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General problem of limiting diffusion–migration currents in a system with ions of three arbitrary charge numbers

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Abstract

The conditions for the appearance of limiting currents in an electrochemical system in the cases of excess and no supporting electrolyte have been studied theoretically. It is shown that the partial currents of parallel reactions are interdependent not only because of their competition for common reactants but also because of the influence of the electric field on the transport processes of the charged reagents and reaction products. The system containing ions of three arbitrary charge numbers has been analyzed in detail for the cases of one, two and three parallel electrochemical reactions. Explicit expressions for partial and total limiting currents have been determined. A geometrical interpretation of the evolution of the system with changing potential difference is given.

1. Introduction

The study of transport processes in electrochemical systems occupies one of the central places in electrochemical kinetics. Nernst [1] proposed subdividing the whole volume of the electrochemical cell into a bulk solution, where the convective motion takes place, and a thin boundary layer near the electrode surface, where the fluid motion is negligible owing to finite viscous forces. In the bulk solution convective transport of ions is much faster than the other types of transport, and hence uniform concentration can be assumed. Convection can be neglected in the thin boundary layer, which is known as the "Nernst layer" or "diffusion layer". For relatively large electrodes, compared with the thickness of the Nernst layer, it is possible to neglect transport in the lateral directions and hence the transport equations become one-dimensional.

In the Nernst model the limiting current appears when the concentration of electroactive ions on the surface becomes negligible compared with the bulk concentration. Of course, the Nernst layer model is the simplest possible and is severely restricted. For example, in this treatment the layer thickness is a phenomenological parameter. However, this model provides a satisfactory explanation of all phenomena in which transport of reagents and reaction products plays a significant role.

Later, Levich [2] found that ion transport near the surface of a rotating-disk electrode proceeds in the same way as in the Nernst layer. The disk electrode then became one of the most important tools in the study of electrochemical kinetics, and the concept of the Nernst layer was widely applied in theoretical investigations of ionic transport [3-7]. We shall use the disk electrode as the main example in this paper. Like the Nernst layer, the system with a spherically symmetric electrode can also be reduced to a one-dimensional problem. The results obtained in these two models are usually very similar [8-12]. One-dimensional steady-state transport is also the typical model used in investigations of transport through membranes [13-15]. All other systems must be solved in two or three dimensions which requires complicated numerical calculations [16] (Thus only a relatively small number of possible situations can be investigated. Sometimes these are not sufficiently representative to derive the proper-

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ties of the general solution which, however, can easily be understood from a simplified analytical solution [17].)

The transport equations in the Nernst layer have a simple solution in some classic cases, such as the one-to-one binary electrolyte which appears in processes of metal electrodeposition. In the more general case of reduction–oxidation electrodes at least three kinds of ions with different charge numbers appear in the system (e.g. two electroactive species Mn^{3+} and Mn^{4+} and electroinactive anions [13]). In this case the solution becomes much more complicated. We present the general solution for an arbitrary charge number because there is no other way of finding the simplest expression if at least one ion species in the system has a charge number different from that of the others.

One of the main purposes of this work is to calculate the limiting current density for a single complicated electrochemical reaction. A reaction of this type often has one or two satellites, i.e. reactions occurring simultaneously with that under investigation. For example, anion reduction can take place in a number of ways (more than six different reduction reactions are possible for NO;, two or three of which proceed simultaneously).

The rates of parallel reactions depend on each other for two main reasons: (a) the competition for reactants; (b) the migration force which depends on the potential distribution which, in turn, depends on the concentration of all species in a self-consistent way.

In Section 3 we discuss a system with a large excess of supporting electrolyte, where only condition (a) holds. A formal description of the general algorithm, which allows both effects to be taken into account is given in Section 4. This algorithm gives a finite but rather complicated solution for the system with three different types of ions (Sections 5 and 6). The mathematical details of the solutions are given in the appendices. A qualitative description of possible ways of reaching a limit for the cases of one and two reactions is given in Section 7. Readers who are interested in examples of real systems are referred to the literature cited, where particular cases are discussed.

2. Statement of the problem

Let us consider an electrochemical system comprising cations with the charge number $z_a(A_1^{z_a+}, A_2^{z_a+},\ldots)$, cations with the charge number $z_b(B_1^{z_b+}, B_2^{z_b+},\ldots)$ and anions $R_1^{z_r-}$, $R_2^{z_r-}$ with the charge number z_r. * Several electrochemical reactions take place on the electrode surface, each of which can be presented in the following form:

$$\sum_i a_{ki}A_i^{z_a+} + \sum_i b_{ki}B_i^{z_b+} + \sum_i r_{ki}R_i^{z_r-} + \sum_i s_{ki}S_i = m_k e^- \tag{1}$$

where S_i are neutral substances which take part in the electrochemical reaction, m_k is the number of electrons transferred in the kth reaction, and a_{ki}, b_{ki}, r_{ki} and s_{ki} are the stoichiometric coefficients. According to the generally accepted rules we assume that stoichiometric coefficients are positive for reactants, negative for reaction products and zero for substances not taking part in the reaction of interest [18].

Consider stationary transport in the Nernst diffusion layer. The Nernst–Planck equation for the ith ion with charge $z_\alpha(\alpha = \text{a, b, r})$ is

$$I_{\alpha i} = Fz_\alpha\left(D_{\alpha i}\frac{dc_{\alpha i}}{dy} + z_\alpha c_{\alpha i}D_{\alpha i}\frac{F}{RT}\frac{d\phi}{dy}\right) \tag{2}$$

where D„ and $c_{\alpha i}$ are the diffusion coefficient and concentration of ion αi (the index $\alpha = $ a, b, r corresponds to the different charge numbers, and the index i indicates different substances with the same charge number), $I_{\alpha i}$ is the current density transported by this ion, F is the Faraday constant, ϕ is the electrical potential, R is the gas constant, T is the absolute temperature and y is the coordinate directed from the electrode surface into the solution. The Einstein relation for ion mobility (which is strictly valid for dilute solutions) has been assumed. The activity coefficients were taken as unity and the diffusion layer was assumed to be the same thickness for all ions.

Equation (2) should be supplemented with the equation defining the electric potential, i.e. the Poisson equation. However, in the case of underlimiting and limiting currents the Poisson equation can be replaced with rather good accuracy by the condition of local electroneutrality:

$$z_a\sum_i c_{ai} + z_b\sum_i c_{bi} + z_r\sum_i c_{ri} = 0 \tag{3}$$

The electroneutrality condition is satisfied everywhere except in close proximity to the electrode in the case when all reactant concentrations become small, i.e. in the regime of the limiting current. However, it has been shown [2,19] that this has a negligible effect in the regime of the limiting current and requires only a small correction in the "regime of overlimiting currents". Therefore eqn. (3) is applied to the whole volume of the diffusion layer. The boundary conditions for eqns.

