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QUALITATIVE ANALYSIS OF ELECTRO-HYDRODYNAMIC CHARACTERISTICS OF WEAKLY CONDUCTING FLUIDS*

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A motion of weakly conducting fluids such as various type electrolytes, petroleum, petroleum products, etc., is investigated. The difficulties encountered in the course of describing such media arise, to begin with, from the presence of the electrochemical reactions of dissociation, ionisation and recombination which have significant effect on the distribution of the electrodynamic parameters /1/; the rate of reaction is determined not only by the temperature and concentration of the particles, but also by the electric field strength /2,3/. Secondly, since the media in question are weakly conducting, they can therefore form and retain volume charge over long periods, the charge determining, in general, the electric field distribution.

A system of equations is written for the weakly conducting electrolyte fluid of nature in the presence of electrochemical dissociation and recombination reactions. The motion of the neutral particles is neglected. The influence of the electric field on the rates of these reactions is taken into account. It is shown that for a wide class of fluids the conducting fluid is quasineutral when the electrochemical reactions are equilibrium reactions. When the ratio of the temperature of the medium to the product of absolute magnitude of the ionic charge and characteristic electric potential difference is small, then terms proportional to the concentration gradients can be neglected in the equations for the concentrations of charged particles and diffusion equations everywhere except in the narrow layers near the boundaries. A complete qualitative analysis of the integral curves of such simplified equations in the phase plane is carried out for the one-dimensional case. Integral curves are found, corresponding to the solutions of the boundary value problems under various boundary conditions. The boundary conditions at the solid wall-electrolyte interface are discussed. Cases are shown in which the boundary conditions can be formulated for the simplified system of equations on the boundaries of the diffusion layers external to the electrodes. The results are used to obtain an analytic solution for the problem of electrolytic cell with flat electrodes.

1. System of equations for weakly conducting fluids. We shall assume that the weakly conducting fluid represents a multicomponent mixture of nonelectrolyte liquids of nature, neutral electrolyte molecules and singly charged anions and cations. Electrochemical dissociation and recombination reactions can take place in this mixture. We shall deal with the liquids in which the concentration of charged particles is low, so that the effect of the ions on the motion of the neutral molecules can be neglected.

We assume that the concentration $n_a{}^*$, velocity of the neutral molecules $\mathbf{u}^*$ and temperature T in the energy units are all known. The effect of the reactions on the concentration of neutral molecules of the electrolyte is neglected. The equations describing the events taking place in the medium in question have the form ($\alpha = +, -$ and the indices $+, -$ and a denote, respectively, the parameters associated with the positive and negative ions and the neutral particles):

$$\frac{\partial n_\alpha{}^*}{\partial t} + \operatorname{div} \mathbf{j}_\alpha{}^* = \omega^*, \qquad \omega^* = k_d n_a{}^* \exp A^* \sqrt{E^*} - k_r n_+{}^* n_-{}^* \tag{1.1}$$

$$\mathbf{j}_\alpha{}^* = -D_\alpha{}^* \nabla n_\alpha{}^* + n_\alpha{}^* b_\alpha{}^* \mathbf{E}^* + n_\alpha{}^* \mathbf{u}^*; \qquad A^* = 2e^{3/2}/(T\varepsilon^{1/2}) \tag{1.2}$$

$$\operatorname{div} \mathbf{E}^* = 4\pi e \varepsilon^{-1} (n_+{}^* - n_-{}^*), \quad \operatorname{rot} \mathbf{E}^* = 0 \tag{1.3}$$

Here $n_\alpha{}^*$ denotes the volume concentration, i.e. the number of particles per unit volume, $\mathbf{j}_\alpha{}^*$, $D_\alpha{}^*$, $b_\alpha{}^*$ is the stream density, diffusion and mobility coefficients of the α-components, $\alpha = +, -$; $b_+{}^* > 0$, $b_-{}^* < 0$; ω^* are the volume densities of the ion sources and sinks, k_d and k_r are the dissociation and recombination coefficients, $\mathbf{E}^*$ is the electric field strength, e is the

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*Prikl.Matem.Mekhan.,46,No.3,pp.435-444,1982 charge of a proton and ε is the dielectric permeability of the electrolyte. The expression for the sources appearing in the right-hand sides of the equations of continuity (1.1) describing the dissociation and recombination processes was given in /3/.

