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Theory of Concentration Polarization. II[1]

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1. Non-streamlined electrodes

The first part of the present investigation was restricted to the discussion of phenomena at electrodes of good streamline shape such as an infinite plate or a disc. It was shown there that the magnitude of the limiting current flowing towards the electrode (or the rate of dissolution) is determined primarily by the mode of stirring of the electrolyte in the vicinity of the electrode, in other words, by the conditions under which the liquid flows past the electrode. In the case of a plate the limiting current density was shown to be proportional to the resistance coefficient.

We consider now the cases when the shape of the electrode is that of a non-streamlined body, as, for instance, a cylinder located transversely to the flow, a sphere, or an electrode with salient angles.

The manner in which the stream flows past the electrode and thus the manner of stirring will in these cases essentially differ from that of the flow past a plate. It may be, therefore, expected that in the case of non-steamlined electrodes new phenomena will be observed and that the laws governing them will differ considerably from those observed in the case of plates and discs. The latter may also be inferred from data obtained in measuring the heat exchange at the surface of non-streamlined bodies in a liquid flow.

Let us now briefly dwell on the picture of a flow past a solid body of non-streamlined shape immersed in a liquid[2].

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[1] Part I. Acta Phys. Chim. URSS, 17, 257 (1942).

[2] A more detailed description of streamline motion may be found in text books on hydrodynamics, in particular in «Modern Developments in Fluid Dynamics», edited by D. Goldstein, Oxford, 1938.

As in the case of a plate, there will exist a Prandtl laminar boundary layer at the surface of the solid body for sufficiently great Reynolds numbers. This boundary layer differs, however, widely from that at the surface of an infinite plate. Namely, as it is seen from Prandtl's equation $\frac{\partial p}{\partial y}=0$, the pressure inside the boundary layer is equal to the pressure in the external flow. Therefore, if there is no longitudinal pressure difference in the external flow past a solid body, the pressure within the boundary layer will also remain constant along the entire boundary, as in the case of a stream flowing past a plate.

In the case of a non-streamlined body there must necessarily be a pressure drop in the external flow. This is seen, in particular, from the Bernoulli equation

$$\frac{p}{\rho}+\frac{v^2}{2}=\text{const}$$

which shows that in the vicinity of the stagnation point of the flow and at the rear of the body the pressure rises (velocity diminishes), and in the vicinity of the largest cross-section of the body (its middle part) the pressure diminishes (velocity increases). The pressure in the boundary layer varies correspondingly: it falls from the stagnation point towards the part of largest cross-section and then rises towards the rear. This leads to a most important phenomenon, *viz.* the separation of the boundary layer from the surface at the rear of the body. For the reader's convenience we shall recall here the usual explanation of the mechanism of separation[4].

Since the pressure in the boundary layer is equal to that in the main stream, the fluid motion in the boundary layer at the rear will be retarded by the upstream pressure gradient.

The tangential component of velocity inside the boundary layer varies, following a definite law, from zero on the wall to its value in the main stream (Fig. 1, wherein is shown the profile of the tangential component in the boundary layer). On the contrary, the pressure in the boundary layer remains constant over the entire cross-section of the layer, in virtue of Prandtl's equation $\frac{\partial p}{\partial y}=0$.

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[3] See Part I, Section 4, equation (5).

[4] Prof. L. Landau has shown (private information) that the usual treatment of the separation phenomenon is not strict enough. In fact, the separation point is a singularity point in Prandtl's equations.

Therefore, the retarding effect of the upstream pressure gradient will be exerted, first of all, on the motion of the fluid particles at the surface of the body. At a certain point the upstream pressure gradient will completely stop the liquid particles at the wall, and beyond this point the particles will begin to move under the action of the upstream pressure gradient in the reverse direction, *i. e.* also upstream. Fig. 1 shows schematically the gradual variation of the velocity profile and the formation of the upstream current. The more remote particles continue to move downstream, so that at this point the boundary layer will separate from the solid surface and thus be transformed into a jet entering into the bulk of the liquid. The fluid motion in such a jet is unstable and beyond the separation point M it becomes turbulent. Thus at the rear of the solid body there exists a zone of turbulent flow called the turbulent wake of the solid, the stirring conditions in this zone being substantially different from those at the forward part of the solid body.

