GENERALIZED PROBLEM OF THE LIMITING MIGRATION AND DIFFUSION CURRENTS IN THREE-ION SYSTEMS

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Ionic transport by migration and diffusion was analyzed theoretically in systems containing three different sons of ions where several electrode reactions occur in parallel. The general conditions were investigated under which steady-state modes of the process exist, and different cases of control of the process by transport limitations were analyzed.

A number of interesting effects develop when kinetically independent electrochemical reactions occur in parallel at the electrode. They are due to interaction of the charged solution components during their transport by migration and diffusion in the diffusion layers or in films covering the electrode. They include the migration-current exaltation observed when cations and a neutral substance are reduced in parallel [1-3], the correlational migration-current exaltation observed when different sort. of cations are reduced in parallel [2-4], as well as the migration effects observed when metal deposition and anion reduction occur in parallel [5].

In the present work we investigate a general three-component system where all charged components can participate in electrode processes. For the sake of simplicity, we limit ourselves to the case where all ions (two sorts of cations and one sort of anions) are univalent. Another possible case, with two sorts of anions and one sort of cations, can be examined in the analogous manner, and the appropriate relations can be obtained when replacing Ψ by $-\Psi$ in the relations to be reported below.

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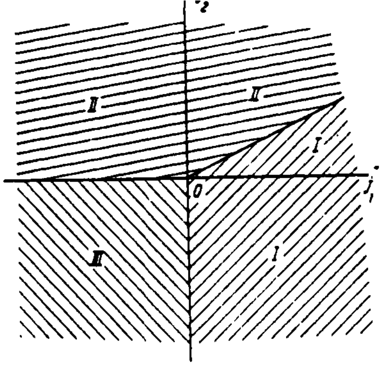

Fig. 1. Scheme of the regions where solutions exist for k = ½ in the plane of j_1 and j_2.

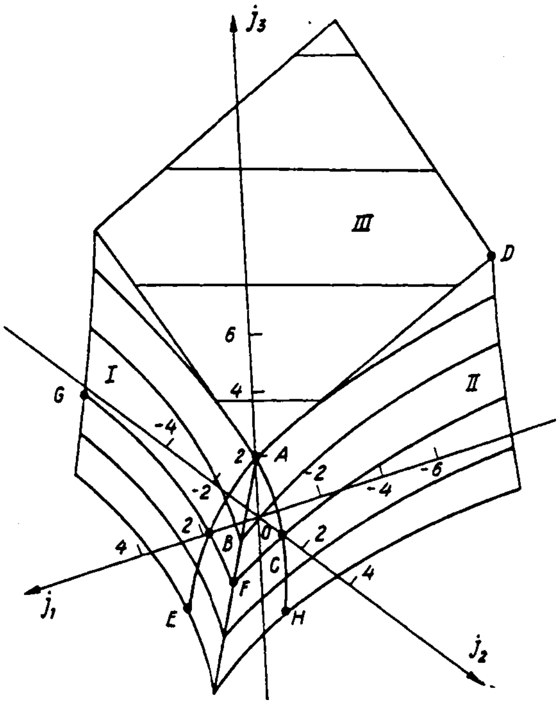

Fig. 2. Scheme of the mutual disposition of limiting-current surfaces I, II, and III in the space of j_1, j_2, and j_3.

diffusion equations describing ionic transport in a diffusion layer of thickness L can be written

$$\frac{dc_1}{dx}+c_1\frac{d\Psi}{dx}=j_1, \tag{1}$$

$$\frac{dc_2}{dx}+c_2\frac{d\Psi}{dx}=j_2, \tag{2}$$

$$\frac{dc_3}{dx}-c_3\frac{d\Psi}{dx}=j_3, \tag{3}$$

$$c_1+c_2=c_3, \tag{4}$$

$$c_3(1)=1,\ c_1(1)=k,\ c_2(1)=1-k. \tag{5}$$

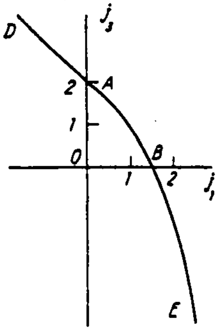

Fig. 3

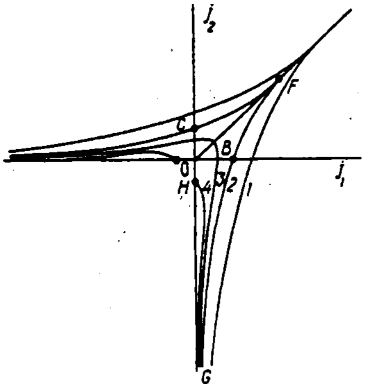

Fig. 4

Fig. **3.** Correlation of the limiting currents of j_1 and j_3 for $j_2 = 0$.

