The light sensitivity of the solutions exhibiting the «halochrome» effect seems to have not been noticed before. The usefulness of infrared spectra for the detection of a photochemical change is demonstrated here. Further investigation along these lines was planned.

Summary

A recording 5-prisms glass spectograph with a differential set-up using a thallofide photocell is described, which permits: 1) the sensitive detection, in the spectral range from λ 0.8 μ to λ 12 μ, of feeble absorption bands (harmonics of the fundamental vibration frequencies), belonging to a component present at low concentration in a solution; 2) the elimination of the disturbing spectrum of a component present in excess in a liquid mixture, and 3) the detection of small changes in the intensity and position of absorption bands, produced by association or formation of molecular compounds (complexes) between the components.

The method has been applied to the identification of intermolecular and intramolecular coupling in the binary system $C_6H_5NH_2 + C_6H_5NO_2$ and for solutions of $(CH_3)_2CO$, $CH_3.C_6H_5.CO$, $(C_2H_5)_2O$ in HCl, H_2SO_4, HNO_3, and CCl_3COOH. Photochemically induced association processes of C_6H_6 molecules in the presence of $AlBr_3$ have been revealed by changes in their vibration frequency.

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The Theory of Concentration Polarization

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1. General remarks

It is known that the rate of an electrochemical process on the surface of an electrode submerged into a solution is determined by two factors: by the rate with which the substance comes in contact with the electrode, and by the rate of the electrochemical reactions on the electrode. The rate of supply is in itself determined not only by the rate of diffusion (and migration in the case of ions), but by the character of stirring of the solution as well.

The purpose of the present work is to investigate the processes of stirring of the solution and their influence on the rate of supply of the ions to the electrode. The question of the rate of supply to the electrode has been discussed in literature many times. There is a considerable amount of experimental work[1] dealing with this question, while the theoretical investigation in the case of stationary processes is confined to two papers of this kind. These are: Nernst's paper[2] which offers a qualitative theory of the diffusion layer, at present generally accepted, and Eucken's[3] that contains an atempt at an exact hydrodynamical theory. Besides these investigations, there is a number of others dealing with the non-stationary processes, which we shall not consider here.

Nernst's theory has a qualitative character. According to this theory, the main change of the concentration takes place in a very

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[1] Noyes and Whitney, Z. physik. Chem., **23**, 689 (1897); Brunner and Tolloczko, *ibid.*, **35**, 283 (1904); Centnerszwer, *ibid.*, A, **141**, 297 (1929); Roller, J. Phys. Chem., **29**, 221 (1938); also Moelwyn-Hughes, «The Kinetics of Reactions in Solution», Oxford, 1933.

[2] Nernst, Z. physik. Chem., **47**, 52 (1904); Nernst and Merriam, *ibid.*, **53**, 235 (1905).

[3] Eucken, Z. Elektrochem., **38**, 341 (1932).

thin layer of the fluid close to the electrode, which is called the diffusion layer. It is supposed here that the thickness of the diffusion layer is so small that the motion of fluid within it may be neglected, and the motion of the ions may be regarded as taking place in a resting medium. This supposition reduces the solution of the problem of the passage of the ion towards the electrode to the solution of the problem of diffusion and migration of ions in an immobile layer of a fluid of a certain small thickness δ; on the boundary of the diffusion layer the concentration of ions must be equal to the average concentration of the solution.

Eucken has integrated the equations for the diffusion and the migration of ions in the diffusion layer for the case when the ions of only one kind are the carriers of the current and pass through the solution.

The value of the thickness of the diffusion layer and its dependence on the character of the flow of fluid and on the geometrical conditions cannot be calculated by means of Nernst's theory which thus turns out to be but a qualitative theory.

The Nernst's diffusion layer theory fails to be satisfactory not only because of the insufficiently clear foundation of its premises and because of its qualitative character, but also since it involves the theoretically inadmissible supposition as to the existence of an immobile layer of a fluid of considerable thickness close to the electrode. At the same time, Nernst himself discovered experimentally the dependence of the thickness of the diffusion layer on the character of stirring of the fluid and also on the temperature, the concentration of the solution and on other factors.

On the other hand, the main conclusion of Nernst's theory as to the existence of a limiting diffusion current, *i. e.* the greatest current that can pass through the solution, is remarkably well confirmed by a number of experiments and does not cause any doubts.

It will be shown later on that, while the fundamental supposition of Nernst's theory, as to the existence of an immobile layer of the fluid close to the electrode, does not correspond to the true state of things, still there is a region of fluid with linear drop of concentration that corresponds to Nernst's diffusion layer.

We shall also find the dependence of the thickness of this region of the fluid, also named by us the boundary diffusion layer, on the character of motion of the fluid.

Eucken's work contains an attempt at building up an exact hydrodynamical theory of the diffusion towards a plane electrode, surrounded by the solution moving with a relatively high velocity. However, in establishing the original equation, Eucken has allowed an inaccuracy which turns out to be essential for further investigation. Namely, as we shall show later on during the investigation of this problem, the equation of the convection diffusion towards a plane electrode in a flowing liquid reads as

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

where the x axis is directed along the electrode, while the y axis is perpendicular to it; u and v stand for the xth and the zth components of the velocity of motion of the fluid and c is the concentration of solution.

Here both of the terms on the left hand side of the equation have exactly the same order of magnitude. Although close to the wall itself u is large as compared with v, still in the same ratio $\frac{\partial c}{\partial y}$ is large as compared with $\frac{\partial c}{\partial x}$.

However, Eucken puts the term $v\frac{\partial c}{\partial y}$ as small without any proof and omits it. This changes essentially the entire picture and influences on the final conclusions.

Therefore, we are justified in considering that at present there is no theory that would allow us to find with sufficient foundation and accuracy the rate of supply of matter to the electrode at definite geometrical conditions, and at a given regime of flow of solution. The building up of such a theory seems to be of obvious interest.

It ought to be mentioned that besides the electrochemical interest, the calculation of the rate of supply of the substance to the electrode, of the rate of the diffusion in particular, offers a purely hydrodynamical interest as well. In the case of diffusion, particularly the diffusion of ions, the quantity $\mathrm{Pr}=\frac{\nu}{D}$, called Prandtl's diffusion number, reaches the value of several thousands. Thus, in this case we deal with a peculiar limiting case of hydrodynamics, which may be called the hydrodynamics of Prandtl's large numbers. The investigation of these diffusion phenomena with Prandtl's large numbers at a solid-liquid boundary and at a liquid-liquid boundary, that is of interest in the theory of heat transfer, may apparently be carried out in adequately pure conditions only by means of the electrochemical methods.

The direct investigation of these processes in the phenomena of heat transfer is exceedingly difficult, due to the great dependence of the viscosity of fluids on the temperature.

2. The general equations

Let us, first of all, obtain the general equations for the concentration of ions in the solution and for the distribution of the potentials in the mixed solution. Considering the motion of the solution being given, for each kind of ions present in the solution we may write down the equation of the transfer as

$$\frac{\partial c_i}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_i = D_i \Delta c_i + u_i e n_i \,\mathrm{div}\,(c_i\,\mathrm{grad}\,\varphi), \tag{1}$$

where c_i is the concentration of ions of the ith kind, D_i and u_i — the coefficients of the diffusion and the mobility, n_i — the valency, φ — the potential of the electric field.

The potential φ satisfies the Poisson equation:

$$\Delta\varphi = -\frac{4\pi e}{\varepsilon}\sum_i n_i c_i, \tag{2}$$

where ε is the dielectric constant of the medium.

The set of equation (1) for each kind of ions present, equation (2) and the Navier-Stokes equations together with the boundary conditions determining the velocity of the fluid $\mathbf{v}$, give the complete system of equations, the integration of which allows to determine the unknown concentrations c_i and the potential φ in the solution.

Since, however, equations (1) are non-linear partial differential equations, the solution of this system of equations in a general form meets with unsurmountable mathematical difficulties. Therefore, we shall confine ourselves to the simplest cases of the binary electrolyte (two kinds of ions) and to the case of three kinds of ions, with the number of ions of one kind being very small as compared with the number of ions of other kinds.

Let us investigate, first of all, the case of a binary electrolyte. Let c_1 and c_2 stand for the concentrations of both kinds of ions, D_1 and D_2 for their coefficients of diffusion, and n_1 and n_2 for their valencies. Further, let $\mathbf{v}$ be the velocity of the fluid and φ the electric potential. Then, regardless of the character of the motion of the fluid, we may write down the general equations of the transfer of ions in the electrolyte:

$$\frac{\partial c_1}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_1 = D_1\,\Delta c_1 + \frac{n_1 e D_1}{kT}\,\mathrm{div}\,(c_1\,\mathrm{grad}\,\varphi), \tag{3}$$

$$\frac{\partial c_2}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_2 = D_2\,\Delta c_2 + \frac{n_2 e D_2}{kT}\,\mathrm{div}\,(c_2\,\mathrm{grad}\,\varphi). \tag{4}$$

Here, in the second member on the right-hand side, the mobilities of ions u_1 and u_2 were substituted by their expressions through the diffusion coefficients D_1 and D_2, the well-known Einstein relation having been made use of.

The potential φ satisfies the Poisson equation:

$$\Delta\varphi = -\frac{4\pi e}{\varepsilon}\,(n_1 c_1 + n_2 c_2), \tag{5}$$

where ε is the dielectric constant of the solution and e — the elementary charge of the ion.

Equations (3), (4) and (5) taken together serve, in the case of a given $\mathbf{v}$, for determining the three unknown functions c_1, c_2 and φ.

Since the equations (3) — (5) are non-linear partial differential equations, the solution in a general form would offer unsurmountable mathematical difficulties, being at the same time of no physical interest. However, these equations may be considerably simplified by means of simple transformations.

First of all, we may suppose that the solution, in the main of its bulk at any rate, is electroneutral, so that instead of equation (5) we may write

$$(n_1 c_1 + n_2 c_2) = 0. \tag{6}$$

As it is known, the condition (6) is fulfilled everywhere with a sufficient degree of accuracy, with the exception of the region of the double layer close to the surface of the electrode.

Putting

$$c_1 = -n_2 c \tag{7}$$

and

$$c_2 = +n_1 c \tag{7'}$$

we can write the following equations for the quantity c, which, for the sake of brevity, we shall call also the effective concentration of the solution:

$$\frac{\partial c}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c = D_1 \Delta c + \frac{n_1 e D_1}{kT}\,\mathrm{div}\,(c\,\mathrm{grad}\,\varphi), \tag{8}$$

$$\frac{\partial c}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c = D_2 \Delta c + \frac{n_2 e D_2}{kT}\,\mathrm{div}\,(c\,\mathrm{grad}\,\varphi). \tag{8'}$$

Subtracting the lower equation from the upper one, we find

$$(D_1 - D_2)\,\Delta c + (n_1 D_1 - n_2 D_2)\,\frac{e}{kT}\,\mathrm{div}\,(c\,\mathrm{grad}\,\varphi) = 0.$$

Thus

$$\mathrm{div}\,(c\,\mathrm{grad}\,\varphi) = -\frac{kT\,(D_1 - D_2)}{e\,(n_1 D_1 - n_2 D_2)}\,\Delta c. \tag{9}$$

Substituting this value of $\mathrm{div}\,(c\,\mathrm{grad}\,\varphi)$ into the equation for c, we may eliminate altogether the electric potential. We get here, in fact,

$$\frac{\partial c}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c = D_1 \Delta c - \frac{n_1 D_1 (D_1 - D_2)}{(n_1 D_1 - n_2 D_2)}\,\Delta c$$

or

$$\frac{\partial c}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c = D \Delta c, \tag{10}$$

where

$$D = \frac{(n_1 - n_2)\,D_1 D_2}{n_1 D_1 - n_2 D_2}. \tag{11}$$

It is called the effective coefficient of diffusion.

Equation (10) represents the equation of convective diffusion and with the given $\mathbf{v}$ wholly determines the concentration of the solution c as a function of the coordinates and time, while equation (9) allows to find the distribution of the electric potential in the solution. Thus the electric field is to be totally eliminated, and the problem of finding the distribution of the field and the concentration in the solution splits into two parts: a purely diffusion part, where the solution of the problem of convective diffusion is obtained and where the distribution of concentration does not depend on the field explicitly, and a subsequent determination of

the electric field in the solution, according to the already known distribution of concentration by means of equation (9).

Equation (9) at once allows the integral

$$\frac{e^2}{kT}\,(n_1 D_1 - n_2 D_2)\,c\,\mathrm{grad}\,\varphi + e\,(D_1 - D_2)\,\mathrm{grad}\,c = -\frac{\mathbf{j}}{n_1 n_2}, \tag{12}$$

where $\mathbf{j}$ stands for the vector of current density.

The integration of equation (12) allows to find the connection of the difference of potentials between the electrodes with the current passing through this solution, which, in fact, is our final purpose.

Further on, we shall solve the equations (10) and (9) in the geometrically simple and at the same time experimentally important cases of electrodes in the form of a revolving flat discs and of a liquid flowing past a plate. We shall confine ourselves here to the case of a stationary current, so that we shall consider the concentration of ions and the velocity of fluid as independent of time explicitly.

