THE DIFFUSION KINETICS OF ELECTROCHEMICAL REACTIONS

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The kinetics of electrochemical reactions resemble those of all other heterogeneous processes and are determined by the rates of the three basic steps: 1) transfer of reagent ions and atoms from the body of the solution to the electrode surface, 2) electrochemical reaction proper, and 3) movement of the final reaction products away from the electrode surface.

The transfer of the reagents to the electrode and the removal of the reaction products will be grouped together arbitrarily and designated as the "diffusional" step of the reaction, even though the first of these processes is not usually considered as being purely diffusional. The diffusional step is not of direct significance for the kinetics of the electrochemical reaction itself but is rather a factor which makes for complications in the process. In practice, however, it is the diffusional step which very frequently determines the over-all reaction rate and this is particularly true under the conditions which prevail in industrial electrolyses. Moreover, the study of electrode reactions at higher velocities is always complicated by the fact that diffusion is then the slow step in the process and the one which limits the rate of over-all reaction. It is customary to speak of diffusion reaction kinetics in the last case.

The importance of the diffusional step for electrochemical kinetics has led to numerous experimental and theoretical studies of diffusion processes in solution. The basic laws applying to the diffusional step of the electrochemical process can now be considered as established through the combined efforts of various workers. A quantitative theory has been developed for the diffusional processes which are involved in the over-all electrochemical reaction under various operating conditions.

This report will attempt to characterize the present state of the theory of the diffusion kinetics of heterogeneous reactions in solution (and of electrochemical reactions, in particular) and to give a more complete quantitative test of this theory by comparing it with certain new experimental data.

The first papers on the diffusional processes in electrolysis (these date back to 1890) considered the solution in the cell to be at rest. It quickly became evident (as will be shown below) that the case of the immobile solution was the exceptional one, and attention was therefore directed to the problem of diffusion in moving solutions. There has recently been a renewal of interest in the study of the transfer of reagents through a stationary solution to a surface. This situation has arisen because of the development of a new technique of measurement which observes the electrochemical reaction over a period which is so short that liquid convection does not have the opportunity to develop. There is, moreover, the formal possibility of reducing the problem of diffusion at the dropping electrode to the companion problem of diffusion in a stationary medium. Thus there is a close relation between the study of the theory of the dropping electrode and a consideration of diffusion problems in stationary media. Solutions have been developed for the diffusion through stationary media in electrolyses and electrochemical reactions under various conditions and these have been presented in a number of papers. A review of this group of papers has been given in the monograph of Delehaye [1].

We will now consider briefly the background of the problem of the transfer of reagents through a stationary medium to the electrode surface. The general case is that in which both diffusion and migration of ions contribute to current passing through the solution.

The ion currents of the first and second type in a binary electrolyte are respectively expressed by equations of the form:

$$j_1 = -D_1\frac{\partial c_1}{\partial x} - u_1 n_1 F c_1 E,$$
$$j_2 = -D_2\frac{\partial c_2}{\partial x} + u_2 n_2 F c_2 E, \tag{1}$$

in which E is the field strength and u, the ionic mobility. The concentration of ion outside the double layer must be such as to satisfy the condition of electrical neutrality:

$$n_1 c_1 = n_2 c_2. \tag{1a}$$

The law of conservation of the number of ions has the form:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial j_i}{\partial x}. \tag{2}$$

Two equations are obtained on introducing the molar concentration, $c = \frac{c_1}{n_2} = \frac{c_2}{n_1}$, combining (1) and (2), and eliminating the electrical field:

$$\frac{\partial c}{\partial t} = D_{\text{eff.}}\frac{\partial^2 c}{\partial x^2}; \tag{3a}$$

$$\frac{\partial}{\partial x}(cE) = -\frac{D_1 - D_2}{F(n_1 u_1 + n_2 u_2)}\frac{\partial^2 c}{\partial x^2}, \tag{3b}$$

here

$$D_{\text{eff.}} = \frac{D_1 n_2 u_2 + D_2 n_1 u_1}{n_1 u_1 + n_2 u_2}. \tag{3c}$$