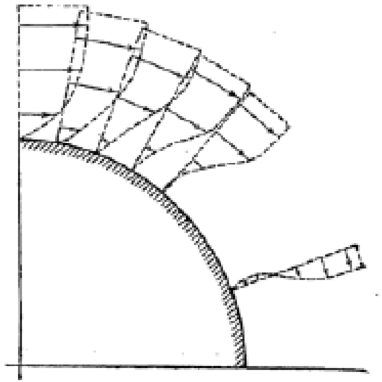

Fig. 1.

The position of the separation point on the body is obviously determined from the condition

$$\left(\frac{\partial u}{\partial y}\right)_{y=0}=0$$

expressing that the tangential velocity at the wall increases with the distance from the latter beyond this point upstream and diminishes from this point downstream (*i. e.* increases in absolute value but is of opposite direction). Methods of calculation used in hydrodynamics allow to find the separation point from this condition in the simplest cases.

The general picture of stirring is thus much more complicated than, for instance, in the case of a plate, and it is therefore difficult to draw any general conclusions on the magnitude of the limiting current and its distribution over the electrode surface. In particular,

in the case of a non-streamlined electrode proportionality between limiting current and resistance coefficient no longer holds as it does for a plate.

In the simplest case of a cylindrical electrode placed perpendicularly to the electrolyte flow, a number of interesting conclusions may, however, be drawn on the distribution and partly even on the value of the limiting current.

Let us consider a cylindrical electrode which is located transversely to the electrolyte flow. As it was just pointed out, for sufficiently large Reynolds numbers a Prandtl boundary layer will be formed in the front part of the cylinder, at its rear the boundary layer will separate from the surface, and behind it a zone of turbulent stirring will arise.

Measurements show that the separation point is situated 8 degrees in front of the equator, the boundary layer thus embracing the cylinder only in the 164° zone. The limiting current densities may be calculated theoretically for the front part of the cylinder.

For the case when heat transmission is involved, a computation is given in Goldstein's book, however, in the limiting case of large Prandtl numbers, in which we are interested, the result obtained differs somewhat from that of Goldstein.

The equations of the boundary layer under action of a pressure gradient may be written[5]

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\nu\frac{\partial^2 u}{\partial y^2}+u_1\frac{\partial u_1}{\partial x},$$

$$\frac{\partial p}{\partial y}=0,$$

where x and y are the tangential and normal coordinates with regard to the cylinder surface, u and v — the tangential and normal velocity components, and the term $u_1\frac{\partial y_1}{\partial u}$, equal to $-\frac{1}{\rho}\operatorname{grad} p$ in virtue of Bernoulli's equation, represents the pressure gradient in the main stream.

Near the stagnation point the velocity of the outer flow (with regard to the boundary layer) may be written $u_1=\frac{4u_0}{d}\frac{x}{}$ where u_0 is the velocity in the unperturbed flow remote from the cylinder, d is

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[5] «Modern Developments in Fluid Dynamics», Vol. II, p. 631, edited by Goldstein, Oxford, 1938.

the cylinder diameter and x — the arc distance from the stagnation point.

The solution of the boundary layer equations valid for comparatively small arc distances x can be regarded as a function of coordinate y only. Computation yields

$$u=\frac{4u_0 x}{d}f'(\eta)\,; \qquad v=-\left(\frac{4\nu u_0}{d}\right)^{1/2}f(\eta)\,,$$

where $\eta=\left(\frac{4u_0}{\nu d}\right)^{1/2}y$, and the function f satisfies equation

$$f'^2-ff'=1+f''' \tag{1}$$

with boundary conditions

$$f(0)=f'(0)=0; \quad f'(\infty)=1. \tag{1'}$$

The equation of convective diffusion is

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}=D\frac{\partial^2 c}{\partial y^2} \tag{2}$$

with $c=c_{-}^{l}$ at $y\rightarrow\infty$ and $c=c_s$ at the cylinder surface (at $y=0$). Passing to a new variable η and substituting v, there obtains

$$c''+\mathrm{Pr}\,fc'=0, \tag{3}$$

where $\mathrm{Pr}=\frac{\nu}{D}$ is the Prandtl number.