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* The case of an electrochemical system comprising anions with different charge numbers z_a and z_b and cations with the charge number z_r can be solved in a similar way.

(2) and **(3)** at y = L (the boundary between the diffusion layer and the bulk solution) are

$$c_{\alpha i}(y=L)=c_{\alpha i}^{0} \qquad \phi(y=L)=\phi_0 \tag{4}$$

It is possible to find the distribution of concentrations $c_{\alpha i}(y)$ and potential $\phi(y)$ from eqns. (2) and **(3)** with boundary conditions (4), but these functions depend on $I_{\alpha i}$ as parameters. One of the conditions for defining parameters $I_{\alpha i}$ is

$$\sum_i I_{\mathrm{a}i}+\sum_i I_{\mathrm{b}i}+\sum_i I_{\mathrm{r}i}=I \tag{5}$$

where I is the integral current density passing through the system. Expression (5) can be transformed into

$$\sum_k I_k=\mathrm{I} \tag{6}$$

where I, is the current density produced in the kth electrochemical reaction. It is easy to obtain the relationship between I_k and $I_{\alpha i}$ from the stoichiometric correlations (1) [20]:

$$I_{\mathrm{a}i}=z_{\mathrm{a}}\sum_k a_{ki}\frac{I_k}{m_k} \qquad I_{\mathrm{b}i}=z_{\mathrm{b}}\sum_k b_{ki}\frac{I_k}{m_k}$$

$$I_{\mathrm{r}i}=\sum_k r_{ki}\frac{I_k}{m_k} \tag{7}$$

Therefore the number of unknown parameters in eqns. (2)–(4) is defined by the number of electrochemical reactions proceeding simultaneously. If the integral current value is known, the number of unknown parameters is reduced to one.

3. Limiting diffusion currents

The following assumption is often used in the determination of the partial currents I,: the slowest stage of one (or several) electrode reaction(s) is the diffusion transport of reactants to the electrode, and the electrode reaction proceeds so fast that the concentration of the reactant at the electrode becomes very small. In the case of excess supporting electrolyte, when the electric field strength is low, it is possible to neglect the migration term in (2) and to determine the limiting value I_k^l of the current of the kth reaction:

$$I_k^l=\frac{Fm_k}{L}\min_i\left(D_{\mathrm{a}i}\frac{c_{\mathrm{a}i}^0}{a_{ki}};\ D_{\mathrm{b}i}\frac{c_{\mathrm{b}i}^0}{b_{ki}};\ D_{\mathrm{r}i}\frac{c_{\mathrm{r}i}^0}{r_{ki}};\ D_{\mathrm{s}i}\frac{c_{\mathrm{s}i}^0}{s_{ki}}\right) \tag{8}$$

This minimum value is taken only among the reactants, i.e. among the substances with positive stoichiometric coefficients (a_{ki}, b_{ki}, r_{ki}, $s_{ki}>0$).

Expression (8) is valid for one reaction only or for several parallel reactions with no common reactants. Generally, when one or more reactants are common to several reactions, it is possible to assume that parallel reactions reach the limiting regime consecutively (one by one). It is convenient to arrange reactions (1) in order of increasing half-wave potentials. Then the limiting current I_1^l for the only electrode reaction with the index k = 1 can be determined from expression (8). The value of the current $I_{\alpha i}$ transported by each of the reactants in the first reaction can be determined by substituting I_1^l into eqn. (7). The limiting current of the second reaction can also be found from eqn. (8), with all the terms reduced by the corresponding values of the currents consumed in the first reaction:

$$I_2^l=\frac{Fm_2}{L}\min_i\left(D_{\mathrm{a}i}\frac{c_{\mathrm{a}i}^0}{a_{2i}}-\frac{a_{1i}I_1^lL}{F};\ D_{\mathrm{b}i}\frac{c_{\mathrm{b}i}^0}{b_{2i}}-\frac{b_{1i}I_1^lL}{F};\right.$$
$$\left.D_{\mathrm{r}i}\frac{c_{\mathrm{r}i}^0}{r_{2i}}-\frac{r_{1i}I_1^lL}{F};\ D_{\mathrm{s}i}\frac{c_{\mathrm{s}i}^0}{s_{2i}}-\frac{s_{1i}I_1^lL}{F}\right) \tag{9}$$

Equation (9) is valid only if all the terms on the right-hand side are positive. If this condition is not satisfied, this reaction is impossible because of the absence of free accessible reactants. In other words, the reaction cannot proceed if it requires a reactant whose transport is already limited because of the previous electrode reaction.

After I_2^l has been found, application of eqn. (8) is repeated until all the I_k^l are determined. Let us once more emphasize the fact that the values of I_k^l depend on the order of the half-wave potentials of all the reactions. This means that the integral limiting current I^l also depends on the values of half-wave potentials of all the reactions (1) when they reach their limiting diffusion regimes. The limiting current I^l equals the sum of the limiting diffusion currents of the individual reactions only for reactionally independent electrochemical systems where each substance either participates in no more than one electrochemical reaction or is in excess.

4. Limiting diffusion–migration currents

A much more complex interaction of the electrochemical reactions takes place in the absence of supporting electrolyte. The following particular case of the electrochemical system (1) has been considered in ref. 21:

$$\mathrm{A}^{z_1+}+z_1\mathrm{e}^-\rightarrow \mathrm{A}_{(\mathrm{s})} \qquad \mathrm{B}^{z_1+}+z_2\mathrm{e}^-\rightarrow \mathrm{B}_{(\mathrm{s})} \tag{10}$$

It includes the parallel precipitation of two species of cations from the solution provided that anions are electroinactive. Let us consider the case when the current produced by the first reaction reaches its limiting value I_1^l under a certain potential difference. As the potential difference increases, the current of the second reaction gradually increases. Consequently, the potential distribution in the diffusion layer is changing. It causes a change in the migration term in expression **(3)** for the first cation species. Therefore we find that the limiting current of the first reaction is a function of the second reaction current, $I_1^1 = I_1^1(I_2)$, and the totally limiting current is described by the expression $I^1 = I_1^1(I_2^1) + I_2^1$.

In the general case of electrochemical system (1), the limiting current of a particular reaction must be considered a function of the currents of all the other electrode reactions that have not yet reached their limiting value. If N reactions (1) are arranged in the order in which they reach the limiting regime, the expression for the integral current in the system (under the condition that the kth reaction has reached the limiting regime) becomes

$$I = I_1^1(I_2^1; ,\dots, I_k^1, I_{k+1},\dots, I_N)$$
$$+I_2^1(I_3^1,\dots, I_k^1, I_{k+1},\dots, I_N) + \dots + I_k^1(I_{k+1},\dots, I_N)$$
$$+ I_{k+1} + \dots + I_N \qquad (11)$$

In order to find the value of the current **I** from (11) it is necessary to know the values $I_{k+1},\dots, I_N$, and this requires information about the kinetics of the electrode reactions $k+1,\dots, N$.