The first of these equations determines the concentration distribution, while the second can be used to fix the spatial distribution of the electric field strength once the concentration distribution is known. The partial differential equation (3a) is known as the Diffusion Equation. Most electrolyses are carried out with an excess of a foreign or inert, electrolyte. This increases the conductivity of the solution to the point where the migrational contribution to the current becomes small in comparison with that due to diffusion. The usual diffusion equation can then be used to describe the transfer of ions, as well as neutral particles

$$\frac{\partial c}{\partial t} = D\cdot\frac{\partial^2 c}{\partial x^2}. \tag{4}$$

The actual physical conditions of electrolysis must be known if the concentration distribution in space and time is to be found and the current passing through the electrolyzer determined. These conditions are characterized by the initial concentrations and by the boundary conditions which the concentrations and particle currents must satisfy at the electrode surface. The concentration is usually uniform throughout the electrolyzer at the beginning of electrolysis.

$$c = c_0 = \text{const} \qquad \text{at} \quad t = 0. \tag{5}$$

The boundary conditions will depend on the nature of the electrochemical reactions which occur on the electrode surface and on the conditions of the electrolysis. The well-known Nernst Equation relates the potential and the solution concentration near the electrode for the case of a reversible reaction.

The relation between the concentrations and the potentials in irreversible reactions is essentially complex. It is frequently possible to assume that an irreversible electrochemical reaction is of the first order with respect to

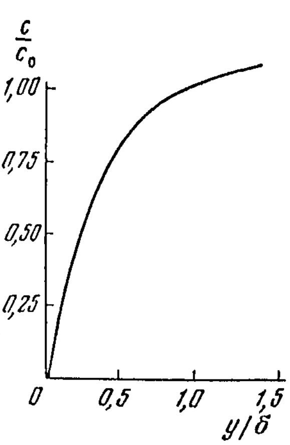

Fig. 1. Concentration distribution at the surface of a disc.

the concentration. Under these conditions, the diffusion current on the electrode surfaces, $j = D(\frac{\partial c}{\partial n})$, is equal to the rate of reaction so that:

$$D\left(\frac{\partial c}{\partial n}\right) = A(\varphi)\,c, \qquad (6)$$

with $A(\varphi)$ a function of the potential and n,a normal to the surface. In practice, electrolysis is so carried out that: 1) the electrode potential is constant, or 2) the potential increases linearly with time, or 3) the potential varies with time, more particularly, varies periodically, or 4) the current flowing through the electrolyzer is constant, or 5) the current flowing through the electrolyzer fluctuates.

The various boundary conditions correspond to various concentration distributions in time and space. The simplest cases of reversible processes at constant potential, or reversible processes with constant current flow through the electrolyzer, were investigated by A. I. Sokolov [2] and by Sand [3] in 1890 (boundary conditions, $j = D(\frac{\partial c}{\partial n}) = \text{const.}$ on the electrode surface. A theory of stationary electrolysis in a binary electrolyte was given by Eiken in 1905 [4]. The theory of a reversible process on the dropping electrode was developed by Ilcovic in 1934, and more exactly, by MacGillavry and Rideal in 1937 [6], and it was shown that this case could be reduced to the problem of diffusion in a stationary medium. These last results are widely known in the field of electrochemistry, for they give a theoretical basis for polarography. The principal interest of recent years has been directed to irreversible reactions since their study is of fundamental interest for electrochemistry. In 1948, N. N. Maiman and the present author developed a method for reducing the equation of convectional diffusion to the dropping mercury electrode to the diffusion equation [7]. This made it possible for N. N. Maiman to solve the complex mathematical problem of developing the polarographic wave for an irreversible electrochemical reaction at the dropping mercury electrode in this same year [8]. The work of N. N. Maiman was tested experimentally by V. S. Bagotskii [9] and the theory shown to be in excellent agreement with experiment. A similar solution for the dropping mercury electrode was obtained in 1953 by Koutetskii [10] while a solution for the case of the stationary solution containing an excess of neutral electrolyte was developed by Delahaye [1], Smutek [11], and Evans and Hush [12]. Much theoretical and experimental work has been done by American and Czech investigators in an attempt to describe electrolysis under a potential varying linearly, or periodically, with time. Note should first be made of the work of Delehaye [1], Sevcik [13] and Randles [14]. Methods involving periodically altering potentials have given good results; these were introduced in the work of B. V. Ershler [15] and were developed in the theoretical and experimental investigations of Delehaye [1], Grahame [16], Jaffe [17], Gerisher [18], and others. More complex cases of the diffusional kinetics of electrode processes which are complicated by the presence of reactions in the body of the solution have been studied by Koutetskii and other Czech investigators [1, 10, 19]. An additional member must be here appended to the diffusion equation to cover the production, or consumption, of diffusing particles in the body of the solution which results from the bulk reaction (i.e., to account for the existence of volume sources).