The solution of equation (3) for a concentration c is

$$c(\eta)=\frac{\int\limits_0^\eta \exp\left(-\mathrm{Pr}\int\limits_0^\eta f d\eta\right)d\eta}{\int\limits_0^\infty \exp\left(-\mathrm{Pr}\int\limits_0^\eta f d\eta\right)d\eta}\,. \tag{4}$$

Correspondingly, the current density j is

$$j=DF\left(\frac{\partial c}{\partial y}\right)_{y=0}=FD\left(\frac{4u_0 d}{\nu}\right)^{1/2}\frac{1}{\int\limits_0^\infty e^{-\mathrm{Pr}\int\limits_0^\eta f d\eta}\,d\eta}\,. \tag{5}$$

Thus with small angular distances from the stagnation point, the current density on the cylinder is independent of the distance to this point. The integral in (5) may be calculated numerically from the numerical solution of equation (1) for $f(\eta)$.

The results of this calculation shall not be presented here being of no special practical interest, and only the manner in which the integral depends upon the Prandtl number will be outlined. Namely, since $f(\eta)$ is very large compared with unity, the integral in (5) converge rapidly. Therefore, in order to establish this dependence, it is sufficient to expand $f(\eta)$ in a power series in η and restrict ourselves to the first terms of the series.

In virtue of the boundary conditions (1′) for f, the expansion will be of the form $f=a\eta^2+\ldots$ Therefore, for j there obtains

$$j\sim FD\left(\frac{u_0 d}{\nu}\right)^{1/2}\frac{1}{\mathrm{Pr}^{1/3}}\,. \tag{6}$$

Formula (6) is valid only for the front part of the cylinder. It is not possible to derive a formula for the diffusion current density valid for large distances from the stagnation point.

One may only expect that near the separation point the current density is less than at the stagnation point because of the more favourable stirring conditions. Beyond the separation point, however, the stirring conditions are appreciably improved owing to the turbulent nature of the flow.

Therefore, the current density must increase and remain approximately constant over the entire rear part. Since it is not possible to calculate the current density in the separation zone, measurements acquire in this case a special interest. The current density distribution over the cylinder surface described here is in agreement with measurements of heat transmission.

With very large Reynolds numbers (of the order of 10^5), the picture of the flow past the cylinder changes: the flow inside the boundary layer becomes turbulent. Owing to the vigorous stirring occurring in the turbulent flow, its interaction with the external flow and its carrying off by the latter is stronger, so that the separation of the turbulent boundary layer occurs later, *i. e.* further downstream, than in the case of a laminar boundary layer. Turbulence in the boundary layer causes the separation point to be displaced downstream beyond the equator to an angle of about 240°, so that the boundary layer is now adjacent to the cylinder over a much greater surface. This is related to a considerable decrease of the hydrodynamic resistance coefficient (so-called resistance crisis) the latter diminishing four times with turbulence appearing in the boundary layer.

The transition from laminar to turbulent boundary layer will be of no less importance in relation to the phenomena in which we are interested. Since the stirring conditions improve markedly with the appearance of turbulence in the boundary layer, the current to the cylindrical electrode must also appreciably increase. Therefore, turbulence in the boundary layer is a very useful method of reducing the polarization concentration. The fall of the resistance coefficient occurs, it is true, at very high Reynolds numbers, so that, for example, in water, with $\nu = 10^{-2}$, and a cylinder diameter $d \sim 1$ cm., the corresponding velocity will be of the order of 10^5 cm. per second, which is very seldom realized in electrochemical practice. Hydrodynamical researches have shown, however, that the occurrence of the resistance coefficient fall may be forwarded by means of an artificial increase of turbulence in the fluid flow past the cylinder.

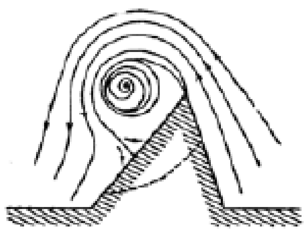

Fig. 2.

With sufficiently intense turbulence of flow the Reynolds number, at which turbulence occurs in the boundary layer, may be decreased by several times. Intensified turbulence of flow is attained either by projecting it through a turbulence grid or by fixing strips or rings at the front part of the cylinder, or simply making its surface sufficiently rough.

Comparing finally a cylindrical electrode with a flat one, we come to the conclusion that, from the standpoint of diminishing the concentration polarization, the former is more advantageous.