2. Reducing the equations to dimensionless form. Electrochemical equilibrium and conditions of quasineutrality.

Substituting (1.2) into (1.1) and assuming that the process is stationary and $\mathbf{u}^* = 0$, we write the system of equations (1.1) — (1.3) in the dimensionless form (the zero subscript denotes the characteristic values of the parameters used as unit values, $\mathbf{r}^*$ is the radius vector and L is the characteristic dimension of the problem)

$$-\delta D_\alpha \Delta n_\alpha + \operatorname{div} n_\alpha b_\alpha \mathbf{E} = \xi^{-1}\omega, \quad \omega = k \exp A\sqrt{E} - n_+ n_- \tag{2.1}$$

$$\xi \operatorname{div} \mathbf{E} = \alpha (n_+ - n_-), \quad \operatorname{rot} \mathbf{E} = 0, \quad \mathbf{j}_\alpha = -\delta D_\alpha \nabla n_\alpha + n_\alpha b_\alpha \mathbf{E} \tag{2.2}$$

$$n_\alpha = \frac{n_\alpha{}^*}{n_0}, \quad \mathbf{E} = \frac{\mathbf{E}^*}{E_0}, \quad D_\alpha = \frac{D_\alpha{}^*}{D_0}, \quad b_\alpha = \frac{b_\alpha{}^*}{b_0}, \tag{2.3}$$

$$\mathbf{r} = \frac{\mathbf{r}^*}{L}, \quad \delta = \frac{D_0}{b_0 E_0 L}$$

$$\xi = \frac{b_0 E_0}{k_r n_0 L}, \quad A = \frac{2e^{3/2}E_0^{1/2}}{\varepsilon^{1/2}T}, \quad k = \frac{k_d n_a{}^*}{k_r n_0^2}, \quad \alpha = \frac{4\pi e b_0}{\varepsilon k_r}$$

The parameter $\delta = \tau_e/\tau_d$ represents the ratio of the characteristic time $\tau_e = L/b_0E_0$ of transport of ions by electric field to characteristic time $\tau_d = L^2/D_0$ of diffusive transport of ions, and the parameter $\xi = \tau_{ch}/\tau_e$ represents the ratio of the characteristic time of change in the ionic concentration caused by the electrochemical reactions $\tau_{ch} = k_r^{-1}n_0^{-1}$, to τ_e. The parameter A is the ratio of the change in the energy of dissociation of the molecules in the characteristic electric field to the characteristic energy of thermal motion /3/, k is the ratio of the dissociation rate unrelated to the presence of electric field to the recombination rate, and α is a characteristic parameter of the elctrolyte independent of the process in question.

The conditions of electrochemical equilibrium under which the ion source and sink intensities in the equations of continuity (2.1) can be assumed equal, are written as follows:

$$\delta\xi = \tau_{ch}/\tau_d \ll 1, \quad \xi = \tau_{ch}/\tau_e \ll 1 \tag{2.4}$$

In this case, neglecting the left-hand part in (2.1), we obtain a reaction connecting the ion concentrations with the electric field strength, valid everywhere except perhaps the narrow layers in the "external" region

$$n_+ n_- = k \exp A\sqrt{E} \tag{2.5}$$

Assuming that the concentrations n_+ and n_- are of the same order, we can obtain from (2.5) the estimates for the order of the magnitude of the concentration n_0 relative to the electric field strength valid, as implied by (2.4), at sufficiently high and low values of the electric field strength.

In majority of known cases $\alpha = O(1)$. In particular, when the relation connecting the recombination coefficient k_r with ionic mobility b_0 and dielectric permeability ε is described by the Langevin formula $k_r = 8\pi e b_0/\varepsilon$, the parameter $\alpha = 0.5$. In this case the first equation of (2.2) and second inequality of (2.4) together yield $n_+ \approx n_-$. Therefore the following assertion holds: in the presence of electrochemical equilibrium the conducting fluid is quasineutral everywhere except perhaps narrow layers.

