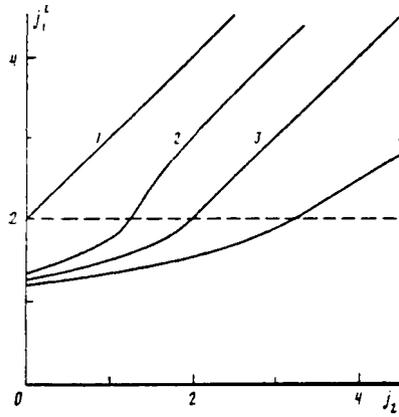


Fig. 4. Limiting currents,  $j_1^L$ , of cation discharge as functions of current  $j_2$ : 1)  $k = 0$ , 2)  $0 < k < \nu$ , 3)  $k = \nu$ , and 4)  $k > \nu$ .

$$j_1^L = 2 [1 + k + J(\nu + 1) \sqrt{(1 - k/(\nu J))(1 + k)/(1 - J)}] / (1 + \nu J), \quad (30)$$

where quantity  $J = j_2/j_1^L$  is limited by the inequality of  $J < 1$  which, together with the condition (24), is realized when  $k < \nu$ . The function  $j_1^L(j_2)$  defined by relation (30) when  $k < \nu$  is shown in Fig. 1. We stress that the curve of  $j_1^L(j_2)$  for  $k < \nu$  runs below the straight line of  $j_2 = k j_1^L / \nu$  corresponding to the condition of  $G = 0$ , and hence the curve of  $j_1^L(j_2)$  constitutes the upper limit of region I where a solution with  $0 \leq \theta \leq 1$  exists. It starts in the point Q in Fig. 1, and at  $j_2 \gg 1$  changes asymptotically to the straight line of  $j_1^L = B + j_2$  where  $b = 2\sqrt{(1 - k\nu)(1 + k)}$ . The concentration distributions of all components corresponding to the condition of  $c_1(0) = 0$  and relation (30) are shown in Fig. 3c.

In the case of  $k > \nu$ , concentration  $c_1(0)$  will not become zero whatever the values of  $j_1$  and  $j_2$ . Here an increase in current  $j_1$  at fixed  $j_2$  has the effect that the value of  $c_1(\theta) = G$  decreases ahead of  $c_1(0)$ . At the same time the value of  $x = \theta^*$  where  $c_1(x)$  has a minimum approaches  $x = \theta$ , and at sufficiently high values of  $j_1 = j_1^L$  the point  $\theta^*$  merges with  $\theta$  and  $c(\theta^*) = G$  becomes zero. This occurs when  $j_1 = j_1^L$  and  $\theta = \theta^*$ :

$$j_1^L = \nu j_2 / k, \quad (31)$$

$$\tilde{\theta} = \theta^* = 1 - 2/j_1^L = 1 - 2k/\nu j_2. \quad (32)$$

In this case the region I is limited by the conditions of  $G = 0$  and  $\theta = 0$ .

The situations where  $c_1(\theta) = G = 0$  correspond to the distributions of ionic concentrations and electric field following from relations (14) to (16) and (21) to (23):

$$c_1 = (x - \tilde{\theta}) / (1 - \tilde{\theta}), \quad c_2 = (1 + k)c_1, \quad c_3 = 0, \quad c_4 = kc_1, \quad (33)$$

$$\mathcal{E} = -1/(x - \tilde{\theta}) \text{ for } x > \tilde{\theta},$$

$$c_1 = c_3 = j_2(1 - \nu/k)(\tilde{\theta} - x)/2, \quad c_2 = c_4 = 0, \quad (34)$$

$$\mathcal{E} = -(k + \nu) / [(k - \nu)(\tilde{\theta} - x)] \text{ for } x < \tilde{\theta}.$$

We notice that in the region of  $0 < x < \tilde{\theta}$  there are no salt anions when  $j_1 = j_1^L$ , ie,  $c_2(x) = 0$  and the solution behaves as a binary electrolyte consisting of the cations undergoing discharge and the  $\text{OH}^-$  ions generated at the electrode. The concentration distributions (33) and (34) are shown in Fig. 3d.

Limiting currents of cation discharge are shown as functions of the current of oxygen reduction at different values of  $k$  and  $\nu$  in Fig. 4. When  $j_2 = 0$  the values of  $j_1^L$  follow the relations of the theory of correlational migration current exaltation up to  $j_1^L = 2$ . The further behavior of  $j_1^L$  depends on the relative values of parameters  $k$  and  $\nu$ . For  $k \geq \nu$  (curves 3 and 4)  $j_1^L$  is a linear function of  $j_2$  in accordance with (31). For  $0 < k < \nu$  (curve 2)  $j_1^L$  is determined by relation (30).

As  $k/\nu$  decreases to zero point Q in Fig. 4 moves toward the vertical axis along the horizontal line of  $j_1 = 2$ . Under these conditions the curve of  $j_1^L$  changes into the straight line of  $j_1^L = j_2 + 2$  corresponding to the theory of migration current exaltation of [4, 5].