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Problems of the Theory of Transport Processes in Systems with Intensive Mass Exchange

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The principles of the macroscopic theory of processes of convective heat and mass transfer in systems with mass exchange, taking place under conditions of large concentration gradients, have been presented. For these systems, the structure of the hydrodynamic fluxes (in particular the velocity profile in the boundary layer next to the wall) shows a marked dependence on the concentration field of the substance being transferred. Studies in which the effect of the interaction between the processes of mass transfer and momentum transfer has been analysed quantitatively in relation to problems of chemical and electrochemical technology have been reviewed. The bibliography contains 68 references.

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I. INTRODUCTION

Present-day chemical and electrochemical technology, and many other fields of science and technology (for example thermophysics, hydrometallurgy, nuclear and electrochemical energetics, purification of gases, etc.) are engaged in the search for methods of intensifying interphase heat and mass transfer. Extensive possibilities in this connection are being opened up by the development of effective methods of dispersing and mixing, and the use of hydrodynamically non-stabilised conditions of convective transport and input regions of heat and mass exchange. High rates of the processes of interphase exchange are realised when these processes are carried out under markedly non-equilibrium conditions, that is with high temperature and concentration gradients.

Traditional methods of mathematical description, based on the separate solution of the equations of hydrodynamics and convective heat and mass transfer, are not applicable to systems in which transfer processes are taking place under conditions of intense mass exchange. In the traditional approach, the distribution of hydrodynamic velocities is found first (for example by solving the Navier–Stokes equations in the case of laminar flow conditions), after which this distribution is substituted in the equation of convective heat or mass exchange and solved for specific boundary conditions to determine the rate of interphase exchange. When applied to systems having large concentration gradients, however, this method of solution is not correct, since convective motion induced by mass exchange takes place[1,2]. The velocity of the induced movement is at right angles to the interphase boundary and the movement takes place in the direction of mass transfer. The physical factor responsible for this movement is the mechanical momentum, which is transferred from one phase to the other by the particles responsible for mass exchange. Since the transmitted momentum is proportional to the diffusion flow of the particles involved is mass transfer, the velocity field close to the interphase boundary depends on the concentration field. The specific form of this dependence is determined by the system of equations for the simultaneous transfer of momentum and mass, and also by the boundary conditions relating the fluxes of momentum and mass at the interphase boundary.

II. CHARACTERISTIC FEATURES OF THE HYDRODYNAMIC CONDITIONS OF INTENSIVE MASS EXCHANGE

The mechanical momentum, proportional to the velocity of interphase mass exchange, influences primarily the boundary conditions for the equations of hydrodynamics and mass transfer: these equations, unlike the case of systems with low velocities of interphase mass exchange, cannot be solved separately. To establish the relationship between the local velocity of movement of a continuous medium (liquid or gas) at the phase interface and the rate of interphase mass exchange, it is possible to take as an example the isothermal transfer of a solute from phase 1 to phase 2. For simplicity it will be assumed that each of the phases is a two-component liquid mixture (a solution of substance m in the corresponding solvent), and that the solvents are immiscible. The diffusion flux $j_m^{(i)}$ of the substance m at any point in space within the phase i is defined as follows[3]:

$$j_m^{(i)} = M_m c_m^{(i)} (\mathbf{v}_m^{(i)} - \mathbf{v}^{(i)}). \quad (1)$$

Here, $c_m^{(i)}$ is the molar concentration of the substance being transferred in the phase i; M_m the molecular mass of this substance; $\mathbf{v}_m^{(i)}$ the mean statistical velocity of the movement of the particles of the substance m in an arbitrary but fixed system of coordinates; and $\mathbf{v}^{(i)}$ the velocity of movement of the centre of mass of the entire liquid mixture in the same system of coordinates.

The velocity $\mathbf{v}^{(i)}$ is described by the system of equations of hydrodynamics (in the case of laminar flow conditions by the Navier–Stokes system of equations). At the same time, this velocity, by definition, is related to the velocities of the movement of the components of the mixture by

the relationship

$$\rho^{(i)}\mathbf{v}^{(i)} = M_m c_m^{(i)}\mathbf{v}_m^{(i)} + M_0 c_0^{(i)}\mathbf{v}_0^{(i)}, \qquad (2)$$

where the quantities having the subscript "0" refer to the corresponding solvent, and $\rho^{(i)} = M_m c_m^{(i)} + M_0 c_0^{(i)}$ is the total density of the solution in the phase i (in the general case this density is a function of the spatial coordinates and time). Each velocity in Eqn.(2) is represented as the sum of the velocity of movement of the interphase surface $d\mathbf{r}_s/dt$ ($\mathbf{r}_s$ is the radius vector of an arbitrary point at the phase interface) and the velocity relative to this surface $\mathbf{v}_{rk}^{(i)}$ ($k = m, 0$). Since the solvents are immiscible, the normal components of the velocities $v_{rn}^{(1)}$ and $v_{rn}^{(2)}$ at the interphase boundary should be equal to zero. Thus Eqn.(2), projected on to the direction of the normal $\mathbf{n}$ to the interphase boundary, has at each point on this boundary the following form:

$$\rho^{(i)}(\mathbf{v}_r^{(i)}, \mathbf{n}) = M_m c_m^{(i)}(\mathbf{v}_{rm}^{(i)}, \mathbf{n}); \quad i = 1, 2. \qquad (3)$$

The analogous operation of projecting Eqn.(1) on to the direction of the normal $\mathbf{n}$ leads, with allowance for Eqn.(3), to the equation

$$(\mathbf{v}_s^{(i)}, \mathbf{n}) = \left(\frac{d\mathbf{r}_s}{dt}, \mathbf{n}\right) + \frac{(J_{ms}^{(i)}, \mathbf{n})}{\rho_s^{(i)} - M_m c_{ms}^{(i)}}, \qquad (4)$$

applicable for any point on the interphase surface. The subscript "s" in this equation indicates that the corresponding quantity refers to the interface between the phases. If the form of the interface is given by one of the equations

$$y = f_1(x, t), \; z = f_2(r, t), \; r = f_3(\vartheta, t),$$

the following expressions give the first term on the right-hand side of Eqn.(4)

$$\left(\frac{d\mathbf{r}_s}{dt}, \mathbf{n}\right) = \begin{cases} \left[1 + \left(\frac{\partial f_1}{\partial x}\right)^2\right]^{-1/2} \frac{\partial f_1}{\partial t} & \text{(in a rectangular system of coordinates);} \\ \left[1 + \left(\frac{\partial f_2}{\partial r}\right)^2\right]^{-1/2} \frac{\partial f_2}{\partial t} & \text{(in a cylindrical system of coordinates);} \\ \left[1 + \left(\frac{\partial f_3}{f_3 \partial \vartheta}\right)^2\right]^{-1/2} \frac{\partial f_3}{\partial t} & \text{(in a spherical system of coordinates).} \end{cases}$$

The condition (4) can readily be generalised to the case where several substances are transferred simultaneously through the interface. According to this condition, the normal component of the velocity of the movement of a continuous medium close to the interphase boundary is determined by the rate of displacement of the boundary itself, the rate of interphase mass exchange, and the surface values of the concentrations of the substance, responsible for mass exchange. It follows from Eqn.(4) that in the case of sufficiently high rates of mass exchange, the hydrodynamic problem cannot be solved independently of the problem of convective diffusion.

A large number of examples of systems of practical interest have been described, in which intensive mass exchange leads to a significant change in the hydrodynamic conditions of heat and mass transfer[4-13]. The most typical examples in this connection are the condensation of a mixture of vapours on a cooled wall[4], the evaporation of a liquid on the surface of drops and bubbles[8,9], and the crystallisation and dissolution of salts[10-13]. One of the theoretical problems in which the velocity field being calculated is found to depend on the concentration field of the particles responsible for mass exchange is the problem of the anodic dissolution of a metal surface in a stream of electrolyte solution at a high electrical current density. This problem is directly related to the theory of the technique of three-dimensional electrochemical machining of metals and alloys which has wide practical uses[14-19]. Existing approaches to the analyses of the processes of intensive anodic dissolution are examined in the next section.

III. ANODIC DISSOLUTION OF METALS IN A STREAM OF ELECTROLYTE

The mathematical description of the macrokinetics of the processes of anodic dissolution, used in practice for the three-dimensional machining of metals, is usually based on the so-called model of the "ideal" electrochemical process[20-22]. This model assumes that: 1) Ohm's law applies throughout the entire space occupied by the solution, as far as the actual electrode surfaces; 2) the distribution of electrical potential in solution is everywhere described by the Laplace equation (in other words, the existence of regions of bulk charge close to the electrodes is not taken into account); and 3) the ionisation of the atoms of the dissolving metal takes place at a constant current efficiency (generally 100%). This means that calculations within the framework of the model of the "ideal" process can lead to satisfactory results only for systems in which the effects of chemical and concentration overvoltage do not play a significant role, and the basic electrical resistance is determined by the bulk properties of the solution, which are constant at all points in the gap between the electrodes.

Mathematically, the problem of the "ideal" process of anodic dissolution does not differ in principle from the problem of the filtration of liquids through porous media under conditions in which the hydrodynamic resistance of the medium is described by Darcy's law[23]. The main difficulty in this case lies in finding the solution of the Laplace equation for the region, the boundaries of which are related to this solution by a familiar differential equation. Even in this simplified formulation, the problem of determining the form of the gap between the electrodes is still extremely complex, and its solution usually requires the use of numerical methods. The problem can be solved in analytical form only in individual cases, mainly for regions having two-dimensional geometry, to which the methods involving the theory of the functions of a complex variable are applicable[24-28]. An elegant analytical method, based on the establishment of the relationship between the components of the complex potential being sought and the solution of the characteristic hypergeometric equation, was developed by Polubarinova-Kochina[23] for application to problems of the theory of filtration. This method can be used without any modification to solve the stationary problems of electrochemical machining within the framework of the model of the "ideal" process (the given values of the flux at the boundaries of the filtration region, the configuration of which is to be determined, are direct analogues of the given values of the potential at the electrodes of the electrochemical cell).

Since in practice it is necessary to deal with non-ideal processes, the calculations carried out on the basis of the "ideal" model generally do not give satisfactory results. It has been shown[18] that Ohm's law cannot be extrapolated from the bulk of the solution to the region of the diffusion boundary layer next to the anode. The results[18] indicate that the true value of the electric potential gradient next to the anode at current densities of the order of 10 A cm^{-2} and electrolyte concentrations of the order of 1 M may differ by several factors of tens from the value obtained without allowance for the effect of concentration overvoltage. For this reason, published methods[17,29,30] for solving the problems of electrochemical machining can hardly be regarded as corresponding to the actual conditions. This statement will be illustrated below by a specific example.

1. Electrochemical Dissolution of a Surface Uniformly Accessible for Ionic Mass Exchange

The problem of the anodic dissolution of a metal in a solution of its own salt (for example the dissolution of iron in iron chloride solution) can be considered. To obtain the analytical solution of this problem, the following simplifying assumptions are made[31-33].