Fig. **4.** Schematic drawing of the projections of level lines j_3 = const on the surfaces I, II, and III onto the plane of j_1 and j_2: 1) $j_3 = 0$; 2) $j_3 < 0$; 3) $0 < j_3 < 2$; 4) $j_3 > 2$.

Here c_1, c_2, and c_3 are the concentrations of cations of the first and second sort and of the anions made dimensionless through c_0, which is the concentration of anions in the bulk solution; Ψ is the electrical potential in units of RT/F; x is the dimensionless coordinate $(0 \leq x \leq l)$, $j_{1,2,3} = i_{1,2,3}L/FD_{1,2,3}c_0$ are the dimensionless current densities for discharge of the ions, and $D_{1,2,3}$ are the corresponding diffusion coefficients ($j_{1,2,3} > 0$ correspond to ionic fluxes toward the electrode). 'Parameter k in boundary condition *(5)* expresses the fraction of cations of the first sort in the total concentration of cations in the solution $(0 \leq k \leq 1)$.

The system of Eqs. (1) to *(5)* can be integrated by the method described in [6]. Adding (1) *to (3)* while allowing for the electroneutrality relation *(4)* and boundary conditions (5) we obtain

$$c_3 = 1 + j(x-1), \tag{6}$$

where the notation of

$$j = (j_1 + j_2 + j_3)/2 \tag{7}$$

was introduced. We point out that the condition of $c_3 \geq 0$ implies that $j \leq 0$.

Substituting *(6)* into *(3)* we obtain

$$\frac{d\Psi}{dx} = \frac{j - j_1}{1 + j(x-1)} \tag{8}$$

Using (8) we can reduce Eqs. (1) and *(2)* to linear equations for $c_1(x)$ and $c_2(x)$. Their integration with boundary conditions *(5)* yields

$$c_1(x) = [j(x-1)+1]^{(j_1-j)/j}\left\{k + \frac{j_1}{j_1+j_2}[(j(x-1)+1)^{(j_1+j_2)/j} - 1]\right\}, \tag{9}$$

$$c_2(x) = [j(x-1)+1]^{(j_2-j)/j}\left\{1 - k + \frac{j_2}{j_1+j_2}[(j(x-1)+1)^{(j_1+j_2)/j} - 1]\right\}. \tag{10}$$

We shall analyze the conditions under which $c_1(x)$ and $c_2(x)$ of *(9)* and *(10)* are physically meaningful, i.e., when the inequalities of $c_1(x) \geq 0$ and $c_2(x) \geq 0$ are satisfied for $0 \leq x \leq 1$. Because of the condition of $j \leq 1$, the expressions in Square brackets in *(9)* and *(10)* are not negative. We shall 'first examine the case when $j < 1$. Then said expression in square brackets will always be positive, so that the only limitation to j is that of $j \neq 0$. The condition of positive $c_1(x)$ and $c_2(x)$ then is reduced to positive expressions in curly brackets.

We point out first of all that for $x = 1$, the two expressions in curly brackets in (9) and (10) are positive. The derivatives of both expressions with respect to x have constant signs for $j < 1$, i.e., they vary monotonically when $0 \leq x \leq 1$. At first, therefore, $c_1(x)$ and $c_2(x)$ could basically become zero with increasing j, only when $x = 0$. Hence $c_1(x)$ and $c_2(x)$ can only become zero when $x = 0$. This implies $c_1(0) = 0$ and $c_2(0) = 0$, which are the conditions where partial limiting currents of components c_1 and c_2 are realized.

The condition of $c_1(0) = 0$ corresponds to the equation of

$$j=1-\left[1-\frac{k(j_1+j_2)}{j_1}\right]^{j/(j_1+j_2)} \tag{11}$$

Introducing the notation of

$$\nu=j_2/j_1 \quad \text{and} \quad \eta=j_3/(j_1+j_2), \tag{12}$$

we can reduce (11) to a form where current j_3 can be expressed explicitly in terms of η and ν:

$$j_3=\frac{2\eta}{\eta+1}[1-(1-k-k\nu)^{(\eta+1)/2}]. \tag{13}$$

Relation (13) is defined for

$$\nu<\frac{1-k}{k} \tag{14}$$

owing to the condition of $j < 1$.

