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# Electrochemical Methods of Studying Transfer Processes in Liquids

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The theoretical basis of the electrochemical method of studying mass and momentum transfer in solid-liquid systems is outlined. Published work on the most important practical applications of the method is reviewed, including electrochemical modelling of heat and mass transfer processes, measurement of averaged and spectral hydrodynamic characteristics of the interaction between a flow of liquid and a solid surface, and the study of the fine structure of turbulent boundary layers. Theoretical and practical problems arising in electrochemical transducers are discussed. 135 references.

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## I. INTRODUCTION

Modern scientific research relies increasingly on new instrumental means of obtaining information without using transducers liable to distort (to a greater or lesser extent) the phenomenon under study. Notable new techniques in the field of hydrodynamics and convective heat and mass transfer, which includes processes of outstanding importance in chemical and electrochemical technology, are laser anemometry, the radioactive indicator method, shadow photography, flow visualisation, etc. A special place among these methods belongs to the electrochemical method, in which an electric current is used as a measure of the rate of mass transfer from a flow of electrolyte solution to a conducting solid surface (the electrode).

The first attempts at electrochemical modelling of mass transfer processes in systems with a given configuration of hydrodynamic flows took place in the late 1940's and early 1950's [1,2]. More recently numerous groups of workers have demonstrated and examined in detail the possibilities of the method, and established its power in studies of transfer and exchange processes in liquid–solid and gas–liquid systems. The electrochemical method allows us to probe the structure of laminar and turbulent boundary layers (where the main resistance to heat and mass exchange resides), to obtain information on the fine structure of the turbulent flow in the viscous sub-layer of the boundary layer, to measure local values of the electrokinetic potential and of the rate of mass transfer, to investigate spatial and time correlations between local properties of hydrodynamic, concentration, and thermal fields, and to model the dynamic characteristics of many types of heterogeneous process of practical interest. As well as being very accurate and reproducible, electrochemical measurements are free from heat losses, they do not alter the area of the interfacial surface, and they are simple and convenient.

In recent years the electrochemical method of measuring viscous friction and of modelling heat and mass transfer processes in turbulent and in laminar flows has attracted the attention of researchers in many countries, including the USSR, USA, Germany, France, Japan, and others. The aim of this paper is to review the most important developments in the use of the electrochemical measurement method and of electrochemical modelling, to present the most interesting and useful results, and to discuss some problems in the theory of electrochemical transducers and some practical difficulties encountered in the application of this very valuable method of investigation.

## II. PRINCIPLES OF THE MEASUREMENT OF THE RATE OF ELECTROCHEMICAL MASS TRANSFER UNDER STABILISED FLOW CONDITIONS

The electrochemical method of studying mass transfer relies on measuring the current density of an oxidation–reduction reaction at the surface of an electrode mounted in the wall of the vessel or exposed to the flow in some other way: under the chosen conditions the magnitude of the reaction current is determined by the hydrodynamic conditions of the process by which the reacting ions are supplied to the working electrode (concentration polarisation regime). In this case all the processes occurring at the working electrode (and therefore also the current flowing in the electrochemical cell consisting of a current source, anode, cathode, and flowing electrolyte) are described with sufficient precision by a system of hydrodynamic equations combined with the equations of convective mass transfer. The reaction rate is usually much greater than the rate of arrival of ions at the electrode surface by convective diffusion and migration, and therefore we can assume to a very good approximation that the concentration of reacting ions at the surface of the transducer is zero ($c_w = 0$). Hence the driving force of the ionic mass transfer ($c_0 - c_w$) is equal to the concentration of the ions at a point far removed from the electrode ($c_0$). Purely diffusional mass transfer is achieved by adding to the working solution an excess of an indifferent electrolyte which does not react electrochemically at the electrode

but minimises the contribution of electromigration to the transport of reacting ions. A typical current–voltage characteristic for a reaction showing concentration polarisation is reproduced in Fig. 1 together with a diagram of the circuit arrangement. In most cases the momentum associated with the substances taking part in the electrochemical reaction is small compared to the momentum of the solvent. Hence the properties of the hydrodynamic flow surrounding the electrode are practically unaffected by the electrochemical reaction.

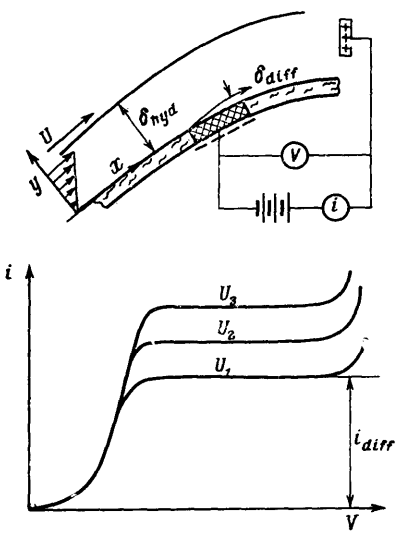



**Figure 1.** Schematic of the electrochemical measurement method and current–voltage characteristics for different flow rates of the solution ($U_1 < U_2 < U_3$): $x$ is the spatial co-ordinate in the flow direction, $y$ is the co-ordinate at right angles to the flow, $\delta_{hyd}$ is the effective thickness of the hydrodynamic boundary layer, $\delta_{diff}$ is the effective thickness of the diffusion boundary layer, $i$ is the measured current, $V$ is the voltage applied to the measuring cell, $i_{diff}$ is the limiting diffusion current.