Still another case, when the migration of ions in the field may be separated from the diffusion and the convective transfer, is the case of three kinds of ions, when the concentration of one kind is low as compared with the concentrations of the two other kinds. The equations of transfer have the form:

$$\frac{\partial c_1}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_1 = D_1 \Delta c_1 + \frac{n_1 e D_1}{kT}\,\mathrm{div}\,(c_1\,\mathrm{grad}\,\varphi), \tag{13}$$

$$\frac{\partial c_2}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_2 = D_2 \Delta c_2 + \frac{n_2 e D_2}{kT}\,\mathrm{div}\,(c_2\,\mathrm{grad}\,\varphi), \tag{14}$$

$$\frac{\partial c_3}{\partial t} + (\mathbf{v}\,\mathrm{grad})\,c_3 = D_3 \Delta c_3 + \frac{n_3 e D_3}{kT}\,\mathrm{div}\,(c_3\,\mathrm{grad}\,\varphi) \tag{15}$$

and the condition of electroneutrality

$$n_1 c_1 + n_2 c_2 + \alpha n_3 c_3 = 0, \tag{16}$$

where α is a small coefficient as compared with unity.

Usually, it is the current carried by the ions of the third kind, the concentration of which is low, that offers practical interest.

In solving the set of equations (13) — (16) two cases must be distinguished. The first case is that one when only the ions of the third kind are liberated at the electrode, and the other case is the case when two kinds of ions are liberated at the electrode, for instance, the second and the third ones.

In both cases we shall solve the equations (13)—(16) by the method of successive approximations.

Let there be no ions of the third kind at all in the solution, in the zero approximation. Then the concentrations of ions of the first and the second kind will have the values c_1^0 and c_2^0, while the potential—φ_0, all of these values being obtained from the equations (8) for a binary electrolyte. It is easy to see, however, that if the ions neither of the first nor of the second kind are liberated at the electrode, then the only possible solution for c_1^0, c_2^0 and φ_0 shall read:

$$c_1^0 = \text{const}, \quad c_2^0 = \text{const}, \quad \varphi_0 = \text{const}.$$

If, however, one of the ions present in large amounts is liberated at the electrode, then the corresponding expressions from the solution of the case of a binary electrolyte problem must be taken for c_1^0, c_2^0 and φ.

In the first approximation we shall look for the solution of equations (13)—(16) in the form:

$$c_1 = c_1^0 + c_1', \qquad c_3 = c_3,$$
$$c_2 = c_2^0 + c_2', \qquad \varphi = \varphi_0 + \varphi',$$

where c_1', c_2' and φ' are small additions, having the same order of magnitude as c_3.

Inserting these values of c_1, c_2 and φ into equations (13)—(16), we get

$$(\mathbf{v}\,\text{grad})\,(c_1^0 + c_1') = D_1 \Delta\,(c_1^0 + c_1') + \frac{n_1 e D_1}{kT}\,\text{div}\,[(c_2^0 + c_1')\,\text{grad}\,(\varphi_0 + \varphi')],$$
$$(\mathbf{v}\,\text{grad})\,(c_2^0 + c_2') = D_2 \Delta\,(c_2^0 + c_2') + \frac{n_2 e D_2}{kT}\,\text{div}\,[(c_2^0 + c_2')\,\text{grad}\,(\varphi_0 + \varphi')],$$
$$(\mathbf{v}\,\text{grad})\,c_3 = D_3 \Delta c_3 + \frac{n_3 e D_3}{kT}\,\text{div}\,[c_3\,\text{grad}\,(\varphi_0 + \varphi')];$$

and the equation of electroneutrality will evidently be rewritten thus:

$$n_1 c_1' + n_2 c_2' + \alpha n_3 c_3 = 0. \tag{17}$$

Neglecting all the members containing the products of small quantities c_1', c_2', φ and c_3 and taking into consideration the equations for c_1^0 and c_2^0, we find

$$(\mathbf{v}\,\text{grad})\,c_1' = D_1 \Delta c_1' + \frac{n_1 e D_1}{kT}\,\text{div}\,(c_1'\,\text{grad}\,\varphi_0 + c_1^0\,\text{grad}\,\varphi'), \tag{18}$$
$$(\mathbf{v}\,\text{grad})\,c_2' = D_2 \Delta c_2' + \frac{n_2 e D_2}{kT}\,\text{div}\,(c_2'\,\text{grad}\,\varphi_0 + c_2^0\,\text{grad}\,\varphi'), \tag{19}$$
$$(\mathbf{v}\,\text{grad})\,c_3 = D_3 \Delta c_3 + \frac{n_3 e D_3}{kT}\,\text{div}\,(c_3\,\text{grad}\,\varphi_0). \tag{20}$$

If we are dealing with the first case, when only the ions c_3 are liberated, then grad $\varphi_0 = 0$ and the equations are reduced to the following:

$$(\mathbf{v}\,\text{grad})\,c_1' = D_1 \Delta c_1' + c_1^0 \frac{n_1 e D_1}{kT}\,\text{div}\,\text{grad}\,\varphi',$$
$$(\mathbf{v}\,\text{grad})\,c_2' = D_2 \Delta c_2' + c_2^0 \frac{n_2 e D_2}{kT}\,\text{div}\,\text{grad}\,\varphi',$$
$$(\mathbf{v}\,\text{grad})\,c_3 = D_3 \Delta c_3.$$

If, however, the ions present in the solution in large amounts are liberated, then c_1^0, c_2^0 and φ are certain given functions of z, and no longer constants.

The concentration c_3 in this case must be found by means of the direct solution of equation (20). c_3 being known, it is possible by means of equation (15) to express c_1' through c_2' and c_3, for instance, and to eliminate the potential φ' from equations (18) and (20) by multiplying the first by n_1, the second by n_2, and subtracting them one from another. This allows, in principle, to find c_1', c_2' and later φ', thus solving the problem to the end.

In other cases we have not as yet succeeded in simplifying the equation of the transfer by separating the migration in the presence of convection of the fluid.

3. A rotating electrode

Our next problem consists in solving for particular geometrical conditions and with a given character of stirring the general equations of transfer written down in the preceding section.

In practice, the stirring of the solution is realized by means of natural or forced convection

As far as natural convection is concerned, it originates in the solution mainly because of the influence of two factors: the non-homogeneity of the solution between the electrodes and the non-uniform distribution of temperature in the solution, which, if other causes are excluded by means of placing of the solution in a thermostat, may be connected with the evaporation from the surface of the fluid.

It is quite difficult to get rid of the natural convection; however, on the other hand, the motion of the fluid in the condition of natural convection may be very easily distorted by various secondary factors. Therefore a theoretical investigation of the influence of natural convection on the current passing in a fluid would scarcely seem reasonable. A much greater interest is offered by the case of forced convection, when the most energetic stirring of the solution takes place, and the influence of subordinate factors may be reduced to a minimum.

Artificial stirring of the solution is realized in practice by various methods, the theoretical advantage and shortcomings of which shall be discussed in next section, dealing with the theory of the boundary diffusion layer.

Here we shall confine ourselves to the case when the stirring of the electrolyte is realized by means of an electrode which has the shape of a flat disc of a sufficiently large area, rotating about an axis perpendicular to the plane of the disc with a constant angular velocity ω.

It turns out here that the problem of finding the rate of supply of the substance to the electrode may be solved exactly, without any approximations, and therefore offers great interest.

At the same time, the revolving disc is very often used in practice and its theory has a practical value as well. Further on, we shall suppose that the area of the electrode is sufficiently large; and that it is placed in a vessel with a solution of an infinite volume, so as to be in a position to neglect all the effects connected with the edges of the disc and the influence of the walls of the vessel.

The problem of the motion of fluid in such conditions has been solved by **Kárman**[4]. We shall reproduce here this solution briefly inasmuch as the expressions for the velocities of the fluid shall be needed further on.

Here we shall restrict ourselves only to the case of sufficiently small Reynolds numbers, so that the motion of the fluid might be considered as laminar. As has been established by **Kempf's** experiments[5], the flow of the fluid dragged by a rotating disc remains laminar up to Reynolds number $\mathrm{Re} \sim 10^5$. It scarcely seems reasonable to consider the convective transfer when there is a turbulent flow of the fluid in the case of a rotating disc, since the calculation of the regime of flow itself is not in a sufficiently good accordance with the experiment.

Let us choose cylindrical coordinates r, φ and z, directing the z axis vertically upwards, and let us investigate only the upper half space above the disc. Then the Navier-Stokes equations for a stationary current of the fluid will have the following form:

$$v_r \frac{\partial v_r}{\partial r} - \frac{v_\varphi^2}{r} + v_z \frac{\partial v_r}{\partial z} = \nu \left(\frac{\partial^2 v_r}{\partial z^2} - \frac{v_r}{r^2} \right) - \frac{1}{\rho} \frac{\partial p}{\partial r}, \tag{1}$$

$$v_r \frac{\partial v_\varphi}{\partial r} + \frac{v_r v_\varphi}{r} + v_z \frac{\partial v_\varphi}{\partial z} = \nu \left(\frac{\partial^2 v_\varphi}{\partial z^2} - \frac{v\varphi}{r^2} \right), \tag{2}$$

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = \nu \frac{\partial^2 v_z}{\partial z^2} - \frac{1}{\rho} \frac{\partial p}{\partial z}, \tag{3}$$

and the continuity equation

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0. \tag{4}$$

Here v_r, v_φ and v_z are the components of the velocity, p is the pressure, ρ and ν are the density and the kinematic viscosity of the fluid.

The following conditions serve as the boundary conditions of equation (1).

On the surface of the disc (the plane $z=0$):

$$v_r = 0, \quad v_\varphi = \omega r, \quad v_z = 0. \tag{5}$$

At $z = \infty$ (far away from the disc)

$$v_r = 0, \quad v_\varphi = 0, \quad v_z = -c. \tag{6}$$

The last condition shows that there is far away from the disc a constant current of fluid flowing towards the disc (Fig. 1).

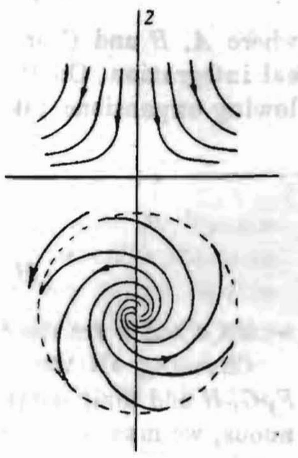

Fig. 1. The lines of flow of a liquid flowing past a rotating disc.

Let us introduce a new non-dimensional variable and let us look for the solution of equations (1)—(4), satisfying the boundary conditions (5)—(6) in the form

$$v_r = r\omega F(\zeta); \quad v_\varphi = r\omega G(\zeta); \quad v_z = \sqrt{\nu\omega}\, H(\zeta),$$
$$p = P(\zeta). \tag{7}$$

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[4] **Goldstein**, «Modern Hydrodynamics», Vol. I and II, Oxford, 1938. See also **Kárman**, Z. angew. Math. und Mech., 1, 244 (1921).

[5] **Kempf**, «Reibungswiderstand rotierender Scheiben», Berlin, 1924, p. 168.

The functions F, G, H and P of the argument ζ evidently satisfy the following equations:

$$F^2-G^2+HF'=F'', \tag{8}$$

$$2FG+HG'=G'', \tag{9}$$

$$HH'-H''=P', \tag{10}$$

$$2F+H'=0, \tag{11}$$

with the boundary conditions

$$\begin{aligned} &F(0)=0, \quad G(0)=1, \quad H(0)=0,\\ &F(\infty)=0, \quad G(\infty)=0, \end{aligned} \tag{12}$$

the value of H at $\zeta=\infty$ being finite.

The most exact and complete solution of this system belongs to Cochrane. At large values of the non-dimensional coordinate ζ for F, G and H the following asymptotic expansions take place:

$$F=Ae^{-C\zeta}-\frac{A^2+B^2}{2C^2}e^{-2C\zeta}+\frac{A(A^2+B^2)}{4C^4}e^{-3C\zeta}+\ldots,$$

$$G=Be^{-C\zeta}-\frac{B(A^2+B^2)}{12C^4}e^{-3C\zeta}+\ldots,$$

$$H=-C+\frac{2A}{C}e^{-C\zeta}-\frac{A^2+B^2}{2C^3}e^{-2C\zeta}+\ldots,$$

where A, B and C are constants determined by means of numerical integration. On the other hand, at small values of ζ, the following expansions take place:

$$F=a\zeta-\frac{1}{2}\zeta^2-\frac{1}{3}b\zeta^3-\ldots, \tag{13}$$

$$G=1+b\zeta+\frac{1}{3}a\zeta^3+\ldots, \tag{14}$$

$$H=-a\zeta^2+\frac{1}{3}\zeta^3+\frac{b}{6}\zeta^4, \tag{15}$$

where a and b are some other constants.