1. The dissolving surface is uniformly accessible with respect to diffusion.

2. The dissolution process is stationary, that is the concentration of each component of the solution at any fixed distance from the surface of the anode (this surface will be regarded as planar) is independent of time.

3. Ionic mass transfer in the solution takes place at very large Schmidt numbers, so that the velocity profile within the diffusion boundary layer may be approximated by a uniform distribution with a constant velocity, equal to the velocity of the movement of the solution directly at the anode surface.

4. The ratio of the effective thicknesses of the diffuse and diffusion boundary layers next to the anode is negligibly small, so that the solution can be regarded as electrically neutral at all points up to the interphase boundary.

5. The physical and transport properties of the solution are independent of the local concentration of cations of the dissolving metal.

6. Dissolution takes place under isothermal conditions.

The condition of uniform accessibility with respect to mass exchange means that the local concentration of each component of the solution depends only on the distance to the surface of the anode:

$$c_k = c_k((\boldsymbol{r} - \boldsymbol{r}_s), \boldsymbol{n}).$$

The stationary form of the equation for the differential mass balance of the kth component of the solution is as follows:

$$\operatorname{div} \boldsymbol{j}_k + M_k(\boldsymbol{v}, \nabla c_k) = 0,$$

where the quantities $\mathbf{j}_k$, $\mathbf{v}$, and c_k are functions of the spatial coordinate $\boldsymbol{r}$. The replacement of $\boldsymbol{r}$ by the new independent variable $x = (\boldsymbol{r}, \boldsymbol{n}) - (\boldsymbol{r}_S, \boldsymbol{n})$ gives

$$\left\{(\boldsymbol{v}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\}\frac{\mathrm{d}c_k}{\mathrm{d}x} + \frac{1}{M_k}\frac{\mathrm{d}}{\mathrm{d}x}(\boldsymbol{j}_k, \boldsymbol{n}) = 0.$$

The assumption that the velocity field next to the anode is uniform makes it possible to replace the expression in braces by the right-hand side of Eqn.(4):

$$\frac{M_k(\boldsymbol{j}_1^{(s)}, \boldsymbol{n})}{\rho^{(s)} - M_1 c_1^{(s)}}\frac{\mathrm{d}c_k}{\mathrm{d}x} + \frac{\mathrm{d}}{\mathrm{d}x}(\boldsymbol{j}_k, \boldsymbol{n}) = 0; \quad k = 1, 2, 3. \tag{5}$$

Here, the subscripts $k = 1,2,3$ refer to the cations of the dissolving metal, the anions of the salt, and the solvent molecules respectively.

From the definition of the diffusion flux (1) and the mass-average hydrodynamic velocity (2) it follows that the vector sum of the diffusion fluxes of all the components present in the solution is equal to zero:

$$\sum_k \boldsymbol{j}_k = 0.$$

This means that in the three-component system being considered here, only two fluxes are independent. Subsequently, therefore, the mass transfer problem will be solved only for two components of the solution (for example 1 and 2).

In the formulation of the boundary conditions for Eqns.(5) it will be assumed that at a certain fixed distance $x = \delta$ from the surface of the anode, the ion concentrations c_1 and c_2 take their constant bulk values $c_1^{(0)}$ and $c_2^{(0)}$. The quantity δ in this approach is equivalent to the effective thickness of the diffusion boundary layer.

If the only electrochemical reaction taking place at the anode is the ionisation of the metal atoms, the normal component of the total mass flux of the metal cations at the surface of the anode

$$(\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) + M_1 c_1^{(s)}\left\{(\boldsymbol{v}^{(s)}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\},$$

should be proportional to the anodic current density i with proportionality coefficient equal to M_1/z_1F (F is the Faraday number):

$$\frac{iM_1}{z_1F} = (\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) + M_1 c_1^{(s)}\left\{(\boldsymbol{v}^{(s)}, \boldsymbol{n}) - \left(\frac{\mathrm{d}\boldsymbol{r}_s}{\mathrm{d}t}, \boldsymbol{n}\right)\right\}.$$

Allowance for Eqn.(4) gives

$$(\boldsymbol{j}_1^{(s)}, \boldsymbol{n}) = \frac{iM_1}{\rho^{(s)}z_1F}(\rho^{(s)} - M_1 c_1^{(s)}). \tag{6}$$

The normal $\mathbf{n}$ in the last expression, and subsequently throughout, is assumed to be directed from the anode towards the solution, and the current density is assumed to be positive.

When an analogous expression is written for the total mass flux of the electrochemically inert anion and this flux is put equal to zero at the anode surface, the following relationship is obtained:

$$(\boldsymbol{j}_2^{(s)}, \boldsymbol{n}) = -M_1M_2ic_2^{(s)}/\rho^{(s)}z_1F. \tag{7}$$

Eqns.(6) and (7) can be regarded as the boundary conditions for Eqns.(5). According to condition (7), the diffusion flux of an electrochemically inert anion at the interphase boundary is nonzero. The physical factor responsible for this fact is the existence of a nonzero normal component of the rate of movement of the centre of mass of the solution at the anode surface; this component leads to a diffusion of the anion from the solution to the surface.

Single integration of Eqn.(5) with boundary conditions (6) and (7) gives:

$$(\boldsymbol{j}_k, \boldsymbol{n}) = \frac{iM_1}{\rho^{(s)}z_1F}(\rho^{(s)}\delta_{1k} - M_k c_k); \quad k = 1, 2, \tag{8}$$

where δ_{1k} is the Kronecker symbol.

The fluxes $\mathbf{j}_k$ are related to the ionic concentration gradients by the following expressions[18]:

$$\boldsymbol{j}_1 = -\frac{D_{\mathrm{eff}}M_1M_3c}{\rho}\zeta(c_1, c_2)\nabla c_1 + \frac{M_1D_{13}\boldsymbol{i}}{F(z_2D_{23} - z_1D_{13})}\left[\frac{c_1}{\rho D_{13}}(M_1D_{13} - M_2D_{23}) - 1\right], \tag{9}$$

$$\boldsymbol{j}_2 = -\frac{D_{\mathrm{eff}}M_2M_3c}{\rho}\zeta(c_1, c_2)\nabla c_2 - \frac{M_2D_{23}\boldsymbol{i}}{F(z_2D_{23} - z_1D_{13})}\left[\frac{c_2}{\rho D_{23}}(M_1D_{13} - M_2D_{23}) + 1\right]. \tag{10}$$

Here, $\mathbf{i} = F[(z_1\mathbf{j}_1/M_1) + (z_2\mathbf{j}_2/M_2)]$ is the vector of the electric current density, related to the scalar current density i by the relationship $(\mathbf{i},\mathbf{n}) = i$, $\rho = M_1c_1 + M_2c_2 + M_3c_3$ is the local density of the solution, $c = c_1 + c_2 + c_3$ the total concentration of the liquid phase, D_{ik} the coefficients of mutual diffusion in the corresponding binary mixtures, and D_{eff} the effective coefficient of ionic mass transfer, defined by the expression

$$D_{\mathrm{eff}} = \frac{\rho(z_2 - z_1)D_{13}D_{23}}{(z_1c_1 + z_2c_2)(M_1D_{13} - M_2D_{23}) + \rho(z_2D_{23} - z_1D_{13})}. \tag{11}$$

The function $\zeta(c_1, c_2)$ is expressed in terms of the mean activity coefficient of the electrolyte γ_{12} by the relationship

$$\zeta(c_1, c_2) = 1 + \frac{\mathrm{d}\ln\gamma_{12}}{\mathrm{d}\ln(c_1/c_1^{(0)})}. \tag{12}$$

Using the fourth simplifying assumption above, which postulates that the condition of local electrical neutrality is fulfilled, the mass transfer problem will subsequently be examined only for the cations "1" (the concentration of the anions c_2 in this case is determined directly from the electrical neutrality condition). Substitution of Eqn.(9) in Eqn.(8) and simple transformation give:

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}+\frac{i}{F(z_1-z_2)M_2D_{23}c}\times$$
$$\times\left\{\frac{M_1D_{13}-M_2D_{23}}{D_{13}}c_1-\rho\left[1-\frac{(z_1-z_2)D_{23}}{z_1D_{\text{eff}}}\left(1-\frac{M_1c_1^{(s)}}{\rho^{(s)}}\right)\right]\right\}=0. \quad (13)$$

If the functional form of the relationship $\gamma_{12}=\gamma_{12}(c_1, c_2)$ is known, it follows that Eqn.(13), together with the condition of local electrical neutrality and the boundary condition (6), determines completely the solution of the problem posed. Since however the published[34] empirical correlations for the relationships $\gamma_{12}(c_1, c_2)$ have an extremely complex form, the rigorous integration of Eqn.(13) is impossible without using numerical methods.

To analyse the most characteristic features of ionic mass exchange under conditions of intensive anodic dissolution, a number of further simplifications can be carried out. Thus it is possible to examine the particular case of a solution composition at which, on the one hand, the local concentrations of the ions are low compared with the concentration of the solvent ($c\cong c_3$) and on the other hand, as a consequence of the high molecular mass of the dissolving metal, the local density of the cations M_1c_1 is comparable with the local density of the solution ρ. Putting $c=c_3=$ const. in Eqn.(13) gives

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}-\frac{iM_1c_1}{Fz_1\rho^{(s)}D_{\text{eff}}}=$$
$$=\frac{i}{F(z_1-z_2)D_{23}}\left[1-\frac{(z_1-z_2)D_{23}}{z_1D_{\text{eff}}}\left(1-\frac{M_1c_1^{(s)}}{\rho^{(s)}}\right)\right]. \quad (14)$$

If the influence of the mass flux of the cations on the hydrodynamics [this influence is described by the boundary conditions (6) and (7)] were not taken into account, the transfer equation would have the form

$$\left(1+\frac{d\ln\gamma_{12}}{d\ln(c_1/c_1^{(0)})}\right)\frac{dc_1}{dx}=\frac{z_2i}{Fz_1(z_1-z_2)D_{12}}. \quad (15)$$

Comparison of Eqns.(14) and (15) shows that the effect of the mutual influence of the processes of momentum and mass transfer begin to be observed under conditions of intensive anodic dissolution, when the partial density of the cations $M_1c_1^{(s)}$ in the layer next to the anode becomes comparable with the density of the solution next to the anode $\rho^{(s)}$.