It has already been emphasized that the stationary solution is met only rarely. The passage of current through the electrolytic cell is accompanied by an alteration in the concentration in the solution. This leads in turn to natural convection in the liquid. Other factors which can give rise to liquid convection are the evolution of thermal energy during electrolysis, the presence of a free non-isothermal surface in the liquid, etc. Thus it can be considered that the liquid will be in motion unless the natural convection is limited by special measures such as the immobilization of the solution with structure-forming substances. On the other hand, forced and energetic agitation of the solution is required in order to obtain the highest possible currents in the electrolytic cell. These facts have attracted special attention to a study of the diffusional kinetics of moving liquids. This type of work has been carried out with special intensity in the Soviet Union in recent years.

Experimental studies on the dissolving of solid bodies in liquids led Nernst to the formulation of a theory of the stationary diffusion layer on the solid surface. This theory has received wide acceptance in electrochemistry; according to it, all of the concentration changes in the diffusing substances are localized in a stationary layer of solution of thickness δ on the solid object's surface. The diffusion current per sq. centimeter of electrode surface is given by:

$$j = D\frac{c_0 - c_1}{\delta}, \tag{7}$$

where c_1 is the equilibrium concentration at the electrode; c_0 is the concentration in the body of the solution; and D is the diffusion coefficient.

Agitation of the solution leads, according to Nernst, to a diminution in the depth of the diffusion layer which follows an emprical law:

$$\delta \sim \frac{1}{v^n}, \tag{8}$$

in which $\underline{v}$ is the rate of movement of the liquid. The exponent $\underline{n}$ of this equation falls between the limits $1/2 \leq n \leq 1$ and is dependent on the experimental conditions. The value of δ can be obtained from measurements of the current $\underline{j}$. The magnitude of δ proves to be so large as to show the incompatibility of the concept of a stationary layer and the hydrodynamic data on liquid mobility. Direct measurements have shown the liquid to be in movement at distances from the solid surface which are considerably smaller than the δ values obtained from the electrochemical data. The inadequacies of the Nernst Theory have led the author to apply modern hydrodynamics to a study of this problem [7].

The formulation of a theory of convectional diffusion in liquids must take account of the fact that the diffusion coefficient in a liquid is quite small in comparison with the coefficient of kinematic viscosity. This indicates that convection plays a major role in the transport of matter in liquids. Convection predominates over the slow diffusion processes in transporting matter, even at low rates of movement. The stationary state in the convectional diffusion of a dissolved substance through a liquid is described by the equation:

$$\vec{v}\,\mathrm{grad}\, c = D\,\Delta c, \tag{9}$$

in which $\vec{v}$ designates the liquid velocity and $\underline{c}$, the concentration.

The equation of convectional diffusion must be supplemented by the boundary conditions which are imposed on the concentrations. The concentration has the fixed value $c = c_0 =$ constant at points far removed from the reaction surface. The concentration must satisfy the condition.

$$D\left(\frac{\partial c}{\partial n}\right)_S = Q, \tag{10}$$

on the reaction surface (the derivative is evaluated on this surface, S, and Q designates the rate of the heterogeneous reaction). The boundary condition (10) expresses a balance between the rates of supply and consumption of a substance in the course of reaction. The reaction rate, Q, is proportional to the concentration of the substance at the reaction surface, c_1, raised to a certain power $\underline{m}$. Thus

$$D\left(\frac{\partial c}{\partial n}\right)_S = kc_1^m. \tag{11}$$

It is possible to pass to the limit $Q \to \infty$ in the simplest case where the reaction rate is very great in comparison with the rate of supply of the material and then write

$$c_1 \to 0 \text{ on surface S} \tag{12}$$

in place of (11). Equation (12) can be replaced by

$$c_1 = \text{const. on surface S}$$

(c_1 is the concentration of a saturated solution) when the heterogeneous reaction proceeds with the formation, rather than consumption, of particles in solution, as would be the case in dissolution.