Similar qualitative considerations allow of drawing certain conclusions on the manner in which objects with considerable roughness of the surface are dissolved. If the dimensions of the salients are large enough, so that they project beyond the boundary layer limits, the fluid will flow past each such salient as past a body with an angle. Fig. 2 shows the nature of the fluid flow close to such a salient. Eddies are seen to break away from its top, so that in the zone directly behind it the fluid motion at the body surface will be turbulent. Because of the more vigorous stirring in the zone of the salients, dissolution will proceed more rapidly and they will tend to be smoothed out (Fig. 2, dotted line). It is easily seen that the polishing of the object dissolved, attained thereby, will continue only until the size of the roughness remains larger than the thickness of the boundary layer at the surface of the body. These considerations pertain, of course, only to the dissolution of chemically uniform samples.

Let us apply, finally, similar qualitative considerations in the discussion of the dissolution or corrosion of an angular electrode under natural convection. Dissolution (Fig. 3) is known to occur in such a manner that the region of the angle itself dissolves faster than faces remote from it.

At first glance, it may seem that such phenomena cannot be the result of the stirring conditions and have to be accounted for on the basis of other considerations. Usually, in a fluid flowing past a concave angle the region of the angle itself is in fact the region of stagnation of the fluid and the stirring conditions are here most unfavourable for dissolution. However, with sufficiently vigorous natural convection, occurring usually under dissolution, the picture might change. The downward flow of liquid in the boundary layer will meet a counter-pressure exerted by the horizontal wall.

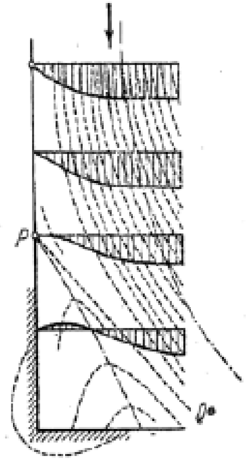

Fig. 3.

In fact, at the wall the vertical fluid velocity is zero, and, correspondingly, close to it the pressure in the fluid is higher than at a distance. Therefore, the flow in the boundary layer will be exactly in response with the picture described above of the flow at the back of a non-streamlined body.

Counter-pressure in the boundary layer will result in its separation from the wall and in the formation of a zone of turbulent stirring.

A calculation of the position of the separation point does not seem to be possible. This point may, however, be expected to be not very far from the angle, so that in the angle itself a sufficiently vigorous stirring of the solution will obtain (Fig. 4). An experimental verification of these concepts of the dissolution of angles would be of great interest.

We presume that such qualitative considerations may be also useful in other cases, when the general picture of the flow in the solution is clear enough.

2. Spontaneous stirring

In practice a current is very often passed through a solution subject to no artificial stirring. In some cases the solution is prevented from being stirred in order to eliminate entirely convective transport of ions in the solution; in other cases, mostly in industrial processes, stirring is not carried out because of the cumberness of the respective apparatus.

It is, therefore, of interest to discuss the problem of the passage of current through a solution under natural convection. Two principal reasons can be indicated to which natural convection is due; firstly non-uniform heating of various parts of the solution when current is being passed, and, secondly, variable density of the solution which is associated with the non-uniform distribution of concentration over the space between electrodes.

Non-uniform heating of the solution is commonly associated with the fact that a greater current passes through some parts of the solution, resulting in a more intensive heating of these zones than others. Apart from this effect, non-uniform heating of the solution may be due to another source. If heat is poorly transmitted from the electrodes, they may become, under the passage of current, either heated or cooled because of the evolution or absorption of heat during the chemical reactions taking place at their surfaces. The latter effect may become quite important when ions with a high overvoltage are liberated on the electrode.

Stirring of the solution associated with the non-uniform heating within its bulk depends essentially upon the geometry of the apparatus, as well as upon various casual factors (evaporation from the solution surface, fluctuation of ambient temperature, etc.); therefore it can hardly be given a theoretical discussion. However, successful selection of the apparatus geometry and low current densities can make this kind of stirring sufficiently small and thus its effect on the passage of current may be neglected.

As far as stirring associated with local heating of the solution near the electrode is concerned, it can, as will be seen later, become important only when the electrode is intensely heated; usually it is of less importance than the concentration effect. We restrict ourselves therefore to the discussion of the latter kind of stirring, the electrode under consideration being assumed in form of an infinite plate

disposed vertically in the gravitation field. We assume, besides, a limiting current to pass through the solution so that the concentration of the solution at the electrode surface itself is zero. Far from the electrode, in the bulk of the solution, the concentration is c^l. The density of the solution near the electrode will then obviously be less than in the bulk of the solution.