Often the size of the electrode in the flow direction (along the $x$ axis) can be made much smaller than the characteristic hydrodynamic dimension, e.g. the cross-sectional diameter of a streamlined body or the distance from the electrode to the point of entry of the hydrodynamic flow. Hence, and with very few exceptions (for example, when very high pressure gradients are present in the system), the potential due to viscous fraction remains practically constant over the electrode surface. Constant tangential stress at the wall is a characteristic condition of systems consisting of a body immersed in a flow of liquid. A system of this type has been used[3] to study, by the electrochemical method, the detachment of a transverse flow surrounding a circular cylinder.

In any practical application of the electrochemical method it is important to bear in mind the following limitations, which apply to the chosen electrochemical reaction and electrolyte.

1. The reaction should not generate any products capable of disturbing the hydrodynamic conditions near the electrode.
2. The concentration polarisation at the measuring electrode should not be large enough to give rise to side reactions, which would alter the limiting diffusion current.
3. The reaction rate should be high enough to ensure that the effect of activation polarisation is negligible.
4. The reaction at the anode should be the inverse of the reaction at the cathode, to ensure that the concentration of the ions reacting at the working electrode remains constant during the experiment.
5. The composition of the electrolyte should be chosen so as to minimise the contribution of migration to the ionic mass transfer.
6. The electrolyte should be readily available in a pure form, adequately stable in solution, and it should offer a wide range of physical properties (viscosity, molecular diffusion coefficient, etc.).
7. The physical properties of the electrolyte (density, viscosity, diffusion coefficient, etc.) as well as their temperature and concentration dependence should be known with sufficient precision.
8. The electrolyte composition and the electrode reaction should be chosen so as to ensure reliable measurement of the limiting diffusion current in the concentration polarisation regime.

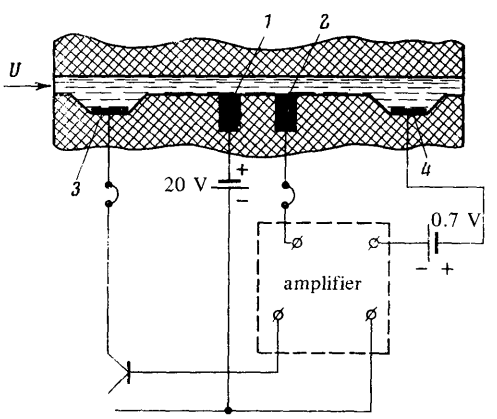



**Figure 2.** Electrochemical method employing two measuring electrodes: *1*) electrode for injecting electrically active material into the solution, *2*) electrode for monitoring the rate of transport of electrically active material by the flow, *3*) and *4*) auxiliary electrodes.

Two modifications of the electrochemical method have been described. The first relies on a single measuring electrode (transducer), which forms a reversible redox system with the electrolyte (see Fig. 1). The output signal of this transducer is the limiting diffusion current. Most of the published work on hydrodynamics and mass transfer was done by this method. However, the one-electrode transducer has a number of shortcomings, including excessive sensitivity of the calibration to the concentration of the species responsible for charge transfer at the interface, and also to the blocking of surface sites during the experiment.

The second modification of the electrochemical measuring system comprises two electrodes located at different points in the flow (Fig. 2). The first two-electrode flow-through cell (in the "disk and ring" configuration) was proposed by Frumkin and Nekrasov[4] for electro-analytical measurements. The electrically active products are generated by an electrochemical reaction in the central area of a rotating disk electrode, and detected by a peripheral, annular electrode mounted on the same disk. Many alternative forms of this system were subsequently developed for investigating the transport properties of liquids and gases and the special features of homogeneous and heterogeneous processes complicated by ionic mass transfer in solutions[5].

A cell consisting of a plane-parallel channel with two parallel strip electrodes separated by a narrow gap and mounted in one wall at right angles to the flow[6] offers a number of advantages over the "disk and ring" configuration. It is easier to construct, and it gives a theoretical description of the velocity and concentration profiles in a convenient analytic form. If the inter-electrode gap is small enough to allow the boundary diffusion layers to overlap, the measured current densities can give information on the hydrodynamic structure of the boundary layers under both the laminar and the turbulent flow regime. If the relationship between the measured limiting diffusion current and the parameters of the boundary layer velocity profiles is known in an analytic form we can determine the local hydrodynamic parameters of the flow with high precision (for example, the distribution of the average tangential stress at the wall, the spectral characteristics of the velocity and surface friction pulsations, etc.). Analytic solutions of the convective mass transfer problem, applicable in correlation measurements under laminar flow conditions, have been obtained for both the above forms of the two-electrode measuring cell[7-12].

## III. CAPABILITIES AND ADVANTAGES OF THE ELECTROCHEMICAL METHOD

Electrochemical transducers are most effectively employed in modelling convective heat and mass transfer processes in liquids[1-12], and also in measurements of viscous flow stresses at the boundary between a turbulent liquid and a solid wall[13-18]. Electrochemical measurements are free from many of the difficulties associated with the methods traditionally used in experimental hydrodynamics, thermo-physics, and chemical technology. Thus even the first attempts at modelling mass exchange[1-3] were successful in demonstrating and exploiting the advantages of the electrochemical method. From a practical standpoint the most important of these advantages are the following.

1. Absence of thermal gradients, which introduce variations in the physical properties of the liquid across the thickness of the boundary layer.
2. The experimental analysis can be extended to the region of relatively high Prandtl numbers, where the temperature dependence of the properties of the liquid becomes most important.
3. In contrast to methods based on dissolution of the wall followed by measurement of weight loss, the electrode surface remains unchanged throughout the experiment.
4. Local measurements of the rate of mass transfer can be attempted because the electrode is only a few microns long in the direction of the flow.