The quantitative assessment of the contribution of this effect can be carried out, without loss of generality, by examining a restricted range of concentrations close to the minimum of the function giving the dependence of $\ln\gamma_{12}$ on c_1 (for most aqueous electrolyte solutions this minimum lies at concentrations of ~1 M,[34] that is in the range where the ratio $M_1c_1^{(s)}/\rho^{(s)}$ may amount to several tens %). In this case, putting $d\ln\gamma_{12}/d\ln(c_1/c_1^{(0)})=0$ in Eqn.(14) and integrating gives

$$c_1=(c_1^{(0)}+\chi)\exp\left[-\frac{iM_1(\delta-x)}{z_1F\rho^{(s)}D_{\text{eff}}}\right]-\chi, \quad (16)$$

where

$$\chi=c_1^{(s)}+\frac{z_2\rho^{(s)}D_{23}}{M_1(z_1D_{13}-z_2D_{23})}. \quad (17)$$

Eqns.(16) and (17) can be used to obtain an equation for determining the concentration of cations $c_1^{(s)}$ next to the anode:

$$[2z_1M_1D_{13}-(z_1M_2+z_2M_1)D_{23}]c_1^{(s)}+z_2M_3D_{23}c=$$
$$=[(z_1D_{13}-z_2D_{23})M_1c_1^{(0)}+z_1(M_1D_{13}-M_2D_{23})c_1^{(s)}+z_2M_3D_{23}c]\times$$
$$\times\exp\left(-\frac{z_2iM_1\delta(z_1D_{13}-z_2D_{23})}{z_1(z_1-z_2)FD_{13}D_{23}[(z_2M_1-z_1M_2)c_1^{(s)}+z_2M_3c]}\right). \quad (18)$$

If the diffusion flux had no influence on convective ion mass transfer from the anode surface, it follows from Eqn.(15) that the equation for $c_1^{(s)}$ would have the form

$$c_1^{(s)}=c_1^{(0)}-\frac{z_2i\delta}{z_1(z_1-z_2)FD_{13}}. \quad (19)$$

Analysis of Eqn.(18) shows that the value of $c_1^{(s)}$ which it gives, for any fixed current density i, is less than the corresponding value determined by Eqn.(19). The $c_1^{(s)}(i)$ relationship described by Eqn.(18) is monotonic, and for a formally unrestricted increase in current, in contrast to Eqn.(19), it gives not an infinitely large value of $c_1^{(s)}$ but a finite asymptotic value, defined by the equation

$$c_{1\max}^{(s)}=-\frac{z_2D_{23}\rho^{(s)}}{2M_1(z_1D_{13}-z_2D_{23})}. \quad (20)$$

Fig.1 gives the $c_1^{(s)}(i)$ relationship for the dissolution of bivalent iron in aqueous 1 *N* $FeCl_2$ at $\delta=10^{-3}$ cm, and for comparison the linear graph corresponding to the absence of mass flux at the anode surface. Fig.1 shows that for a given anodic current density, the true value of the concentration of cations in the layer next to the anode is always lower than the value calculated without allowance for the mutual influence of the processes of mass and momentum transfer. An important conclusion from this result is the prediction of the possibility of achieving higher current densities (compared with those obtained within the framework of the traditional theory of convective diffusion, applicable for systems having low rates of interphase mass exchange) for a given "critical" value of the concentration of metal cations next to the anode. The existence of this "critical" value under real conditions may be related either to supersaturation of the solution or to other restrictions, for example complex formation or bulk chemical reactions, the formation of passivating films, etc.

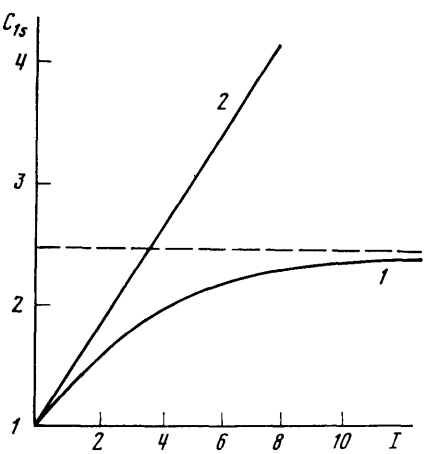


Figure 1. Dependence of the concentration of iron cations next to the anode (curve *1*) on the dimensionless current density $I=i\delta/Z_1FD_{13}c_2^{(0)}$ under the conditions of the dissolution of iron in 1 *N* aqueous $FeCl_2$ solution for $\delta=10^{-3}$ cm; the straight line corresponds to the conditions in which there is no mass flux at $x=0$ and no translational movement of the anode; $C_{1S}=c_1^{(s)}/c_2^{(0)}$.

Thus the above analysis indicates that it is necessary to take account of the interaction of the processes of mass and momentum transfer in the mathematical description of intensive electrochemical mass exchange. Estimates show that this interaction has a significant influence on the accuracy of the calculations at current densities of the order of 10 A cm^{-2} or more in molar (or more concentrated) solutions.

2. Macrokinetics of Intensive Electrochemical Mass Exchange in Solutions Containing Three Kinds of Ion

In many cases of practical interest, the process of anodic dissolution takes place in solutions containing ions of three kinds: the cations of the dissolving metal and the ions of the indifferent electrolyte. The latter is used to ensure that the electrical conductivity of the solution is sufficiently high. Since the intensive mass exchange accompanying the dissolution process can make the concentration of the cations of the dissolving metal close to the anode surface comparable with the local concentration of the ions of the indifferent electrolyte, it follows that in the equations for ionic mass transfer, even within the electricially neutral diffuse layer, it is necessary to consider the mechanism of electromigration.

It is appropriate to use the Nernst diffusion model[35] as a completely satisfactory approximation for application to the processes involved in the steady-state dissolution of surfaces uniformly accessible for mass exchange, when the local concentrations c_k and mass diffusion–migration fluxes j_k of all the ionic components of the solution depend only on the distance x to the anode surface. This model postulates the existence of a layer of a certain thickness δ next to the anode, in which the main change in the concentration of the components of the solution, limiting the rate of mass exchange, occurs.

The results obtained within the framework of the Nernst model show good agreement with the results of a theoretical analysis, based on the correct non-model allowance for the hydrodynamic conditions of mass transfer, if it is assumed that the effective thickness of the diffusion layer δ depends, in a definite manner, on the coefficient of molecular diffusion of the component being transferred. This relationship is a power dependence with exponent varying from 0.33 to 0.25 with change from laminar to turbulent mixing conditions[36]. Estimates based on the published equations[36] show that in the case of turbulent mixing conditions, the values of the thickness δ corresponding to different ionic components of the solution differ from one another by not more than 20%, if the coefficients of molecular diffusion of these components differ by a factor of not more than three. For this reason, in the examination of mass transfer in solutions containing ions of three kinds, it has been assumed[37–40] that the thickness δ is the same for all three kinds.

In the case of steady-state conditions of dissolution of a surface uniformly accessible for mass exchange, the system of equations of ionic mass transfer can be represented as follows[18]:

$$j_k = \frac{M_1 i}{z_1 F}\left(\delta_{1k} - \frac{M_k c_k}{\rho^{(s)}}\right); \quad k = 1, 2, 3. \tag{21}$$

Here, the subscript "1" for all quantities refers to the cations of the dissolving metal, and the subscripts "2" and "3" to the anions and cations respectively of the indifferent electrolyte. As before, the fluxes j_k are assumed to be positive if they are directed from the anode to the solution.

The fluxes j_k are related to the gradients of the ionic concentrations c_k and the electric potential ϕ by Onsager's equations[41]. In the case of solutions containing ions of three kinds, however, these equations contain the coefficients of mutual diffusion D_{12}, D_{13}, and D_{23}, which cannot be calculated theoretically or determined experimentally. It is therefore appropriate to examine as a first approximation the case of a sufficiently dilute solution, when it is possible to neglect the mutual influence of the ion fluxes and to approximate these fluxes by the expression

$$j_k = -M_k D_k \frac{dc_k}{dx} - \frac{z_k M_k D_k c_k F}{RT}\frac{d\varphi}{dx}; \quad k = 1, 2, 3, \tag{22}$$

where D_k is the diffusion coefficient of the ions of type k in the pure solvent, and z_k the valency of the ions. Substituting Eqn.(22) in Eqn.(21) gives the set of equations

$$\frac{dc_k}{dx} + \left(\frac{z_k F}{RT}\frac{d\varphi}{dx} - \frac{M_1 i}{z_1 F \rho^{(s)} D_k}\right) c_k + \frac{i\delta_{1k}}{z_1 D_1 F} = 0. \tag{23}$$

This set must be supplemented by the equation for the electric potential ϕ and by boundary conditions defining the values of the ion concentrations and the potential in the bulk of the solution (more accurately, beyond the limits of the diffusion layers). In the case of sufficiently high concentrations of the indifferent electrolyte, when the ratio of the effective thicknesses of the diffuse and diffusion boundary layers next to the anode is small, the Poisson equation describing the electrical field distribution can be replaced by the condition for local electrical neutrality of the solution:

$$\sum_{k=1}^{3} z_k c_k = 0. \tag{24}$$

It will be assumed that beyond the limits of the diffusion layer, the concentrations of the ions of the indifferent electrolyte are uniform, and that the concentration of the ions of the dissolving metal is equal to zero. Since outside the diffusion layer the electric field is purely ohmic, the potential can be measured from the plane $x = \delta$ (the value of the potential in the region next to the cathode can be determined if the magnitude of the ohmic electric field and the thickness of the gap between the electrodes are known). Thus the boundary conditions for the system of equations (23) and (24) can be formulated as follows:

$$c_1 = 0, \; c_2 = c_2^{(0)}, \; c_3 = -\frac{z_2}{z_3} c_2^{(0)}, \; \varphi = 0 \text{ for } x = \delta.$$

It is convenient to look for solutions using the following dimensionless variables:

$$y = x/\delta, \; C_k = c_k/c_2^{(0)}, \; \psi = F\varphi/RT, \; I = i\delta/z_1 F D_1 c_2^{(0)}, \; \xi_k = M_1 D_1 c_2^{(0)}/D_k \rho^{(s)}.$$

In these variables, the system of equations (23) and (24) has the form

$$\frac{dC_k}{dy} + \left(z_k \frac{d\psi}{dy} - \xi_k I\right) C_k + \delta_{1k} I = 0, \tag{25}$$

$$\sum_{k=1}^{3} z_k C_k = 0, \tag{26}$$

with boundary conditions

$$C_1 = 0, \; C_2 = 1, \; C_3 = -z_2/z_3, \; \psi = 0 \text{ for } y = 1. \tag{27}$$

The system of equations (25) and (26) has an analytical solution when the diffusion coefficients of all types of ion present in the solution are equal ($D_1 = D_2 = D_3 = D$). In this case, the following expressions are obtained for the distributions of the ionic concentrations and the electric potential:

$$C_1 = \frac{1}{2\xi Y}\left\{\frac{4 z_2 z_3 Y^2}{(z_1 - z_2)(z_2 - z_3)} + \frac{\xi^2 (z_1 - z_2)(z_2 - z_3)}{z_1^2}\exp\left[-2\xi I (1 - y)\right]\right\}, \tag{28}$$

$$C_2 = -\frac{2 z_1 z_3 Y}{\xi (z_1 - z_2)(z_2 - z_3)}, \tag{29}$$

$$C_3 = -\frac{\xi (z_1 - z_2)(z_2 - z_3)}{2 z_1 z_3 Y}\exp\left[-2\xi I (1 - y)\right], \tag{30}$$

$$\psi = \frac{z_2 - z_3}{2z_2z_3}\left\{\xi I(1-y) + \frac{1}{2}\ln\frac{a_1\exp[-2\xi I(1-y)] + a_2\exp[-\xi I(1-y)] + a_3}{a_1 + a_2 + a_3}\right\}. \quad (31)$$

Here, the following symbols are introduced:

$$Y = 1 - \left[1 - \xi\left(1 - \frac{z_2}{z_3}\right)\right]\exp[-\xi I(1-y)];$$

$$\xi = \frac{M_1 c_2^{(0)}}{\rho^{(s)}};$$

$$a_1 = 2 + \frac{z_3}{\xi(z_2 - z_3)} + \frac{\xi(z_2 - z_3)}{z_3}\left[1 + \frac{z_3(z_1 - z_2)(z_1 - z_3)}{4z_1^2 z_2}\right];$$

$$a_2 = -\frac{2}{\xi(z_2 - z_3)}[\xi z_2 + z_3(1 - \xi)];$$

$$a_3 = \frac{z_3}{\xi(z_2 - z_3)}.$$

When the charges of all the ions are the same ($z_1 = z_3 = -z_2 = z$). Eqns.(28)–(31) are transformed into the corresponding equations obtained in Ref.38.