The analogous partial limiting current of cations of the second sort corresponds to the condition of

$$j_3=\frac{2\eta}{\eta+1}\{1-[k-(1-k)/\nu]^{(\eta+1)/2}\}. \tag{15}$$

Relation (15) is defined for

$$\nu>\frac{1-k}{k} \quad \text{as} \quad \nu<0. \tag{16}$$

owing to the condition of $j < 1$.

We call attention to the fact that in the case being considered, the dimensionless current j_1 should be positive when $c_1(0) = 0$ and $c_2(0) > 0$. In fact, negative j_1 should imply that $d\Psi/dx$ in (1) will tend toward $-\infty$ when $c_1(0) \to 0$. However, this is at variance with the condition of finite $d\Psi/dx$ that follows from (8) for $j < 1$. It follows that $j_1 > 0$ when $c_1(0) = 0$ and $c_2(0) > 0$. We can see in an analogous way that flux j_2 should be positive when $c_2(0) = 0$ and $c_1(0) > 0$.

We shall examine the geometric significance of conditions (14) and (16) in the plane of j_1 and j_2 (Fig. 1) while taking into account the inequalities obtained.

Region I corresponds to realization of the condition (14) with $j_1 > 0$; this region is delimited by the negative semiaxis of j_2 and by the half straight line of

$$j_2=j_1\frac{1-k}{k}, \quad j_1>0, \quad j_2>0. \tag{17}$$

Region II corresponds to realization of the condition (16) with $j_2 > 0$; this region is delimited by the negative semiaxis of j_1 and by the same half straight line. We stress that the boundaries themselves are not included into the definitions of the regions, since all inequalities used were rigorous.

We shall now examine the case of $j = 1$. In this case it will be convenient to write relations (9), (10), and (6) for $c_1(x)$, $c_2(x)$, and $c_3(x)$ in the form of

$$c_1(x)=x^{j_3-1}\left(k-\frac{j_1}{j_1+j_2}\right)+\frac{j_1}{j_1+j_2}x, \tag{18}$$

$$c_2(x) = x^{j_3-1}\left(1-k-\frac{j_2}{j_1+j_2}\right)+\frac{j_2}{j_1+j_2}x, \tag{19}$$

$$c_3(x) = x. \tag{20}$$

It is important to notice the following special features of relations (18) to (20). For x tending toward zero, the leading terms in (18) and (19) should be the terms which are linear in x. Otherwise one of the concentrations, c_1 or c_2, would have to become negative at small x, since it is easy to see that the expressions in the brackets of (18) and (19) are equal in size and opposite in sign. It follows that j_3 should be larger than two. The condition of $j_3 > 2$ unambiguously yields the inequality of $j_1 + j_2 < 0$, from which it follows that j_1 and j_2 are both negative. In the plane of parameters j_1 and j_2, the region of solutions which correspond to the case of $j = 1$ (i.e., to the totally limiting current) corresponds to the "negative" quadrant (region III in Fig. 1). It is readily seen from (18) and (19) that the boundaries of the quadrant are included into region III.

In addition to the possibilities considered above, a further possibility exists for the problem to have a solution for $j = 1$, viz., the case where the expressions in parentheses of (18) and (19) are zero. This is realized on the straight line (17) separating regions I and II. Physically, the condition of (17) is entirely natural, since the conditions of $c_1(0) = c_2(0) = 0$ are fulfilled on the straight line (17) as we go from region I [where ($c_1(0) = 0$ and $c_2(0) > 0$] to region II [where $c_2(0) = 0$ and $c_1(0) > 0$]. The coefficients of the terms in (18) and (19) which are linear in x are positive at j_1 and j_2 which satisfy (17).

We shall now discuss cases where limiting currents can be attained in the three-component, three-current problem being examined. It will be convenient for this purpose to represent the surface defined by relations (13) and (15) in the three-dimensional space of j_1, j_2, j_3 (Fig. 2). At given values of parameter k, relations (13) and (15) can be described by the surfaces of the partial limiting currents which intersect along the straight line corresponding to relation (17) and the condition of $j = 1$. It follows from the above investigation, moreover, that the region where the problem has a solution is delimited by the plane of $j = 1$ (III in Fig. 2), which corresponds to the condition of a totally limiting current,

$$j = (j_1+j_2+j_3)/2 = 1. \tag{21}$$

The above investigation of possible steady-state modes of the electrochemical process in a three-component, three-current system is the generalization of results obtained in a number of prior papers [1-7].