Choosing all the constants pointed out so that the functions F, G, H and their derivatives with respect to ζ should remain continuous, we may obtain the following numerical values of constants[6]:

$$\begin{aligned} &a=0.510, \quad b=-0.616, \quad C=0.886,\\ &A=0.934, \quad B=1.208. \end{aligned} \tag{16}$$

As the limiting expressions for H show, the velocity component normal to the surface of the disc increases rapidly as we move away from the disc, and then tends to the constant limit C.

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[6] Cochrane, Proc. Cambr. Phil. Soc., **30**, 365 (1934).

As far as the functions F and G are concerned, G diminishes rapidly down to zero as we move away from the disc, while F has its maximum close to the disc, after which it also diminishes down to zero. Therefore, an exact solution of the problem gives the following picture of the motion of the liquid. Away from the rotating infinite disc the fluid moves vertically in the direction of the electrode; in a thin layer directly adjacent to the surface of the disc, the fluid is dragged and acquires a rotating motion, with the angular velocity increasing when approaching the disc up to the value of ω. Finally, because of the centrifugal effect in the region where it is dragged, the fluid acquires also a radial velocity The lines of the flow of the fluid join in the infinity.

The thickness of the region of dragging is not large. As may be seen from the graph, already at $\zeta\sim 2.7$—2.8, G becomes very small, diminishing tenfold as compared with its value on the disc itself at $\zeta=0$.

If this point be determined conventionally as a boundary of the region of dragging, then its thickness δ will be equal

$$\delta\sim 2.7\sqrt{\frac{\nu}{\omega}}. \tag{17}$$

At $\omega=25$, in water at room temperature

$$\delta\sim 2.7\frac{0.1}{5}\sim 0.05 \text{ cm}.$$

Let us turn now to the solution of the problem of the transfer of ions in the electrolyte to the revolving electrode. For the cases enumerated in the preceding section, the problem of the motion of ions splits into two problems; into a purely diffusion part, consisting of the solution of equation (10) of section 2, and into the problem of finding the distribution of the electric field in the solution.

Our final problem is to find the relation between the electromotive force in the circuit and the electric current flowing through the solution (the volt-ampere characteristic of the process).

The equation of the convective diffusion written in cylindrical coordinates has the form

$$v_r\frac{\partial c}{\partial r}+\frac{1}{r}v_\varphi\frac{\partial c}{\partial \varphi}+v_z\frac{\partial c}{\partial z}=D\left(\frac{\partial^2 c}{\partial r^2}+\frac{\partial^2 c}{\partial z^2}+\frac{1}{r^2}\frac{\partial^2 c}{\partial \varphi^2}\right). \tag{18}$$

Inasmuch as in our case, due to axial symmetry of the problem, c cannot depend on the angle φ explicitly, the equation is simplified and acquires the form:

$$\omega r F_{(z)} \frac{\partial c}{\partial r} + \sqrt{\nu\omega}\, H_{(z)} \frac{\partial c}{\partial z} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} \right), \tag{19}$$

where for v_r and v_z their values from equation (15) are inserted.

The equation of the field, according to equation (10) of section 2 may be written down in cylindrical coordinates in the form:

$$(D_1 - D_2)\, e \frac{\partial c}{\partial r} + \frac{(n_1 D_1 - n_2 D_2)\, e^2}{kT} c \frac{\partial \varphi}{\partial r} = - \frac{j_r}{n_1 n_2}, \tag{20}$$

$$(D_1 - D_2)\, e \frac{\partial c}{\partial z} + \frac{(n_1 D_1 - n_2 D_2)\, e^2}{kT} c \frac{\partial \varphi}{\partial z} = \frac{j_z}{n_1 n_2} \tag{21}$$

where j_r and j_z are the radial and the vertical components of the current.

For the sake of simplicity we shall consider only the upper plane of the disc and the half space above it filled by the fluid. The situation at the lower plane of the disc shall be identically the same and shall correspond simply to the doubling of the disc area. The current j_z to the electrode in the upper half plane flows against the positive direction of the axis z and is considered by us as negative. Therefore, there is a plus sign in the right-hand side of equation (21). The current j_r flows along the positive direction of the r axis and is therefore positive.

The following conditions serve as the boundary conditions: the potential φ of the second electrode (anode) situated away from the revolving electrode, at $z = l$, is chosen as zero:

$$\varphi_{z=l} = 0. \tag{22}$$

The concentration of the solution is designated here through $c^{(l)}$. Evidently

$$c^{(l)} = \frac{c_2^{(l)}}{n_1} = - \frac{c_1^{(l)}}{n_2},$$

where $c_1^{(l)}$ and $c_2^{(l)}$ is the concentration of both kinds of ions in the bulk of the solution:

$$z = l, \quad c = c^{(l)}. \tag{23}$$

Close to the surface of the electrode, near the plane $z = 0$, the total current transferred to the electrode by those ions which are not liberated at this electrode must vanish. We shall admit that the ions of the first kind are liberated at the electrode, so that for the ions of the second kind we may write

$$D_2 \frac{\partial c_2}{\partial z} + \frac{n_2 e D_2}{kT} c_2 \frac{\partial \varphi}{\partial z} = 0 \quad \text{at} \quad z = 0. \tag{24}$$

This relationship, generally speaking, does not take place within the solution itself close to the electrode, since even if the ions of the second kind are not liberated at the electrode, still they may carry a current differing from zero due to convection. On the electrode itself, the convection velocity vanishes and the equality (24) must hold.

Multiplying (24) by $\frac{1}{n_1}$, we find, evidently, the boundary condition for c:

$$\frac{\partial c}{\partial z} + \frac{n_2 e}{kT} c \frac{\partial \varphi}{\partial z} = 0 \quad \text{at} \quad z = 0. \tag{24'}$$

We shall attempt to look for the solution of equations (19), (20), (21) satisfying the boundary conditions (22), (23), (24′) in the form

$$c = c(z) \quad \text{and} \quad \varphi = \varphi(z), \tag{25}$$

i. e. depending only on the z coordinate. If such a solution were found and would turn out not to be contradictory, on the basis of the uniqueness theorem, it might be considered as the correct solution of our problem. Physically, supposition (25) means nothing else but that the radial motion of the fluid cannot carry the ions beyond the electrode, and consequently may, with a fair degree of exactness, be fulfilled only for large dimensions of the disc, when the influence of the edges may be neglected and the disc may be considered infinitely large.

If the supposition (25) is fulfilled, then the equations (19)—(21) will evidently acquire the following form:

$$v_z \frac{dc}{dz} = D \frac{d^2 c}{dz^2}, \tag{26}$$

$$(D_1 - D_2)\, e \frac{dc}{dz} + \frac{(n_1 D_1 - n_2 D_2)\, e^2}{kT} c \frac{d\varphi}{dz} = \frac{j_z}{n_1 n_2} = j, \tag{26'}$$

$$j_r = 0. \tag{26''}$$

Integrating (26) we find, successively

$$\frac{dc}{dz}=a_1e^{\int\limits_0^z \frac{v_z}{D}dz}, \tag{27}$$

$$c=a_1\int\limits_0^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+a_2, \tag{28}$$

where a_1 and a_2 are the constants of integration.

The boundary condition (22) gives

$$c^{(l)}=a_1\int\limits_0^l e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+a_2,$$

so that it is convenient to write the expression for c in the form

$$c=a_1\int\limits_l^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+c^{(l)}. \tag{29}$$

Equation (26′) may be written as:

$$d\varphi=\frac{jkT}{e^2(n_1D_1-n_2D_2)}\,\frac{dz}{c}-\frac{(D_1-D_2)\,kT}{e\,(n_1D_1-n_2D_2)}\,\frac{dc}{c}.$$

Integrating within the limits from l to z, we find the following expression for the potential φ:

$$\varphi=-\frac{kT\,(D_1-D_2)}{e\,(n_1D_1-n_2D_2)}\lg\frac{c}{c^{(l)}}+\frac{kTj}{e^2(n_1D_1-n_2D_2)}\int\limits_l^z\frac{dz}{c}+a_3. \tag{30}$$

The constant a_1 may be found from the boundary condition (24′). Substituting into (24′) the value of $\frac{dc}{dz}$, c and $\frac{d\varphi}{dz}$ for $z=0$, we get, after simple transformations:

$$a_1=\frac{n_2}{n_2-n_1}\cdot\frac{j}{D_1e}, \tag{31}$$

whence, substituting into (29) and (30), we get:

$$c=\frac{n_2}{n_2-n_1}\,\frac{j}{D_1e}\int\limits_l^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+c^{(l)}, \tag{29′}$$

and

$$\varphi=-\frac{kT\,(D_1-D_2)}{e\,(n_1D_1-n_2D_2)}\lg\frac{c}{c^{(l)}}+$$

$$+\frac{kTj}{e^2(n_1D_1-n_2D_2)}\int\limits_l^z\frac{dz}{\frac{n_2j}{(n_2-n_1)D_1e}\int\limits_l^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+c^{(l)}}. \tag{30′}$$

The potential difference between the anode and the cathode $\varphi_a-\varphi_k$, where φ_a is the potential of the anode, and φ_k—the potential of the cathode, is evidently equal to the applied potential difference V minus the concentration polarization P. The latter is equal to

$$P=-\frac{kT}{en_1}\lg\frac{c_1^{(0)}}{c_1^{(l)}}=-\frac{kT}{en_1}\lg\frac{c_0}{c^{(l)}}. \tag{32}$$

Since we have chosen the zero of potential on the anode ($z=l$), we get evidently

$$\varphi_k=-\frac{kT\,(D_1-D_2)}{e\,(n_1D_1-n_2D_2)}\lg\frac{c_0}{c^{(l)}}+$$

$$+\frac{kTj}{e^2(n_1D_1-n_2D_2)}\int\limits_l^0\frac{dz}{\frac{n_2j}{(n_2-n_1)D_1e}\int\limits_l^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+c^{(l)}}.$$

Therefore

$$V=(\varphi_a-\varphi_k)+P=-\varphi_k+P=+\frac{kT\,(D_1-D_2)}{e\,(n_1D_1-n_2D_2)}\lg\frac{c_0}{c^{(l)}}-$$

$$-\frac{kT}{en_1}\lg\frac{c_0}{c^{(l)}}-\frac{kTj}{e^2(n_1D_1-n_2D_2)}\int\limits_l^0\frac{dz}{\frac{n_2j}{(n_2-n_1)D_1e}\int\limits_l^z e^{\frac{1}{D}\int\limits_0^z v_z\,dz}\,dz+c^{(l)}}. \tag{33}$$

Let us now turn to the calculation of the last integral. Substituting the values v_z from equations (15) and (27), we get

$$I = \int\limits_{l}^{0} \frac{dz}{\frac{n_2 j}{(n_2 - n_1) D_1 e} \int\limits_{l}^{z} e^{\frac{1}{D}\int\limits_{0}^{z} v_z \, d\zeta} dz + c^{(l)}} =$$

$$= \int\limits_{l}^{0} \frac{dz}{\frac{n_2 j}{(n_2 - n_1) D_1 e} \int\limits_{l}^{z} e^{-\left[\frac{a_0 \nu}{} \frac{z^3}{\left(\sqrt{\frac{\nu}{\omega}}\right)^3} + \dots\right]} dz + c^{(l)}} . \qquad (34)$$

Let us introduce into the integral (34) a new variable t, determined as

$$t = \frac{z}{\delta'}, \qquad (35)$$

where

$$\delta' = \frac{\sqrt{\frac{\nu}{\omega}}}{\left(\frac{a_0}{3} \frac{\nu}{D}\right)^{1/3}} = \left(\frac{D}{\nu}\right)^{1/3} \frac{\delta}{\sqrt[3]{\frac{a_0}{3}}} = 1.82 \left(\frac{D}{\nu}\right)^{1/3} \delta. \qquad (35')$$

Here $\delta = \sqrt{\frac{\nu}{\omega}}$ is a quantity which, except for the coefficient, is equal to the thickness of the boundary layer of fluid, determined by formula (17). Thus, for the distance between the electrodes always $l \gg \delta'$. Then we get

$$I = \int\limits_{l/\delta'}^{0} \frac{dt}{\frac{n_2 j}{(n_2 - n_1) D_1 e} \int\limits_{l/\delta'}^{t} e^{-[t^3 + \beta t^4 + \dots]} dt + \frac{c^{(l)}}{\delta'}} +$$

$$+ \int\limits_{1}^{0} \frac{dt}{\frac{n_2 j}{(n_2 - n_1) D_1 e} \int\limits_{l/\delta'}^{t} e^{-(t^3 + \beta t^4 + \dots)} dt + \frac{c^{(l)}}{\delta}} = I_1 + I_2 \qquad (36)$$

Here β stands for a certain numerical coefficient.

In the integral I_1 the variable t is greater than unity. Because of the rapid convergence of the exponential expressions, the first integral in the denominator is extremely small as compared with the second member and may be omitted. Therefore

$$I_1 \cong \int\limits_{l/\delta'}^{1} \frac{dt}{\frac{c^{(l)}}{\delta'}} \cong -\frac{(l - \delta')}{c^{(l)}} \cong -\frac{l}{c^{(l)}}, \qquad (37)$$

inasmuch as $l \gg \delta'$.