As noted above, the chief difference between the equations describing the transfer phenomena in electrolyte solutions under conditions of intensive interphase mass exchange and the traditional equation of ionic mass transfer, which assumes that the hydrodynamics are independent of mass exchange, lies in the allowance for additional convective transfer, associated with the existence of the normal component of the hydrodynamic velocity at the interphase surface. The additional convective flux arises as a consequence of the influence of mass exchange on the hydrodynamics, and this process is more intense, the higher the value of the parameter ξ. To illustrate quantitatively the effect brought about by the influence of ionic mass exchange on hydrodynamics, it is possible to compare the values of the concentrations, next to the anode, of the ions of the dissolving metal $C_1(0)$ and $C_1^*(0)$ determined by Eqn.(28) for a certain finite value of ξ and for $\xi = 0$ (that is under conditions where the solution "adheres" to the anode) respectively. Table 1 gives the values of these concentrations as functions of the current density for the cases of the dissolution of bivalent iron in 1 M and 5 M aqueous solutions of a 2–2-valent indifferent electrolyte.

Table 1. Dependence of the quantities $C_1(0)$ and $C_1^*(0)$ on the anodic current density and the concentration of the indifferent electrolyte.

I	$C_1^*(0)$	$C_1(0)$		I	$C_1^*(0)$	$C_1(0)$	
		$c_2^{(0)}$=1 M	$c_2^{(0)}$=5 M			$c_2^{(0)}$=1 M	$c_2^{(0)}$=5 M
0	0	0	0	10	5.83	4.29	1.74
1	0.833	0.802	0.716	15	8.38	5.46	1.77
5	3.21	3.06	1.56	20	10.9	6.30	1.79

Table 1 shows that the existence of a mass flux of solution to the anode surface decreases the concentration gradient of the ions of the dissolving metal next to the anode. Eqns.(28) to (31) lead to the predicted[38] effect of increase in the electric field intensity close to the anode compared with conditions in which dissolution is not accompanied by the transfer of the mechanical momentum of the solution. In fact, the extent of the increase in the intensity can be characterised by the parameter τ, given by

$$\tau = (d\psi/dy)_{x=0}/(d\psi^*/dy)_{x=0},$$

where $\psi^*(y)$ is the distribution of the potential, calculated without allowance for the influence of mass exchange on hydrodynamics. In the particular case where the charges of all the ions are equal ($z_1 = z_3 = -z_2 = z$), this distribution has the form[38]:

$$\psi^* = \frac{1}{z}\ln\left[1 + \frac{1}{2}I(1-y)\right].$$

It can readily be shown that the parameter τ is always greater than unity, and with an unrestricted increase in the current density it increases according to the law $\tau = \xi I$. Table 2 gives the numerical values of the parameter τ, calculated for the dissolution of nickel in a 2 *N* aqueous solution of a 2–2-valent indifferent electrolyte.

Table 2. Influence of the mass flux of the solution at a nickel surface dissolving in 2 *N* aqueous $CuSO_4$ solution on the electric field intensity next to the anode.

I	0	1	5	10	15	20	40
τ	1.00	1.12	1.41	1.80	2.21	2.68	4.70

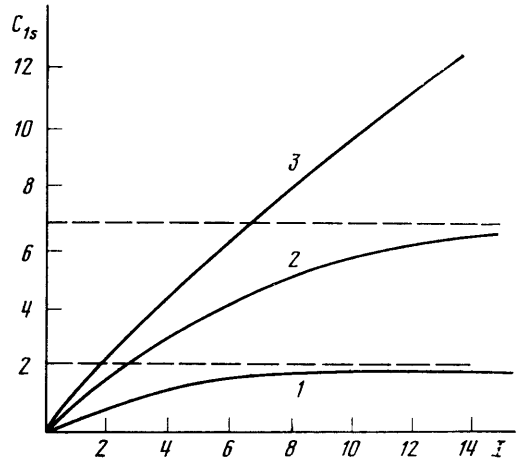


Figure 2. Concentration of nickel cations next to the anode during the dissolution of nickel in 5 *N* (curve *1*) and 1 *N* (curve *2*) aqueous $CuSO_4$ solutions; curve *3* was calculated without allowance for the influence of mass exchange on hydrodynamics; $C_{1S} = c_1^{(s)}/c_2^{(0)}$; $I = i\delta/z_1FD_1c_2^{(0)}$.

Eqn.(28) leads to the effect, described in the previous section, of "saturation" of the layer next to the anode by cations of the dissolving metal. Fig.2 gives graphs showing the change in the value of C_{1S} with change in the current density for the system $Ni^{2+}/CuSO_4$. These graphs were calculated with the assumption that the density of the solution is constant ($\rho = \rho^{(s)} = 1$ g cm^{-3}) for $\delta = 10^{-3}$ cm. According to the results obtained[32,38], the maximum deviation of the value of the concentration of nickel cations next to the anode is independent of the concentration of the indifferent electrolyte and amounts to ~9 M. Calculations show that for $\delta = 10^{-3}$ cm, the limiting value of the cation concentration can be achieved only at current densities greater than 100 A cm^{-2}. At current densities less than 10 A cm^{-2}, however, the concentration of nickel cations close to the anode, according to estimates carried out, does not exceed 0.8 M for $c_2^{(0)} = 1$ M, and 3.6 M for $c_2^{(0)} = 5$ M.

The physical factor responsible for the effect of "saturation" of the layer next to the anode is that at high anodic current densities, the rate of removal of cations from the anode by a convective transport mechanism, associated with the influence of mass exchange on hydrodynamics, becomes equal to the rate of accumulation of cations close to the anode as a result of dissolution.

3. Dissolution of the Wall of a Plane-Parallel Channel

The problem of intensive mass exchange between the wall of a circular or plane-parallel channel and a liquid flux moving along this channel is of interest from the viewpoint of the quantitative description of the elementary act of processes of dissolution and precipitation, which find extensive application in chemical and electrochemical technology. Problems of analogous type have been examined in the thermophysical literature[42–45] in connection with the analysis of systems in which gas is blown in or sucked out via a porous wall in order to intensify heat transfer. An analysis of this kind is applicable to osmotic membranes[46]: in all these cases, at the interphase boundary, there is a normal component of the hydrodynamic velocity, related either to the pressure drop on different sides of the permeable wall or to the diffusion flux of substance responsible for mass exchange. The difference between the problem of intensive electrochemical dissolution in a stream of electrolyte and the problem in which an inert medium is blown into the main stream lies in the fact that the mechanical momentum transferred to the liquid phase on dissolution is not independent of the conditions of mass exchange, as in the case where an inert medium is blown in, but is determined by the solution of the convective–diffusion problem.

A typical example of systems in which there is intense electrochemical dissolution of a metal in a stream of electrolyte is a plane-parallel channel, along which a concentrated electrolyte solution is flowing, where one of the walls of the channel (the anode) is dissolving under the influence of an electric current of high density. The dissolving surface in this case is not uniformly accessible for mass exchange, and the Nernst diffusion model is not applicable to it. Correct allowance for the contribution of convective mass transfer to the resulting rate of interphase mass exchange in this system is possible only by simultaneous solution of the system of equations of hydrodynamics and convective diffusion[47].

A plane-parallel channel $-a \leqslant x \leqslant a$ can be considered, along which a laminar flow of a solution of an indifferent electrolyte is moving in the positive direction of the z axis (the ions of this electrolyte do not take part in heterogeneous processes at the walls of the channel). It is assumed that the following quantities are given at the inlet to the channel (at $z = 0$): the average rate of flow of the electrolyte u_0, the pressure $p = p_0(x)$, the longitudinal pressure gradient $(\partial p/\partial z)_0 = \gamma_0$, and the average bulk concentration of the indifferent electrolyte c_0. It is also assumed that the wall $x = a$ consists of a metallic anode, which is dissolving under the influence of an electric current of density $i(z)$. Under real conditions, the average density $\bar{i}$ of the current flowing through the gap between the electrodes is usually fixed:

$$\bar{i} = \frac{1}{l}\int_0^l i(z)\,dz,$$

where l is the length of the channel.

It will be assumed that the concentration of the cations M^{z_1+} of the dissolving metal (z_1 is the charge of the cations) is equal to zero at the inlet to the channel, and that at the cathode surface ($x = \mp a$) the liquid adheres to the surface ($v_x = v_z = 0$) and there is no mass flux of the cations M^{z_1+}. It will also be assumed that in the dissolution process, the anode is kept in a fixed position (at $x = a$) by means of a special regulating device. In accordance with condition (4), the x component of the velocity of the liquid v_x at $x = a$, in the case of a stationary anode, is related to the current density i by the expression

$$v_x = -\frac{M_1 i}{z_1 \rho^{(s)} F}, \tag{32}$$

where M_1 is the atomic mass of the dissolving metal, and $\rho^{(s)}$ the local density of the solution at $x = a$.