In the simplest particular case when only one sort of ions is electroactive, the state of the system can be described by a point located on one of the three axes, j_1, j_2, or j_3, in the three-dimensional diagram shown in Fig. 2, while the case of a limiting current with respect to this electroactive component corresponds to the intersection of these axes with the calculated composite (I + II + III) threedimensional surface. The point A where all three surfaces (I, II III) intersect corresponds to a limiting current $j_3^l = 2$ which arises when the anions are the electroactive ions. Essentially, this is the ordinary dimensionless limiting current in a binary electrolyte (where the two sorts of species, c_1 and c_2, function as the inactive cations).

The limiting currents are determined by Eucken's relation [8, 9] when any one of the cations is electroactive; points B and C on surfaces I and II correspond to these two cases.

Next in complexity is the particular case where two sorts of ions are electroactive. We consider first the case when these are the anions and one sort of cations (for the sake of definition: c_1). Setting $j_2 = 0$ and $j_1 < 0$ in relation (21) we obtain an equation linking the limiting current j_3 and the current j_1:

$$j_3 = 2 - j_1. \tag{22}$$

Relation (22) describes the well-known effect of migration-current exaltation [1-3] seen when cations and a neutral substance are reduced (or anions and a'neutral substance are oxidized) at the same time. On the three-dimensional surface (j_1, j_2, j_3), straight line (22) is given by the intersection of plane III with surface II. On the plane of j_1 and j_2, relation (22) is reflected by the half straight line AD (Fig. 3).

It appears that the case where cations are supplied to the electrode in the presence of electroactive anions has not been investigated in detail previously. The interrelation between currents j_1 and j_3 corresponding to this case follows from relation (13) for $\nu = 0$ and $\eta = j_3/j_1$; it is shown in Fig. 3. The section of the curve between points A and B which describes the joint reduction of cations and oxidation of anions corresponds to a situation where currents j_3 are depressed when j_1 is raised. Cations are reduced while anions appear at the electrode when $j_3 < 0$ and $j_1 > 0$. Section BE of the curve corresponds to the limiting current for this process. This section describes a process which in its nature is akin to the effect of migration-current exaltation, but which is not linear. The absolute value of j_3 increases monotonically with increasing j_1 from the value of $2[1 - \sqrt{(1 - k)}]$ (point B) given by Eucken's relation to arbitrarily large values of j_1.

We call attention to the fact that the limiting current in section AD implies that the concentrations of all three components become zero at the electrode, while in sections AB and BE of the curve, only the concentration c_1 becomes zero at the electrode surface in the limiting-current mode while $c_3(0) > 0$ and $c_2(0) > 0$.

We now shall consider the particular case of $j_3 = 0, j_1 > 0, j_2 > 0$. Plots of j_1 against j_2 and of j_2 against j_1 which correspond to the partial limiting currents with respect to the first and second sort of cations are shown in Fig. 4. Section FB of the plot of j_1 against j_2 which will be discussed below, for the sake of definition, corresponds to the function provided by the theory for the correlational migration-current exaltation [2, 4]. Section BG corresponds to reduction of cations of the first sort occurring while cations of the second sort are generated in parallel at the electrode surface by electrodissolution. It can be seen from Fig. 4 that here the first process is suppressed (or depressed) when the rate of the second process increases.

The case where $j_3 \neq 0$ is the generalization of the case discussed above, where it was defined that $j_3 = 0$. It will be convenient when plotting the corresponding curves of $j_1(j_2)$ for fixed values of j_3 to write v in terms of η and j_3 with the aid of relation (13):

$$\nu = \frac{1}{k}\left[1 - k\left(1 - j_3\frac{\eta+1}{2\eta}\right)^{2\cdot(\eta+1)}\right]. \tag{23}$$

Picking some value of η in (23) one readily finds the corresponding value of ν; then one finds j_1 and j_2 from (12). Plots of j_1 against j_2 obtained in this way for a number of values of the parameter j_3 are shown in Fig. 4. It is important to note that the shape and position of the curves substantially depend on the sign of $(j_3 - 2)$. The curves are similar to that for the case of $j_3 = 0$ when $j_3 < 2$. They start on the half straight line AD, intersect the axis of j_1, and asymptotically tend toward the negative semiaxis of j_2. However, the curves corresponding to $j_3 > 2$ issue from points defined by the condition of $j_2 + j_3 = 2$; they also tend asymptotically toward the negative semiaxis of j_1.

The plots of j_2 against j_1 defined by relation (15) with fixed j_3 are analogous. We must point out in addition that for $j_1 < 0$ and $j_2 < 0$, the relation between j_1 and j_2 which corresponds to a totally limiting current in the system is given by relation (21), and can be pictured as shown in Fig. 4 by the straight-line segments uniting the points from which the plots of $j_1(j_2)$ and $j_2(j_1)$ issue when $j_3 > 2$.