The second integral I_2 is calculated in the appendix. The result is

$$I_2 = \frac{(n_2 - n_1) D_1}{n_2 j} \lg \frac{c^{(0)}}{c^{(l)}}, \qquad (38)$$

and consequently, due to equations (38), (37) and (36),

$$I = I_1 + I_2 = -\frac{l}{c^{(l)}} + \frac{(n_2 - n_1) D_1 e}{n_2 j} \lg \frac{c^{(0)}}{c^{(l)}} \qquad (39)$$

Inserting this value of I into equation (36), we get:

$$V = \frac{kT (D_1 - D_2)}{e (n_1 D_1 - n_2 D_2)} \lg \frac{c^{(0)}}{c^{(l)}} - \frac{kT}{e n_1} \lg \frac{c^{(0)}}{c^{(l)}} - \frac{kT}{e} \frac{(n_2 - n_1) D_1}{n_2 (n_1 D_1 - n_2 D_2)} \lg \frac{c^{(0)}}{c^{(l)}} +$$

$$+ \frac{kTj (l - \delta')}{e^2 (n_1 D_1 - n_2 D_2) c^{(l)}} = \frac{kT}{e} \left(\frac{1}{n_2} - \frac{1}{n_1}\right) \lg \frac{c^{(0)}}{c^{(l)}} + \frac{kTj (l - \delta')}{e^2 (n_1 D_1 - n_2 D_2) c^{(l)}} . \qquad (40)$$

The second member of equation (40) has a simple physical meaning; it is nothing else but the usual ohmic potential drop in a solution, while the first member represents the potential drop connected with concentration polarization and the ohmic drop in the solution of variable concentration. From the form of the second member containing the usual ohmic drop in a solution with a constant concentration $c^{(l)}$ over the length $(l - \delta')$, we see that a noticeable change of concentration takes place only over the region of the solution between the electrode itself $(z = 0)$ and the plane $z \sim \delta'$.

Thus, we come to the following fundamental result: all the solution may be split into two regions. In the first region, in the interval between $z \sim \delta'$ and $z \sim l$, the concentration of the solution remains constant and equal to $c^{(l)}$. In the second region, between the electrode and $z = \delta'$, the concentration varies from the value of c_0 on the electrode to the value of $c^{(l)}$ in the solution.

It is necessary to emphasize here that such a picture of the distribution of concentration in the solution is by no means obvious and we did not postulate it as was done in Nernst's theory, but came to it as a result of precise analysis. At not very low concentrations of the solution and at usual distances between the electrodes l, the ohmic resistance of the solution is extremely small and the second member in formula (40) may be omitted. Then we get, from equation (40):

$$V=\frac{kT}{e}\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\lg\frac{c_0}{c^{(l)}},$$

or, substituting the value of $c^{(0)}$ from equation (29′) we get:

$$V=\frac{kT}{e}\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\lg\left(1+\frac{n_2 j\delta'}{(n_2-n_1)D_1ec^{(l)}}\int\limits_{l/\delta'}^{0}e^{-(t^3+\beta t^4+\dots)}dt\right).$$

Since the distance between the electrodes l is great as compared with δ', we may approximately substitute infinity for the lower limit of the integral. Then we get:

$$\int\limits_{\infty}^{0}e^{-(t^3+\beta t^4+\dots)}dt\cong-\int\limits_{0}^{\infty}e^{-t^3}dt=-\Gamma\left(\frac{1}{3}\right)=-\Gamma\left(\frac{4}{3}\right)=-0.89,$$

where Γ is the gamma function.

Here we have taken the advantage of the fact that at great values of t, when the higher powers in the polynome in the exponent prevail, the integrated expression vanishes, therefore the integral converges very rapidly. Thus, finally

$$V=\frac{kT}{e}\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\lg\left(1-\frac{n_2 j\cdot 0.89\,\delta'}{(n_2-n_1)\,D_1c^{(l)}\,e}\right)=$$
$$=\frac{kT}{e}\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\lg\left(1-\frac{j}{j_{\text{lim}}}\right), \tag{41}$$

where j_{lim} denotes the quantity:

$$j_{\text{lim}}=\frac{(n_2-n_1)\,D_1c^{(l)}\,e}{0.89\cdot n_2\delta'}. \tag{42}$$

Formula (41) shows that to the revolving electrode there may flow a current, the intensity of which does not exceed the value of j_{lim}, called, therefore, the limiting current, or the current of saturation. In the case of passage of a current exceeding the limiting current, there would arise a deviation of the solution from electroneutrality, accompanied by the appearance of a very high stopping resistance, as a result of which the density of the current would be diminished down to the values of j_{lim}. Rewriting formula (41) in the form

$$j=j_{\text{lim}}\left(1-e^{\frac{eV}{kT\left(\frac{1}{n_2}-\frac{1}{n_1}\right)}}\right), \tag{43}$$

we see (inasmuch as $n_2<0$) that at an electromotive force significant to any extent and exceeding $\frac{kT}{e}$, there passes through the solution a limiting current, which is independent of the electric field strength.

Since the limiting current does not depend on the field strength, there is no need, in order to find its value alone, to perform all the preceding calculations. In fact, since the limiting current is a pure diffusion process, we can, in order to find it, make use of the following arguments.

Equation (43) connects the current j flowing in the solution with the difference of concentrations at the electrodes and the parameters characterizing the motion of the fluid and of the ions. It is clear that the highest possible value of the current j_{lim} would correspond to the highest value of the difference of concentrations, *i. e.* to the value of $c^{(0)}$ equal to zero.

Thus, equation (29′) gives directly

$$j_{\text{lim}}=\frac{c^{(l)}(n_2-n_1)\,D_1e}{n_2\int\limits_0^l e^{\frac{1}{D}\int\limits_0^z v_z dz}dz}=\frac{c^{(l)}(n_2-n_1)\,D_1e}{n_2}\cdot\frac{1}{\delta'\int\limits_0^{l/\delta'}e^{-(t^3+\beta t^4+\dots)}dt}=$$
$$=\frac{c^{(l)}(n_2-n_1)D_1e}{0.89\cdot n_2\delta'}. \tag{42′}$$

The full current flowing through the solution is proportional to the area of the electrode and equals

$$I=2\pi r^2 j_{\text{lim}},$$

where factor 2 is introduced in order to take both sides of the disc into account.

It follows from formula (42′) that the value of the limiting current $j_{\lim}$ turns out to correspond to such a picture of the distribution of ions, in which there would take place a linear drop of concentration from the value corresponding to the average concentration in the bulk of the solution down to zero close to the revolving electrode, this drop occurring within the layer of the thickness of

$$\delta'' = 0.89\,\delta' = 0.89 \times 1.82 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}} = 1.62 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}}. \qquad (44)$$

The existence of the quantity δ'', called the thickness of the diffusion layer, was postulated by Nernst[7].

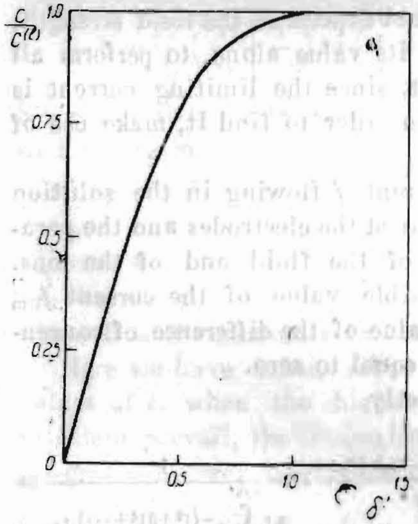

Fig. 2. The depedence of the concentration of solution on the distance from the disc.

We see that the exact theory is in accord with Nernst's qualitative theory and leads to a quite definite dependence between the thickness of the diffusion layer, on the one hand, and the properties of ions of the fluid and the character of its motion, on the other hand. At the same time, the essential difference between the present theory and Nernst's theory lies in the fact that in the former, no incorrect assumptions are made concerning the immobility of the fluid within the diffusion layer. It only turns out that also in the case of a fluid moving with respect to the electrode, there is a region of a very abrupt, almost linear drop of concentration.

It is necessary to emphasize that with an exactness up to a coefficient of the order of unity, between the thickness of the diffusion layer δ'' and the thickness of the boundary layer of fluid δ, dragged by the rotating disc, there exists the relation

$$\delta'' \cong \left(\frac{D}{\nu}\right)^{1/3} \delta. \qquad (45)$$

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[7] E u c k e n, Z. physik. Chem., **59**, 72 (1907); B a a r s, Handb. d. Phys., **13**, 559 (1928).

As will be shown in the following section, this relation has a general character.

For the particular case of a univalent electrolyte and cathode deposition ($n_1 = 1$, $n_2 = -1$) we have the following expression for the volt-ampere characteristic of the discharge:

$$j = j_{\lim}\left(1 - e^{-\frac{eE}{2kT}}\right)$$

where

$$j_{\lim} = \frac{ND_1}{\frac{0.89}{2}\delta'} = \frac{ND_1 e}{0.81 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}}}. \qquad (46)$$

If, instead of the angular velocity ω, we should introduce the number of revolutions $Z = \frac{\omega}{2\pi}$, then

$$j_{\lim} = \frac{ND_1 e}{2.2 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{Z}}}.$$

With respect to the order of magnitude $D \sim 10^{-5}$, $\nu = 10^{-2}$ and

$$\delta'' \cong \frac{0.022}{\sqrt{Z}}. \qquad (45')$$

A more detailed comparison with experimental data on hand shall be given in the following section.

4. The general theory of the boundary layer

A laminar boundary layer. In the preceding section devoted to the theory of a rotating electrode we have developed an exact theory of the limiting current passing through the solution. It turned out there that although, strictly speaking, the decrease of concentration takes place throughout the solution, there exists a relatively thin layer of fluid in which a very rapid drop of concentration takes place. Further, beyond the limits of this layer, concentration may be considered as almost constant. This circumstance is closely bound with the character of the flow of the fluid dragged by a rotating electrode. Indeed, the Kárman theory given at the beginning of the chapter shows that the fluid is dragged by the disc only within a very thin layer, beyond the limits of which there is but a steady flow of the fluid towards the electrode.

It was found there [equation (45)] that between the thickness of the diffusion boundary layer and the thickness of the boundary layer of fluid there exists a simple connection.

This circumstance is not a peculiar characteristic of the rotating electrode, but apparently is of an universal character. It turns out that in case of any geometrical conditions of flow of fluid with sufficiently high Reynolds numbers, there is close to the surface of the electrode a thin diffusion layer within which the main change of concentration takes place.

For the sake of convenience we shall consider the electrode at rest and the solution as flowing past the electrode with a given velocity which equals at a great distance from the electrode U_0.

The flow of the fluid is described by Navier-Stokes equation which for a stationary flow of the fluid have the form

$$(\mathbf{v}\,\mathrm{grad})\,\mathbf{v} = -\mathrm{grad}\,\frac{p}{\rho} + \nu\Delta\,\mathbf{v}, \qquad (1)$$

$$\mathrm{div}\,\mathbf{v} = 0, \qquad (2)$$

where $\mathbf{v}$ is the vector of velocity of the fluid, p—the pressure, ρ—the density and ν—the kinematic viscosity of the fluid. As is known, the character of flow of the fluid is determined by the value of the only non-dimensional parameter that may be obtained by means of the basic quantities entering the Navier-Stokes equations, *i. e.* of the Reynolds number $\mathrm{Re} = \frac{Ul}{\nu}$, where v is a characteristic velocity of the flow, and l is a characteristic length (in our case, the dimensions of the body past which the fluid flows). The Reynolds number, as far as the order of magnitude is concerned, represents the ratio of the convective term $(\mathbf{v}\,\mathrm{grad})\,\mathbf{v}$ in the left-hand side of equation (1) to the viscous term $\nu\Delta\mathbf{v}$ in the right-hand side of equation (1). Indeed

$$\mathrm{Re} \sim \frac{|(\mathbf{v}\,\mathrm{grad})\,\mathbf{v}|}{|\nu\Delta\mathbf{v}|} \sim \frac{U\cdot\frac{1}{l}\,U}{\nu\,\frac{U}{l^2}} \sim \frac{Ul}{\nu}.$$

If the Reynolds number is large (but not large enough to set in the turbulent flow), then the viscous term is small as compared with the convective member and may be omitted. Here the Navier-Stokes equations reduce to the equations of motion of a perfect fluid, whence it may be seen that the influence of viscosity does not tell at all on the flow of the fluid in volume. Thus, next to the surface of a solid body, there moves with great velocity a flow of a quasi-perfect fluid, that may slip along its surface without any loss of velocity caused by friction. On the other hand, however, the experiment shows that on the surface of a solid body there is no slip between the solid body and the fluid, so that the velocity of the latter drops to zero on the boundary with the solid body. Therefore, in the immediate vicinity of the surface of the solid body, the velocity of the fluid must change from the comparatively high value of the velocity of the stream flowing past the surface down to zero at the solid wall. In this region called, as is known, Prandtl's boundary layer, because of the very high gradient of velocity in the direction normal to the wall, it is no longer possible to neglect the influence of viscosity, and the term $\nu\Delta\mathbf{v}$ turns out here to be of the same order of magnitude as the convective term. Thus, the entire stream of the fluid with large Reynolds numbers may be divided into two regions: the region of potential flow, in which viscosity does not play any essential part, and the region of Prandtl's boundary layer, where, on the contrary, the influence of viscosity is very essential and the viscous terms in Navier-Stokes equation may not be dropped. However, due to the circumstance that the thickness of the boundary layer δ is very small, the Navier-Stokes equations here may be considerably simplified[4]. It is clear, indeed, that the variation of velocity along the wall within the boundary layer is very small as compared with its variation along the normal.