The steady-state conditions for the transfer of the momentum and mass of the metal cations within the channel is described by the system of Navier–Stokes, continuity, and convective diffusion equations. It is convenient to write this system of equations using the following dimensionless variables:

$$X = \frac{x}{a}, \quad Z = \frac{D_1 z}{a^2 u_0}, \quad V_x = \frac{a}{D_1} v_x, \quad V_z = \frac{v_z}{u_0},$$
$$P = \frac{D_1 p}{\mu u_0^2}, \quad C = \frac{c}{c_0}, \quad \mathrm{Re} = \frac{a u_0 \rho}{\mu}, \quad \beta = \frac{D_1}{a u_0}.$$

Here, c is the local concentration of ions of the dissolving metal, and μ the dynamic viscosity of the solution. In dimensionless variables, the system of transfer equations has the form

$$\beta^3 \mathrm{Re}\left\{V_x \frac{\partial V_x}{\partial X} + V_z \frac{\partial V_x}{\partial Z}\right\} = -\frac{\partial P}{\partial X} + \beta^2\left\{\frac{\partial^2 V_x}{\partial X^2} + \beta^2 \frac{\partial^2 V_x}{\partial Z^2}\right\},$$
$$\beta \mathrm{Re}\left\{V_x \frac{\partial V_z}{\partial X} + V_z \frac{\partial V_z}{\partial Z}\right\} = -\frac{\partial P}{\partial Z} + \frac{\partial^2 V_z}{\partial X^2} + \beta^2 \frac{\partial^2 V_z}{\partial Z^2},$$
$$\frac{\partial V_x}{\partial X} + \frac{\partial V_z}{\partial Z} = 0,$$
$$V_x \frac{\partial C}{\partial X} + V_z \frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial X^2} + \beta^2 \frac{\partial^2 C}{\partial Z^2}.$$

This system does not take account of the influence of the gravitational field.

The mathematical analysis of the problem is simplified considerably by examining a region of the channel separated by a sufficient distance from the inlet section $z = 0$; it can be shown that for the region $z \geqslant a^2 u_0/D_1$, where D_1 is the diffusion coefficient of the ions of the dissolving metal, it is possible to omit terms containing second derivatives with respect to the coordinate Z in the original system of transfer equations. Moreover, according to condition (32), the x component of the velocity can be represented in the form

$$v_x = \frac{\bar{i} M_1}{z_1 \rho^{(s)} F} V_x = \beta \varepsilon u_0 V_x,$$

where $\varepsilon = a\bar{i}M_1/z_1 F \rho^{(s)} D_1$.

The boundary conditions for this system are:

$$V_x = -(i/\bar{i}) = -W(Z) \quad \text{for } X = 1; \tag{33}$$

$$V_z = 0 \text{ for } X = \pm 1; \; V_x = 0 \text{ for } X = -1; \tag{34}$$

$$P = P_0' = \frac{D_1 p_0}{\mu u_0^2}, \quad \frac{\partial P}{\partial Z} = \Gamma_0 = \frac{a\gamma_0}{\mu} \quad \text{for } Z = 0; \tag{35}$$

$$C = 0 \text{ for } Z = 0; \tag{36}$$

$$\frac{\partial C}{\partial X} = 0 \text{ for } X = -1; \tag{37}$$

$$\frac{\partial C}{\partial X} = \frac{a\bar{i}}{z_1 F D_1 c_0}\left(1 - \frac{M_1 c_0}{\rho^{(s)}} C_s\right) \quad \text{for } X = 1. \tag{38}$$

Since by definition[18] the current density i is related to the diffusion flux of the cations M^{z_1+} by the expression

$$j_1^{(s)} = -D_1\left(\frac{\partial c}{\partial x}\right)_s = -\frac{i}{z_1F}\left(1-\frac{M_1c_s}{\rho^{(s)}}\right) = \frac{\rho^{(s)}D_1}{aM_1}V_x^{(s)}\left(1-\frac{M_1c_s}{\rho^{(s)}}\right),$$

it follows that conditions (33) and (38) are essentially identical and give the relationship between the velocity and concentration profiles.

The parameter β is inversely proportional to the Peclet number, and for many systems of practical interest it is negligible compared with unity. For example, for the flow of pure water at an average velocity of 1 m s^{-1} along a channel of width 1 mm, this parameter is of the order of 10^{-6}. It is therefore possible to neglect terms containing the parameter β in the original system of equations, and to write this system in the following simplified form:

$$\frac{\partial P}{\partial X} = 0,\ \frac{\partial P}{\partial Z} = \frac{\partial^2 V_z}{\partial X^2},\ \frac{\partial V_x}{\partial X} + \frac{\partial V_z}{\partial Z} = 0,$$
$$V_x\frac{\partial C}{\partial X} + V_z\frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial X^2}. \qquad (39)$$

To simplify the problem further and obtain a solution in analytical form, it will also be assumed that the parameter ε is small.

The numerical value of this parameter depends to a significant extent on the average anodic current density $\bar{i}$. Thus in the case of the dissolution of bivalent iron for a width of the gap between the electrodes equal to 1 mm, the parameter ε satisfies the relationship $\varepsilon \cong 0.3\,\bar{i}$, where the current density is expressed in units of A cm^{-2}; this means that for $\bar{i} < 1$ A cm^{-2}, the parameter ε can in fact be regarded as small. By representing the functions being sought in the form of the expansions

$$V_x = V_x^{(0)} + \varepsilon V_x^{(1)} + \ldots$$
$$V_z = V_z^{(0)} + \varepsilon V_z^{(1)} + \ldots$$
$$P = P^{(0)} + \varepsilon P^{(1)} + \ldots$$
$$C = C^{(0)} + \varepsilon C^{(1)} + \ldots$$

and using the boundary conditions (33)–(38), it is possible to obtain in the zeroth approximation the following solution of the hydrodynamic problem:

$$P^{(0)} = P_0^{(0)} + \Gamma_0^{(0)}Z,\ V_x^{(0)} = 0,\ V_z^{(0)} = -\frac{1}{2}\Gamma_0^{(0)}(1-X^2), \qquad (40)$$

where the quantities $P_0^{(0)}$ and $\Gamma_0^{(0)}$ are the first nonzero terms of the expansions

$$P_0 = P_0^{(0)} + \varepsilon P_0^{(1)} + \ldots,\quad \Gamma_0 = \Gamma_0^{(0)} + \varepsilon\Gamma_0^{(1)} + \ldots$$

Equating the terms linear with respect to the parameter ε in Eqns.(39) and in the boundary conditions (33)–(35) gives

$$P^{(1)} = P_0^{(1)} + \Gamma_0^{(1)}Z - \frac{3}{2}\int_0^Z d\xi \int_0^\xi W(\xi')\,d\xi',$$
$$V_x^{(1)} = -\frac{1}{2}W(Z)\left(1+\frac{3}{2}X-\frac{1}{2}X^3\right), \qquad (41)$$
$$V_z^{(1)} = (1-X^2)\left[\frac{3}{4}\int_0^Z W(\xi)\,d\xi - \frac{1}{2}\Gamma_0^{(1)}\right].$$

Analysis of Eqns.(41) shows that, for sufficiently large values of Z at least, the existence of the normal component of the hydrodynamic velocity at the surface of the anode leads to an increase in the velocity of the flux in the direction Z.

With the assumptions made, the concentration field is described by the equations

$$V_z^{(0)}\frac{\partial C^{(0)}}{\partial Z} - \frac{\partial^2 C^{(0)}}{\partial X^2} = 0, \qquad (42)$$

$$V_z^{(0)}\frac{\partial C^{(1)}}{\partial Z} - \frac{\partial^2 C^{(1)}}{\partial X^2} = -V_x^{(1)}\frac{\partial C^{(0)}}{\partial X} - V_z^{(1)}\frac{\partial C^{(0)}}{\partial Z} \qquad (43)$$

with boundary conditions

$$C^{(0)} = 0,\ C^{(1)} = 0 \quad \text{for } Z = 0; \qquad (44)$$

$$\frac{\partial C^{(0)}}{\partial X} = 0,\ \frac{\partial C^{(1)}}{\partial X} = 0 \quad \text{for } X = -1; \qquad (45)$$

$$\frac{\partial C^{(0)}}{\partial X} = J_0(Z),\ \frac{\partial C^{(1)}}{\partial X} = -C_s^{(0)}(Z) \quad \text{for } X = 1, \qquad (46)$$

where $J_0(Z) = a\bar{i}W(Z)/z_1FD_1c_0$.

The function $J_0(Z)$ in the general case cannot be regarded as small, since for any fixed value of Z it is proportional to the product of two parameters, ε and $\rho^{(s)}/M_1c_0$. The latter, even for extremly concentrated solutions (1 M and above), may be significantly greater than unity.

The extreme problems defined by Eqns.(42)–(46) are solved by the standard methods of mathematical physics. The solution obtained is very cumbersome, however, and it is not appropriate to give it here. Nevertheless, it is appropriate to analyse the asymptotic behaviour of the concentration profile for large values of the longitudinal coordinate Z under conditions of uniform distribution of the current density at the anode (J_0 = const). Using the published method[48], the solution of Eqn.(42) can be sought in the form

$$C^{(0)} = A^{(0)}Z + B^{(0)}(X), \qquad (47)$$

where $A^{(0)}$ and $B^{(0)}(X)$ are the unknown constant and function. It can readily be seen that the first boundary condition (44) cannot be satisfied by Eqn.(47). Thus the boundary condition (44) is replaced by the condition

$$J_0Z = \int_{-1}^{1} C^{(0)}V_z^{(0)}\,dX. \qquad (48)$$

This condition means that in the zeroth approximation with respect to the parameter ε, the quantity of metal cations entering the channel in unit time as a result of the dissolution of its wall is equal to the quantity of cations transferred by the flux through a given transverse cross section in the same time interval.

Substituting Eqn.(47) in Eqn.(42), integrating the latter twice with respect to X, and using the boundary conditions (45), (46), and (48) give:

$$C^{(0)} = \frac{1}{2}J_0\left\{-\frac{3}{\Gamma_0^{(0)}}Z + X + \frac{3}{4}X^2\left(1-\frac{1}{6}X^2\right) - \frac{117}{280}\right\}. \qquad (49)$$

Sine $\Gamma_0^{(0)} < 0$, the concentration $C^{(0)}$ increases linearly with distance from the channel inlet.

The correction to the concentration, associated with the existence of the normal component of the hydrodynamic velocity at the anode surface, can be found analogously. For large values of the argument Z, this correction can be sought in the form

$$C^{(1)} = A^{(1)}Z^2 + B^{(1)}(X)\,Z + G^{(1)}(X). \qquad (50)$$

Here, instead of the second boundary condition (44), it is necessary to use the condition

$$-C_s^{(0)}Z = \int_{-1}^{1}(C^{(0)}V_z^{(1)} + C^{(1)}V_z^{(0)})\,dX, \qquad (51)$$

which has the same physical significance as condition (48), but is written in a higher linear approximation with respect to the parameter ε.

Simple but cumbersome operations give the expression

$$C^{(1)} = -\frac{9}{4}\frac{J_0}{(\Gamma_0^{(0)})^2}Z^2 + \frac{3}{4}\frac{J_0}{\Gamma_0^{(0)}}Z\left\{\frac{3}{4}X^2\left(1-\frac{1}{6}X^2\right)+X-\frac{39}{280}\right\}+ \\ +\frac{1}{64}J_0\left\{-\frac{1}{8}X^8+\frac{3}{2}X^6-\frac{4}{5}X^5-\frac{669}{140}X^4-12X^3- \right. \\ \left. -\frac{443}{70}X^2+\frac{568}{35}X+\frac{519919}{333400}\right\}. \qquad (52)$$

From this expression it follows that at a sufficient distance from the channel inlet, the additional convective transfer induced by interphase mass exchange leads to a decrease in the concentration of the ions of the dissolving metal next to the anode. This is illustrated by Fig.3, where the broken line corresponds to the solution of the problem of ionic mass transfer with allowance for the convective flux described above.