3. Simplifying the system of equations.

Using the Einstein formula and introducing $\Delta\varphi = E_0L$ we can write the parameter δ in the form $\delta = T/(e\Delta\varphi)$. We can always give the value of the characteristic potential difference for which $\delta \ll 1$. Thus, when $\Delta\varphi = 1$ B and the temperature is 300 K, the parameter $\delta \approx 10^{-2}$. When $\delta \ll 1$, the distribution of the concentrations and electric field can be described everywhere, except in the narrow diffusion layers, by the following system of equations:

$$\xi \operatorname{div} n_\alpha b_\alpha \mathbf{E} = k \exp A\sqrt{E} - n_+ n_- \tag{3.1}$$

$$\xi \operatorname{div} \mathbf{E} = \alpha (n_+ - n_-), \quad \mathbf{j}_\alpha = n_\alpha b_\alpha \mathbf{E}, \quad \operatorname{rot} \mathbf{E} = 0 \tag{3.2}$$

In the case when all parameters depend on a single Cartesian coordinate x, the difference between the equations (3.1) for $\alpha = +$ and $\alpha = -$ can be integrated. Introducing the total dimensional $\mathbf{j}^*$ and dimensionless $\mathbf{j}$ current with help of the formulas $\mathbf{j}^* = e(\mathbf{j}_+{}^* - \mathbf{j}_-{}^*)$, $\mathbf{j} = \mathbf{j}^*/en_0b_0E_0$ and using the second equation of (3.2), we can write ($j_x = j$, $E_x = E$, $j_y = j_z = E_y = E_z = 0$; here and henceforth we assume, without loss of generality, that $b_+{}^* = |b_-{}^*| = b_0$)

$$j = (n_+ + n_-)E \tag{3.3}$$

In the one-dimensional case the closed system of equations consists of the equation (3.3) and equations

$$\xi \frac{dn_+E}{dx} = k \exp A\sqrt{E} - n_+n_-, \qquad \xi \frac{dE}{dx} = \alpha (n_+ - n_-) \tag{3.4}$$

4. Qualitative investigation of the system of equations in the phase space.

From (3.3) and (3.4) we can obtain the equation for the curves in the phase planes En $(n = n_\pm)$ as well as equations describing the variation of electric field E and concentrations $n_\pm$ along the x-coordinate

$$\frac{dn}{dE} = \frac{n^2E(1-2\alpha) - nj(1-\alpha) + kE\exp A\sqrt{E}}{\alpha E(2nE - j)} \tag{4.1}$$

$$\frac{dE}{dx} = \frac{\alpha(2n_+E - j)}{\xi E} = \frac{\alpha(j - 2n_-E)}{\xi E} \tag{4.2}$$

$$\frac{dn_\pm}{dx} = \pm \frac{n_\pm^2E(1-2\alpha) - n_\pm j(1-\alpha) + kE\exp A\sqrt{E}}{\xi E^2} \tag{4.3}$$

From (4.1) and (4.2) we see that the phase patterns in the planes En_+ and En_- coincide, and phase velocities of the points are equal in magnitude and opposite in direction. Figs.1—4 show, for definiteness, the phase planes En_+ and the direction of motion along the integral curves is indicated by arrows. Let us introduce the notation