If the X axis is directed along the surface of the body, which for the sake of simplicity we shall consider as having a very large radius of curvature, and the Y axis is directed normal to the wall, then the equations of motion of the fluid in the boundary layer (Prandtl's equations) would have the form:

$$U\frac{\partial U}{\partial x} + V\frac{\partial U}{\partial y} = \nu\frac{\partial^2 U}{\partial y^2} - \frac{1}{\rho}\frac{\partial p}{\partial x}, \quad \frac{\partial p}{\partial y} = 0, \quad \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} = 0,$$

where U and V denote the tangential and the normal components of velocity.

On the surface of the body $U = V = 0$, while far away from it, on the limits of the boundary layer, U turns into the given velocity of the outer stream flowing past the body, U_0. The thickness of the boundary layer δ is determined as such a distance from the wall, in which the tangential component of velocity U becomes with a sufficient degree of accuracy equal to U_0. A simple analysis shows that always by the order of magnitude the thickness of the boundary layer is equal to

$$\delta \sim \sqrt{\frac{\nu x}{U_0}} \tag{3}$$

where x denotes the distance from a front stagnation point.

The second Prandtl's equation shows that the pressure in a boundary layer does not change in the direction normal to the wall. Therefore, the term $\frac{\partial p}{\partial x}$ in the first equation represents the gradient of pressure along the wall in an exterior potential stream.

In a particular case, when in the exterior stream there is no gradient of pressure $\frac{\partial p}{\partial x}$, and Prandtl's equations are still more simplified, acquiring the form:

$$U\frac{\partial U}{\partial x} + V\frac{\partial U}{\partial y} = \nu\frac{\partial^2 U}{\partial y^2}, \tag{4}$$

$$\frac{\partial p}{\partial y} = 0, \tag{5}$$

$$\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} = 0. \tag{6}$$

Solutions of Prandtl's equation (4)—(6) for the component of the velocity with small (as compared with δ) values of y, may be represented in the form

$$U \sim \frac{U_0}{\delta} y + \dots; \quad V \sim \frac{\nu y^2}{\delta^3} + \dots \tag{7}$$

Let us turn now to the equations of convective diffusion of ions in the solution. According to preceding statements, they shall have the form

$$U\frac{\partial c}{\partial x} + V\frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right), \tag{8}$$

D being the effective coefficient of diffusion. The form of equation (8) is very similar to the form of Navier-Stokes equations, when in the latter the gradient of pressure is absent. Here, coefficient of diffusion D plays the rôle of the kinematic viscosity ν. Therefore, the character of convective diffusion shall be determined by the value of the only non-dimensional quantity entering equation (8) $\frac{Ul}{D}$, analogous to the Reynolds number. The quantity $\frac{Ul}{D}$ is called the Pekle number and has a simple meaning—it represents, in the order of magnitude, the ratio of the convective term in equation (8) to the diffusion term:

$$\mathrm{Pe} \sim \frac{U\frac{\partial c}{\partial x}}{D\frac{\partial^2 c}{\partial y^2}} \sim \frac{Ul}{D}.$$

In the case of great values of the Pekle number, we may apply to the equation of convective diffusion considerations wholly similar to those brought forward above, concerning the boundary layer in the case of an obstacle with a large Reynolds number Re. In fact, when $\mathrm{Pe} \gg 1$ at great distances from the surface of the obstacle, the diffusion term in equation (8) may be neglected, so that in this region the value of concentration shall be determined exclusively by the convection of the fluid. In particular, in the case of the usual stirring of the solution, the concentration at a distance from the electrode shall be constant.

On the other hand, on the surface of the electrode, concentration c is also constant, but it is different from the volume concentration (in particular, for the case of the limiting current $c = 0$ on the electrode). Therefore, the main change of concentration must take place within a thin layer of the solution, adjacent to the surface of the electrode. In this thin layer of fluid the diffusion term in equation (8), due to large values of concentration gradient occurring here, turns out to be of the same order of magnitude as the convective term. Thus, we see that in the case of high Pekle number Pe, there must exist a region of abrupt change of concentration of the solution—a region similar to that of the abrupt change of the velocity of the fluid—the Prandtl boundary layer. We shall call it following Nernst the region of the boundary diffusion layer.

These considerations refer equally to the diffusion of neutral particles and to the diffusion of ions in those cases, enumerated in section 2, when the electric field may be separated from the general equations of transfer.

Our problem at present is to obtain the equations of convective diffusion in a boundary diffusion layer and to determine the thickness of the latter δ'. The solution of the first problem does not offer any difficulties; it is clear that in a diffusion layer the change of concentration along the direction perpendicular to the wall shall be great in comparison with the change of concentration along the wall, so that

$$\frac{\partial^2 c}{\partial x^2} \sim \frac{c}{x^2}; \quad \frac{\partial^2 c}{\partial y^2} \sim \frac{c}{\delta'^2}; \quad \frac{\partial^2 c}{\partial y^2} \gg \frac{\partial^2 c}{\partial x^2}.$$

Therefore, the equation of convective diffusion in the boundary diffusion layer has the form

$$U \frac{\partial c}{\partial x} + V \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}. \tag{9}$$

In finding the thickness of the diffusion layer, it is necessary to distinguish between two cases, different in principle: the case when the non-dimensional ratio $\frac{\nu}{D}$, called the Prandtl's diffusion number Pr, is great as compared with unity, and the case when, on the contrary, it is a number of the order of unity.

Strictly speaking, the latter case is never realized in practice in the phenomenon of diffusion. However, it is widely known in phenomena of heat conduction, where the coefficient of heat conduction is usually of the same order of magnitude as the viscosity of the fluid.

Besides, as shall be seen below, in order that there should be between the two cases a difference essential in practice, it is necessary that not only the Prandtl number itself, but $(\mathrm{Pr})^{1/3}$ also were large as compared with unity, *i. e.* that Pr were at least of the order of a thousand.

We shall consider here only the case of very large Prandtl numbers in which we are directly interested, and which is always realized in electrochemistry.

Inasmuch as the thickness of the boundary layer $\delta \sim \sqrt{\nu}$, and for the process of diffusion the rôle of kinematic viscosity is played by the coefficient of diffusion D, it is clear that the thickness of the boundary diffusion layer δ' is smaller than δ, since $D \ll \nu$. This may also be seen directly from equation (8).

This circumstance allows us, in investigating the diffusion layer, to take advantage of the expansion for the components of velocity (7), in which only the first term is retained, since in the diffusion

layer certainly $y \ll \delta$. In equation (9) the member $V \frac{\partial c}{\partial y}$ must be of the same order of magnitude as the member $D \frac{\partial^2 c}{\partial y^2}$.

On the other hand, according to the order of magnitude, with $y \sim \delta'$ we have:

$$V \frac{\partial c}{\partial y} \sim V_{y=\delta'} \left(\frac{\partial c}{\partial y}\right)_{y=\delta'} \sim \frac{Vc}{\delta'} \sim \frac{\nu c \delta'}{\delta^3},$$

while

$$D \left(\frac{\partial^2 c}{\partial y^2}\right)_{y=\delta'} \sim \frac{Dc}{\delta'^2}.$$

From both the expressions obtained, we get

$$\delta' \sim \left(\frac{D}{\nu}\right)^{1/3} \delta \sim \frac{\delta}{(\mathrm{Pr})^{1/3}}. \tag{10}$$

We can see from the relationship (10) that the thickness of the diffusion boundary layer is connected with the thickness of Prandtl's boundary layer by an universal relations, independent of the Reynolds number.

Due to the smallness of the coefficient of diffusion, δ' is always small as compared with δ, the use of formula (10) being justified, inasmuch as $(\mathrm{Pr})^{1/3} \gg 1$.

It is easy to see here that the first term in the left-hand side of equation (9) is of the same order of magnitude as the second one, *i. e.*

$$U \frac{\partial c}{\partial x} \sim V \frac{\partial c}{\partial y}.$$

Indeed

$$U \frac{\partial c}{\partial x} \sim \frac{U_0 y}{\delta} \frac{c}{x} \sim \frac{U_0 c \nu \delta'}{U_0 \delta^3} \sim \frac{Dc}{\delta'^2} \sim D \frac{\partial^2 c}{\partial y^2} \sim V \frac{\partial c}{\partial y}$$

on the basis of equations (3) and (7).

Comparison of equation (9) with equation (4) in Eucken's work[3] shows that he made an error neglecting a term of the same order of magnitude as that one retained in the equation.

The case of Prandtl's numbers Pr of the order of unity, considered in the theory of heat conduction, leads to a different relation between δ' and δ. Indeed in this case[4]

$$\delta' \sim \sqrt{\frac{\varkappa}{\nu}}\, \delta \sim \frac{\delta}{\mathrm{Pr}^{1/2}}$$

where $\varkappa$ is the coefficient of heat conduction.

Equations (10) and (3) show by the way that the thickness of the diffusion layer in the case of a solution flowing past the electrode depends, generally speaking, on the coordinate x on the electrode surface. Namely, δ increases as the square root of the distance from the front stagnation point of the body. Therefore, for instance, the thickness of electrolytical deposits must vary according to this law, as we move away from the end of the electrode — a statement that has a considerable technical interest for certain cases of deposits on precise instruments.

It is clear, of course, that the formulae for thicknesses δ' and δ may be made use of only in cases of sufficiently large values of x, since in the opposite case the requirement $\mathrm{Re} \gg 1$, or $\mathrm{Pe} \gg 1$, correspondingly, shall not be fulfilled.

Knowledge of the expression for the thickness of the diffusion layer enables to write down at once the expression for the order of magnitude of the limiting current that may flow to the electrode. It is the limiting current, exactly, that corresponds to the greatest drop of concentration between the solution and the electrode, *i. e.* it evidently takes place when the concentration of ions liberating at the electrode vanishes. Here, as to the order of magnitude, the limiting current density j_{lim} is equal to

$$j_{\mathrm{lim}} = D\frac{c^{(l)} - c^0}{\delta'} = \frac{Dc^{(l)}\,\mathrm{Pr}^{1/3}}{\delta} \sim \frac{Dc^{(l)}\,\mathrm{Pr}^{1/3}}{\sqrt{\frac{\nu x}{U_0}}}. \qquad (11)$$

The limiting current density depends, generally speaking, on the chosen point on the electrode surface, since the thickness itself of the diffusion layer changes from point to point.

The total limiting current flowing down the electrode is

$$J_{\mathrm{lim}} = \int j_{\mathrm{lim}}\, dS$$

where the integration is performed over the surface of the electrode. If we should consider that the curvature of the latter is sufficiently small, *i. e.* consider that it has the shape of a plate l in length and h in width, then evidently

$$J_{\mathrm{lim}} \sim Dec^{(l)}\left(\frac{\nu}{D}\right)^{1/3}\sqrt{\frac{U_0 l}{\nu}}\,h. \qquad (12)$$

Exact calculations of the limiting current may be performed only in simple geometrical cases. Particularly, in the case of the electrode in the form of a plate of dimensions sufficiently great as to allow to ignore the influence of the ends, an exact solution leads to the expression for the total limiting current intensity [4]:

$$J_{\mathrm{lim}} = \frac{0.67ec^{(l)}hD^{2/3}U_0^{1/2}l^{1/2}}{\nu^{1/6}} \qquad (12')$$

coinciding with equation (12) in the order of magnitude.

In other cases, for instance in the case of a rotating cylinder or disc, or in a case when the solution flows past such electrodes, or is drawn past them by means of a stirring apparatus, the formula (12) may be made use of as far as the order of magnitude is concerned. This circumstance is connected with the fact that, as calculations show, the thickness of the boundary layer δ is always, by the order of magnitude, connected with the rate of flow by the relation (3), although, of course, the numerical coefficient shall be different in different geometrical cases.

5. The theory of the diffusion boundary layer in the case of a turbulent flow

In the preceding section we have exposed the theory of the diffusion boundary layer for the case of a laminar flow of a fluid past the electrode. We have not considered there the question as to whether the flow of the fluid outside the boundary layer was laminar or turbulent, inasmuch as only the processes taking place within the boundary layer play a significant rôle for the passage of the current.

However, at very large Reynolds numbers ($\mathrm{Re} \sim 10^5$ for a quiet flow of the fluid and at smaller numbers for a perturbed one), turbulence of the stream of fluid takes place not only in the volume, but inside the boundary layer as well. Here the picture of the current passing through the solution is modified essentially, and the former conclusions lose their force. We shall consider further on the question of the passage of the current in the presence of a turbulent boundary layer [8].