From general considerations related to the Bjerknes theorem it is clear that convection will inevitably arise in the solution, since surfaces of equal fluid density are perpendicular to the surfaces of equal pressure.

Let us choose as plane $y=0$ the electrode directing the y axis into the solution and the x axis vertically upwards. The concentration of the solution and, consequently, its density will, in a general way, be functions not only of the distance from electrode (y), but likewise of the position on the electrode (x).

The change of the concentration from its value c^l in the solution to zero on the electrode surface will take place in a thin layer of the fluid, in the diffusion layer near to the electrode surface. Since in our case this change of concentration is the only cause to which is due the liquid motion, the latter can occur only inside the diffusion layer. Therefore, in order to find the distribution of velocity and concentration in the solution, the equation of the boundary layer may be written[*]

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\nu\frac{\partial^2 u}{\partial y^2}+g\frac{\rho(c)-\rho(c^l)}{\rho(c)}, \tag{7}$$

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0, \tag{8}$$

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}=D\frac{\partial^2 c}{\partial y^2}, \tag{9}$$

where $\rho(c)$ is the density of the solution at the point considered, $\rho(c^l)$ — its density remote from the electrode, u and v — the tangential and normal velocity components.

Assuming the variation of the solution density to be small enough and expanding the last term in (7) in a series, equation (7) may, on neglecting all terms but the first, be written

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\nu\frac{\partial^2 u}{\partial y^2}+g\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial c}\right)_{c=c^l}(c-c^l)\,.$$

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[*] «Modern Developments in Fluid Dynamics», Vol. II, 638, edited by Goldstein, Oxford, 1938.

It is convenient further to introduce instead of the concentration c the dimensionless quantity $\varphi = \frac{c^l - c}{c^l}$. Equations (7) and (9) become then

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} + g\alpha\varphi, \tag{7'}$$

$$u \frac{\partial \varphi}{\partial x} + v \frac{\partial \varphi}{\partial y} = D \frac{\partial^2 \varphi}{\partial y^2}, \tag{9'}$$

where.

$$\alpha = \frac{c^l}{\rho_0} \left(\frac{\partial \rho}{\partial c} \right)_{c = c^l}.$$

The boundary conditions for equations (7') and (9') are

$$\left.\begin{matrix} u = v = 0, \\ \varphi = 1, \end{matrix}\right\} y = 0; \tag{10}$$

$$\left.\begin{matrix} u = 0, \\ v = 0, \end{matrix}\right\} y \to \infty. \tag{11}$$

To solve equations (7') and (9'), we introduce a new dimensionless variable

$$\eta = \left[\frac{g\alpha}{4\nu^2} \right]^{1/4} \frac{y}{x^{1/4}}, \tag{12}$$

and the stream function

$$\Psi = 4\nu \left[\frac{g\alpha}{4\nu^2} \right]^{1/4} x^{3/4} f(\eta).$$

The velocity components being

$$u = \frac{\partial \Psi}{\partial y} = 4\nu \left[\frac{g\alpha x}{4\nu^2} \right]^{1/2} f'(\eta),$$

$$v = -\frac{\partial \Psi}{\partial x} = \nu \left[\frac{g\alpha}{4\nu^2} \right]^{1/4} x^{-1/4} (\eta f' - 3f).$$

The function f satisfies the equation

$$f''' + 3ff'' - 2f'^2 + \varphi = 0. \tag{13}$$

For φ as a function of the dimensionless variable the diffusion equation may be written in the form

$$\varphi'' + 3\Pr f\varphi' = 0, \tag{14}$$

where $\Pr = \frac{\nu}{D}$ is the Prandtl number.

The boundary conditions for f and φ are

$$\left.\begin{matrix} f = f' = 0, \\ \varphi = 1, \end{matrix}\right\} \eta = 0; \tag{15}$$

$$\left.\begin{matrix} f' = 0, \\ \varphi = 0, \end{matrix}\right\} \eta \to \infty. \tag{16}$$

In solving equations (13) and (14) we take advantage of Pr being very large compared with unity.