Recent work on the measurement of boundary layer friction[19-23] has convincingly demonstrated the power of the electrochemical method and highlighted its advantages over the more traditional thermo-anemometric method. Firstly, electrochemical friction transducers are practically free from thermal losses, which are very difficult to estimate in thermo-anemometric transducers (especially the thin-film variety). Secondly, the liquid flowing round the solid body can be used as the working electrolyte in the electrochemical method, whereas the thermo-anemometric method requires a different, often very reactive, liquid. Thirdly, and this is very important, the diffusion coefficient of solutes is often several orders of magnitude smaller than the thermal diffusivity coefficient, and therefore (other conditions being equal) the information on the hydrodynamic flow reaches the electrochemical transducer from liquid layers closer to the solid surface than in the thermo-anemometric method. This is the reason why the electrochemical method was chosen to solve a number of fundamental problems concerning the fine structure of the viscous sub-layer. On of these problems was to establish in a functional form the law governing the change in the effective turbulent transport coefficients near a solid wall.

Some entirely new methods of studying boundary layer transport processes in gas–liquid flows have been developed[24] on the principle of electrochemical measurements. The problem of modelling tubular heat exchangers in chemical reactors has been largely resolved by an electrochemical study[25] of the interaction between the surface diffusion layers of closely spaced horizontal cylinders with their axes parallel and in the same vertical plane. The electrochemical method has been used with success also in measurements of large-scale velocity and pressure pulsations in the volume of a turbulent flow[26] and in the boundary layer detachment region[27].

## IV. GENERAL THEORETICAL PROBLEMS

A large number of papers have been written on the theory of the electrochemical method of measuring rates of mass and momentum transfer[2,3,9-18,28-33]. Since the greatest theoretical and practical interest resides in the turbulent flow case we shall confine the discussion which follows to the present status of the theory of electrochemical transducers operated in the turbulent flow regime of the electrolyte solution.

### 1. Description of the Operation of Electrochemical Transducers in Terms of the Diffusional Boundary Layer Theory

The transducers best suited to the measurement of local characteristics of boundary layers have small dimensions in the direction of the mean flow. It becomes even more important to minimise the size of the transducer when we wish to measure the pulsation characteristics of the boundary layer, because in these measurements the sensitivity of the transducer decreases as its size increases (owing to the random changes in the magnitude of boundary layer friction along the transducer surface). An alternative explanation of the decrease in sensitivity with increase in size of the transducer is the averaging (over the transducer surface) of the current oscillations produced by various perturbations over distances smaller than the characteristic dimension (length) of the mass transfer region. For this reason the diffusion transducer is insensitive, in this region of geometrical dimensions,

to the fine structure of the spectrum of turbulent pulsations. We shall therefore discuss, in the first instance, only those transducers having sufficiently small dimensions in the direction of flow.

Consider an electrode of width $h$ and length $l$, integral with the surface exposed to the flow, and located in the region of uniform tangential stresses. We shall impose the condition $l \ll h$, so that end effects at right angles to the flow direction can be ignored. This condition is satisfied, for example, by a ring electrode mounted flush with the tube wall in the region of hydrodynamically stabilised flow. We shall assume that the liquid flowing past the transducer contains a uniformly distributed passive additive at concentration $c_0$ (i.e. an additive which does not affect the flow dynamics). Let the origin of the spatial co-ordinates be at the front edge of the transducer, with the $x$ axis along the direction of flow and the $y$ axis at right angles to the planar wall. The stationary diffusion equation for planar turbulent two-dimensional flow, which applies in the regions where the passive additive is neither being generated nor consumed, can be written

$$\bar{u}_x \frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial \bar{c}}{\partial x} - \overline{u_x'c'}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial \bar{c}}{\partial y} - \overline{u_y'c'}\right), \qquad (1)$$

where the primes denote the pulsations of the instantaneous values with respect to their mean values. This equation can be solved by a number of procedures, the simplest of which (proposed by Boussinesq [34]) assumes a linear relation between the turbulent flows $\overline{u_x'c'}$, $\overline{u_y'c'}$ and the gradient of the mean concentration of additive. In the general case of an anisotropic velocity field Boussinesq's hypothesis can be formulated as

$$\overline{u_x'c'} = -K_{xx}\frac{\partial \bar{c}}{\partial x} - K_{xy}\frac{\partial \bar{c}}{\partial y}, \quad \overline{u_y'c'} = -K_{yx}\frac{\partial \bar{c}}{\partial x} - K_{yy}\frac{\partial \bar{c}}{\partial y}, \qquad (2)$$

where the coefficients of the turbulent diffusion tensor ($K_{ij}$) are functions of the $x$ and $y$ co-ordinates. Most of the published theoretical work based on the hypothesis (2) assumes, often without justification, that the $x$ and $y$ axes are the main axes of the $K_{ij}$ tensor, i.e. that $K_{xy} = K_{yx} = 0$. Other supplementary conditions have also been postulated, for example $K_{xx} = 0$ or $K_{xx} = K_{yy}$. Some workers assume diagonality of the $K_{ij}$ tensor on the grounds that the directions of the $x$ and $y$ axes are defined by the same conditions as the hydrodynamically stabilised flow. None of these arguments is really strict [35]. We can only state that under stabilised flow conditions and near the walls, when the viscous flow stress $\tau_w$ does not vary in the direction of the flow, the components of the $K_{ij}$ tensor are independent of the longitudinal co-ordinate $x$, i.e. that $K_{ij} = K_{ij}(y)$.