It is useful to reformulate Equation (9) for convectional diffusion by introducing the dimensionless velocity $\vec{V} = \vec{v}/u$, and the coordinates $X_i = x_i/L$, u and L being, respectively, the characteristic flow rate and dimension of the system.

We then have:

$$\vec{V}\overset{\text{grad } c}{\Delta c} - \frac{1}{\text{Pe}}\Delta c = 0, \tag{13}$$

where differentiation has been carried out with respect to the dimensionless variables X_i. Pe designates the dimensionless Peclet number:

$$\text{Pe} = \frac{u \cdot L}{D} = \frac{u \cdot L}{\nu} \cdot \frac{\nu}{D} = \text{Re} \cdot \text{Pr}, \tag{14}$$

Re being the Reynolds number and Pr, the Prandtl number. Pr is of the order of 10^3, or greater, for diffusion in such liquids as water. Thus, the Peclet number is very large unless the Reynolds number is quite small. This indicates that the second member of (13), the equation for convectional diffusion, is small in comparison with the first if the concentration c does not alter very rapidly in passing from one point to another. A solution of (13) which will satisfy the boundary conditions far from the reaction surface is

$$c = c_0 = \text{const.}$$

It is clear, however, that this solution cannot be valid in the neighborhood of the reaction surface. This indicates that there is a narrow region near the reaction surface within which the alteration of the concentration is so rapid that it is no longer permissible to neglect Δc. It is essentially within this region that the concentration changes from c_0 to zero, or c_1. We will designate this region of rapid concentration change as the diffusional boundary layer. It is clear that the depth of the diffusional boundary layer, δ', is very minute in comparison with the dimension of the system, L. This detail can be employed in bringing about a simplification in the equation for convectional diffusion in the diffusional boundary layer. Thus, the last member of $\Delta c = \partial^2 c/\partial x^2 + \partial^2 c/\partial y^2$ expresses the alteration of the concentration in a direction perpendicular to the reaction surface, whereas the first member gives the alteration in the concentration along this reaction surface. It is clear that $\partial^2 c/\partial y^2 \gg \partial^2 c/\partial x^2$ when the alteration in the concentration c perpendicular to the reaction surface is limited to an interval $\delta' \ll L$, so that it is then possible to write

$$v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}. \tag{15}$$

in place of (9). Estimates show that the two members of the left hand member of (15) differ by no more than one order of magnitude; although the derivative $\partial c/\partial y$ is large in comparison with $\partial c/\partial x$ the component v_y is small in comparison with v_x in this same expression. Thus the entire solution can be arbitrarily divided into two regions; the thin diffusional boundary layer of depth δ', in which the principal alteration in the concentration takes place, and the region lying outside of this boundary layer where the concentration is practically constant. It is to be understood that the concept of a boundary layer of definite depth is an artificial one and that the two regions of the liquid are not sharply separated from one another. The depth of the diffusional boundary layer will depend on the rate of agitation of the liquid and on the properties of the diffusing particles. It must be emphasized that the rate of movement of the liquid plays an essential role in determining the concentration distribution in the boundary layer through Equation (15). The diffusional boundary layer is thus fundamentally different from the Nernst diffusion layer. The diffusional boundary layer is the analog of the Prandtl hydrodynamic boundary layer. The retardation of liquid flow by the forces of friction is known to occur within the Prandtl boundary layer. The liquid velocity changes from the value u in the interior of the flow around the object to zero on the surface of this object over a distance which is equal to the depth, δ_0, of the Prandtl layer. Liquid viscosity does not appear outside of the Prandtl boundary layer where the velocity slowly alters from point to point according to the law of ideal liquids. Theory shows the depth of the Prandtl layer to be given by the equation

$$\delta_0 \sim \sqrt{\frac{\nu x}{u_0}} = \frac{x}{\sqrt{\mathrm{Re}}}, \tag{16}$$

in which x is the distance measured from the point of incidence of the flow.