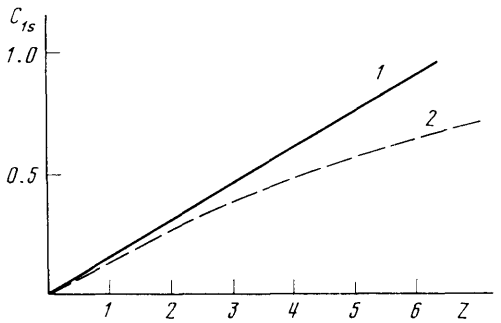


Figure 3. Theoretical profiles of the concentration of the cations of a dissolving metal next to the anode as a function of distance from the inlet to the gap between the electrodes at a given anodic current density: *1*) assuming that the liquid adheres to the anode surface; *2*) with allowance for the normal component of the hydrodynamic velocity, induced by the mass exchange.

The above analysis confirms the results obtained in the two previous sections for the dissolution of surfaces uniformly accessible with respect to mass exchange. They lead to the conclusion, important in practice, that it is possible to achieve higher current densities under conditions in which the concentration of the cations of the dissolving metal cannot, for various reasons, exceed a particular value.

IV. INFLUENCE OF DIFFUSION OF HYDRODYNAMICS UNDER CONDITIONS OF MASS TRANSFER TO THE SURFACE OF A ROTATING DISC

A disc rotating in a laminar liquid represents a typical example of a surface uniformly accessible with respect to mass exchange. Surfaces of this kind are often examined using the Nernst diffusion model[35], which makes it possible to obtain clear and simple expressions for describing the kinetics of mass transfer. In many cases, however, this model cannot reflect the quantitative aspect of the relationship between the processes of mass and momentum transfer. The reason for this is that convective mass transfer, which is essentially not included in the equations postulated by this model, not only leads to a change in the dependence of the thickness of the diffusion layer on the transport properties of the solution but also leads to a change in the actual type of mass transfer equations. For this reason, attempts have been made to develop a method which on the one hand would make it possible to take correct account of the contribution of convective mass transfer to the resulting rate of interphase mass exchange, and on the other hand could be used to estimate the accuracy of the results given by the Nernst model.

The equations of hydrodynamics for a rotating disc with allowance for the mass flux, induced by mass exchange, and the variable transport properties, have been formulated and solved for various specific cases[10–13,16,43,44,49]. The most general method of solution, based on a procedure involving "splicing" of the asymptotic expansions for the velocity field, was developed in Refs.13 and 16. The application of this method to the case of mass exchange limited by the resistance of convective diffusion in a liquid phase for large Schmidt numbers is examined below.

The Navier–Stokes equations are written in a cylindrical system of coordinates with a polar axis x passing through the centre of the disc. The property of uniform accessibility of the surface of the disc with respect to diffusion makes it possible to assume that the density ρ and kinematic viscosity ν of the solution, which depend on the concentration of the substance responsible for mass exchange, are functions only of the coordinate x. The coordinate x is replaced by the new independent variable ζ, defined by the expression

$$\zeta = \sqrt{\omega}\int_0^x \frac{dx'}{\sqrt{\nu(x')}},$$

where ω is the angular velocity of rotation of the disc. The distributions of the velocities v_r, v_ϑ, and v_x are represented in the form

$$v_r = r\omega F(\zeta),\quad v_\vartheta = r\omega G(\zeta),\quad v_x = \sqrt{\nu\omega}\,H(\zeta).$$

Substitution of these expressions in the system of Navier–Stokes equations, and simple transformations, give[49]:

$$F^2 - G^2 + HF' - F'' = F'\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)', \\ 2FG + HG' - G'' = G'\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)', \qquad (53) \\ 2F + H' = -H\left(\ln\sqrt{\frac{\rho^2\nu}{\rho_0^2\nu_0}}\right)',$$

where ρ_0 and ν_0 are the values of the density and viscosity at a distance from the disc (as $x \to \infty$); the primes denote the corresponding derivatives with respect to ζ. Since the transfer equations do not contain derivatives of the function $H(\zeta)$ higher than the first derivative, it follows that one boundary condition is sufficient for the determination of this function. With allowance for the mass flux of the solution at $x = 0$, due to the movement of the centre of mass of the liquid phase as a consequence of mass exchange (see Eqn.(4)), the boundary conditions for the functions F, G, and H take the form

$$F(0) = 0,\ G(0) = 1,\ H(0) = -\sigma^3 M\left(\frac{\partial c}{\partial\zeta}\right)_s \frac{1}{\rho^{(s)} - Mc^{(s)}}, \qquad (54)$$

$$F(\infty) = 0,\ G(\infty) = 0. \qquad (55)$$

Here, $\sigma = (D/\nu_0)^{1/3}$, M and D are the molecular mass and diffusion coefficient of the substance being transferred, c is its local concentration, and the symbol "s" refers to the conditions at the surface of the disc.

The boundary conditions (54) show that to solve the hydrodynamic problem it is necessary to know the distribution of concentration close to the surface of the disc. At the same time, the equation of convective diffusion, which in the case of stationary conditions of mass transfer has the form

$$(\mathbf{u}, \nabla c) = D \operatorname{div} \nabla c, \qquad (56)$$

contains the hydrodynamic velocity **v**, and therefore cannot be solved independently of Eqns.(53). To find the simultaneous solution of the problem of the transfer of mass and momentum close to the rotating disc it is necessary to substitute the boundary conditions for the concentration field. It is assumed that the values of the concentration at the surface of the disc ($c^{(s)}$) and in the bulk of the solution (c_0) are given. In the case of large Schmidt numbers ($Sc = \nu_0/D \gg 1$), Eqn.(56) can be simplified by making use of the condition that the parameter σ be small. If this parameter is small compared with unity, it can be shown[49] that the concentration c depends only on the single coordinate ξ. Eqn.(56) then takes the form

$$H(\zeta)\frac{dc}{d\zeta} = \sigma^3 \frac{d^2 c}{d\zeta^2},$$

which, with allowance for the above boundary conditions, gives:

$$c(\zeta) = c^{(s)} - (c^{(s)} - c_0)\int_0^{\zeta} \exp\left\{\sigma^{-3}\int_0^{\zeta'} H(\zeta'')\,d\zeta''\right\} d\zeta' \Big/ \int_0^{\infty} \exp\left\{\sigma^{-3}\int_0^{\zeta'} H(\zeta'')\,d\zeta''\right\} d\zeta'. \qquad (57)$$

The determination of the derivative $(dc/d\zeta)_S$ from Eqn.(57) gives for the third boundary condition (54):

$$H(0) = \frac{\sigma^3 (c^{(s)} - c_0) M}{\rho^{(s)} - Mc^{(s)}} \left\{\int_0^{\infty} \exp\left[\sigma^{-3}\int_0^{\zeta} H(\zeta')\,d\zeta'\right] d\zeta\right\}^{-1}. \qquad (58)$$

The analytical solution of the system of equations (53) can be obtained by the method of "spliced" asymptotic expansions, which represent a generalisation of the boundary layer method and has been described in detail[50]. According to this method, the functions F, G, and H are sought in the form of the following expansions:

$$F = F_0(\zeta) + \sigma F_1(y) + \ldots,$$
$$G = G_0(\zeta) + \sigma G_1(y) + \ldots,$$
$$H = H_0(\zeta) + \sigma^2 H_1(y) + \ldots,$$

where $y = \zeta/\sigma$, and the functions F_0, G_0, and H_0 represent the solution of the hydrodynamic problem in the absence of mass exchange, that is for $H(0) = 0$. For $\zeta \ll 1$, these functions are given by the expressions[51]:

$$F_0 = a\zeta,\ G_0 = 1 - b\zeta,\ H_0 = -a\zeta^2,\ a = 0.51,\ b = 0.62.$$

By substituting the expansions introduced above in Eqn. (53) and equating terms with identical powers of σ, it is possible to obtain equations for the functions F_1, G_1, and H_1. These functions should satisfy the following boundary conditions for $y = 0$:

$$F_1(0) = 0,\ G_1(0) = 0,\ H_1(0) = \frac{(a/3)^{1/3} M (c^{(s)} - c_0)}{\Gamma\left(\frac{4}{3}\right)(\rho^{(s)} - Mc^{(s)})},$$

where $\Gamma(4/3)$ is the gamma function. As $y \to \infty$, the "splicing" conditions should be satisfied:

$$\lim_{y\to\infty}[F_0(\sigma y) + \sigma F_1(y)] = a\zeta,$$
$$\lim_{y\to\infty}[G_0(\sigma y) + \sigma G_1(y)] = 1 - b\zeta,$$
$$\lim_{y\to\infty}[H_0(\sigma y) + \sigma^2 H_1(y)] = -a\zeta^2.$$

Simple mathematical operations give the following result[16]: with an accuracy corresponding to terms of order σ^2, the function $H(y)$ is given by

$$H(y) = \sigma^2\left\{H_1(0) - 2a\rho_0\int_0^{y}\int_0^{y'} \frac{\rho(y')\sqrt{\nu(y')}}{\rho(y'')\sqrt{\nu(y'')}}\,dy''\,dy'\right\}. \qquad (59)$$

Substitution of Eqn.(59) in Eqn.(57) gives the solution to the problem of convective mass transfer. Since the quantity $H_1(0)$ is proportional to the difference $\Delta c = c^{(s)} - c_0$, that is the driving force of mass transfer, it follows from Eqns.(57) and (59) that under the conditions of intensive mass exchange, the rate of mass transfer is not a linear function of the driving force. When the values of the difference Δc are not too large, the diffusion flux $j^{(s)} = -D(dc/dx)_S$ can be represented, using Eqns.(57) and (59), as a power series in Δc. In the particular case where the physical properties are constant ($\rho = \rho_0 = \text{const}$, $\nu = \nu_0 = \text{const}$), this series has the form[13]:

$$j^{(s)} = \frac{(a/3)^{1/3}}{\Gamma\left(\frac{4}{3}\right)} MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\left(1 - \frac{0.57M\Delta c}{\rho_0 - Mc^{(s)}} + \ldots\right).$$

The resulting rate of mass transfer w is determined by the sum of the contributions of the diffusion and convective mechanisms of mass transfer:

$$w = j^{(s)} + Mc^{(s)}v_x^{(s)}.$$

Use of the expressions given above for $j^{(s)}$ and $v_x^{(s)}$ gives, with an accuracy corresponding to terms quadratic in the difference Δc:

$$w = 0.62MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\,\frac{\rho_0 - 0.57M\Delta c}{\rho_0 - Mc^{(s)}}. \qquad (60)$$

In the particular case where $c_0 = 0$, Eqn.(60) becomes

$$w = 0.62MD^{2/3}\nu_0^{-1/6}\sqrt{\omega}\,\Delta c\left(1 + 0.43\frac{M\Delta c}{\rho_0}\right).$$

It follows from Eqn.(60) that the existence of additional convective movement, induced by mass exchange, leads, for a given value of the driving force of mass transfer Δc, to an increase in the rate of interphase mass exchange. A measure of this increase is provided by the ratio $(\rho_0 - 0.57M\Delta c)/(\rho_0 - Mc^{(s)})$.