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[8] This section is intentionally written briefly, since the hydrodynamic scope of the question is of less interest for physical chemists. For acquaintance with the theory of turbulence we shall refer the reader to a monography by Goldstein in «Modern Hydrodynamics», Vol. I and II, Oxford, 1938.

Let us write out, first of all, equations of motion of the fluid in a turbulent boundary layer. If we suppose, for the sake of simplicity, that the flow takes place along a wall of small curvature in the direction of x axis, and if we shall represent the tangential and the normal component of velocity as

$$u = \bar{u} + u', \qquad v = \bar{v} + v',$$

where $\bar{u}$ and $\bar{v}$ are average with respect to time values, and u', v' are turbulent pulsations, then the corresponding equations are

$$\bar{u}\,\frac{\partial \bar{u}}{\partial x} + \bar{v}\,\frac{\partial \bar{v}}{\partial y} = \frac{\partial}{\partial y}\left(\nu\frac{\partial \bar{u}}{\partial y} - \overline{u'v'}\right): \qquad (1)$$

The term $\nu\frac{\partial \bar{u}}{\partial y}$ represents the flow of the momentum in the direction perpendicular to the wall due to viscosity, and the term $\overline{u'v'}$ represents the flow of the momentum due to turbulent pulsations (divided by the density of the fluid). At not too small distances from the wall, the latter turns out to be many times greater than the first, so that we may neglect the influence of viscosity. Only at very small distances δ from the wall, due to the great value of the gradient $\frac{\partial \bar{u}}{\partial y}$, both of the terms become equal to each other, after which the term $\nu\frac{\partial \bar{u}}{\partial y}$ begins to prevail over the term $\overline{u'v'}$. In other words, at values of $y < \delta$ the transfer of the momentum in the fluid is conditioned in the main by viscosity.

As is known, this region bears the name of the viscous sublayer. We wish to emphasize that, in spite of the general opinion, the turbulent pulsations of velocities inside the viscous sublayer do not disappear by any means, and the motion does not become laminar. On the contrary, they are of the same order of magnitude as the average velocities. It is only the flow of the momentum transferred by the turbulent pulsations that is small.

Let us turn now to equations of transfer in a turbulent boundary layer.

The equations of transfer will have the former form (8) of section 4, however, all of the quantities shall now change statistically in time. Therefore, in all the final expressions we must average with respect to the time. The effective concentration c may be represented in the form

$$c = \bar{c} + c',$$

where $\bar{c}$ is the average (with respect to time) concentration, and c' is its pulsation part.

Inserting this value of c and also the expressions for u and v given above into equation (8) of section 4, and then averaging with respect to time, we may write the equation of transfer in the form

$$\bar{u}\,\frac{\partial \bar{c}}{\partial x} + \bar{v}\,\frac{\partial \bar{c}}{\partial y} = \frac{\partial}{\partial y}\left(D\frac{\partial \bar{c}}{\partial y} - \overline{v'c'}\right). \qquad (2)$$

We may affirm, first of all, that inasmuch as in the case of a turbulent regime of the flow the migration of ions is separated and the passage of the current through the solution is described by an equation of a purely diffusion type, there remains valid the former conclusion as to the existence of a limiting current that may flow through the solution and corresponds to the boundary condition $c = 0$ on the surface of the electrode.

Due to very energetic stirring of the solution when there is a turbulent flow, the values themselves of the limiting currents are, generally speaking, considerably greater than in the case of a laminar flow.

Considering the equations of the transfer we see further that, away from a solid wall, the flow of the substance transferred by turbulent pulsations of the velocity $\overline{v'c'}$ would be much greater than the flow of a substance transferred by molecular diffusion $D\frac{\partial \bar{c}}{\partial y}$, so that here the latter may be neglected altogether. At very small distances from the wall, when $y < \delta'$, the transfer of the substance would, on the opposite, be realized in the main by molecular diffusion, inasmuch as here the gradient $\frac{\partial \bar{c}}{\partial y}$ would be very great.

We shall name this region the diffusion sublayer.

We see further that away from the wall, when in equations (1) and (2) we may neglect the viscous and the diffusion terms respectively, the equations of motion and of transfer become similar.

Therefore, there is here a full analogy between the transfer of the momentum and the transfer of the matter in a flowing fluid.

This analogy would remain in force in the case of small values of y as well, if the quantities ν and D would have close numerical values, *i. e.* the Prandtl number would be of the order of unity (which is the case usually in heat conduction). Inasmuch, however, as the coefficient of diffusion is always much less than the viscosity, it is clear that the thickness of the diffusion sublayer δ' is less than the thickness of the viscous sublayer δ. Indeed, in the case of transfer of matter the diffusion and the turbulent flows become equal to each other at relatively high values of the gradient $\frac{\partial \bar{c}}{\partial y}$, *i. e.* closer to the wall than takes place usually for similar quantities in the course of transfer of momentum.

Therefore, the entire turbulent boundary layer may be divided into three regions:

1) the region of the nucleus of the turbulent boundary layer $y > \delta$, in which both the transfer of the momentum and the transfer of matter are realized by turbulent pulsations;

2) the region $\delta' \leqslant y \leqslant \delta$, in which the transfer of the momentum is realized by means of a viscous mechanism, while the matter is transferred by turbulent pulsations, and finally

3) the region $y \leqslant \delta'$, in which the transfer of the momentum is as formerly realized by a viscous mechanism, and the matter is transferred by molecular diffusion (diffusion sublayer).

The viscous sublayer includes, evidently, both the latter regions. The exact relationship between δ' and δ shall be given below.

From all that has been said above it is clear that between the phenomena we are interested in of the transfer of matter and the transfer of momentum in a turbulent flow of fluid, revealing itself in the form of the friction stresses acting from the fluid on the solid wall, there is a close connection and even a certain analogy, although not a full one.

This circumstance, as well as dimensionality considerations may be made use of in order to write the general expression for the flow of matter thus found across a turbulent boundary layer. The density of the limiting current shall be evidently equal to q is obtained from the condition $c=0$ on the surface of the body and $c=c^{(l)}$ beyond the limits of the boundary layer.

As is shown in hydrodynamics, the shear stresses acting per cm.² of the solid wall may be always represented in the form of

$$\sigma = c_f(\mathrm{Re})\,\frac{\rho u_l}{2},$$

where ρ is the density of the fluid, u_l is the average velocity of its flow, and $c_f(\mathrm{Re})$ — a certain function of the Reynolds number, bearing the name of local coefficient of resistance.

The form of c_f depends, of course, on the form of the surface flown past and on the distance from the front stagnation point. Analogous relations hold for the total friction forces.

As far as the flow of matter q transferred by the turbulent flow of the fluid to the cm.² of the surface is concerned, it is clear that it cannot depend explicitly on the viscosity of the fluid ν and on the coefficient of diffusion D. Therefore, according to dimensionality arguments, it is clear that q must have the form

$$q = f(\mathrm{Re}, \mathrm{Pr})\, u_l c_l,$$

inasmuch as there are no other dimensional values, except u_l and c_l, by means of which it is possible to compose the quantity having the dimensionality of q.

For the particular case of the smooth plate, we have obtained an exact formula for $f(\mathrm{Re}, \mathrm{Pr})$.

Inasmuch as into these formulae enter unknown constants characterizing the turbulent transfer of matter in a stream, they cannot be made use of for direct finding of q. On the contrary, however, by measuring q it is possible to find the values of these important constants.

For finding the transfer of matter it is necessary to know the law of the distribution of velocities, and concentrations in the different regions of the stream considered above.

As is known, in the region of the turbulent boundary layer, there takes place a logarithmic law of distribution for the average rate of flow $\bar{u}_1$:

$$\bar{u}_1 = \gamma V_0 \lg \frac{V_0 y}{\nu} + u_\delta = \gamma V_0 \lg \frac{y}{\delta} + u_\delta,$$

where u_δ is the velocity on the boundary of a viscous sublayer $\sigma \sim \frac{\nu}{V_0}$, V_0 is the characteristic velocity of the stream equal to $\sqrt{\sigma/\rho}$ and γ is some constant.

Within the viscous sublayer the momentum is transferred by a viscous flow. The velocities of a viscous flow u_{visc} and v_{visc} are, as previously, expressed by formulae (7) of section 4, where, however, δ denotes now the thickness of the viscous sublayer, U_0 is the velocity on its boundary, *i. e.* u_δ, and due to smallness of δ the development may be stopped at the first term.

As concerns the average velocities of the turbulent flow within a viscous sublayer, as L. Landau has pointed out to the author, they may be obtained from the following considerations.

Since on the wall all the velocities vanish, close to it for the average velocities of the turbulent motion it is possible to write (with the exactness up to small quantities of a higher order):

$$\bar{u}_2 = ay, \tag{3}$$

$$\bar{v}_2 = by^2. \tag{3'}$$

In the development $\bar{v}_2$ the terms of the first order are absent, inasmuch as, as is seen from the equation of continuity (see also section 4) the order of magnitude of the normal component of the velocity exceeds the order of magnitude of the tangential component by an unity.

Inasmuch as when $y \sim \delta$ we have definitely $u_{\text{visc}} \sim \bar{u}_2$ and $v_{\text{visc}} \sim \sim \bar{v}_2$, the constants a and b must be of the order:

$$a \sim \frac{u_\delta}{\delta}, \quad b \sim \frac{\nu}{\delta^3},$$

so that in the entire second region the velocities of the viscous and the turbulent motions are exactly of the same order of magnitude.

It is easy to see, however, that the transfer of momentum in a viscous sublayer is realized in the main by the viscous motion. Indeed, the flow of momentum transferred by the turbulent pulsations would be equal to (see Goldstein's monography, referred to above)

$$\sigma_{\text{turb}} = -\rho\overline{u'v'} = -\rho\lambda\bar{v}\frac{d\bar{u}}{dy} = -\frac{\alpha\rho\nu u_\delta}{\delta^4}y^3$$

and small as compared with the flow of the momentum transferred by viscous motion

$$\sigma_{\text{visc}} = \rho\nu\frac{\partial u_{\text{visc}}}{\partial y} = \frac{\rho\nu u_\delta}{\delta}$$

at $y < \delta$, so that here

$$\sigma \sim \sigma_{\text{visc}} = \frac{\rho\nu u_\delta}{\delta}.$$

The distribution of velocities being known, we may find the transferred flow of matter.

According to what has been said above, in the first and second regions the flow of matter is transferred by a turbulent motion of the fluid. As follows from the general theory of transfer in the course of turbulent motion, for the flow of matter we may write (similarly to the way it is done in the dynamic theory of gases)[9]

$$q = -\overline{v'c'} = -\lambda\bar{v}\frac{d\bar{c}}{dy}, \tag{4}$$

where the quantity λ represents the mean free path of turbulent pulsations (mixture length).

Close to the wall, throughout the boundary layer, λ may be developed into series of power of the distance to the wall, and we may limit ourselves to the first term, having written

$$\lambda = \alpha y.$$

As far as v is concerned, it has a different value in the first and second regions. Precisely, in the first region we may, according to Kárman, write

$$\sqrt{\overline{u^2}} = \sqrt{\overline{v^2}} \cong v = l\frac{d\bar{u}}{dy} = \alpha\gamma V_0.$$

Substituting this value of $\bar{v}$ and λ into (4) and integrating, we get

$$\bar{c}_1 = \frac{\beta Q}{V_0}\lg\frac{y}{\delta} + c_\delta, \tag{5}$$

where c_δ is the value of c at $y = \delta$ and $\beta = \frac{1}{\alpha\gamma}$. In the second region $\bar{v}_2$ is expressed by formula (3'). Therefore here

$$q = -\frac{\alpha\nu}{\delta^3}y^3\frac{dc}{dy}.$$

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[9] Kárman, Proc. of the 4th Int. Congr. for Appl. Mech., Cambridge, p. 77, 1934.

For the average concentration we get

$$\bar{c}_2 = \frac{Q\delta^3}{2\nu\alpha}\left(\frac{1}{y^2} - \frac{1}{\delta'^2}\right) + c_{\delta'}$$

where $c_{\delta'}$ is the value of c at $y = \delta'$.

Finally, in the third region, when $y < \delta'$ the transfer of matter is realized by molecular diffusion and for q we get

$$q = -D\,\frac{dc}{dy}$$

and

$$c_3 = -\frac{q}{D}\,y \qquad (y < \delta').$$

When $y = \delta'$ the flows of matter transferred by turbulent pulsations and by molecular diffusion become of the same order of magnitude. Therefore, for δ' we obtain:

$$\delta' \sim \left(\frac{D}{\nu}\right)^{1/3}\delta. \qquad (6)$$

The relationship written down here is similar to the one written down by us for the case of a laminar boundary layer.