The velocity distribution within the boundary layer is known from the solution of the corresponding hydrodynamic problem. The velocity distribution of convectional diffusion in liquids can be essentially simplified when the Prandtl number is small in comparison with unity. It is natural to suppose that the depth of the diffusional boundary layer, δ', is essentially less than the depth of the hydrodynamic boundary layer, δ_0, since the Peclet number for convectional diffusion is always considerably larger than the Reynolds number and the depth of the boundary layer diminishes with increasing Re according to (16). Thus, the velocities v_x and v_y of Equation (15) can be approximated by $v_x \sim u_0 y/\delta_0$, and $v_y \sim \nu z^2/\delta_0^3$ at very small distances from the surface. The depth of the diffusional boundary layer can be estimated by setting expressions for v_x and v_y into (15) and then comparing the orders of magnitude of the members of this equation. This depth proves to be equal to

$$\delta' \sim \sqrt{\frac{\nu \cdot x}{u_0}} \cdot \left(\frac{D}{\nu}\right)^{1/3} \sim \delta_0 \cdot \left(\frac{D}{\nu}\right)^{1/3}, \tag{17}$$

i.e., it is only one-tenth as large as the depth of the hydrodynamic boundary layer δ_0. The principal change in the concentration occurs in this layer of depth δ' and the density of the diffusion current can be therefore be written as

$$j \sim D \cdot \frac{c_0 - c_1}{\delta'} \sim D \cdot \frac{c_0 - c_1}{\left(\frac{D}{\nu}\right)^{1/3} \cdot \sqrt{\frac{\nu x}{u_0}}}. \tag{18}$$

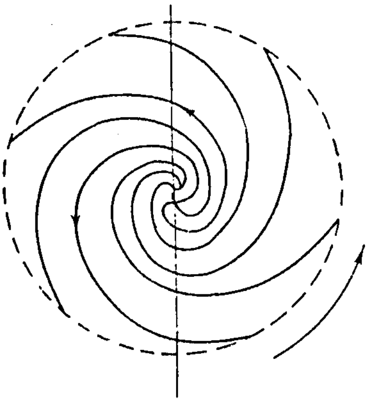

Fig. 2. Velocity distribution in a liquid which is flowing around a disc.

In addition to such estimations, a number of our papers have carried out quantitative solutions of the equation of convectional diffusion for cases of heterogeneous, or electrochemical, reactions which are simple from the hydrodynamic point of view.

Experimental test of the theoretical work has been made in various investigations and has shown such good agreement that it is possible to apply these formulas in practice with a high degree of confidence. A brief review of certain theoretical work and its experimental confirmation will be given below.

Theoretical studies have shown that a rotating disc is an especially suitable surface for investigating heterogeneous reactions. Such a disc has the advantage that all of the points on its surface (with exception of those in a thin layer at the edge) are equally accessible for diffusion. This means that the depth of the diffusion layer and the density of the particle current are constant over the entire surface of the disc. The problem of convectional diffusion to the disc surface is one which admits of an exact solution. The current density at the disc surface is expressed by the equation

$$j = \frac{D \cdot (c_0 - c_1)}{1{,}616 \left(\frac{D}{\nu}\right)^{1/3} \left(\frac{\nu}{\omega}\right)^{1/2}} = \frac{F \cdot (c_0 - c_1)}{\delta'}, \tag{19}$$

in which ω is the angular velocity of rotation.

The calculated distribution of concentrations at the surface of a disc is shown in Fig. 1 and the distribution of velocities in a liquid which is flowing around the disc, Figure 2. The velocity of the liquid at a distance δ' from the disc is only 10% of the velocity at infinite distance.

B. N. Kabanov and Yu. G. Siver [20] (Fig. 3) and, later, Hogge and Krichmen [21], E. A. Aikazyan and A. I. Fedorova [22], and Tobiash [23], have measured the maximum diffusion current to a rotating disc electrode and thus subjected Equation (19) to a very careful check.