Thus, it is readily seen that the curves shown in Fig. 4 are the projections of level lines on the composite surface of limiting currents, I + I + III, in the three-dimensional space pictured in Fig. 2. With a value of 0.5 for parameter k, this surface is symmetric relative to the plane of $j_1 = j_2$. This symmetry is upset when parameter k assumes different values; then the position of plane III remains unchanged, but half straight line ***AF*** changes in its slope relative to the coordinate axes. The "steepness" of surfaces I and II changes at the same time; surface I becomes less steep, and surface II becomes steeper with increasing k.

It had been assumed in the above analysis that generally, all three ion types could be electroactive. We shall discuss in more detail possible cases of electrode processes involving said ions.

Suppose that a single electrode reaction involving all three components occurs in the system:

$$\nu_1 A_1^+ + \nu_2 A_2^+ + \nu_3 A_3^- + ne = 0. \tag{24}$$

Then the fluxes of these components should be interrelated via the stoichiometric coefficients and the two linear relations

$$j_2/j_1 = \nu_2/\nu_1 = \nu; \quad j_3/(j_1 + j_2) = \nu_3/(\nu_1 + \nu_2) = \eta. \tag{25}$$

In the space of j_1, j_2, j_3, relations (25) define a straight line issuing from the coordinate origin. Depending on the values of ν_i, it may or may not intersect with any one of the surfaces I, II, and III. When an intersection occurs, this implies that a limiting current arises in the system because one of the conditions: $c_1(0) = 0$, $c_2(0) = 0$, or $c_3(0) = 0$, is fulfilled. When intersections are lacking, this corresponds to a system where the current can assume any value. We point out that, if some substance is the product of the electrode process, i.e., has a negative stoichiometric coefficient, it will not be able to limit the overall process. Generally, a limiting current is not assured to occur in the system when just one of the stoichiometric coefficients is positive. For instance, when $\nu_1 = \nu_2 = -1$ and $\nu_3 = 1$, the corresponding straight line does not intersect with any of the surfaces I, II, and III.

When a limiting current exists in the system, i.e., when the straight line intersects with one of the surfaces (I, II, or III), the value of this current can be found from one of the relations corresponding to the loci of points of intersection between the straight line and the surfaces: (13), (15), or (21), where relations (25) are used for ν and η.

Consider now the case when two electrode reactions occur in the system, one of them involving any two sorts of electroactive ions and the other producing the third sort of ions. Here the fluxes of the two components involved in the first reaction are mutually proportional, which geometrically, in the space of j_1, j_2, j_3, corresponds to some plane P passing through one of the coordinate axes. This plane generally intersects with two of the three surfaces I, II, and III. Plane P will cross the axis of j_3 when the ions involved in the reaction have the same sign. Then it intersects with plane III and either the surface I or the surface II (in which case the limiting-current situation is similar to that pictured in Fig. 3), or it intersects with the surfaces I and II but not with III (in which case the limiting-current situation is described by two branches looking like the nonlinear sections *ABE* of the curve in Fig. 3).

Plane P crosses the axis of j_1 (or of j_2) and intersects with surfaces I and II, in certain cases even with plane III, when ions of different sign are involved in the reaction. Plane P may then either intersect with the half straight line *AF* or intersect with its extension in the plane III, or it may be situated parallel to the half straight line AF. In the last two cases, a region exist where the currents j_1 and j_2 can have any (positive) value while currents j_3 can increase to any value. Here we can draw an analogy to the migration-current exaltation in a more complex system where two reactions occur in parallel and two solution components are involved in one of these reactions. We remark that, when j_1 and j_2 are negative, j_1, j_2, and j_3 can always assume whatever (absolute) value.

In a system where two electrode reactions occur which have reactants in common, the state of the system can be characterized by a plane P the position of which depends on the values of the stoichiometric coefficients of these reactions, and which by necessity passes through the coordinate origin, of $j_1 = j_2 = j_3 = 0$. The resulting admissible regions where the reactions can occur under limiting-current conditions, are defined by the intersections between plane P and the surfaces I, II, and III; they are qualitatively similar to those described above.

Finally, in the general case when three parallel reactions occur in the system, the surfaces I, II and III themselves constitute the boundaries for the admissible partial currents j_1, j_2, and j_3. For a specific system of three parallel electrode reactions, surfaces of this sort have been analyzed in [10].

Thus, the above analysis provides a generalized picture for the limitation of electrode processes in three-component systems by diffusion and migration when several (generally coupled) electrochemical reactions occur.

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