At very large values of the Prandtl diffusion number (the usual condition for mass transfer in liquid drops) the main resistance to mass transfer is concentrated in a thin boundary layer within which the velocity distribution can be assumed to be linear in the transverse co-ordinate $y$:

$$\bar{u}_x(y) = \frac{u_*^2}{\nu} y. \qquad (3)$$

Here $u_*$ is the characteristic turbulent pulsation velocity, related to the frictional stress $\tau_w$ at the wall by the expression $u_* = (\tau_w/\rho)^{1/2}$ where $\rho$ is the density of the liquid and $\nu$ is the molecular kinematic viscosity. The components of the turbulent diffusion coefficient tensor in the boundary layer are given with sufficient precision by the first term of a Taylor series expansion in powers of $y$:

$$K_{ij} = \nu b_{ij}\left(\frac{yu_*}{\nu}\right)^{n_{ij}} = \nu b_{ij} y_+^{n_{ij}}.$$

An analysis of Eqn. (1) with the hypothesis (2) has shown [36] that at Prandtl numbers greatly in excess of unity the structure of the diffusion layer near the surface of the transducer is such that $K_{yy}$ is the only components of the $K_{ij}$ tensor making a significant contribution to the rate of mass transfer. Hence Eqn. (1) can be simplified, retaining only the component

$$K_{yy} = \nu b y_+^n, \qquad (4)$$

where the exponent $n$ is some effective value averaged over the thickness of the diffusion boundary layer, and in principle could be a function of the Prandtl number (note that for finite Prandtl numbers the expression of the $K_{yy}$ coefficient in a Taylor series will contain, in general, more than one power of the dimensionless distance $y_+$). The experimental determination of the numerical value of the parameter $n$ has been discussed several times in the literature [35-40], but there are still differences of opinion. The majority view is that the most probable range of $n$ values is $3 \leqslant n \leqslant 4$. Thus an electrochemical investigation aiming to determine [41-45] "the limiting damping law of the turbulence" gave $n \simeq 3$. Other workers [46,47] find that $n \simeq 4$.

The general boundary conditions needed to ensure a unique solution of Eqn. (1) assume a constant concentration of the passive additive in the region far removed from the transducer surface

$$\bar{c}(x, \infty) = c_0; \ \bar{c}(-\infty, y) = c_0$$

and they also assume a balance between the rate of the electrochemical reaction $k$ and the mass flow of ions $j_w$ to the surface of the planar diffusion transducer, determined by the rate of diffusion under conditions such that ionic migration under the influence of an electric field can be ignored:

$$D\frac{\partial \bar{c}}{\partial y}\bigg|_w = \begin{cases} 0 & \text{for } x < 0 \text{ and } x > l; \\ kF(c_w) & \text{for } 0 \leqslant x \leqslant l. \end{cases}$$

The form of the function $F(c_w)$ is determined by the kinetics of the surface reaction. We shall assume in what follows that this reaction is of the first order, i.e. that $F(c_w) = c_w$, where the subscript $w$ denotes conditions at the wall (i.e. for $y = 0$).

In the dimensionless variables of boundary layer theory

$$\vartheta = \frac{c_0 - \bar{c}}{c_0}, \ X = \frac{x}{l}, \ Y = \frac{y}{l}\left(\frac{u_*^2 l}{9Dvx}\right)^{1/3} = \frac{1}{\alpha}\frac{y}{l}$$

and introducing the above approximations Eqn. (1) becomes, for $\alpha \ll 1$,

$$(1 + \chi X^{n/3}Y^n)\frac{\partial^2\vartheta}{\partial Y^2} + 3Y^2\left(1 + \frac{\chi n}{3}X^{n/3}Y^{n-3}\right)\frac{\partial\vartheta}{\partial Y} - 9XY\frac{\partial\vartheta}{\partial X} = 0, \qquad (5)$$

where $\chi = b\mathrm{Pr}^{(3-n)/n}(9lu_*/\nu)^{1/3}$ is the dimensionless parameter of the problem. The boundary conditions in dimensionless variables are

$$\vartheta(-\infty, Y) = 0; \ \vartheta(X, \infty) = 0;$$
$$\frac{\partial\vartheta}{\partial Y}(X, 0) = \begin{cases} 0 & \text{for } X < 0 \text{ and } X > 1; \\ KX^{1/3}[\vartheta(X, 0) - 1] & \text{for } 0 \leqslant X \leqslant 1. \end{cases} \qquad (6)$$

Here the symbol $K = k(9l\nu/u_*^2 D)^{1/3}$ denotes the dimensionless rate constant of the electrochemical reaction. If this constant is formally allowed to approach infinity the last of the boundary conditions (6) becomes

$$\vartheta(0 \leqslant X \leqslant 1, \ 0) = 1, \qquad (7)$$

which corresponds to the limiting case of a fully polarised transducer. Kader and Dil'man [36] have obtained an analytic solution of Eqn. (5) for this case.