However, for an approximate solution of the problem it is possible to assume that the potentials of all reactions are significantly different and the currents of all reactions that have not reached the limiting regime are equal to zero: $I_{k+1} = \dots = I_N = 0$. In this case the solution procedure is similar to that in Section 3. However, the comparatively simple expressions (8) and (9) for the limiting current I_k^1 must be replaced by the following algorithm:

(1) Assuming $I_{k+}, = \dots = I_N = 0$, find the distribution of concentrations of all the components in the diffusion layer as functions of k parameters $I_1,\dots, I_k$.

(2) At $y = 0$, set the concentrations of those reactants which are limiting for reactions $1,\dots, k-1$ equal to zero. This results in a system of $(k-1)$ equations for the unknown parameters $I_1,\dots, I_k$.

(3) Solve this system of equations and express $I^l,\dots, I_{k-1}^1$ as a function of the single parameter I_k.

(4) Substitute $I_1^1(I_k),\dots, I_{k-1}^1(I_k)$, **I,** into the expressions for the concentrations in the diffusion layer and find expressions for the concentrations of all the reactants at $y = 0$ as a function of I,.

(5) Determine the value of I_k, which corresponds to zero concentration of one component at the electrode while the others are not negative. This value of I_k is the limiting value.

Usually, this value of I_k is the only one that is a minimum among all possible values defined by the conditions $c_i(I_k, y = 0) = 0$. However, this rule is not always fulfilled. An example of an electrochemical system with two parallel reactions where a double limiting current (when the concentrations of the reactants for each reaction become equal to zero near the electrode) can have three different values is given in ref. 22. This case can be explained in terms of the appearance of multiply connected domains of possible current values I_k and is discussed in more detail at the end of Section 7.

5. Concentration distribution in the diffusion layer

As already mentioned above, the concentration distribution in the diffusion layer can be obtained by solving eqns. (2) and (3) with the boundary conditions (4). The best way of solving this problem is to introduce a new independent coordinate ψ, the dimensionless potential, using the technique described in detail in ref. 23.

The main aim of this method is to find the inverse function $y = y(\psi)$ instead of determining the potential distribution ψ as a function of the coordinate y. Similarly, the concentrations can also be found as functions of the dimensionless potential. This procedure results in the following expression for $c_{\alpha i}$ in parametrical form:

$$c_{\alpha i} = \left[c_{\alpha i}^0 + \frac{I_{\alpha i} L}{z_\alpha j_\mathrm{a} F D_{\alpha i}} f\left(\psi;\ \lambda' + \frac{z_\alpha}{|z_\mathrm{r}|};\ \lambda'' \right) \right] \times \exp\left(\frac{-z_\alpha \psi}{|z_\mathrm{r}|} \right) \qquad (12)$$

$$y = L\left[1 - f(\psi, \lambda', \lambda'')/j_\mathrm{a}\right] \qquad (13)$$

where new designations are introduced for dimensionless currents transported by ions of the same charge

$$j_\alpha = \frac{L}{z_\alpha F c^0} \sum_i \frac{I_{\alpha i}}{D_{\alpha i}} \qquad \alpha = \mathrm{a, b, r} \qquad (14)$$

for the integral concentration

$$c^0 = \sum_i c_{\mathrm{r}i}^0 \qquad (15)$$

and for the dimensionless electrical potential

$$\psi = -\frac{|z_\mathrm{r}| F}{RT} (\phi - \phi_0) \qquad (16)$$

The function $f(\psi,\ ', \lambda'')$ included in eqns. (12) and (13) is just a linear combination of two exponential functions of the potential in the form $\exp[(\lambda' \pm \lambda'')\psi]$. The procedures for deriving expressions (12) and (13) and the explicit form of the function $f(\psi,\ ', \lambda'')$ are given in Appendix A. It should be noted here that the function f is dimensionless and depends only on the ratio of the boundary concentrations $c_{\alpha i}$ and the ratio of currents j_α as parameters, and not on the currents themselves.

Equating the right-hand sides of (12) in turn to zero, we can find values of the potentials ψ_0 that correspond to zero concentrations. After determining the value of the potential using the algorithm given in Section 4, the dimensionless value of the limiting current $j_a = f(\psi_0, \lambda', \lambda'')$ can be derived from (13) and then, using the stoichiometric relations, the values of all other currents can be obtained.

Unfortunately, the numerical solution of a transcendental equation is necessary for calculating the potential ψ_0, because the right-hand side of (12) is the sum of three exponential functions with different exponents.

In order to investigate the main properties of the system without performing numerical calculations, we shall discuss in detail an important case of a system containing three ion species with different charges in which each species reduces (or oxidizes) on the electrode independently of all others. We then discuss the behavior of a three-ion system with arbitrary stoichiometry. The analytical solution is obtained for another specific case when the total flow of ions with a particular charge is zero. Finally, the general features of the problem are discussed.

6. System containing three ion species with different charge numbers

We consider the case when three kinetically independent electrochemical reactions take place on the electrode and exactly one ion species takes part in each of them. Let us assume that ion species $A_1^{z_a+}$ (for simplicity A) takes part in the first reaction, ion species B^{z_b+} (for simplicity B) takes part in the second reaction and ion species R^{z_r-} (R) takes part in the third reaction. In this case the concentration distribution (12) is given by (see Appendix A)

$$c_a = c_a^0\, e^{\lambda'\psi}[\cosh(\lambda''\psi) + \beta_1 \sinh(\lambda''\psi)] \tag{17}$$

$$c_b = c_b^0\, e^{\lambda'\psi}[\cosh(\lambda''\psi) + \beta_2 \sinh(\lambda''\psi)] \tag{18}$$

$$c_r = (c_a z_a + c_b z_b)/z_r \tag{19}$$

Equating the right-hand side of eqn. (17) to zero, we find the value of the potential ψ_0 which relates to the limiting current produced by the component of species A^{z_a+}: $\psi_0 = 1/\lambda''$ arccoth β_1. Introducing ψ_0 into (13) at y = 0 we find the dimensionless limiting current of the first reaction:

$$j_a = f(1/\lambda'' \operatorname{arccoth} \beta_1, \lambda', \lambda'') \tag{20}$$

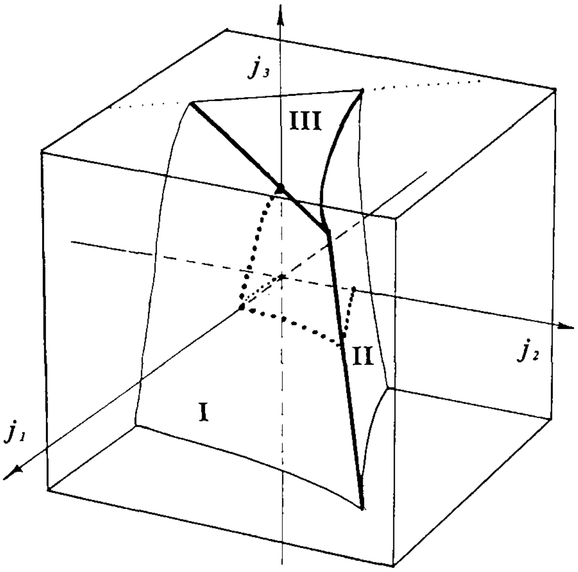

Fig. 1. Surfaces corresponding to the limiting regimes of the electrochemical system for $z_1 = 2$, $z_2 = 1$ and k = 0.3.