$$L(n, E) = n^2E(1-2\alpha) - nj(1-\alpha) + kE\exp A\sqrt{E} \tag{4.4}$$

$$L_1(n, E) = 2nE - j, \quad L_2(n, E) = nE - j$$

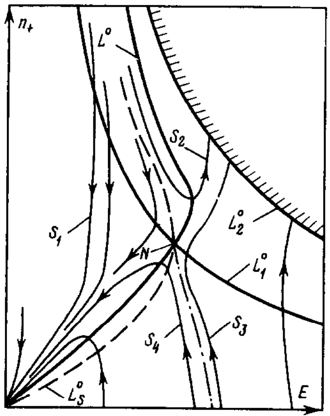

Fig.1

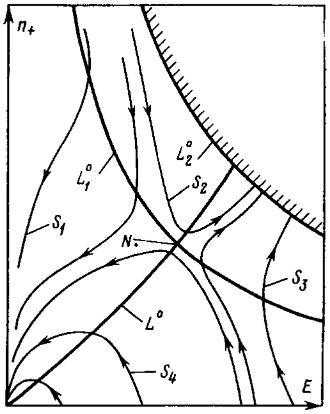

Fig.2

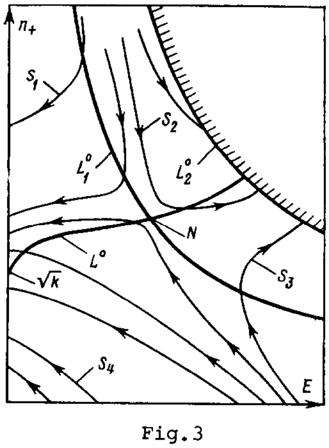

Fig.3

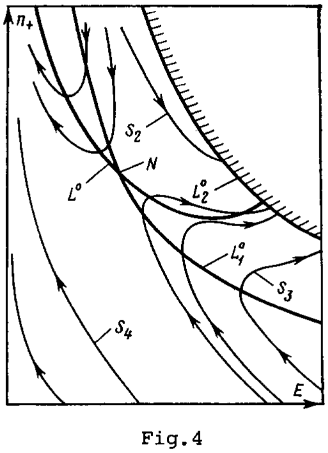

Fig.4

In what follows, the curves $L(n, E) = 0$, $L_1(n, E) = 0$, $L_2(n, E) = 0$ are denoted by L°, L_1° and L_2° respectively. The line L_1° represents the isocline of the vertical tangents and is a hyperbola with the asymptotes represented by the coordinate axes. The equation of this line together with (3.3) imply that $n_+ = n_-$ on this line. We shall call L_1° the quasineutrality line. We note that when $\alpha \neq 1$, the axis $E = 0$ is also isocline of the vertical tangents. The curve L_2° is a hyperbola lying above L_1° and possessing the same asymptotes. The segments of the phase curves lying above the line L_2° have no physical meaning since, according to (3.3), when $n_\pm > j/E$ we have $n_\mp < 0$. The curve L° at $E \neq 0$ is an isocline of the horizontal tangents. It intersects at any value of parameter α the line L_1° at the point N, which is a saddle-type singularity of equation (4.1) with the coordinates $E_N(j)$, n_N, where $E_N(j)$ is a root of the equation

$$j = 2E(k\exp A\sqrt{E})^{1/2}, \tag{4.5}$$

$$n_N = \frac{j}{2E_N(j)}$$

In Fig.1, which corresponds to the case $\alpha \ll 1$, the dashed depict the line L_s° which also passes through the point N on which the concentrations n_+ and n_- and electric field all satisfy the condition of electrochemical equilibrium and the Ohm's Law, represented by the formulas (2.5) and (2.3) respectively. The integral curves of the phase plane are divided by four separatrices emerging from the saddle point N, into four families. We shall denote the families of the phase curves intersecting the line L_1° above and below the saddle point N by S_1 and S_3 respectively, and the families not intersecting the line L_1° and lying above and below it by S_2 and S_4.The separatrix separating the families S_3 and S_4 is shown in Fig.1 by a dashed line.

4.1. Case $\alpha \ll 1$. The phase pattern is shown in Fig.1. The coordinate origin is a node-type singularity and the integral curves come at this point into tangential contact with the straight line $n = kE / j\,(1 - 2\alpha)$. The line L° passes through the coordinate origin and saddle point N. The abscissa of the point at which the curve L° has a vertical tangent satisfies the equation

$$j^2\,(1 - \alpha)^2 = 4kE^2\,(1 - 2\alpha) \exp A \sqrt{E}$$

The point lies above N and tends to N as $\alpha \to 0$. The dependence of the asymptotics of the upper and lower branch of L° on α as $E \to 0$ is, in its principal term,

$$n \to j\,(1 + \alpha) / E \quad \text{and} \quad n \to kE\,(1 + \alpha) / j$$

Outside the α-neighborhood of the curve L° the integral curves become almost vertical $dn / dE \sim \alpha^{-1}$. Here and henceforth under the term α-neighborhood of the curve $f\,(x, y) = 0$ we understand the geometrical position of the points the coordinates of which satisfy the condition $|\,f\,(x, y)\,| \lesssim \alpha$.

From (4.1) it follows that the parts of the integral curves lying in the α-neighborhood of the line L° along which the variation $\Delta E \sim 1$ and $\Delta n \sim 1$, have the corresponding order of the function $L\,(n, E) \sim \alpha$. When $\alpha \to 0$, the curve L° becomes the line L_s°. The behavior of the lines L_1° and L_2° is independent of the parameter α. The line L_s° passes through the saddle point N, has a vertical tangent at this point, and lies in the $\alpha n\,(j - 2nE)$-neighborhood of the line L°. A quasiequilibrium mode of the electrochemical volume reactions corresponds, with the accuracy of up to terms of order α, to the segments of the integral curves passing through the α-neighborhood of the line L°, with $n\,(j - 2nE) \sim 1$. Despite the fact that the quasineutrality is absent from everywhere outside the line L_1°, the result obtained does not contradict, when $\xi \ll \alpha \ll 1$, the assertion of Sect.2, since as shall show below, the flow corresponding to the segments of the integral curves in question occurs not in the "external" region, but in the narrow boundary layers.