## 2. The Problem of Describing Small Transducers

Analysis of Eqn. (5) shows that the turbulent diffusion mechanism plays a negligibly small role if the longitudinal co-ordinate $x$ is small enough. This conclusion has a simple physical significance: the pulsations of the hydrodynamic and of the concentration field are quickly damped near the wall, and have no effect on the rate of mass transfer at the wall itself (i.e. within the thickness of the diffusional boundary layer). It is important in practice to estimate the length of the electrode for which the contribution of turbulent mass transfer in the viscous layer can be ignored (allowing, however, for the real velocity profile, which can be quite different from the purely laminar profile). An exact solution of this problem for arbitrary values of $n$ and $b$ has been obtained[36]. The critical transducer length $l_1$, up to which the effect of turbulent transfer can be ignored, is given by the expression

$$l_1 = \left[\frac{3r_*(2n+3)\,\Gamma(1/3)\,\Gamma(2n/3)}{bn\,\Gamma^2(n/3)\,\Gamma\left(\frac{n+1}{3}\right)}\right]^{n/3} \frac{\nu}{9u_*}\,\mathrm{Pr}^{\frac{n-3}{3}}, \qquad (8)$$

where $\Gamma(x)$ is a gamma-function, and the quantity $r_*$ denotes the precision (expressed as a percentage) of the experimental determination of the tangential stress at the wall.

Formula (8) becomes much simpler for $n = 3$, enabling the parameter $b$ to be evaluated from experimental results (a value of approximately $10^{-3}$ was obtained by Kader and Dil'man[36]):

$$l_1 = 30\frac{\nu r_*}{u_*}. \qquad (8a)$$

In order to arrive at an estimate of the order of magnitude of the critical length $l_1$ under practical conditions we shall consider a transducer mounted in the wall of a tube of diameter $d = 1$ cm. Assuming that the transducer can measure the tangential stress with a precision $r_* = 10\%$, the critical length $l_1$ calculated by formula (8a) will vary with the Reynolds number Re for the flow in the tube (Re = $Ud/\nu$, where $U$ is the mean velocity of the flow) over the following range

| $\mathrm{Re}\cdot 10^{-3}$ | 5 | 10 | 50 | 100 | 500 | 1000 |
|---|---|---|---|---|---|---|
| $l_1$, cm | 8.82 | 4.84 | 1.18 | 0.632 | 0.149 | 0.079 |

If the length of the electrode is less than $l_1$ there is a difficulty arising from the leading and the trailing edge of the transducer. In most of the papers quoted above the theory of diffusion transducers is developed in the boundary layer approximation, involving the assumption that the transducer is polarised over its entire length. It is well known, however, that the boundary layer approximation does not adequately describe the real distribution of the concentration near the edges of the transducer, i.e. in the regions of steeply changing wall conditions, where calculations based on this approximation can be seriously in error as a result of molecular diffusion in directions parallel to the wall. Thus the error becomes more significant with smaller transducers. Furthermore, since every point on the electrode surface is not equally accessible, and the reaction rate is finite, the concentration of reacting ions at the surface in the region of the leading edge must vary from its initial value to zero, i.e. some parts of the electrode are not polarised. Since the influence of the finite reaction rate is strong near both edges of the diffusion transducer, the two effects must be considered together.

However, all the work published so far deals with the two effects separately. Ling[48] has made a numerical analysis of the influence of edge effects in small, fully polarised transducers, while other workers[9,32] studied the concentration distribution along the surface of the transducer in the boundary layer approximation. The only fairly comprehensive numerical analysis of edge effects in systems designed for the measurement of stationary mass transfer and friction was published only recently[33]. On the other hand the effects are completely ignored in papers dealing with the sensitivity of electrochemical transducers to pulsations in the viscous sub-layer of the turbulent boundary layer[15,16,31,49].

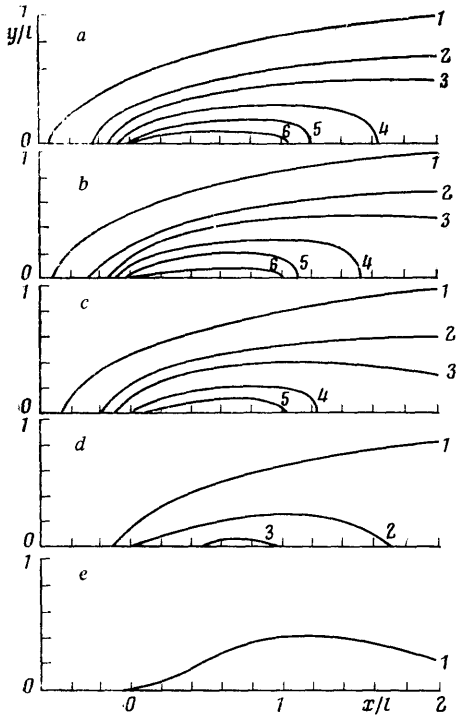



**Figure 3.** Concentration field above a thin-film diffusion transducer of dimensionless length $L = u_* l\sqrt{\mathrm{Pr}}/\nu = \sqrt{50}$ for different values of the dimensionless rate of electrochemical reaction $K_0$: *a*) $K_0 = \infty$, *b*) $K_0 = 10$, *c*) $K_0 = 1$, *d*) $K_0 = 0.1$, *e*) $K_0 = 0.01$; curves *1–6* correspond to $\theta$ values of 0.01, 0.1, 0.2, 0.4, 0.6, and 0.8 respectively.

Kader and Gukhman[33] solved the problem of mass transfer to the surface of an electrochemical transducer having a short length in the direction of the flow by using the average velocity profile of formula (3) and ignoring the influence of turbulent pulsations, but allowing for molecular diffusion in the longitudinal direction. Fig. 3, taken from that paper, shows the lines of equal concentration near the surface of diffusion transducers of equal length $l = (\nu/u_*)\,(50/\mathrm{Pr})^{1/2}$ for different values of the dimensionless complex parameter $K_0 = k\sqrt{\mathrm{Pr}}/u_*$ ($0.01 \leq K_0 < \infty$). The arbitrary edge of the diffusional boundary layer, corresponding to $\theta = 0.01$, is discussed in the same paper.