An expression for the limiting current corresponding to cation species B can be obtained from eqn. (20) by interchanging β_1 and β_2 (the definitions of constants λ', λ'', k, β_1 and β_2 are given in Appendix A).

The condition for the limiting current for anions has a completely different form:

$$j_a + j_b + j_r = 1 + k/z_1 + (1-k)/z_2 \tag{21}$$

This is why, in accordance with the condition of electroneutrality, as soon as the anion concentration approaches zero, the concentrations of both cations also approach zero. Therefore a totally limiting current is attained in this system. In this case the potential drop in the diffusion layer formally becomes unlimited. In the physical sense this means that the potential drop in the diffusion layer is comparable with that in the double layer in the range of high values of potential difference between the working electrode and a test electrode in the bulk solution. The conditions stipulating the limiting regimes of the electrochemical system under discussion are plotted in three-dimensional space (j_a, j_b, j_r) in Fig. 1. We now consider the picture obtained qualitatively (a strict analytical consideration is given in Appendix B). An inclined plane III is situated in the space region where j_a, $j_b < 0$ and characterized by expression (21). When the flow values j_a, j_b, j_r correspond to the points on this plane, concentrations of all the components approach zero near the electrode. In a certain sense it is possible to designate it a totally limiting current for all j_a, $j_b < 0$. The straight line given by expressions

$$\begin{aligned} j_a &= k(1 + z_r/z_a - j_r) \\ j_b &= (1-k)(1 + z_r/z_b - j_r) \end{aligned} \tag{22}$$

lying in the plane (21) and continuing into the area of positive j_a and j_b should also be noted. This straight line is the boundary between two curvilinear surfaces corresponding to the limiting regimes for cations of species A (surface I) and species B (surface II). Surfaces I and II both have variable curvature and become steeper as $j_a \to -\infty$ and $j_b \to -\infty$ respectively. The junction point of the three surfaces has the following coordinates:

$$\begin{aligned} j_a &= 0 \\ j_b &= (1-k)(|z_r|/z_b - |z_r|/z_a) \\ j_r &= 1 + |z_r|/z_a \end{aligned} \tag{23}$$

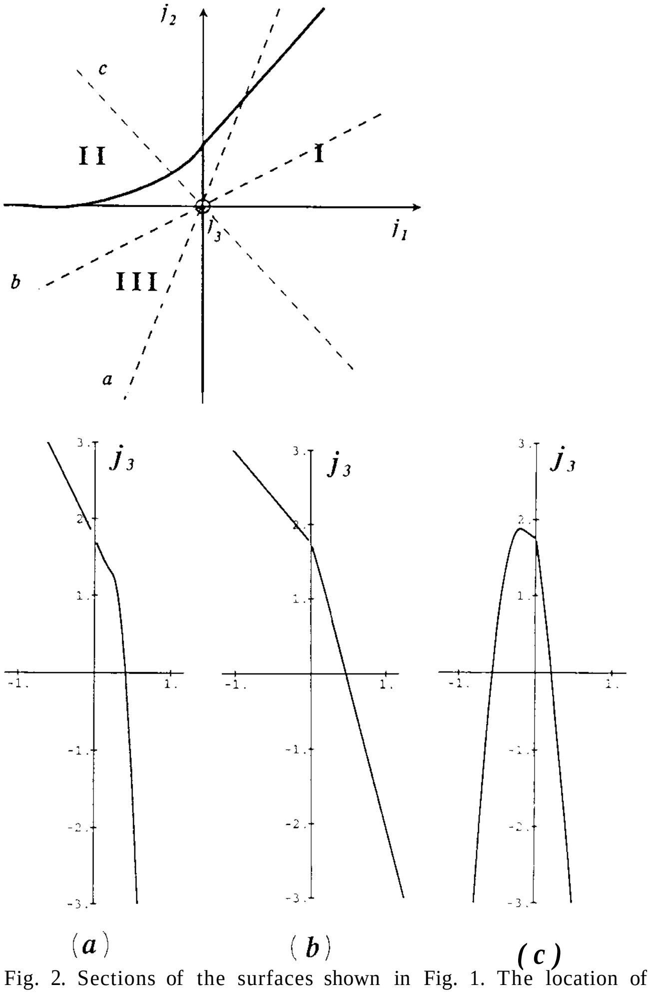

Fig. 2. Sections of the surfaces shown in Fig. 1. The location of sections a–c is indicated on the scheme.

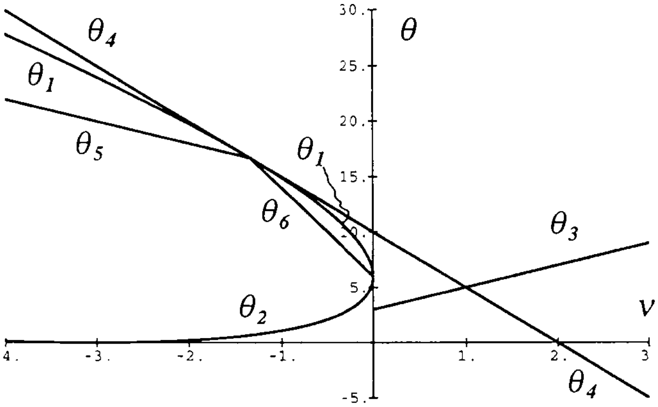

Fig. 3. Boundaries between different regions characterizing the behavior of the system.

The boundary between surfaces III and I is half the straight line beginning at the junction point and lying in the surface $j_2 = 0$. The boundary between surfaces II and III is much more complicated. This curve is a tangent to the straight line (23) at the junction point, then approaches the plane $j_1 = 0$ tangentially and finally continues along the half-straight line analogously to the boundary between III and I.

Some axial sections of the surfaces I, II and III are shown in Fig. 2. It should be noted that the results shown in Figs. 1 and 2 are obtained from precise analytical expressions, i.e. the coordinate of any point can be obtained with the aid of a pocket calculator.

Each domain of surfaces I-III is "projected" onto the corresponding area of the surface (ν, θ) (see Figs. 3 and 4 and Appendix B). The simplifying factor is that the lines of the changing regime (where the concentrations are expressed by trigonometrical and hyperbolic functions) do not affect the form of surfaces I and II and hence they are not plotted in Fig. 4.