4.1.1. Let us inspect the behavior of the parameters $n_\pm$ and E in the physical $xn_\pm$ and xE planes. From (4.1) it follows that in the α-neighborhood of the line L° the increment $\Delta n \sim \Delta E$ and outside it $\Delta E \sim \alpha \Delta n$. This, together with (4.2) and (4.3) imply that on moving along the segments of the integral curves lying in the α-neighborhood of L°, the variation in n and E in the physical xn and xE planes by a quantity of the order of unity takes place over the lengths $\Delta x_n \sim \Delta x_E \sim \Delta x \sim \xi\alpha^{-1}$. In the course of deriving this estimate we assumed that the quantity $L\,(n, E)$ cannot be smaller than α along the integral curve passing through the α-neighborhood of the line L°. Indeed, if $L\,(n, E) \sim \varkappa \ll \alpha$, then $\Delta n \sim \Delta E \varkappa \alpha^{-1}$. When $\Delta n \sim 1$, $\Delta E \sim \alpha\varkappa^{-1} \gg 1$, the integral curve becomes almost horizontal and does not follow L° since the slope of L° is different from zero everywhere.

When $\xi \ll \alpha \ll 1$, the segments of the phase curves in question have the corresponding lengths $\Delta x \sim \xi\alpha^{-1} \ll 1$ in the physical planes. They represent the boundary layers, so that these segments of the integral curves cannot describe the solution of the boundary value problem formulated on the segment (0.1). This also applies to the segments of integral curves lying outside the α-neighborhood of the line L° and having the corresponding lengths of the order of ξ on the physical xn and xE planes when $\Delta n \sim 1$, $\Delta E \sim \alpha$. The segments of the phase curves with corresponding lengths $\Delta x \sim 1$ on the physical planes when $\xi \ll \alpha \ll 1$, lie only in the small neighborhood of the saddle point N. Indeed, the system of equations (4.2), (4.3) linearized in the small neighborhood of the point N can be reduced by nondegenerate linear change of variables to the form (J is the Jacobian of the transformation)

$$J\,\frac{du}{dx} = u, \quad J\,\frac{dv}{dx} = -v, \quad J = \frac{1}{\sqrt{a^2 + bc}}$$

$$E = \frac{aJ^2 + J}{2}\,u + \frac{aJ - 1}{bJ}\,v + E_N, \quad n = \frac{bJ^2}{2}\,u + v + n_N$$

$$a = \frac{2\alpha n_N}{\xi E_N}, \quad b = \frac{[4\,(\alpha - 1) + A\sqrt{E_N}]\,n_N{}^2}{2\xi E_N}, \quad c = \frac{2\alpha}{\xi}$$

Integrating the first equation of this system we obtain

$$J \ln \left| \frac{u\,(x_2)}{u\,(x_1)} \right| = x_2 - x_1$$

In the new variables the point N has a corresponding saddle at the coordinate origin, with the asymptotics coinciding with the coordinate axes. The last equation implies that by choosing a phase curve in the uv-plane passing near the coordinate origin so that the value of the coordinate u at the entry to the neighborhood of the coordinate origin, denoted by $u(x_1)$, is sufficiently small, we can attain an arbitrarily large value of $\ln|u(x_2)/u(x_1)|$. (The quantity $u(x_2)$ denotes the value of coordinate u at the exit from the neighborhood and will obviously be of the order of the circle radius). Consequently we can always choose the phase curve in such a manner that its segment lying in some small neighborhood of the coordinate origin will have a corresponding, predetermined length in the physicl plane.

Thus we have shown that when $\xi \ll \alpha \ll 1$, a solution of the boundary value problem on the interval $[0, 1]$ can be represented by a quasineutral electrochemical equilibrium mode, deviating from the equilibrium inside narrow layers. When $\alpha \lesssim \xi \ll 1$, the quantities Δx can be of the order of unity not only in the neighborhood of the singularity N, but also in the α-neighborhood of the line L°. The integral curves which do not pass near the singularity N can also serve as solutions of the boundary value problem on the interval $[0, 1]$. In this case the segments of the phase curves lying outside the α-neighborhood of the line L° have the corresponding boundary layers with thickness of the order of ξ. When $\xi \gtrsim 1$, then in the present case $(\alpha \ll 1)$ as well as in the cases discussed below in which the parameter α is not small, the segments of any integral curves can serve as a solution of the problem on the interval $[0, 1]$.