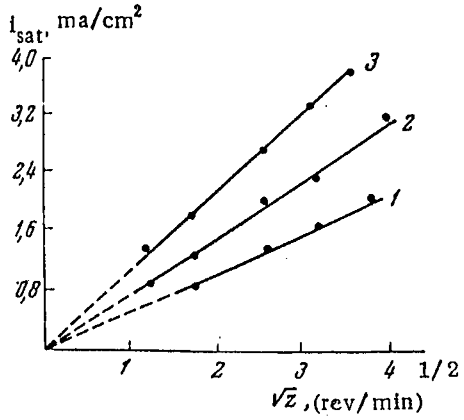

Fig. 3. The relation between the maximum current density for the discharge of hydrogen ions and the square-root of the rate of rotation of the disc: 1) $H_2SO_4 + 0.5\ N\ Na_2SO_4$; 2) $H_2SO_4 + 0.1\ N\ K_2SO_4$; 3) $HCl + 0.1\ N\ KCl$.

The agreement between the experimental data and this theoretical equation is so good that the rotating disc electrode can be successfully applied for measuring ionic diffusion coefficients and for quantitative analysis of solutions.

The accuracy of measurements made with the disc is no less than those carried out with the dropping mercury electrode. Not only has the maximum diffusion current corresponding to the boundary condition c = 0 been obtained but also a solution of the problem of convectional diffusion to the disc under the general boundary condition of (11).

This latter solution was used in the work of A. N. Frumkin and É. A. Aikazyan [24] for analyzing the ionization of molecular hydrogen on a platinum anode. These authors were able to obtain important information on the reaction mechanism from a determination of the reaction order. Ya. V. Durdin and Z. U. Dukhnyakova [25], Bircumshaw and Riddiford [26], and Galpern [27] have used the rotating disc in studying the dissolution of a number of metals. From the agreement between the dissolution rates and the predictions of Equation (19) it could be established that the dissolution of zinc, manganese, and magnesium proceeds according to diffusion kinetics in many acids.

Another case of a heterogeneous surface reaction in which we have obtained a solution for the equation of convectional diffusion is that of a sheet surrounded by a laminar liquid flow. Pohlhausen [28] has treated a similar problem in heat transfer. The Prandtl number is usually close to unity in the case of heat transfer. Thus the above-mentioned simplification of Equation (15) could not be applied in Pohlhausen's work and a solution was there obtained by numerical methods. The density of the flow to the sheet proved to be equal to

$$j = 0.33 D \Delta c \left(\frac{D}{\nu}\right)^{-1/3} \left(\frac{u}{\nu x}\right)^{1/2}. \tag{20}$$

The flow of density varies from point to point in the case of the sheet. Equation (20) has been experimentally tested in the work of Trumpler and Zeller [29] and shown to be in good agreement with the experimental results.

An important instance of agitation is that of the natural convection which arises from an alteration in the concentration (and density, ρ) of the solution in the neighborhood of a surface of heterogeneous reaction. We have carried out calculations on the current density for natural convection to a vertical sheet using the equation

$$j = \frac{Dc_0}{\delta'} = \frac{Dc_0 \cdot 0{,}54 \cdot \mathrm{Pr}^{1/4}}{x^{1/4}} \left[\frac{g\alpha}{4\nu^2}\right]^{1/4} \tag{21}$$

Here α designates the quantity $\alpha = c_0/\rho_0\,(\partial\rho/\partial c)$. The current density under natural convection is proportional to the 5/4 power of the solution concentration and varies from point to point.

Equation (21) has been subjected to careful test in the work of Ibl [30]. There is good agreement between theory and experiment. Numerous other instances of convectional diffusion have also been considered. Solutions have been obtained for the special case of diffusion to a heterogeneous reaction surface on which the boundary conditions vary from one section to another, for convectional diffusion in solutions which are so moving as to have low values of the Reynolds number, for diffusion to the inner surface of a tube, etc.

A number of experimental studies have aimed at confirming the results of these latter calculations. Much theoretical work has been devoted to the problem of diffusion at liquid – liquid and liquid – gas interfaces. An outline of this work would lead beyond the limits of the present report.