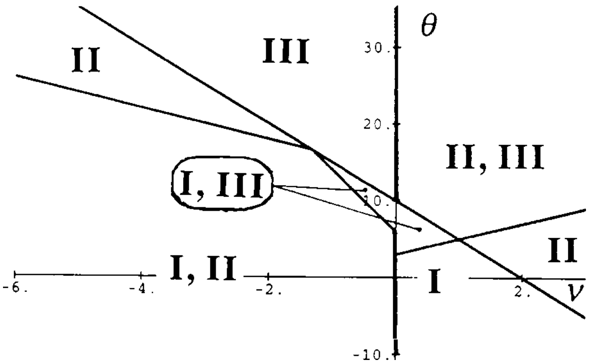

Fig. 4. "Map" for the construction of the surface of limiting current regimes.

7. Discussion

The different types of system behavior depending on the sequence of standard potentials of the reactions can easily be described qualitatively using the figures given above.

For example, let us assume that the reduction reaction of the first cation species begins with an increase in potential difference. This corresponds to movement of the point (j_a, j_b, j_r) from the origin along the axis j_a. At a particular value of the potential this point reaches surface I, i.e. the system becomes limited by cations of the first species. If the reduction reaction of the second cation species then "switches on", the point characterizing the state of the system stays on surface I and at the same time begin to move along the curve on the plane $j_3 = 0$ towards the straight line (22) that divides surfaces I and II. After the anion reaction is "switched on", this point can move along the straight line (22). To determine the final state of the system it is necessary to define the correlation between the kinetics of three electrode reactions. If the reaction potentials do not differ significantly, the trajectory of the point on the curves deviates to some extent from that described above.

If the anion reaction "switches on" after the reduction reaction of cation species 1, the point (j_a, j_b, j_r) moves along the line of intersection of the vertical plane $j_b = 0$ and surface 1 towards surface 111, and then continues along the straight line separating surfaces II and III.

The phenomenon of the increase in the reduction limiting current of the cations when anion reduction appears was first described by Heyrovsky and Bures [24] and denoted "exaltation of the migration current". Calculations of the line separating surfaces 11 and III have been performed by Newman **[6].** The solutions for the system of transport equations in the case of two parallel cation reduction reactions (for the range where $j_a, j_b > 0$) are also given in the literature [21]. Our solution allows us to calculate values of limiting diffusion–migration currents for an arbitrary three-ion electrochemical reaction. Evidently, the ion fluxes (of both products and reagents) of a given electrochemical reaction are proportional to each other with coefficients defined by stoichiometric coefficients. The solution given above depends only on the ratio of the fluxes. Therefore it is possible to calculate the values of one or two limiting diffusion–migration currents (depending on the stoichiometry of the reaction).

The physical meaning of the existence of two different limiting currents for the same electrochemical reaction (1) is evident. The reaction can proceed in two different directions (cathodic or anodic). Therefore the process can be limited by different ion species. If the reactants are not all present in excess (e.g. H_2O), a limiting current is obviously impossible for this type of reaction (in the region $j_a, j_b, j_r > 0$).

A geometrical interpretation can also be given. The definite stoichiometric coefficient makes it possible to construct a straight line in the space (j_a, j_b, j_r) which passes through the origin and comprises the points corresponding to physically possible states of the system. If this line intersects two surfaces, the maximum rates of both reactions (cathodic and anodic) are subject to restrictions. However, if the line intersects only one surface, one of the reactions can generally proceed at an unlimited rate (electrodissolution of the metal).

The most useful results obtained from the analysis of limiting current surfaces are those for the common case of two parallel electrochemical reactions. Each of the reactions is represented by a separate straight line in the space (j_a, j_b, j_r) (a set of covectors from the origin in terms of analytical geometry). The superposition of two reactions corresponds to the superposition of their vectors. As a result, the physically available area is the whole plane "stretched" on the vectors. The only boundaries of this area are the curves of intersection of the plane and the limiting current surfaces.

For example, let us assume that during the first reaction that reaches a limiting current, ions of species 1 are consumed. Then the system can evolve in three different ways.

(1) Owing to the stoichiometry of the two reactions, the total flux of ions of species 2 is directed towards the electrode. Then the system moves towards the state of a completely limiting current (points of intersection of "the straight line of limiting current" (22) and the physically realized plane) [25]. This state of limitation satisfies both generally accepted criteria of the limiting current: (a) the integral current flowing in the system achieves its maximum value; (b) concentrations of all reacting components approach zero.

(2) The cation flux (from one side) and the anion flux (from the other) are in opposite directions. Then the two electrochemical reactions "help" each other. Even when all concentrations near the electrode approach zero, the electric current can increase owing to transformation of the electric field in the diffusion layer.

(3) Fluxes of cations of different species are in opposite directions, and the cations produced on the electrode (e.g. species A) force out the cations of the other species when the potential difference increases. The result is that the reaction consuming cation species B has to correlate with the reaction which produces them. In this case we are dealing with an integral electrochemical reaction where the intermediate (ions of species B) should be excluded. If ions of species B are not produced at all, the reaction under consideration is completely suppressed. It should be emphasized that this suppression is due to diffusion–migration restrictions for ion transport and not to the reactional restrictions. In. the absence of the second (hindering) reaction, this reaction could proceed at a significant rate. Such a limitation of one reaction by the other owing to the diffusion–migration kinetics was first described by Sokirko and Kharkats [25].

Reactions which proceed in only one direction, either cathodic or anodic, are frequently encountered in electrochemistry. In this case another restriction appears. First, the plane corresponding to two other reactions should be identified in the current space (j_a, j_b, j_r). One of the semi-spaces formed in this way is chosen to correspond to one direction of the reaction. If the second reaction also proceeds only in one direction, it is necessary to impose similar restrictions. For example, if only the cation reduction reactions take place on the electrode (precipitation of metal alloys on an electrode which is not consumed) only a quarter of the space, namely the region $j_1, j_2 > 0$, should be left. These supplementary planes also impose certain restrictions on the evolution of the system, depending on potential difference. However, in contrast with the limiting current surfaces, if a certain point (j_a, j_b, j_r) reaches this plane it indicates only the absence of the corresponding reaction [26]. The easier case, when there are only two parallel reactions in the electrochemical system and the restricting planes degenerate into restricting semi-straight lines, has been studied earlier [22].

We have discussed the cases of one, two and three parallel reactions. These results can be generalized to the case of four or more parallel reactions. In fact, the additional fourth reaction differs from the simple superposition of the first three reactions only in the presence of neutral reactants $S_{\alpha i}$. Therefore the location of the characterizing point at the onset of the fourth and subsequent reactions will not change in principle. It will still be located on the straight line corresponding to the limiting current or on the other restricting surface. This means that new reactions would probably replace other reactions (suppressing them), i.e. there would be no significant changes in current values.