4.1.2. Integral curves belonging to family S_1 emerge from the coordinate origin, pass above the line L° through its α-neighborhood, then verge away from it and move almost vertically $dn/dE \sim \alpha^{-1}$, making a vertical tangential contact with the line L_1°, to the upper branch of the line L°. The curves cannot intersect L° and continue to move along it in its α-neighborhood, gradually departing from it with increasing slope of L°. When $E \to 0$, the upper branch of L° intersects the curve L_2° and tends asymptotically to the hyperbola $n_+ = j(1+\alpha)/E$, and the phase curves belonging to S_1 tend to L_2° asymptotically without intersection. The lines belonging to S_2 emerge from L_2°, move towards L° with the tangent to it in almost vertical direction, intersect it and continue along it within its α-neighborhood. As the slope of L° increases they leave its α-neighborhood and tend asymptotically from below to the line L_2°. The lines belonging to family S_4 progress in the α-neighborhood of the lower branch of L°, intersect L° and move almost vertically to the intersection with the axis $n_+ = 0$. The lines of family S_3 emerge from the line $n_+ = 0$ and move almost vertically, up to the line L_2° intersecting L_1° on the way.

4.2. Case $\alpha = 0.5$. The case corresponds to the Langevin relation connecting the coefficients of recombination, mobility and dielectric permeability. The phase pattern is shown in Fig.2. The line L° passes through the coordinate origin into the saddle point N and intersects the line L_2°. The coordinate origin is a degenerate node. The integral curves make a tangential contact with the axis $E = 0$. The upper branches of the curves belonging to S_1 and S_2 tend asymptotically to the line L_2° as $E \to 0$. In the present case and in further cases where α is not small, a reasoning analogous to that of Sect.4.1 can show that when $\xi \ll 1$, then the segments of the phase curves which have the corresponding lengths in the physical planes of the order of unity, lie in some small neighborhood of the point N. Thus outside the narrow ξ-layers the parameters n_+, n_- and E are connected in this case by the conditions of electrochemical equilibrium and quasineutrality, which agrees with the assertion made in Sect.2.

Case $\alpha = 1$ (Fig.3). The line L° passes throught the point with coordinates $0, \sqrt{k}$ and through N. The singularity at the coordinate origin degenerates and the phase curves belonging to S_4 are transformed near it into a family of parallel straight lines. The lines belonging to family S_1 emerge not from the coordinate origin, but from the points on the axis $E = 0$ lying above the point with coordinates $0, \sqrt{k}$. When $E \to 0$, the upper branches of the curves belonging to S_1 and S_2 tend asymptotically to the hyperbolas of the form $n_+ = j/E - \text{const}$ (the constant depending on the line under consideration).

Case $\alpha \gg 1$ (Fig.4). The line L° emerges from L_2°, intersects the line L_1° at the saddle point N and tends asymptotically, as $E \to 0$, to the hyperbola $n_+ = j(2 - \alpha^{-1})/4E$ from above (the principal term describes the dependence of the asymptote on α). The coordinate origin is a saddle singularity with the local asymptotes $E = 0$ and $n = -kE/j(2\alpha - 1)$. The upper and lower branches of the curves belonging to S_1 tend to infinity as $E \to 0$. The lines belonging to S_3 emerge from the axis $n_+ = 0$ and progress to the intersection with L_1°. Those which approach the line L° to the left of its minimum intersect it and continue along it in the downward direction, intersect it once again and then move upwards to intersect the line L_2°. The lines which approach L° to the right of its minimum, do not intersect it.