The solution of equation (14) satisfying boundary conditions (15) and (16) may be presented as

$$\varphi = 1 - \frac{\int_0^\eta e^{-3\Pr \int_0^\eta f d\eta} d\eta}{\int_0^\infty e^{-3\Pr \int_0^\eta f d\eta} d\eta}. \tag{17}$$

The function f in (17) is unkown. It can be ascertained, however that as Pr is very high, the integrals converge quite rapidly, and their value is chiefly determined by the form of f at small η.

Owing to this fact, we may consider here as in the case of forced convection the thickness of the diffusion layer, and with $\eta > \eta'$ assume that $\varphi \sim 1$, the concentration being constant and equal to c^l. In this case the boundary condition (11) may be presented as

$$\left.\begin{matrix} f' = 0 \\ \varphi = 0 \end{matrix}\right\} \eta = \eta'. \tag{18}$$

With $\eta < \eta'$ the step-by-step method may be used in solving equation (13). At small values of η the expansion of f may be written

$$f = \frac{\beta\eta^2}{2} + \gamma\eta^3 + \ldots \tag{19}$$

The terms of zero and first power in η must be absent in virtue of the boundary condition (15). Coefficient β has so far not been determined.

On account of the rapid convergence of the integrals in (17) we may substitute the first term of expansion (19) with sufficient approximation. There follows

$$\varphi = 1 - \frac{\int\limits_0^{\eta} e^{-\beta \mathrm{Pr} \eta^3} d\eta}{\int\limits_0^{\infty} e^{-\beta \mathrm{Pr} \eta^3} d\eta}. \tag{20}$$

Introducing the new variable $t = (\beta \mathrm{Pr})^{1/3}\eta$ we get

$$\varphi = 1 - \frac{\int\limits_0^{(\beta \mathrm{Pr})^{1/3}\eta} e^{-t^3} dt}{\frac{1}{3}\Gamma\left(\frac{1}{3}\right)} = 1 - \frac{\int\limits_0^{(\beta \mathrm{Pr})^{1/3}\eta} e^{-t^3} dt}{0.89}. \tag{21}$$

With $(\beta \mathrm{Pr})^{1/3}\eta > 1$, $\varphi = 0$ owing to the rapid convergence of the integral. On the contrary, with $(\beta \mathrm{Pr})^{1/3}\eta < 1$ we may approximately write

$$\varphi \cong 1 - \frac{(\beta \mathrm{Pr})^{1/3}\eta}{0.89}. \tag{22}$$

Obviously, the thickness of the diffusion layer may in this case be defined as

$$(\beta \mathrm{Pr})^{1/3}\eta' = 0.89$$

or

$$\delta' = \frac{0.89 x^{1/4}}{(\beta \mathrm{Pr})^{1/3}\left[\frac{g\alpha}{4\nu^2}\right]^{1/4}}. \tag{23}$$

For function f with $\eta < \eta'$ the following equation may be approximately written

$$f''' + 3ff'' - 2f'^2 + \left(1 - \frac{(\beta \mathrm{Pr})^{1/3}\eta}{0.89}\right) = 0. \tag{24}$$

Equation (24) can be solved by the step-by-step method. Since we are not interested in a high accuracy of coefficient values we may restrict ourselves to the zero approximation. In the zero approximation the value of f is

$$f = \frac{\beta\eta^2}{2} - \frac{\eta^3}{6} - \frac{(\beta \mathrm{Pr})^{1/3}\eta^4}{0.89 \times 24},$$

and

$$f' = \beta\eta - \frac{\eta^2}{2} - \frac{(\beta \mathrm{Pr})^{1/3}\eta^3}{0.89 \times 6}.$$

In virtue of (18) with

$$\eta = \eta' = \frac{0.89}{(\beta \mathrm{Pr})^{1/3}}; \quad f' = 0,$$

so that

$$\beta = (0.59)^{3/4} \frac{1}{\mathrm{Pr}^{1/4}}.$$

Hence from (21)

$$c = 0.54\ \mathrm{Pr}^{1/4}\eta = 0.54\ \mathrm{Pr}^{1/4}\left[\frac{g\alpha}{4\nu^2}\right]^{1/4}\frac{y}{x^{1/4}}. \tag{25}$$

From (23) there obtains

$$\delta' = \frac{x^{1/4}}{0.54\ \mathrm{Pr}^{1/4}\left[\frac{g\alpha}{4\nu^2}\right]^{1/4}}. \tag{23'}$$