From equations (2) and (5) we get, evidently,

$$\frac{q}{(\bar{c}_1 - c_\delta)} = \frac{\alpha^2\gamma^2 V_0^2}{(\bar{u}_1 - u_\delta)} = \frac{\alpha^2\gamma^2\sigma}{\rho\,(\bar{u}_1 - u_\delta)} .$$

Eliminating c_δ, we find

$$q = -\frac{V_0^2 c_1}{\frac{\rho}{\alpha^2\gamma^2}\,[\bar{u}_1 - u_\delta] - \left[\frac{\delta^3}{2\nu\alpha}\left(\frac{1}{\delta^2} - \frac{1}{\delta'^2}\right) - \frac{\delta'}{D}\right]\rho\sigma} .$$

After simple tranformations we get

$$q \cong -\frac{c_f\bar{u}_1\bar{c}_1}{2\left[A + (\mathrm{Pr}_p^{2/3} - A)\,B\sqrt{\frac{c_f}{2}}\right]} , \qquad (7)$$

where

$$c_f = \frac{\rho\,\frac{V_0^2}{2}}{\frac{\rho\bar{u}_1^2}{2}}, \quad A = \frac{1}{\alpha^2\gamma^2} \quad \text{and} \quad B = \frac{u_\delta}{V_0} = \text{const.}$$

Thus, we have established the form of the function φ (Re, Pr) for the case of a smooth plate. It really depends slightly on Re. The value of constants A and B cannot be determined from the experimental data available at present and calls for new scrupulously performed measurements of the limiting currents at high Reynolds numbers. Our formula differs considerably from a similar formula obtained by Kárman[10] for high Prandtl numbers. However, we cannot be convinced by its derivation, since in the course of this derivation the difference between δ and δ' was not taken into account, while unfounded supposition as to the existence of a wide intermediate region between the viscous sublayer and the turbulent nucleus of the stream was assumed. Besides, Kárman takes for granted, without any grounds for it, that the constants in the logarithmic laws of distribution of velocities and concentrations have the same value.

In the case of low Prandtl numbers, the formula obtained by us differs little from that one deduced by Prandtl[10]. However, the latter is not wholly correct, since Prandtl also made use of the supposition of the equality of constants in the logarithmic laws for $\bar{c}$ and $\bar{u}$.

In conclusion, we wish to emphasize that in the case of rough plates the above results lose their force. From the character of the conclusion it is clear that the critical dimensions of the roughnesses that may change noticeably the character of stirring of the fluid will be of order of δ' (but not of δ), *i. e.* very small.

Making use of the expression, obtained as a result of the best measurements, we get:

$$K \sim \left(\frac{D}{\nu}\right)^{1/3}\frac{30\nu}{V_0} = \left(\frac{D}{\nu}\right)^{1/3}\frac{30\nu}{\sqrt{c_f\,\frac{\rho\bar{u}_1^2}{2}}} .$$

It is clear, from the physical viewpoint, that the roughness of the electrode, hindering the motion of the fluid and hampering the stirring in the course of the turbulent flow, must also diminish, *ceteris paribus*, the magnitude of the limit current.

In other cases f (Re, Pr) represents a certain function of Reynolds and Prandtl's numbers, the form of which may to a certain extent be determined from considerations connected with the existence of the analogy pointed out above between the transfer of matter and of momentum.

Precisely, if the Prandtl number Pr were equal to unity, so

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[19] Prandtl, Physik. Z., 29, 487 (1928).

that this analogy would be complete, then, evidently, there would hold the relation

$$f(\mathrm{Re},\, 1) = \alpha c_f,$$

where α is a numerical factor (by no means equal to unity, generally speaking, as is usually erroneously assumed in similar calculations of the theory of heat conduction).

If, however, $\mathrm{Pr} \neq 1$ and the similarity of the transfer of matter and of the momentum is not complete, we may still write

$$f(\mathrm{Re},\, \mathrm{Pr}) = \varphi(\mathrm{Re},\, \mathrm{Pr})\, c_f(\mathrm{Re}),$$

where $\varphi(\mathrm{Re},\, \mathrm{Pr})$ is some new function of Re and Pr, concerning which we may but affirm that it depends to a relatively slight degree on the Reynolds number and, moreover, in such a way that at $\mathrm{Pr} = 1$, $\varphi(\mathrm{Re},\, 1)$ turns into a constant α. Therefore, for the density of the limiting current in the general case we may write

$$j_{\mathrm{lim}} = e\varphi(\mathrm{Re},\, \mathrm{Pr})\, c_f u_l c_l. \qquad (1')$$

Already from the latter very general expression, important electrochemical consequences may be derived. Precisely, inasmuch as the coefficient of resistance itself usually decreases slowly with the increase of Re or does not depend on Re at all, it is possible to affirm that the limiting current must be proportional to u_l^n, where the power index n is somewhat less than unity or simply equal to it. Here, inasmuch as the character itself of the dependence of c_f on Re turns out usually different in different regions of Reynolds numbers, the value of n may depend on Re.

Let us consider three cases important from a practical viewpoint: an electrode having the form of a smooth plate of large dimensions, a rotating disc and a cylinder rotating inside another coaxial cylinder at rest. The total coefficient of resistance of a plate with a degree of exactness sufficient for our purpose may be written in the form of

$$c_f \sim 0.07\, \mathrm{Re}^{-1/5},$$

so that the total limiting current may be proportional to the velocity of the flow u_l to the power $^4/_5$. The turbulization of the flow takes place when $\mathrm{Re} \sim 3 \times 10^5$ in a quiet flow, but may occur also at much smaller values of $\mathrm{Re} \sim 10^4$, if the flow running on the plate is highly perturbed.

In the case of a disc, the coefficient of resistance is expressed by an approximate formula of the type $c_f \sim \mathrm{Re}^{-1/5}$, so that the limiting current is again proportional to $u_l \sim r\omega$ to the power $^4/_5$. Turbulence sets when $\mathrm{Re} \sim 5 \times 10^5$.

Finally, for a rotating cylinder, it is possible to consider very roughly $c_f \sim \mathrm{Re}^{0.4}$ $\left[\text{where } \mathrm{Re} = \frac{\omega r}{\nu}(r_2 - r_1)\right]$, r_1 being the radius of the inner rotating cylinder and r_2—the radius of the outside resting one, so that the limiting current is proportional to the rate of rotation to the power 0.6. As is known, the motion of the fluid in this case is unstable and turbulence sets on relatively very early.

6. Discussion of the results obtained and comparison with the experiment

In order to check the theory exposed above, we may make use of a large number of papers published at different periods, in which the concentration polarization in the course of electrolysis in various conditions, or the rate of heterogeneous reactions, in particular, the rate of the dissolution of metals, were studied.

In the case of electrolysis, usually the full volt-ampere characteristic (polarization curve) of the discharge with various kinds of stirring of the solution had been obtained.

As far as the rates of heterogeneous reactions are concerned, in order to check the theory we may make use of the data relating to the cases, when the general rate of the reaction is determined by the rate of the convective diffusion of some agent, either from the solution towards the surface upon which the reaction takes place or away from it into the solution.

A great number of heterogeneous reactions is described in literature, the rate of which is determined by the supply of reactant to or away from the region where the reaction takes place, but not by the rate of the chemical reaction itself, which may be considered here arbitrarily high. The quantity of the matter that has participated in the reaction will in these cases be determined by the diffusion current of that reactant, the supply of which to the reaction region determines its full rate.

Prior to proceeding directly to compare the theory of the diffusion boundary layer with the experiment, it is necessary to discuss the possible sources of inaccuracies of the theory and the limits of its applicability. The application of the theory is limited first of all by the requirement that the Reynolds numbers of the flow of the fluid past the electrode be sufficiently large as compared with unity, so that the Prandtl theory of the boundary layer might be made use of. Practically this condition is always realized.

The dependence of the diffusion coefficients on the concentration of the solution that has not been taken into account by us is a source of a possible inaccuracy of the theory. In reality the diffusion of ions is realized with a varying diffusion coefficient, inasmuch as the concentration of the solution changes noticeably from point to point within the diffusion layer. The dependence of the diffusion coefficient on the concentration is relatively slight and cannot change the order of magnitude of the quantities obtained. It can, however, tell on the value of numerical coefficients. Also, in the theory the influence of natural convection on the transfer of ions in the solution was not taken into account. It is clear, however, that in the case of a sufficiently energetic stirring this influence would be insignificant.

The most serious shortcoming of the theory exposed above is the fact that the expressions obtained for the limiting current hold only for such a case, when there are two kinds of ions in the solutions, or when the concentration of ions liberating at the electrode is small as compared with the concentration of the other ions.

Already in the case of three kinds of ions, we have been forced to restrict ourselves to the investigation of the motion of ions in a resting diffusion layer, as was done in the old Nernst theory[11]. We may, however, assert that qualitatively the formulae for the effective thickness of the diffusion layer obtained for a binary electrolyte hold also for the case of a solution containing three or more kinds of ions.

Therefore, although in this case we have not succeeded in finding an exact solution of the equations of convective diffusion, and, consequently, the exact expression for the diffusion current, still qualitatively we may, as previously, make use of the expressions obtained above.

As we have emphasized more than once, of essential significance is the circumstance that the formulae for the diffusion current hold

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[11] Levich, to be published shortly.

qualitatively not only for an electrode representing a plate in a flowing liquid or a rotating disc, for which cases they were derived, but also for electrodes that represent a cylinder rotating around one of the axes.

Both of the circumstances pointed out play a very essential rôle in comparing the theory with the experiments performed usually in complicated geometrical conditions and in the presence in the solution of a great number of different kinds of ions, as well as in the application of the theory to the practice of electrolysis or electrode position.

As far as the character of stirring is concerned, the greater part of the performed measurements may be naturally divided into three groups: experiments in which mixing was realized by revolving an electrode of any shape; experiments with mixing of the solution by a mixer; and experiments in which attempts were made to exclude mixing altogether.

In section 3 we have already pointed out that it is practically impossible to get rid of the natural convection, with the exception of the case of non-Newtonian fluids. Therefore, we shall not consider here at all the experiments of the last type.

As far as experiments in which the mixing of the solution is performed by a mixer are concerned, they have a number of serious shortcomings. The most important of these is the indefiniteness of geometrical conditions of the experiment. It is clear that the character of stirring will in this case depend on the shape of the mixer, on its size and the distance from the electrode, on the shape of the latter, etc.

Besides this, in the case of very high rates of rotation of the mixer, the mixing of solution will be strongly influenced by the formation of the regions of rarifications behind the paddles of the mixer, due to the cavitation phenomenon—a phenomenon well studied in the case of propelling screws.

Therefore experiments with the mixing of the solution by a mixer are unsatisfactory from a theoretical viewpoint.

However, it is possible, apparently, to make use for a qualitative control of the theory, of the data of such experiments with mixing by means of a mixer in which the size of the mixer was sufficiently large as compared with the gap between the electrode and the mixer paddles.

In this case the electrode may be regarded as a plate past which moves a given plane-parallel stream of the fluid dragged by the mixer. From the theoretical point of view, stirring by a flat revolving disc is the simplest method of mixing the electrolyte. The theory of this method may be developed to the end, as was shown in section 3. At the same time, it is exactly this method that is used most frequently in practice of electroanalysis. Unfortunately, up to now there have been no sufficiently precise experiments performed with a revolving disc. Realization of such experiments would be of great interest.

In a large number of published papers the measurements were performed without a sufficiently clear comprehension of the hydrodynamic picture, in complicated geometrical conditions, that made difficult the quantitative analysis of the obtained results. In the majority of the experiments, in particular, there was used as a revolving electrode a cylinder revolving about an axis passing through its centre and parallel to the generatrix. Apparently, the geometrical conditions of flow were considered to be simplest in this case. In reality, however, the investigation of convective diffusion in the case of a revolving cylinder is bound with considerable difficulties. For an infinite cylinder the problem has no stationary solutions at all: the concentration of the solution turns out to be infinitely increasing as the logarithm of the distance from the axis of the cylinder, similarly to the case of an electric potential in an analogous problem of electrostatics. In the case of a cylinder of finite length, the problem becomes mathematically very difficult.

Therefore the data of the experiments with the electrode in the form of a revolving cylinder may be used only for a qualitative control of the theory. After these general remarks, we may go over to a direct comparison of the results of the theory with those of the experiment.

The existence of a limiting current that may pass through the solution at given conditions of mixing is the main conclusion of the theory exposed. This conclusion relates to the case of a binary electrolyte, as well as to the case when there are in the solution additions of indifferent electrolytes, the existence of the limiting current being independent of the specific geometrical conditions, but being connected with the existence of a diffusion boundary layer itself. The curves shown in Fig. 3 demonstrate the general picture of the dependence of the current passing through the solution on the potential difference applied between the electrodes for a revolving electrode.

We see that in full accordance with the theory in the case of a small potential difference V, when the passing current is much less than the limiting one, a linear dependence between V and the current density j takes place, *i. e.* we find ourselves in a region where Ohm's law can be applied. When the applied potential difference increases, the curve bends and becomes parallel to the abcissa at $j = j_{\text{lim}}$ and $V = V_{\text{lim}}$. The value of the critical potential difference V_{lim}, as may be seen from formula (40), section 3, is determined, on the one hand, by the ohmic potential in the solution down to the boundary of a diffusion layer, and, on the other hand, by the universal quantity $\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\frac{kT}{e}$.