Longitudinal molecular diffusion results in a change in the concentration of reacting ions upstream from the

transducer. It is evident from the Figure that the diffusional boundary layer has a finite thickness at the leading edge of the electrode. However the influence of longitudinal molecular diffusion in this region becomes less marked as the parameter $K_0$ decreases. This effect stems from the peculiarities of the polarisation of thin-film diffusion transducers: the polarisation decreases as $K_0$ decreases, and for $K_0 = 0.01$ the arbitrary edge of the diffusional boundary layer ($\theta = 0.01$) coincides with the surface of the transducer. The surface concentration gradient is almost constant along the transducer under these conditions [33]. Calculation shows that even in small transducers operating under activation control the effect of longitudinal molecular diffusion is negligibly small.

An important characteristic of the efficiency of a thin-film diffusion transducer is the magnitude of the local diffusional flow at the leading edge ($x = 0$, $y = 0$). It can be shown [33] that this flow ($j_{wf}$) is given by the expression

$$j_{wf} = A\frac{u_* c_0}{\nu}\mathrm{Pr}^{-1/3}, \qquad (9)$$

where the coefficient $A$ is finite for all values of the transducer length†, and depends on the value of $K_0$. Numerical values of the $A$ coefficient for different characteristic values of $K_0$ are set out below:

| $K_0$ | 0.01 | 0.1 | 1.0 | 10 | $\infty$ |
|---|---|---|---|---|---|
| $A$ | 0.0099 | 0.091 | 0.575 | 1.65 | 2.40 |

### 3. Relative Role of Kinetic and Diffusion Effects for Transducers of Different Size

It follows from the above results that even for $K_0 = 10$ the transducer is not fully polarised ($\theta_W \neq 1$) over its entire length. The situation is illustrated in Fig. 4, which shows the distribution of the dimensionless surface concentration of diffusion transducers of different size ($5 \leq (u_* l\sqrt{\mathrm{Pr}}/\nu) \leq \sqrt{5000}$) for different reaction rates ($0.01 \leq K_0 < \infty$). It can be seen from the curves that the polarisation of the transducer increases with the length of the transducer and with $K_0$, in keeping with the expected decrease in the role of end effects with increase in the length of the transducer. The results of the analytic solution in the boundary layer approximation are also plotted in the Figure (broken lines). As expected, this solution gives a poor description of the real concentration field in the immediate vicinity of the leading and the trailing edge of the transducer, but it agrees very well with the numerical calculation over the central region. It follows from the general propositions of the boundary layer theory that the width of this region must increase with the dimensionless transducer length $L = u_* l\sqrt{\mathrm{Pr}}/\nu$. It is interesting to note that the direction of the difference between the analytic and the numerical solution (theoretical values of $\theta_W$ lower at the leading edge and higher at the trailing edge) suggests that the $\langle\theta_W\rangle$ values obtained by computer averaging over the length of the transducer for the boundary layer approximation should be fairly constant even for relatively short transducers. The present section is devoted to a discussion of these effects.

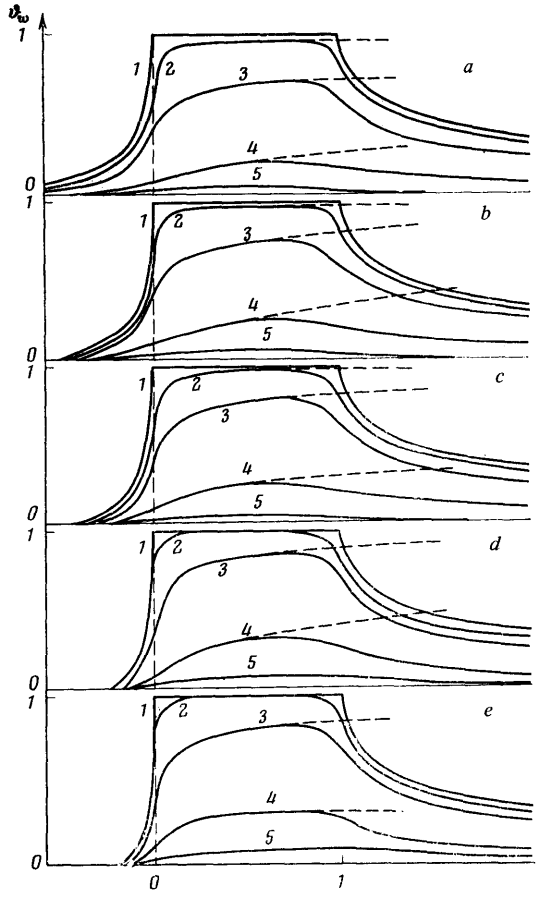



**Figure 4.** Concentration distribution on the surface of a thin-film diffusion transducer. The solid lines are given by the numerical solution, the broken lines by the analytic calculation in the boundary layer approximation: *a*) $L = 5$, *b*) $L = \sqrt{50}$, *c*) $L = 10$, *d*) $L = \sqrt{500}$, *e*) $L = \sqrt{5000}$; curves *1–5* correspond to values of the dimensionless rate $K_0$ of $\infty$, 10, 1, 0.1, and 0.01 respectively.