V. MUTUAL INFLUENCE OF THE COMPONENTS OF A GASEOUS MIXTURE ON CONDENSATION FROM A TURBULENT STREAM

Convective fluxes induced by mass exchange may also arise in systems with mass transfer in multicomponent gaseous mixtures (for example in condensation, evaporation, or rectification). These are usually called "Stefan" fluxes[2]. When Stefan fluxes are present, there is a significant change in the nature of the interaction between the components being transferred in gaseous mixtures, since this interaction may take place through the velocity field, modified by mass exchange. To illustrate this effect, it is possible to examine a multicomponent gaseous phase containing components which differ sharply in their molecular transport properties. Since the transfer of all components of this system takes place under identical hydrodynamic conditions, it is possible in principle, by obtaining quantitative information on the magnitude of the individual mass fluxes, to establish an unambiguous correlation between the effective coefficients of mass transfer for each component of the mixture and the molecular properties of all the other components. This correlation represents a

measure of the mutual influence of the substances being transported[52].

The process involved in the condensation of one component from a fully developed turbulent stream of a three-component ideal gaseous mixture on to the surface of a planar hard wall can be examined. The molecular properties of the component condensing will be denoted by the symbol "1". It will be assumed that the rate of condensation is determined entirely by the resistance of the gaseous phase. It will also be assumed that the surface of the film of condensate is uniformly accessible with respect to mass transfer and that the process of interphase mass exchange takes place under stationary conditions, that is that the concentration of each component of the gaseous phase at any fixed distance from the surface of the film is independent of time. With these conditions, the equation of convective mass transfer for any ith component of the mixture will have the following form:

$$\frac{d}{dx}\left(j_i - M_i D_t \frac{dc_i}{dx}\right) + M_i(v - V)\frac{dc_i}{dx} = 0; \quad i = 1, 2, 3. \tag{61}$$

Here, j_i is the molecular-diffusion flux of the ith component, M_i its molecular mass, c_i the molar concentration, $D_t = D_t(x)$ the coefficient of turbulent diffusion, $v = v(x)$ the velocity of the turbulent stream, averaged over the period of turbulent pulsations, and V the velocity of translational movement of the surface of the film of condensate relative to the solid wall, that is the linear velocity of growth of the condensate film. The coordinate x is measured from the surface of the film in the direction of the gaseous phase.

The relationship between the fluxes j_i and the gradients of the concentrations c_i in the case of ideal mixtures is described by the familiar Stefan–Maxwell equations. In the particular case when one of the inert, that is non-condensing, components of the mixture (for example component 3) is present in excess and it can be assumed that the conditions $c_1 \ll c_3$ and $c_2 \ll c_3$ are fulfilled, there is no direct diffusion interaction between components 1 and 2, determined by the laws of the thermodynamics of irreversible processes. In this case, the simple expressions corresponding to Fick's first law are applicable for the fluxes j_1 and j_2:

$$j_1 = -D_{13}M_1\frac{dc_1}{dx}, \quad j_2 = -D_{23}M_2\frac{dc_2}{dx}.$$

Here, D_{13} and D_{23} are the coefficients of mutual molecular diffusion in the corresponding binary mixtures.

The above-mentioned particular case of an excess of one of the inert components of the mixture will subsequently be examined, and it will be assumed that the mass transfer of components 1 and 2 takes place in a turbulent diffusion boundary layer $0 \leq x \leq d$, beyond which the concentrations of the components being transferred are distributed uniformly:

$$c_1 = c_1^{(0)}, \; c_2 = c_2^{(0)} \text{ for } x \geqslant d. \tag{62}$$

On the surface of the film of condensate, the total mass flux of the component condensing should be equal to the rate of interphase mass exchange. If the latter is denoted by I and it is assumed that the fluxes directed from the surface of the film in the direction of the gaseous phase are positive, the boundary condition for component 1 at $x = 0$ will have the form:

$$\frac{1}{M_1}j_1^{(s)} + c_1^{(s)}(v^{(s)} - V) = -I, \tag{63}$$

where the symbol "s", as before, refers to the values of the liquid–gas interface. The boundary condition for the inert component 2 is formulated analogously:

$$\frac{1}{M_2}j_2^{(s)} + c_2^{(s)}(v^{(s)} - V) = 0. \tag{64}$$

The rate of convective mass transfer, brought about by the Stefan flux, is determined by Eqn.(4) given above:

$$v^{(s)} = V + \frac{j_1^{(s)}}{\rho^{(s)} - M_1 c_1^{(s)}}.$$

Allowance for Eqns.(63) and (64) gives the following boundary conditions for the diffusion fluxes:

$$j_1^{(s)} = -M_1 I\left(1 - \frac{M_1 c_1^{(s)}}{\rho^{(s)}}\right), \tag{65}$$

$$j_2^{(s)} = \frac{M_1 M_2 c_2^{(s)}}{\rho^{(s)}} I. \tag{66}$$

It may be noted that, according to Eqn.(66), the diffusion flux of the inert component at the interphase boundary is non-zero. The physical reason for this is the existence of a non-zero normal component of the rate of movement of the centre of mass of the gaseous mixture at the interphase boundary: this component, in the case where the surface of the film is not permeable to the inert component, brings about diffusion of this component in the direction away from the surface.

To analyse Eqns.(61) it is necessary to obtain the form of the relationship $D_t(x)$ more accurately. According to general theoretical considerations[53] and published[54–58] experimental data on transport phenomena in turbulent streams, the intensity of convective mass transfer brought about by turbulent pulsations of the velocity field decreases with decrease in the distance from the solid interphase boundary approximately according to a power law with exponent lying in the range between 3 and 4. In the case of a mobile interface (liquid–gas and liquid–liquid), the effect of damping of the turbulent pulsations is much less marked: the role of stabilising factor bringing about damping in this case is played by the interphase surface tension. Experimental data[59–62] indicate that the decrease in the effective coefficient of turbulent diffusion as the mobile interphase boundary is approached, as in the case of a solid wall, takes place according to a power law, but with a smaller exponent (equal to approximately two). If allowance is made for the fact[36] that beyond a viscous hydrodynamic sub-layer of thickness δ_0 (in the range $x > \delta_0 \cong \nu/u^*$, where u^* is the characteristic velocity of turbulent pulsations in the direction perpendicular to the interphase boundary), the relationship $D_t(x) \sim x$ should be fulfilled, it is possible to write for $D_t(x)$ the following interpolation equation:

$$D_t(x) = \frac{\varkappa_1 u^* x^n}{x^{n-1} + \varkappa_2 \delta_0^{n-1}}, \tag{67}$$

where $\varkappa_1$, $\varkappa_2$, and n are empirical constants.

Estimation of the relative contribution of the terms of Eqn. (61) responsible for different transfer mechanism shows that in the layer directly adjoining the surface of the film and having a thickness δ_i defined by the expression

$$D_{i3} = D_t(\delta_i) = \frac{\varkappa_1 u^* \delta_i^n}{\delta_i^{n-1} + \varkappa_2 \delta_0^{n-1}}, \tag{68}$$

turbulent mass transfer does not play a significant role, and the rate of convective transfer brought about by the averaged velocity field in a direction perpendicular to the film surface can be approximated with a high degree of accuracy by the velocity of the Stefan flux (4). Thus within the range $0 \leq x \leq \delta_i$, the mass transfer equations (61) can be simplified considerably and written in the form

$$\frac{d}{dx}\left(j_i + \frac{M_i c_i j_1^{(s)}}{\rho^{(s)} - M_1 c_1^{(s)}}\right) = 0; \quad i = 1, 2.$$

With allowance for the boundary conditions (65) and (66), the first integral of these equations has the form

$$\frac{dc_i}{dx} = \frac{M_1 I}{M_i D_{i3}}\left(\delta_{i1} - \frac{M_i c_i}{\rho^{(s)}}\right),$$

where δ_{i1} is the Kronecker symbol. Subsequent integration gives the expression

$$c_i = \frac{1}{M_i}\rho^{(s)}\delta_{i1} + A_1^{(i)} \exp\left(-\frac{M_1 I x}{\rho^{(s)} D_{13}}\right); \quad i = 1, 2, \tag{69}$$

where $A_1^{(i)}$ represents the constants of integration.

In the ranges $\delta_i \leq x \leq d$, molecular diffusion plays no part, and convective mass transfer is brought about chiefly by turbulent pulsations, so that the transfer equations (61) can be approximated as follows:

$$\frac{d}{dx}\left\{D_t(x)\frac{dc_i}{dx}\right\} = 0; \quad i = 1, 2.$$

With allowance for Eqn.(68) and the boundary conditions (62), the following concentration profiles are obtained for the regions $\delta_i \leq x \leq d$:

$$c_i = c_i^{(0)} + \frac{A_2^{(i)}}{\varkappa_1 u^*}\left\{\ln\left(\frac{x}{d}\right) + \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{d^{n-1}} - \frac{1}{x^{n-1}}\right)\right\}, \tag{70}$$

where $A_2^{(i)}$ represents arbitrary constants, which can be found from the conditions for smooth linking of the profiles (69) and (70) at $x = \delta_i$:

$$\left(\frac{dc_i}{dx}\right)_{\delta_i - 0} = \left(\frac{dc_i}{dx}\right)_{\delta_i + 0}, \quad (c_i)_{\delta_i - 0} = (c_i)_{\delta_i + 0}.$$

Simple calculations give the following result:

$$A_1^{(i)} = \left(c_1^{(0)} - \rho^{(s)}\frac{\delta_{i1}}{M_i}\right)\exp\left(\frac{M_1 I \delta_1}{\rho^{(s)} D_{i3}}\right) \times$$
$$\times\left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_i}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_i^{n-1}} - \frac{1}{d^{n-1}}\right)\right]\right\}^{-1}. \tag{71}$$

Eqns.(69) and (71) can be used to obtain the relationship between the rate of condensation I and the concentration of the component condensing on the surface of the film $c_1^{(s)}$ (if condensation is to take place, this concentration must be equal to the saturation concentration):

$$\frac{c_1^{(s)} - \rho^{(s)}/M_1}{c_1^{(0)} - \rho^{(s)}/M_1} = \exp\left(\frac{M_1 I \delta_1}{\rho^{(s)} D_{13}}\right) \times$$
$$\times\left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_1}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_1^{n-1}} - \frac{d}{d^{n-1}}\right)\right]\right\}^{-1}. \tag{72}$$

If the molecular masses of all the components of the mixture are identical and $\delta_1 = d$ (that is within the framework of the film model), Eqn.(72) becomes the familiar Stefan equation[2] for the rate of condensation in the presence of non-condensing gases.