Generalization to the case of a system with ions of more than three types is both much more interesting and much more difficult. For example, assume that there are anions of two different species in the system (with the same charge). All the restrictions discussed above for the region of possible current values (j_a, j_b, j_r) apply in this case. Moreover, new restrictions appear associated with the fact that the concentration of a certain anion species (not just their sum) may become zero on the electrode. These conditions result in the appearance of additional surfaces (in the case of three reactions) or curves (in the case of two reactions) which can have rather complicated shapes.

In particular, it is possible that when all necessary restrictions have been taken into account, the remaining space of possible values (j_a, j_b, j_r) will consist of several unconnected domains. Gradual transition from one domain to another, i.e. under slow changes in the potential, is impossible. Transitions can only occur from a non-stationary state or by "revolutionary" jumps, i.e. by a rapid change in current or transformation of the concentration profile under small potential changes. Therefore, the system described above provides an example of electrochemical instability.

Unfortunately, as mentioned in Section 5, problems of limiting currents in such systems must be solved numerically. In connection with this, we consider two studies [22,26] in which parallel precipitation of copper in an acid solution and the reduction of NO_3^- ions to NO; ions were considered. In this case the integral flux of anions towards the electrode is zero, and it is possible to calculate the surface of the limiting current analytically, using the fact that the NO; concentration approaches zero at the electrode (the case of two parallel electrochemical reactions was considered in ref. 22 and the case of three reactions was considered in ref. 26).

If a homogeneous chemical reaction takes place inside the volume of the transport zone, the region of possible current values is expanded. The effect of the possible influence of the recombination of H^+ and OH^- on copper reduction has been investigated [27], and it was shown that the physically realized area of current values consists of two or even three unconnected domains.

8. Conclusion

The conditions for the appearance of limiting transport currents in an electrochemical system with ions of three arbitrary charges have been studied theoretically. The majority of the experimental systems include ions with two or three different charge numbers. Therefore the results presented in this work, together with results obtained earlier for a system, with ions of two different charges [28], can be used to give full descriptions of existing real system. The cases of both excess and no supporting electrolyte were investigated. In the first case an algorithm for the determination of a step-like current–voltage curve was proposed. In the second case, i.e. in the presence of both diffusion and migration transport in the system, the distribution of concentrations of all components inside the diffusion layer was found, and the general analytical solution for limiting currents in a system containing three different ion species with different charges was given. Cases of one. two and three parallel electrochemical reactions with arbitrary stoichiometry were discussed in detail. It was shown that the region of physically realized currents is restricted by surfaces (curves in the case of two reactions) of various origins:

(a) two curvilinear surfaces and one plane correspond to zero concentrations of cations of either the first or second species and the concentration of anions in proximity to the electrode;

(b) planes (passing the origin) if the reaction (reactions) can proceed in only one direction;

(c) curvilinear surfaces (curves) of a rather complicated shape if there are more than three ion species in the system.

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Nomenclature

$A_i^{z_a+}$(A)	anion species ($i = 1, 2, \ldots$) with charge number z_a
a_{ki}	stoichiometric coefficients of $A_i^{z_a+}$ in the kth reaction
$B_i^{z_b+}$(B)	cation species ($i = 1, 2.. \ldots$) with charge number z_b
b_{ki}	stoichiometric coefficients of $B_i^{z_b+}$ in the kth reaction
c^0	integral concentration in the bulk solution
$c_{\alpha i}$	concentrations of the ion species αi ($\alpha =$ a, b. r; $i = 1, 2, \ldots$)
$c_{\alpha i}^0$	concentrations of ions species αi in the bulk solution
c_1	dimensionless total concentration of cation species $A_i^{z_a+}$
c_2	dimensionless total concentration of cation species $B_i^{z_b+}$
c_3	dimensionless total anion concentration
$D_{\alpha i}$	diffusion coefficients of the ion species αi ($\alpha =$ a, b, r; $i = 1, 2, \ldots$)
F	Faraday constant
f	auxiliary function
I	integral current density
I^1	integral limiting current density
I_k	current density produced in the kth electrochemical reaction
I_k^1	limit value of I_k
$I_{\alpha i}$	current density transported by ion species αi ($\alpha =$ a, b, r; $i = 1, 2, \ldots$)
j_α	dimensionless current transported by ion a ($\alpha =$ a, b, r)
k	dimensionless bulk concentration
L	diffusion layer thickness
m_k	number of electrons transferred in the kth reaction
R	gas constant
$R_i^{z_r}$	anion species ($i = 1, 2, \ldots$)
r_{ki}	stoichiornetric coefficients of $R_i^{z_r-}$ in the kth reaction
S_i	neutral substances ($i = 1, 2, \ldots$)
s_{ki}	stoichiometric coefficient of S_i in the kth reaction
T	absolute temperature
u_1, u_2	combinations of charge number
x	dimensionless coordinate
y	coordinate
z_a, z_b	charge numbers of cation species
z_r	charge numbers of anion species
z_1, z_2	normalized charge numbers of cation species
β_1, β_2	auxiliary dimensionless variables
θ	auxiliary dimensionless variable
θ_i	characteristic curve on the plane (ν, θ) ($i = 1, 2, \ldots$)
$\lambda' \pm \lambda''$	roots of the characteristic equation
ν	auxiliary dimensionless variable
ϕ	electric potential
ϕ_0	electric potential on the boundary
ψ	dimensionless potential
ψ_0	value of ψ corresponding to zero concentration

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Appendix A

The distributions of concentration and potential in the diffusion layer in the case when the currents transported by each of the components are known are determined in this appendix.

Summing eqn. (2) for ions of the same charge number, we obtain

$$\frac{\mathrm{d}c_1}{\mathrm{d}x} + z_1 c_1 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_{\mathrm{a}} \tag{A1}$$

$$\frac{\mathrm{d}c_2}{\mathrm{d}x} + z_2 c_2 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_{\mathrm{b}} \tag{A2}$$

$$\frac{\mathrm{d}c_3}{\mathrm{d}x} - c_3 \frac{\mathrm{d}\psi}{\mathrm{d}x} = j_{\mathrm{r}} \tag{A3}$$

where, in addition to definitions (14), the following new dimensionless functions are introduced:

$$\begin{aligned} &c_1 = \sum_i c_{\mathrm{a}i}/c^0 \qquad c_2 = \sum_i c_{\mathrm{b}i}/c^0 \\ &c_3 = \sum_i c_{\mathrm{r}i}/c^0 \qquad k = \sum_i c^0_{\mathrm{a}i}/c^0 z_1 \\ &x = y/L \qquad z_1 = z_{\mathrm{a}}/|z_{\mathrm{r}}|\,/z_2 = z_{\mathrm{b}}/|z_{\mathrm{r}}| \end{aligned} \tag{A4}$$

The condition of electroneutrality **(3)** in dimensionless form becomes

$$z_1 c_1 + z_2 c_2 = c_3 \tag{A5}$$

and the boundary conditions (4) become

$$\begin{aligned} &c_1(x=1) = k/z_1 \qquad c_2(x=1) = (1-k)/z_2 \\ &c_3(x=1) = 1 \qquad \psi(x=1) = 0 \end{aligned} \tag{A6}$$

It should be noted, that the system of equations (A1)-(A3) and (A5) with the boundary conditions (A6) describe parallel reduction of two cation species and of one anion species. Therefore the full problem (2)–(4) is reduced to an easier form.