4.3. Let us inspect the values of the parameters n_+, n_- and E at some cross section $x = x'$. The values of n_+ and n_- are connected by the relation (3.3), therefore the coordinates of the points in the En_+ and En_- planes corresponding to the values of the parameters at the cross section $x = x'$ and equal to each other only on the line L_1° where $n_+(x') = n_-(x')$. As we showed before, the phase patterns in the En_+ and En_- planes coincide, differing from each other only in the direction of the moiton. Let us consider, on the En phase plane (Figs.1 – 4), the motion of the point M_+ with coordinates $E(x')$, $n = n_+(x')$ and the corresponding motion of the point M_- with coordinates $E(x')$, $n = n_-(x')$. The coordinates of the points M_+ and M_- coincide on the line L_1°. Since the points M_+ and M_- move in the opposite directions, it follows that, as the coordinate x increases, the points will move along the different (upper and lower relative to the line L_1°) branches of the phase curve. Since the line L_1° is intersected only by the curves belonging to S_1 and S_3, it follows that the points M_+ and M_- move in the opposite directions along one and the same curve of the same family (S_1 or S_3). From (3.3) it follows that the relations $n_\pm = 0$ and $n_\mp = j/E$ may hold only simultaneously so that the abscissas of the points of intersection of the curve belonging to S_3 with L_2° and the axis $n_+ = 0$ are the same. Similarly, for a motion of the point M_+ along the curve belonging to $S_2\,(S_4)$ in the phase plane we have the corresponding motion of M_- along the corresponding curve $S_4\,(S_2)$. determined by (3.3).

5. Boundary conditions. Problem of electrolytic cell with flat electrodes.

A concrete physical problem which can be solved with help of the integral curves obtained in Sect.4, is defined by setting out its boundary conditions.

Boundary conditions for the concentrations. We shall assume that the positive and negative ions are transformed into neutral molecules at the solid-electrolyte interface. The number of ions of the α-type reacting on a unit surface in unit time is proportional to the concentration of ions in the power of l_α. The proportionality coefficient k_α can, generally speaking, depend on the temeprature T, electric field E and the properties of the solid-electrolyte pair. To simplify the problem we shall not consider the other type reactions. The surface of solid may serve as the source of ions, and the ion flux densities are determined with help of $j_{\alpha em}$. The boundary conditions for a stationary process at the solid-electrolyte interface can be written in the form ($j_\alpha{}^*$ is given by (1.2) and n is the outer normal to the boundary)

$$j_{\alpha n}^* = j_{\alpha em}(T, E) + k_\alpha n_\alpha^{*l_\alpha} \tag{5.1}$$

In the case of conducting boundaries we must, e.g. specify the potentials of all bodies.

Electrolytic cell with flat electrodes. We consider the problem of distribution of electro-hydrodynamic parameters of the electrolyte solution in a cell with flat electrodes, the coordinates of which are $x^* = 0$ (anode) and $x^* = L$ (cathode). A potential difference $\Delta\varphi = \varphi(0) - \varphi(L) > 0$ is applied across the electrodes. The distribution of parameters between the electrodes outside the boundary diffusion layers is described by (3.3), (3.4), the parameter $\delta = \tau_e/\tau_d \ll 1$, and functions sought are assumed to dependent on a single Cartesian coordinate x^*. We use the distance between the electrodes L and applied field $E_0 = \Delta\varphi/L$ as the characteristic dimensions for reducing the system of equations to its dimensionless form. To solve the equations (3.3) and (3.4) we must transfer the boundary conditions (5.1) to the boundaried of the diffusion layers away from the electrodes, and the number of boundary conditions must be reduced by a number equal to the decrease in the order of the system (2.1), (2.2). Let us consider the case when emission currents are absent, the anode current is determined by the negative ions and cathode current by the positive ions. The boundary conditions (5.1) can now be written in dimensionless form as ($j_n = j_x = j$; $E_n = E_x = E$; $j_y = j_z = E_y = E_z = 0$):

$$j_+ = -\delta D_+ \frac{dn_+}{dx} + n_+ b_+ E = 0, \qquad \Lambda_\pm = \frac{k_\pm n_0^{l_\pm - 1}}{b_0 E_0} \tag{5.2}$$

$$j_- = j = -\delta D_- \frac{dn_-}{dx} + n_- b_- E = \Lambda_- n_-^{l_-}, \qquad x = 0$$

$$j_+ = j = -\delta D_+ \frac{dn_+}{dx} + n_+ b_+ E = \Lambda_+ n_+^{l_+} \tag{5.3}$$

$$j_- = -\delta D_- \frac{dn_-}{dx} + n_- b_- E = 0, \qquad x = 1$$

Replacing in (3.3), (3.4) the independent variable thus $X = x\delta^{-1}$ and multiplying the resulting equations by δ, we neglect terms of the order of δ compared with terms of the order of unity. The resulting system of equations describing the behavior of the inner solution of zero order with respect to δ has the integral $j_+^{(i)}(X) = \text{const}$ (the symbols (i) and (e) denote the parameters of the inner and outer solution respectively). Using the integral obtained, the first boundary condition (5.2) and the condition of asymptotic matching, we write the following system of equations:

$$j_+^{(i)}(X) \equiv j_+(0) = 0; \qquad \lim_{x\to 0} j_+^{(e)}(x) = \lim_{X\to\infty} j_+^{(i)}(X) = 0$$