It follows from Eqn. (5) that the role of the edge effects may vary with $L$. Of course, for any value of $L$ there will always be values of $x$ so small that the product $\alpha^2\partial^2\theta/\partial x^2$ cannot be assumed to be small. Under these conditions the term $\partial^2\bar{c}/\partial x^2$ in Eqn. (1) cannot be ignored near the leading edge of the transducer, and the boundary layer approximation ($\partial^2\bar{c}/\partial x^2 = 0$) cannot be applied in this case. However, the fraction of the transducer surface for which this effect is appreciable decreases with increase of $L$.

†The conclusion from the exact solution of the diffusion problem (with allowance for longitudinal diffusion) that the diffusion flow is finite at the leading edge of the transducer is inconsistent with the results of later approximate calculations [134,135]. The contradiction probably arises from the assumption of a modified velocity profile in the latter work, corresponding to slipping of the liquid on the solid wall. However, even in the limit of a vanishingly small slip velocity the final analytic formula for the diffusional flow at the leading edge is incorrect, because at sufficiently small distances from the transducer surface the convective mass transfer due to slip dominates over the mass transfer associated with laminar flow in the viscous sub-layer.

Hence we may assume that for

$$\langle \alpha^2 \rangle = \int_0^1 \alpha^2(X)\,dX = \left(\frac{9}{L^2}\right)^{2/3} \int_0^1 X^{2/3} dX \ll 1$$

the influence of edge effects on the general mass flow in a thin-film diffusion transducer is negligible. Thus we can say that in a transducer of length

$$l \gg l_2 = 12\,\frac{\sqrt{\nu D}}{u_*} \qquad (10)$$

the analysis based on the boundary layer approximation is quite correct. We note that the exact result obtained by Ling[48] for the case of $k \to \infty$ agrees fairly well with the estimate of Eqn. (10).

In a similar way we can estimate the length $l_3$ for which the rate of the electrochemical reaction plays a significant role. We use the last of the boundary conditions given in Eqn. (6). The electrochemical transducer can be said to be fully polarised when

$$\langle KX^{1/3} \rangle = \frac{k}{u_*}(9\,L\,\mathrm{Pr}^{2/3})^{1/3} \int_0^1 X^{1/3} dX \gg 1,$$

i.e.

$$l_3 = 260\,\frac{u_*^2 D^2}{k^3 \nu}. \qquad (11)$$

The following interesting conclusions can be made from this estimate. As the frictional velocity increases, i.e. as the mean velocity of the flow passing the transducer increases, the length $l_3$ will vary if all other conditions remain the same. Depending on the value of the complex parameter $K_0$, this variation can be quite steep. If the constant $k$ for the electrochemical reaction is small, even relatively long transducers may not be polarised over their entire length for typical working values of the overvoltage.

## V. ELECTROCHEMICAL MODELLING OF MASS TRANSFER PROCESSES

Because of its many advantages, already mentioned, the electrochemical method has proved very successful in studies of mass transfer and phase exchange in solid–liquid systems. Initially the work was aimed at identifying improved solution compositions and the corresponding electrode reactions. It was usually carried out in measuring cells having well known hydrodynamic characteristics (rotating disk[50,51], rotating cylinder[52], flat plate[53], circular tube[54], and others). More latterly a very large number of publications on the electrochemical modelling of mass-transfer processes of practical interest has appeared in the literature (in particular, processes used in the chemical and petrochemicals industries). In many instances the experimental results have led to a broader and deeper physical understanding of the mass transfer mechanism, and have stimulated a great deal of theoretical work.

Both stationary and non-stationary methods have been used in electrochemical investigations of mass transfer. Since the two types of method have a number of individual features, we shall discuss them separately.

### 1. Stationary Methods

Electrochemical modelling has been used to study, with a precision unmatched by other methods, the mass recoil coefficients at the inlet of a circular tube as a function of length and of the Prandtl diffusion number[54–56]. By using thin annular electrodes these coefficients were measured at very small distances from the head of the mass transfer vessel (approximately one-thousandth of the radius of the tube). No previously known method could approach this level of precision.

Mass transfer in the gap between two rotating cylinders has been examined in detail[57–59]. The authors varied (over wide limits) the cell geometry and the rate of rotation of the cylinders, and they studied the influence of surface roughness on the rate of mass exchange between the phases. They were able to obtain quantitative empirical expressions describing not only the kinetics of stationary mass transfer, but also the conditions governing the hydrodynamic stability of the flow.

Interesting and unexpected results were obtained when electrochemical modelling was applied to rough surfaces. It was shown[60] that not only does the rate of mass transfer (relative to that in a smooth-walled system) not increase with flow velocity but it actually decreases, and may fall below unity[61]. These results, which were contrary to all expectations, were subsequently confirmed in more accurate experiments[45]. A theoretical explanation has recently been put forward, and generalised to a full quantitative theory of the phenomenon[62,63].

Very many electrochemical investigations using a rotating disk have been reported[42,64–72]. Some of them[64–67], confined to the purely laminar flow regime at the surface of the disk, were aimed primarily at measuring the diffusion coefficients of ions in electrolyte solutions. On the other hand, studies relying on turbulent mixing have dealt with the damping law of the turbulence in the immediate vicinity of the wall[42,68], with the influence of surface roughness on the rate of mass transfer[69,70], and with the local rates of mass transfer from small regions of various shapes on the surface of the disk[71,72].

Interesting results have been reported also on free convection near vertical and inclined plates with a smooth or a rough surface[73,74], near cylindrical objects under conditions when the curvature of the surface can influence the rate of mass transfer in the turbulent regime of free convection[75], and also on ionic mass transfer under free convection accompanied by heat transfer[76].