The nature of the "hydrodynamic" interaction between components 1 and 2 can be analysed by comparing the surface ($x = 0$) values of the concentration of the inert component 2 in the presence and absence of condensation. According to Eqns.(69) and (71), the surface concentration of component 2 is given by

$$c_2^{(s)} = c_2^{(0)} \exp\left(\frac{M_1 I \delta_2}{\rho^s D_{23}}\right) \cdot \left\{1 + \frac{M_1 I}{\rho^{(s)}\varkappa_1 u^*}\left[\ln\left(\frac{\delta_2}{d}\right) - \frac{\varkappa_2 \delta_0^{n-1}}{n-1}\left(\frac{1}{\delta_2^{n-1}} - \frac{1}{d^{n-1}}\right)\right]\right\}^{-1} \tag{73}$$

and increases sharply with increase in the rate of condensation (in the absence of condensation, that is for $I = 0$, the concentration profile $c_2(x)$ would be completely uniform). It follows from Eqns.(72) and (73) that the driving force for the transfer of component 2 from the surface of the film into the depth of the gaseous phase (proportional to the difference $c_2^{(s)} - c_2^{(0)}$) depends to a significant extent on the molecular transport properties of the condensing component 1. The nature of this relationship can be analysed for the case of the condensation of ethanol from a vapour–air mixture, formed during the convective drying of the polymer carboxymethylcellulose. The main components of the mixture are ethanol ($C_1^{(0)} = 0.1$), oxygen ($C_2^{(0)} = 0.1$), and nitrogen ($C_3^{(0)} = 0.8$). The concentrations $C_i^{(0)}$ are given in mole fractions. The temperature of the surface on which condensation takes place is 20 °C. This temperature corresponds to a saturation concentration $C_1^{(s)} = 0.058$ at atmospheric pressure[63].

The Reynolds number Re for the stream of vapour–gas mixture is 10^4 for an average linear velocity $u_0 = 10$ m s^{-1}. The coefficients of mutual diffusion of the components of the mixture are (m^2 s^{-1}): $D_{13} = 0.10 \times 10^{-4}$, $D_{23} = 0.15 \times 10^{-4}$, $D_{12} = 0.10 \times 10^{-4}$. The rate of condensation I and the difference $c_2^{(s)} - c_2^{(0)}$ were calculated using Eqns.(72) and (73) for the chosen real mixture and four hypothetical mixtures. The only difference between the latter and the real mixture was that the coefficient D_{13} was given the arbitrary values 0.06, 0.08, 0.12, and 0.14 cm^2 s^{-1}. The Schmidt numbers in all cases had an order of magnitude of unity (from 1 to 2.5). In the calculations, the parameter n was put equal to 2.

Table 3 gives the calculated values of the rate of condensation I, the concentration $c_2^{(s)}$, and the driving force of mass transfer $c_2^{(s)} - c_2^{(0)}$.

Table 3. Dependence of the kinetic characteristics of the transfer of an inert component on the coefficient of molecular diffusion of a condensing component.

D_{13}, cm^2 s^{-1}	0.06	0.08	0.10	0.12	0.14
$10^4 I$, kg mole m^{-2} s^{-1}	4.8	5.5	6.0	6.3	6.3
$10^3 c_2^{(s)}$, kg mole m^{-3}	4.73	4.77	4.80	4.82	4.84
$10^3(c_2^{(s)} - c_2^{(0)})$, kg mole m^{-3}	0.27	0.31	0.34	0.36	0.38

Table 3 shows that the difference $c_2^{(s)} - c_2^{(0)}$ increases approximately linearly with increase in the diffusion coefficient D_{13}.

VI. ELECTRODEPOSITION OF METALS FROM CONCENTRATED SALT SOLUTIONS

In the cathodic deposition of metals (in electroplating, the development of electrochemical information transformers, etc.) it is often necessary to predict the magnitude of the limiting diffusion current with respect to the discharging metal cations. This calculation is also of interest for the determination of the mechanism of the electrochemical deposition of a metal; in this case the values of the limiting current calculated for the assumed mechanism, and the experimentally measured values,

should be compared. An analogous calculation is also necessary to determine the concentration dependence of the diffusion coefficient for a known mechanism of the electrochemical reaction.

At diffusion current densities close to the limiting value, the local values of the viscosity and density of the solution, and also of the ionic diffusion coefficients close to the cathode surface, in the diffusion boundary layer, correspond to the conditions of ionic mass transfer in infinitely dilute solutions. With increase in the distance from the cathode surface, however, the local transfer coefficients and the physical properties of the solution, particularly in concentrated solutions, may differ significantly from the values next to the electrode, and this should be reflected in the profiles of the ion concentrations and the electric potential close to the electrode, and also in the magnitude of the limiting diffusion current.

The numerical calculation of the limiting current has been carried out[49] for the electrochemical deposition of copper from copper sulphate solution with allowance for the empirical concentration dependence of the diffusion coefficient of the salt. In a theoretical examination of the same process[64], but under non-stationary conditions, a linear concentration dependence of the diffusion coefficient was postulated. The calculations showed that the theoretical concentration profiles next to the electrode are in much better agreement with the experimental profiles, determined by an optical method, than the relationship given by Sand's familiar equation[65].

To derive an analytical relationship which would make it possible to carry out a more detailed comparison of theory and experimental data and to use this equation to obtain information on the effective transfer coefficients in concentrated electrolyte solutions, it is appropriate to examine the problem of ionic mass transfer to a rotating disc electrode (in this case the problem has one-dimensional geometry) with possibly a more general form of concentration dependence of the transfer properties of the solution. From an analysis of available experimental data on the viscosity ν, density ρ, and activity coefficient g of the salt, the following relationships can be postulated[66–68]:

$$\nu = \nu^s \exp\left[\frac{n}{c_2^{(0)}}(c_1 - c_1^{(s)})\right], \quad \rho = \rho^s \exp\left[\frac{m}{c_2^{(0)}}(c_1 - c_1^{(s)})\right], \quad g = g^s \exp\left[-\frac{k}{c_2^0}(c_1 - c_1^{(s)})\right]. \tag{74}$$

Here, $c_2^{(0)}$ is the bulk concentration of the anions of the salt, c_1 the local concentration of cations, the superscript "s" refers to the conditions at the interphase boundary, and n, m, and k are positive empirical constants.

Equations and boundary conditions have been derived[18], describing the transfer of cations close to the surface of a rotating disc under the conditions of the dissolution of the metal in a concentrated solution of its own salt (for example iron in $FeCl_2$ solution). The problem of the mass transfer of cations, accompanying the cathodic deposition of a metal from a binary electrolyte solution, is formulated analogously, the only difference being that there is a change in the direction of the mass flux of the particles being transferred[67]. If the cathodic current density is denoted by i, and it is assumed that $i < 0$, the equation for the transfer of the cations will have the form

$$(v - V)\frac{dc_1}{dy} - \frac{D_{eff} i (M_1 D_1 - M_2 D_2)}{(z_1 - z_2) F D_1 D_2}\frac{d}{dy}\left(\frac{c_1}{\rho}\right) = \frac{D_{eff} M_3 \nu_0^{1/3}\sqrt{\omega}}{D_1^{1/3}}\frac{d}{dy}\left(\frac{cg}{\rho\sqrt{\nu}}\frac{dc_1}{dy}\right). \tag{75}$$

Here, v is the component of the velocity of the liquid at right angles to the surface of the disc; y the dimensionless distance from the surface of the disc, related to the effective thickness of the diffusion boundary layer; V the linear rate of increase in the thickness of the deposited layer of metal; c the total molar concentration of the solution (as before, the subscript "3" refers to the solvent molecules); and D_1 and D_2 the ionic diffusion coefficients in an infinitely dilute solution.

The boundary conditions for this equation are:

$$\frac{dc_1}{dy} = \frac{z_2 i \rho^s \sqrt{\nu^s}}{z_1 (z_1 - z_2) F \sqrt{\omega} D_1^{2/3} M_3 c^{(s)} g^{(s)}} \quad \text{for } y = 0; \tag{76}$$

$$c_1 = -\frac{z_2}{z_1} c_2^{(0)} \quad \text{for } y = \infty. \tag{77}$$

The integration of Eqn.(75) with boundary conditions (76) and (77) can be carried out in analytical form by expanding the concentration profile as a power series in the distance y. The additional condition that $c_1 = 0$ for $y = 0$ makes it possible to obtain an expression for the limiting diffusion current i_{lim}. This expression has the form[66]:

$$i_{lim} = i_{lim}^{(0)} L, \tag{78}$$

where $i_{lim}^{(0)}$ is the value of the limiting current for the electrochemical deposition of the metal, calculated without allowance for the concentration dependence of the physical properties of the solution:

$$i_{lim}^{(0)} = z_1 F D_1 \left(1 - \frac{z_1}{z_2}\right)\frac{c_1^{(0)}\sqrt{\omega}}{1{,}61 D_{eff}^{1/3} \nu_0^{1/6}}.$$

The coefficient L is given by the expression

$$L = \left\{1 + [0.418m + 0.089n + 0.258k + 0.281B]\frac{z_2}{z_1}\right\} \cdot \left(\frac{\nu_0 \rho_0}{\nu^s \rho^s}\right)^{1/3}, \tag{79}$$

where

$$B = \sqrt{\frac{\nu^s}{\nu_0}}\frac{(z_1 M_2 - z_2 M_1) c_2^{(0)}}{(z_1 - z_2)\rho^s}. \tag{80}$$

Eqn.(79) shows that for $m = n = k = 0$, the coefficient L is not equal to zero, but makes a correction to $i_{lim}^{(0)}$ which is independent of the changes in the physical properties of the solution as the concentration varies and which arises as a result of the more accurate solution of the equation of convective diffusion, which includes terms quadratic in the driving force of ionic mass transfer.

Since one of the most important directions in present-day chemical and electrochemical technology is the development of the theoretical principles of transport phenomena in highly non-equilibrium systems with mass and heat fluxes which are not linear functions of the corresponding driving forces, a rigorous and systematic mathematical theory of processes of intensive mass exchange is undoubtedly urgently required. From the examples examined in the present review it is possible to obtain a picture of the fields of science and technology in which the effects of the interaction between the processes of mass and momentum transfer play the most important role, and the magnitude of these effects. Moreover, the examples given demonstrate the weakness and unsystematic character of the traditional theory of convective diffusion, developed for systems with low rates of interphase mass exchange, for the description of systems in which the hydrodynamic conditions are not an external factor, but are established under the influence of the technological conditions of the process of mass transfer.

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