The need for theoretical work on convectional diffusion in turbulent liquid flow has been brought out in connection with the intensification of heterogeneous processes and in studying heterogeneous processes which take

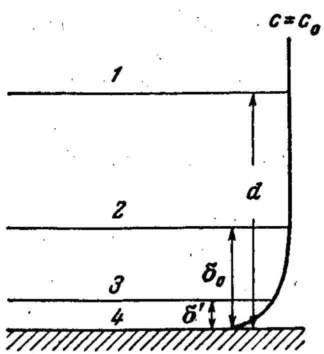

Fig. 4. The structure of turbulent flow. Concentration profile: 1) basic turbulent flow; 2) turbulent boundary layer; 3) viscous sublayer; 4) diffusional sublayer.

place at high velocity. It should be noted that the problem of convectional diffusion in industrial apparatus is one which frequently involves consideration of turbulent flow.

The development of a theory of convectional diffusion in turbulent flow has necessitated a refinement of the hydrodynamic concepts of the nature of the turbulence in the neighborhood of a solid surface. We have proposed a theory of the damping of turbulence in the neighborhood of a solid surface [7] which is essentially different from that suggested earlier by Prandtl and Karman [31]. The structure of the turbulent flow near a solid surface proves to be rather complex. The turbulent pulsations are gradually damped on approaching the surface and the effect of viscosity appears in a narrow film of thickness δ_0, which is known as the viscous sublayer. We have postulated that residual turbulent pulsations are responsible for a transfer of matter even in this viscous sublayer so that the concentration here is approximately the same as in the depth of the solution (Fig. 4).

A solution of the problem of convectional diffusion in turbulent flow has been obtained on the basis of this hypothesis. The principal change in concentration is that which takes place in a very thin liquid film

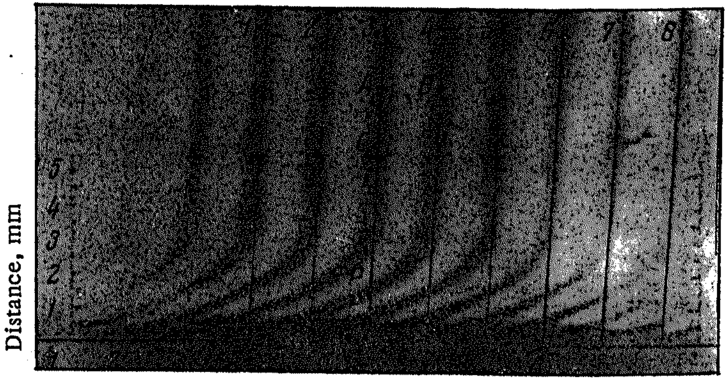

Fig. 5. Interferometer measurements on the distribution of concentration at a wall in turbulent flow.

where molecular diffusion predominates over the transfer due to the turbulent pulsations (Fig. 5). The depth, δ', of this so-called diffusional sublayer proves to be equal to $\delta' \propto \delta_0 / \mathrm{Pr}^{1/4}$

Theory shows that the diffusion current to the disc surface in turbulent flow (which sets in at Re~ 10) is given by

$$j = \frac{0{,}01 c_0 S a \omega}{\mathrm{Pr}^{3/4}} \cdot \left(\frac{\nu}{a^2 \omega}\right)^{1/10}. \tag{22}$$

The experiments of I. A. Bagotskii [32] have shown that Equation (22) correctly reproduces the relation between j, ω and D. A more detailed test of Equation (22) has been set forth in the work of A. I. Fedorova and G. L. Vidovich [33]. Measurements on the temperature dependence of the diffusion current also indicate that Equation (22) correctly reproduces the relation between j, the solution viscosity, ν, and the diffusion coefficient, D.

The relation between j, ν, and D which follows from the Prandtl - Karman theory, and from the recently published work of Vielschtich [34], is not in agreement with the data of A. I. Fedorova and G. L. Vidovich [33].

Thus it can be considered that the various theories of convectional diffusion at a solid – liquid interface which we have developed have now been rather convincingly confirmed by a wide mass of experimental material which has been accumulated in working under various geometrical conditions and with various types of liquid movement. This makes it possible to apply these concepts with assurance in predicting the rate of the diffusional step in heterogeneous reactions under various conditions, and especially in electrochemical reactions. In addition these theoretical concepts of the convectional transfer of matter in moving liquids find successful applications in such neighboring fields as the theory of thermal transfer and the theory of aerosols and colloids.

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