The density of the diffusion current flowing to the electrode (limiting current density) under natural convection is

$$j_{\mathrm{lim}} = zF\left(\frac{\partial c}{\partial y}\right)_{y=0} = 0.54\, zF\mathrm{Pr}^{1/4}\left[\frac{g\alpha}{4\nu^2}\right]^{1/4}\frac{1}{x^{1/4}}. \tag{26}$$

The full current to the electrode will then be

$$I = 0.72\, zF\,\mathrm{Pr}^{1/4}\left[\frac{g\alpha}{4\nu^2}\right]^{1/4} b h^{3/4}. \tag{27}$$

The order of magnitude of α is $\frac{c^l}{\rho_0}\left(\frac{\partial\rho}{\partial c}\right)_{c=c^l} \sim c^l$ since usually $\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial c}\right)_{c=c^l} \sim 1$ if c^l is given in per cent. Therefore, the order of magnitude of the thickness of the boundary diffusion layer is

$$\delta' \sim \frac{h^{1/4}}{\left[\frac{\mathrm{Pr}\, g c^l}{4\nu^2}\right]^{1/4}},$$

with

$$c^l \sim 10^{-3}; \qquad h \sim 1; \qquad \delta' \sim 0.03.$$

As concerns the effect of the temperature difference between electrode and solution on the natural stirring, it may be neglected in comparison with the effect just considered, since the solution density changes with temperature slower than with the concentration, when the temperature difference is not too great.

No quantitative experimental data are available with which the expression obtained for δ' could be compared.

In the well-known book of Glasstone and Hickling[7] the value $\delta' \sim 0.03$ is reported, but no data are given for c^f.

3. Turbulent flow

In our previous investigation (Part I, Section 5) we used, following Prandtl, for the mean free path λ the expression $\lambda = \alpha y$, regarding λ as proportional to the distance from the wall. Further analysis has, however, shown that Prandtl's expression for λ is valid only beyond the limits of the viscous sublayer. Within it a somewhat other expression must be used for the mean free path. The latter may, namely, be apparently presented as

$$\lambda = \overline{v}_{\mathrm{turb}} \overline{\tau} \tag{28}$$

where $\overline{v}_{\mathrm{turb}}$ is the main value of the turbulent (pulsation) velocities and $\overline{\tau}$ is the mean time of motion $\overline{\tau} = \int \frac{1}{\omega} f(\omega)\, d\omega$, where ω are the frequencies of the turbulent motion spectrum, and $f(\omega)$ is their partition function. The dependence of $f(\omega)$ on the distance from the wall is generally unknown. Strictly speaking, to each frequency from the set of frequencies forming the spectrum of turbulent fluid motion there corresponds a definite value of the viscous sublayer thickness; thus the problem of the dependence of λ upon y is very complex and requires the study of the entire turbulent frequency spectrum.

We shall restrict ourselves to a more limited problem, assuming that the integrand has a sharp enough maximum in a region of the frequency spectrum. Although the form of the partition function $f(\omega)$ is so far not known, such an assumption is quite natural. Physically $\overline{\tau}$ cannot diverge, neither in the region of low frequencies nor in the region of high ones. In this case the thickness of the sublayer, corresponding to the frequencies at the spectrum maximum, must be considered the viscous sublayer thickness δ. Further τ will have a quite definite value independent of the distance from the wall, so that the dependence of λ upon y is determined only by its dependence upon the first factor in (28).

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[7] Glasstone and Hickling, «Electrolytic oxidation and reduction inorganic and organic», London, 1935.

However, as it was shown in Part I, the normal component of the mean pulsation velocity $\overline{v}_{\mathrm{turb}}$ is proportional to y^2, so that $\overline{\lambda} \sim y^2$.

Substituting this value of $\overline{\lambda}$ into the expression of the flow of substance transported by turbulent pulsations (I, Sections 5, 4) and carrying out further transformations as it was done in I, there results the following expression for the flow of substance to the electrode

$$q = \frac{c}{\frac{1}{2}\rho u_0^2} \, \frac{\frac{1}{2} u_0 c^f}{\left[A + (\alpha' \mathrm{Pr}^{3/4} - A) B \sqrt{\frac{c^f}{2}}\right]}.$$

This expression differs from (I, Sections 5, 7) in that the dependence upon the Prandtl number is somewhat different. As concerns its dependence upon c_f or the velocity u_0 it agrees with the one written earlier, so that the whole reasoning from part I referring to this point still holds.

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