Thus the boundary condition on the left electrode will have the form

$$j_+^{(e)}(0) \equiv n_+ b_+ E\,|_{x=0} = 0 \tag{5.4}$$

Similarly for $x = 1$ we obtain

$$n_- b_- E\,|_{x=1} = 0 \tag{5.5}$$

Studying the behavior of the integral curves on the phase plane in Figs.1—4 we see, that the latter two relations hold only when

$$n_+(0) = n_-(1) = 0 \tag{5.6}$$

Indeed, if we assume that (5.1) implies $E(0) = 0$, then the phase curve corresponding to such a solution should emerge from the point on the ray $\{n_+, E \mid E = 0,\ n_+ \geqslant 0\}$. However, the direction of the motion along the phase curves is such, that no phase curve exists which emerges from any point lying on this ray, into the region where $n_+ > 0,\ E > 0$. Thus the relations (5.6) represent the boundary conditions for the concentrations for the system of equations outside the diffusion layers.

Assuming that the potential at the electrode-solution interface is continuous, we can write the boundary conditions for the electric field strength in the form

$$\int_0^1 E(x)\,dx = 1 \tag{5.7}$$

In order to rewrite this boundary condition for the equations (3.3), (3.4), we must obtain the estimates for the integrals of $E(x)$ over the intervals $[0, \delta]$ and $[1 - \delta, 1]$. It can be shown that when the following conditions hold:

$$\frac{\alpha\delta}{\xi}\left(\frac{j}{\Lambda_\alpha}\right)^{1/l_\alpha} \lesssim 1 \tag{5.8}$$

then the integrals are small. It follows therefore that the potential drop across the boundary diffusion layers can be neglected in the zero approximation with respect to δ. In this case the relation (5.7) will continue to represent a boundary condition for the electric field strength for (3.3), (3.4). We see that at sufficiently high rates of electro-chemical reactions at the electrodes the relations (5.8) always hold. When $l_+ = l_- = 1$, the conditions (5.8) become particularly simple

$$\frac{4\pi D_0 j^*}{\varepsilon b_0 E_0^2 k_\alpha} \lesssim 1$$

Thus the solution of the problem of electrolytic cell with flat electrodes reduces to that of solving the equations (3.3), (3.4) with boundary conditions (5.6), (5.7). The phase curve in the plane En_+ corresponding to the solution of the problem in question must emergy from a some point on the $0E$ axis where $n_+ = 0$, and terminate at the line L_2^0 where $n_+ = j/E$, i.e. $n_- = 0$. Thus the solution in the plane En_+, and hence in En_-, must belong to S_3.

Let us assume that $\xi \ll 1$. Here the curves belonging to family S_3 and describing the solutions of the system of equations on the segment $[0, 1]$ must pass near the singularity N. This, together with Sect.4, determines the type of behavior of the parameters in question inside the electrolytic cell, but outside the diffusion layers. Outside the narrow layers with thickness of the order of ξ adjacent to the diffusion layers, the concentration $n_+ = n_-$, and the medium is quasineutral. The electric field strength and ionic concentrations are connected by the formula (2.5) expressing the condition of electrochemical equilibrium. Since the curve on the phase plane En_+ corresponding to the solution of the problem in question passes near the point N, it follows that the value of electric field strength outside the layer of thickness of the order of ξ is connected with the constant j, i.e. with the dimensionless current, by the relation (4.5).

In the case of $\alpha \ll 1$ the phase curves of the family move almost vertically, therefore the change in the electric field strength outside the diffusion layers can be neglected with the accuracy to terms of order α. In this case, assuming that according to the boundary condition (5.7) $E \approx 1$ and writing (4.5) in the dimensional form, we obtain the following volt-ampere characteristic of the cell:

$$j^* = 2eb_0E_0\left(\frac{k_d n_a^*}{k_r}\exp\frac{2e^{3/2}E_0^{1/2}}{\varepsilon^{1/2}T}\right)^{1/2} \qquad (\xi \ll 1,\ \alpha \ll 1)$$

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