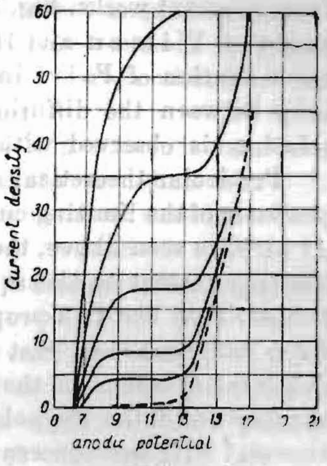

Fig. 3. The typical polarization curves for various concentrations of solution.

The greatest interest is offered by the dependence of the value of the limiting (diffusion) current j_{lim} on the fundamental quantities that determine the properties of the solution and the character of stirring. There are, first of all, the concentration of the solution c_l, then the rate of the flow of the fluid or of the revolving of the electrode U_0, the viscosity of the fluid η and the coefficient of diffusion D. Besides, the dependence of the limiting current on the temperature is also of interest. We shall discuss first qualitatively the general character of the dependence of j_{lim} on the values enumerated, which may be done on the basis of a rich experimental material, inasmuch as the geometrical conditions of mixing (the shape of the electrodes) and the number of the ionic species represented in the solution influence but little the character of the dependence itself. Afterwards, we shall go over to the quantitative comparison of the calculated and the observed values of j_{lim} in the scarce number of cases, when such a comparison is possible.

The direct proportionality between the limiting (diffusion) current and the concentration of the solution called for by the theory was already established by Nernst and Merriam's experiments[2], and served in its time as one of the main arguments in the establishing by Nernst of the diffusion layer theory.

These results by Nernst and Merriam were confirmed repeatedly in more recent works. Fig. 3 shows the results of very exact measurements of Wilson and Hughes[12] of the limiting currents for the reduction of Fe^{+++} in Fe^{+}. In all cases the direct proportionality between the diffusion current and the concentration of the solution is observed with great exactness.

Particular theoretical and practical interest is offered by the dependence of the limiting current on the velocity of motion of the fluid. As we have seen above, the theory leads to a proportionality of the limiting current to the square root of the velocity of the fluid for a laminar flow and to a proportionality to a higher power of velocity for a turbulent flow past the electrode. The power index increases in the latter case from the value of 0.6—0.8 almost up to unity with the increase of the Reynolds number of the flow. As far as the experimental data are concerned, it has been repeatedly pointed out in literature that there is a noticeable difference between the results obtained by different authors concerning this point. For instance, the data obtained by Eucken[3] are in good agreement with the power index $^1/_2$ (see below). Nernst and Merriam gave an empirical formula for a limiting current with the index 0.6[2]. Bruner[1] has obtained a omewhat greater index (0.66). Eucken[7] has pointed to a proportionality of the limiting current to the revolving speed of the electrode to the power 0.5—0.6. In van Name's[13] experiments the diffusion current turned out to be proportional to the velocity to the power 0.7—0.9. According to Wildermann[14], the index is equal to unity. In King's[15], experiments on the rate of dissolution of zinc the peripheral speed of the disolving cylinder was brought up to 27 m./sec. (which corresponds to the value of Reynolds numbers of about 2.7×10^5). Here the obtained results correspond to a proportionality of the diffusion current to the rate of rotation to the power 0.7—0.8.

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[12] Wilson and Hughes, Ind. and Eng. Chem., 607 (1923).
[13] Van Name, Amer. J. of Science, **29**, 237 (1910).
[14] Wildermann, Z. physik. Chem., **66**, 445 (1909).
[15] King and Schack, J. Amer. Chem. Soc., **57**, 1212 (1935).

Such a discrepancy in the experimental results may be naturally explained by the different degree of turbulization of the electrolyte which flows past the electrode

In new experiments by Eucken special precautions were taken in order to insure a laminar flow of the fluid; and the lowest value of the power index of the velocity $^1/_2$ was obtained in good agreement with the theory. In other experiments, no precautions to insure the laminar flow of the electrolyte in the neighbourhood of the electrode were taken.

In Nernst and Merriam's experiments a thin wire was used as a revolving electrode: the number of revolutions was relatively small (up to 600 r. p. m.), so that the Reynolds numbers must have been rather small, and a strong turbulization of the current was not to be expected. In Brunner and van Name's experiments mixing was effected by a mixer moving close to a flat electrode.

In Brunner's experiments the Reynolds numbers were of the order of $Re \sim 2\,000$, so that the turbulization of the flow also should have been still insignificant, but, judging by the results ($n \sim 0.66$), already noticeable because of the poor geometrical conditions.

In van Name's experiments there was, apparently, strong turbulence of the current. The Reynolds numbers in these experiments reached the value of $Re \sim 10^4 - 10^5$, while the geometrical conditions also favoured the turbulence of the current.

King's data relate wholly to a turbulent flow past the electrode Reynolds numbers lie between 3×10^4 and 2×10^5, while the model dissolved in these experiments had the shape of a cylinder or disc. It is known, however, that, when a cylinder is rotating even in the case of relatively small Reynolds numbers, the motion of the fluid is not stable and becomes turbulent.

Thus, it is, apparently, possible to assert that the discrepancy observed in the experimental data is in reality connected not with scarcely probable errors of measurements, but with the different degree of turbulence of the stream of the fluid in different experiments. On the whole, although no systematic measurements of the limiting current in simple geometrical conditions (for instance, for a flat electrode) were performed in a sufficiently wide range of Reynolds numbers, which includes the regions of a laminar as well as of a turbulent flow, the comparison of the data obtained by different authors demonstrates clearly that the character of the dependence of the limiting current on the rate of flow is in a good agreement with the theoretical conclusions.

The dependence of the limiting current on the coefficients of diffusion is in general rather complex. In the case of a binary electrolyte the limiting current, according to formula (42) section 3, varies inversely to the $^1/_3$ power of the effective diffusion coefficient D and is proportional to the diffusion coefficient of the ions which carry the current D_1.

If different kinds of the ions are represented in the solution, this dependence is still more complicated.

Since, however, the diffusion coefficients of different ions, with the exception of ions H_3O^+ and OH^-, differ from each other to a relatively small degree, we may approximately consider that the limiting current j_{lim} is proportional to

$$j_{\text{lim}} \sim D^{0.66}. \qquad (1)$$

Such a dependence is in a good agreement with Eucken's measurements reported in the work referred to above more than once, and also with King's data on dissolution of metals[16], in which there was observed a proportionality between the rate of the dissolution and the diffusion coefficients of different ions to the power of from 0.7 to 0.83. Although the power 0.83 is too large, we ought to bear in mind that the diffusion coefficients depend on the concentration of solution, and in certain cases, as, for instance, in the case of HCl, change considerably in the presence of salts, so that the accuracy of these experiments is not high.

The dependence of the limiting current on the viscosity in the case of a laminar flow may be represented by the semi-empirical formula

$$j_{\text{lim}} \sim \frac{1}{\nu^{5/6}}. \qquad (2)$$

Indeed, according to formulae (46) section 3 the limiting current varies as $j_{lim} \sim \frac{D^{2/3}}{\nu^{1/6}}$. On the other hand, however, with the change of viscosity the coefficient of diffusion also changes, according to the empirical law $D \cdot \mu = \text{const}$.

Inasmuch as the density of the fluid changes with the temperature only to a very small extent, one may approximately consider that $D \sim \frac{1}{\nu}$, whence the formula (1) given above is obtained.

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[16] King and Howard, Ind. and Eng. Chem., **29**, 75 (1937).

Formula (1) is in a good accordance with the data obtained by King[17] when dissolving zinc in an acid. The viscosity of the solution changed by adding sugar. It was found then that the rate of the dissolution varies approximately inversely to the viscosity. Taking into consideration the relative roughness of the experiment, it seems scarcely possible to distinguish between the powers $^5/_6$ and unity.

The measurements of the dependence of j_{lim} on the temperature may be used only for qualitative conclusions as to the nature of the factor determining the rate of a definite heterogeneous reaction but not for quantitative judgments as to the dependence of j_{lim} on the coefficients of diffusion or on the viscosity of the solution.

The rather slight dependence of the rate of heterogeneous reaction on the temperature shows that the rate of reaction is limited by the supply of the substance to the region where the reaction takes place, but not by its kinetics.

Because of the strong dependence of both quantities, entering moreover into the expression for j_{lim} in a complex combination, it does not seem possible basing on the temperature dependence to draw any conclusions as to the proportionality of j_{lim} to some power of the diffusion coefficient or viscosity.

From all the above said we may conclude that the theory of the diffusion boundary layer developed above is in a good qualitative agreement with the experiment. However, as far as the quantitative comparison is concerned, we have succeeded in doing it only for Eucken's experiments[4]. In these experiments the current passed between two platinum electrodes in a solution of KI and KCl in the presence of I^-, Br^- and H_3O^+ playing a rôle of depolarizing agents.

One of the electrodes was represented by a resting plate of large dimensions, so that the current passing through the solution was always small as compared with the limiting current to this plate, therefore it was possible to neglect the polarization phenomena on this electrode.

The second electrode was a plate 0.28 cm. in height and 0.089 cm. in width. The stirring was realized in the following manner: past the second electrode there moved the exterior wall of the cylindrical vessel containing the solution and the electrodes. The distance between the electrode and the moving wall varied from 0.05 up to 0.4 cm.

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[17] King, J. Amer. Chem. Soc., **57**, 828 (1935).

and was thus always greater than the corresponding thickness of the boundary layer. The Reynolds numbers of the flow did not exceed $Re \sim 10^4$. Here, as is emphasized by Eucken, the flow past the plate remained strictly laminar, so that for the limiting current formula (12′) section 4 may be made use of. Table 1 shows that between the theoretical and the experimental values for the limiting current there is a wholly satisfactory agreement.

Table 1

The dependence of the limiting current on the angular velocity

$\omega_1 = 88.3$, $J_{\text{calc}} = 1.33 \times 10^{-4}$ A, $J_{\text{obs}} = 1.15 \times 10^{-4}$ A;
$\omega_2 = 19.3$, $J_{\text{calc}} = 0.671 \times 10^{-4}$ A, $J_{\text{obs}} = 0.685 \times 10^{-4}$ A

$\frac{\omega_1}{\omega_2}$	$\frac{(J_{\text{calc}})_1}{(J_{\text{calc}})_2}$	$\frac{(J_{\text{obs}})_1}{(J_{\text{obs}})_2}$
1.27	1.14	1.09
1.50	1.22	1.15
2.39	1.55	1.33

It ought to be observed that because of probably accidental causes, just as good an agreement exists between the undoubtedly incorrect theoretical formula of Eucken himself and his experimental data.

As far as the quantitative comparison of the above results with other experiments is concerned, this comparison is restricted, as has been pointed out more than once, due to the differences in geometrical conditions.

However, in spite of this, the agreement between the theory and the experimental data turns out even more satisfactory than might have been expected. There is, in particular, a quite good quantitative agreement with Nernst and Merriam's experiments[2]. These authors give for the thickness of the diffusion layer the empirical formula

$$\delta'' = \frac{0.05}{Z^{0.6}}$$

where Z is the number of revolutions, which amounted to several hundreds per minute in these experiments.

In the range of the number of revolutions Z pointed out this formula is in a good quantitative agreement with formula (45′) section 3.

Summarizing all that has been said, we are able to conclude that the exposed theory is in a very good agreement with the experiment. However, a precise experimental study of the phenomena of concentration polarization in a wide range of Reynolds numbers and simple geometrical conditions, allowing to establish decisively the quantitative agreement between the theory and the experiment, is highly desirable.

In conclusion I wish to express my deep gratitude to Prof. L. Landau and Prof. A. Frumkin for interest in this work and valuable discussions of the results.

Appendix to section 3

The integral I_2 is equal

$$I_2 = \int_0^1 \frac{dt}{\frac{n_2 j}{(n_2 - n_1) D_1 e}\left[\int_{l/\delta'}^{0} e^{-(t^3+\beta t^4+\dots)}\,dt + \int_0^t e^{-(t^3+\beta t^4+\dots)}\,dt\right] + \frac{c^{(l)}}{\delta'}}.$$

In the last integral the denominator never exceeds unity. Therefore, the exponential function may be developed into series and we have approximately:

$$I_2 \cong \frac{(n_2 - n_1) e D_1}{n_2 j} \lg \frac{c^{(0)}}{c^{(0)} + \frac{n_2 j \delta'}{(n_2 - n_1) D_1 e}}$$

where $c^{(0)}$ is the value of c at $z = 0$ [in the plane of the disc, see (29′) section 3].

Evidently, in the same approximation we have

$$c^{(0)} + \frac{n_2 f \delta'}{(n_2 - n_1) D_1 e} \cong c^{(l)},$$

so that

$$I_2 \cong \frac{(n_2 - n_1)\, e D_1}{n_2 j} \lg \frac{c^{(0)}}{c^{(l)}}.$$

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