Multiplying eqn. (A1) by z_1, eqn. (A2) by z_2 and eqn. (A3) by -1, summing them and taking (A5) into account, we obtain

$$\frac{\mathrm{d}x}{d\psi} = \left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^{-1} = \frac{u_1 c_1 + u_2 c_2}{j_1 \theta} \tag{A7}$$

where the following variables are introduced for simplicity:

$$\begin{aligned} &u_1 = z_1(z_1+1) \qquad u_2 = z_2(z_2+1) \\ &\theta = z_1 + \nu z_2 - j_{\mathrm{r}}/j_{\mathrm{a}} \qquad \nu = j_{\mathrm{b}}/j_{\mathrm{a}} \end{aligned} \tag{A8}$$

Multiplying (A1) and (A2) by $\mathrm{d}x/\mathrm{d}\phi$ and using the correlation

$$\frac{\mathrm{d}c}{\mathrm{d}x}\,\frac{\mathrm{d}x}{\mathrm{d}\psi} = \frac{\mathrm{d}c}{\mathrm{d}\psi}$$

we obtain, taking (A7) into account,

$$\begin{aligned} &\frac{\mathrm{d}c_1}{\mathrm{d}\psi} = \left(\frac{u_1}{\theta} - z_1\right)c_1 + \frac{u_2}{\theta}c_2 \\ &\frac{\mathrm{d}c_2}{\mathrm{d}\psi} = \frac{u_1\nu}{\theta}c_1 + \left(\frac{u_2\nu}{\theta} - z_2\right)c_2 \end{aligned} \tag{A9}$$

It is not necessary to write down the equation for c_3 because it depends functionally on (A9) and (A7). Equations (A9) form a set of ordinary first-order linear differential equations. The characteristic equation of this system is

$$\theta\lambda^2 - (u_1 + u_2\nu - \theta z_1 - z_2\theta)\lambda + (\theta z_1 z_2 - u_1 z_2 - \nu u_2 z_1) = 0 \tag{A10}$$

After some transformation, the discriminant Δ of the quadratic equation (A10) can be expressed as follows:

$$\Delta = \theta^2(z_1 - z_2)^2 - 2\theta(z_1 - z_2)(u_1 - \nu u_2) + (u_1 + \nu u_2)^2 \tag{A11}$$

The roots A,, A, of the characteristic equation (A10) can be presented in the following form:

$$\lambda_{1,2} = \lambda' \pm \lambda'' \tag{A12}$$

where

$$\begin{aligned} &\lambda' = (u_1 + u_2\nu - \theta z_1 - z_2\theta)/2\theta \\ &\lambda'' = \sqrt{\Delta}/2\theta \end{aligned} \tag{A13}$$

After taking the boundary conditions (A6) into account, the distribution of concentrations $c_1(\psi)$ and $c_2(\psi)$ can be expressed as

$$\begin{aligned} c_1(\psi) &= \frac{k}{z_1} e^{\lambda'\psi}(\cosh \lambda''\psi + \beta_1 \sinh \lambda''\psi) \\ c_2(\psi) &= \frac{1-k}{z_2} e^{\lambda'\psi}(\cosh \lambda''\psi + \beta_2 \sinh \lambda''\psi) \end{aligned} \qquad \text{(A14)}$$

The unknown constants β_1 and β_2 are found by introducing (A14) into eqns. (A9) and comparing the terms at cosh $\lambda''\psi$ (or sinh $\lambda''\psi$):

$$\begin{aligned} &\left(\frac{u_1}{\theta} - z_1 - \lambda' + \frac{u_2}{\theta}\frac{z_1}{z_2}\frac{1-k}{k}\right) \\ \beta_2 &= \frac{1}{\lambda''}\left(\frac{u_2\nu}{\theta} - z_2 - \lambda' + \frac{u_1\nu}{3}\frac{z_2}{z_1}\frac{k}{1-k}\right) \end{aligned} \qquad \text{(A15)}$$

Introducing (A14) into (A7) and integrating, we obtain the relationship between the dimensionless coordinates x and ψ:

$$x = 1 - f(\psi, \lambda', \lambda'')/j_a \qquad \text{(A16)}$$

where the function $f(\psi, \lambda', \lambda'')$ is defined as

$$\begin{aligned} &f(\psi, \lambda', \lambda'') \\ &\quad - \frac{1}{(2\theta\lambda')^2 - \Delta} \\ &\quad\quad \times\Big([k(z_1+1) + (1-k)(z_2+1)] \\ &\quad\quad \times\{\lambda' - [-e^{\lambda'\psi}(\lambda' \cosh \lambda''\psi - \lambda'' \sinh \lambda'\psi)]\} \\ &\quad + [k(z_1+1)\beta_1 + (1-k)(z_2+1)\beta_2] \\ &\quad\quad \times[-\lambda'' - e^{\lambda'\psi}(\lambda' \sinh \lambda''\psi - \lambda'' \cosh \lambda''\psi)]\Big) \end{aligned} \qquad \text{(A17)}$$

If $\Delta < 0$, the characteristic roots λ_1, λ_2 of the equation become complex, but this does not affect the existence of real solutions for concentrations and potentials. Indeed, the only imaginary variable λ'' is included in (A14) in the combinations cosh $\lambda''\psi$ and sinh $\lambda''\psi/\lambda''$, which can be replaced by the real functions $\cos(i\lambda''\psi)$ and $\sin(i\lambda''\psi)/i\lambda''$. A similar transformation can be performed for expression (A17).

Equation (2) for the distribution of a component with charge number z_α can be expressed as follows after replacing the independent variable:

$$\frac{dc_{,,}}{d\psi} + \frac{z_\alpha c_{\alpha i}}{|z_r|} = \frac{I_{\alpha i}L}{FD_{\alpha i}}\frac{dx}{d\psi} \qquad \text{(A18)}$$

This is an ordinary linear differential equation of first order in $c_{\alpha i}$. It can be solved by varying the integration constant. The final result is

$$c_{\alpha i} = \left[c^0_{ai} + \frac{I_{\alpha i}L}{j_\alpha FD_{\alpha i}} f\left(\psi;\ \lambda' + \frac{z_\alpha}{|z_r|};\ \lambda''\right)\right] \exp\left(-\frac{z_a\psi}{|z_r|}\right) \qquad \text{(A19)}$$

It should be emphasized that expressions (A16) and (A19) present an explicit (although rather complex) parametric dependence of concentration profile on the coordinate.

Appendix B

The conditions for the validity of eqns. (20) and (21) are given in this appendix. In addition, we consider the case $z_1 < z_2$ (the case $z_1 = z_2$ can be obtained by applying the limit transition $z_1 \rightarrow z_2$).

The first obvious consideration is that the system can reach the limiting current state relative to any component α only if its current is directed towards the electrode: $j_a > 0$. The solution depends only on the ratio of dimensionless currents j_α, i.e. on parameters ν and θ. Therefore it is convenient to carry out the analysis on the plane (ν, θ). In that coordinate system all boundaries between different regions characterizing the system behaviour are expressed by simple curves (parabolas and straight lines), which are designated $\theta_i = \theta_i(\nu)$ (Fig. 3).

One of the most important curves is the parabola

$$\theta_{1,2} = \frac{u_1 - u_2\nu \pm \sqrt{(-\nu u_1 u_2)}}{z_1 - z_2} \qquad \nu < 0 \qquad \text{(B1)}$$

where the discriminant **A** of the characteristic equation (A10) approaches zero. This parabola is tangential to the axis $\nu = 0$ at $\theta = u_1/(z_1 - z_2)$ and the axis $\theta = 0$ at $\nu = -u_1/u_2$. As was shown, the concentration distribution is expressed by trigonometric functions of the potential inside the parabola $\theta_{1,2}$ and by hyperbolic functions outside it.

It is necessary for the existence of limiting currents produced by cation species A that $\psi_0 = -1/\lambda''$ arccoth β_1 should be real, i.e. $|\beta_1| > 1$ outside the parabola. It can be shown by direct calculation that the condition $|\beta_1| = 1$ is equivalent to the condition that the point (ν, θ) should lie on the straight line

$$\theta_4(\nu) = z_1 + z_2\nu + \frac{z_2\nu(1+z_1)}{(1-k)(z_2-z_1)} - \frac{z_1(1+z_2)}{k(z_2-z_1)} \qquad \text{(B2)}$$

The straight line $\theta_4(\nu)$ is tangential to the upper part of the parabola 0, at the point with the coordinate $\nu = \nu^*$:

$$\nu^* = -\frac{z_1(1+z_2)}{z_2(1+z_1)}\left(\frac{1-k}{k}\right)^2 \qquad \text{(B3)}$$

Let us consider the positive semi-plane $\nu > 0$. In the region above the line θ_4, the condition $|\beta_2| > 1$, $|\beta_1|$

< 1 is valid, and so the limiting current may be produced by the components of the second species but not of the first species. Under the line θ_4 the condition $|\beta_1| > 1$, $|\beta_2| < 1$ is valid, and the limiting current may be produced by the components of the first species only. Thus the quadrant of space (j_a, j_b, j_r) defined by the condition $v > 0$ $(j_a > 0, j_b > 0)$ is divided between variants of "limitation" by cations of one or other species. However, "limitation" by cations is impossible in the quadrant $(j_a < 0, j_b < 0)$, which also agrees with the condition $v > 0$. Condition (21) for the limiting anion current can be expressed as

$$j_a = \frac{1 + k/z_1 + (1-k)/z_2}{1 + \nu + z_1 + \nu z_2 - \theta} \tag{B4}$$

The flow value j_a from (B4) is negative if $\theta > \theta_3(\nu)$, where

$$\theta_3(\nu) = 1 + z_1 + \nu(z_2 + 1) \tag{B5}$$

Therefore one or two different states of the limiting current can correspond to each point on the plane (ν, θ). From the mathematical point of view, this property of the plane (ν, θ) arises because it is the projective space [29] of the three-dimensional space (j_a, j_b, j_r).

The interdependence between different variants of the solution is much more complex when $v < 0$. In this case conditions $|\beta_1| > 1$ and $|\beta_2| < 1$ coincide with each other and are valid for the points lying below $\theta_4(\nu)$: $\theta < \theta_4(\nu)$. Meanwhile, the increase in potential difference ψ from zero at fixed ν and θ (i.e. fixed β_1, β_2, λ', λ'') should be considered. It is obvious that below a certain value of the potential ψ_0 the limiting current will be reached by c_1 or c_2 depending on the values of β_1 and β_2. A further increase in ψ (reaching the other limiting regime) is impossible. This contradiction can be solved by the fact that the potential can change in both positive and negative directions, which leads to two different values of the limiting currents (at the same values of v and θ). The necessary condition for that state of the system is $\beta_1\beta_2 < 0$, which is equivalent to a domain located under the line

$$\theta_5 = \left(u_1 - u_2\nu + 2u_2\frac{1-k}{k}\frac{z_1}{z_2}\right)/(z_1 - z_2) \tag{B6}$$

and under the segment

$$\theta_6 = \left(u_1 - u_2\nu - 2u_1\nu\frac{k}{1-k}\frac{z_2}{z_1}\right)/(z_1 - z_2) \tag{B7}$$

The segment θ_6 connects the two tangent points to parabola θ_1 mentioned above (see Fig. 3), and the line θ_5 begins at the tangent point to θ_4, and θ_1, and is parallel to the axis of the parabola $\theta_{1,2}$. Therefore in the domain restricted by the broken line, composed of θ_5, θ_6 and the axis $v = 0$, two variants of limiting currents determined by c, and c_2 exist. A simple but rather cumbersome analysis shows that in the domain between θ_4 and θ_5 the limitation process is determined only by c_2, and in the triangle between θ_4 and θ_6 it is determined only by c_1.

As the space quadrant j_a, $j_b > 0$ is divided into two parts, corresponding to two regimes limited by c_1 and c_2, the space quadrant $j_a < 0$, $j_b > 0$ is similarly divided into two parts, corresponding to limitation by c_2 and c_3. In this case the condition of the limiting current, determined by c_3 (i.e. $j_1 > 0$ or $\theta > \theta_3$), is valid over the whole domain $\theta > \theta_4$ and in the triangle limited by θ_4, θ_6 and $v = 0$.

Only one surface, according to the condition $c_1(0) = 0$. is located in the space quadrant $j_a > 0$, $j_b < 0$. This occurs because the condition $j_b > 0$, necessary for limitation by c_3, is valid only when $\theta < \theta_3$, i.e. in the region totally "occupied" by c_1 and c_2.

Figure 4 is a "map" showing domains for different regimes of system behavior. This "map" allows the possible regime(s) of limitation to be defined for each point (ν, θ), after which the value(s) of the limiting current can be determined using eqns. (21) and/or (22).