The stationary method has been used with success in system involving transverse flows over cylinders[3,77,78], in measurements of instantaneous local rates of mass transfer between an oscillating liquid film and a solid wall with a direct flow or a counter-flow of gas[79], and in studies of mass transfer in the turbulent flow beyond the point of greatest discontinuity in an annular tube[80]. Lastly, the stationary electrochemical method has been applied in studies of mass transfer in liquids have unusual properties[81].

### 2. Non-stationary Methods

It has been shown theoretically[82] that the stabilisation time of the concentration boundary layer formed at the surface of a flat plate with zero angle of attack by a sudden change in surface concentration is given approximately by

$$t_c \simeq \mathrm{Pr}^{1/3} x/U$$

and under normal conditions is measured in milliseconds. On the other hand the duration of the transient electrical process corresponds to the time constant $t_{el}$ of the circuit

consisting of the double layer capacitance $C_d$ and the ohmic resistance of the electrolyte $R_{el}$ [83]:

$$t_{el} \simeq R_{el} C_d.$$

In most cases of practical interest the time $t_{el}$ is of the order of a microsecond [84]. Hence we may assume that the diffusion-controlled reaction regime is established almost instantaneously. These considerations provide the basic concepts underlying the electrochemical modelling of non-stationary mass transfer processes: the non-stationary situation is modelled either by a sharp change in electrode potential or by a sharp change in hydrodynamic conditions.

The theoretical foundations of modelling non-stationary processes were laid by Lighthill [85], who studied the effect of small periodic perturbations in the main hydrodynamic flow on the surface friction and heat exchange coefficients at the liquid–solid interface. Others [86-89] developed theoretical analyses of heat and mass transfer processes from simple geometrical bodies (sphere and cylinder) oscillating in a liquid with an amplitude small in comparison with the characteristic dimensions of the system. The result of this work was a series of quantitative relationships defining the sensitivity of the electrode to mechanical oscillations in the measuring system. Mitchell and Hanratty [15] carried out numerical calculations of non-stationary models of mass and momentum transfer processes near walls exposed to turbulent flows, and obtained a solution of the convective diffusion equation at the wall of an annular tube in the presence of periodic perturbations of the pressure gradient. A theoretical discussion [90,91] of the convective diffusion of a passive additive in an arbitrary velocity field opens the possibility of measuring large-scale velocity pulsations by a correlation method. Lopatin and coworkers [92] have looked for an analytic form of the function describing the response of the surface of a rotating disk electrode to periodic perturbations of the concentration of reacting ions in the bulk of the solution.

Among the experimental studies of non-stationary mass transfer we should mention, first of all, a systematic investigation of the development of a diffusion boundary layer at a metal plate exposed to a stationary flow of electrolyte solution at different angles of attack [93-95], and also some work on mass transfer to a transversely located cylinder [96,97] and to the wall of an annular tube [98]. Mass transfer in non-stationary flows was studied experimentally near the surface of a vibrating disk [99], and also in the case of pulsating flow in a tube [100,101]. Much of this work was stimulated by the needs of a new and rapidly expanding branch of technology: chemotronic instrumentation, i.e. the construction of apparatus for the translation of non-electrical quantities into electrochemical signals [102-105]. Another important application of non-stationary methods is in the development of electro-diffusion anemometers, whose operating principle has been discussed in detail [28-32,49].

## VI. ELECTROCHEMICAL METHODS OF STUDYING HYDRODYNAMIC PROBLEMS

Accurate methods of determining experimentally the hydrodynamic structure of various flow configurations (mean velocity and tangential stress profiles, fluctuation parameters associated with turbulence, etc.) are needed to provide objective information on the mechanism of turbulent transfer near a solid surface, and thus to test the many hypotheses to be found in the literature on the fine structure of boundary layers. They are also needed for reliable engineering calculations of the hydraulic parameters of turbulent flows in industrial mass exchange apparatus, chemical reactors, thermophysical plant, and other systems.

As pointed out above, the electrochemical method offers very attractive possibilities in all these areas. Its ability to measure with great precision both the averaged and the spectral characteristics of flow near the walls of channels and of submerged bodies has been repeatedly demonstrated. With gas–liquid flows within channels the electrochemical principle offers the only possibility of measuring the true tangential stress at the wall [32,106]: all other known methods (such as the pressure drop method, the floating element method, the Stanton tube methods, etc.) are either totally inapplicable or insufficiently accurate. Electro-diffusion transducers have been used for direct measurements of surface friction and its pulsations for different flow regimes of two-phase media in vertical and horizontal tubes, for accurately establishing "regime charts" of the parameters governing the various flow regimes of two-phase mixtures, and in studies of the hydrodynamic analogy between bubbling and ebullition under forced flow conditions [24,32].

The spherical electrochemical transducer [107,108] has been found very effective for the measurement of velocity profiles in laminar flows. It consists of a spherical platinum electrode 0.5 to 1.0 mm in diameter, located in the flow region of interest and operated under conditions of concentration polarisation. Concentration and temperature errors are avoided by inserting into the flow an auxiliary micro-electrode whose output is independent of the flow rate and is determined by the concentration of the depolariser (oxygen) and by temperature. This transducer can measure local flow rates with a spatial resolution limited by the width of the disturbed hydrodynamic region. For $Re < 1$ this region extends over approximately six electrode radii on either side of the transducer. At higher Reynolds numbers the width of the disturbed region decreases.

Significant advances have been made in the design and practical application of electrochemical surface friction transducers. Some theoretical aspects of the operation of these transducers are discussed in detail in the following sections.

### 1. Measurement of Mean Tangential Stresses

For a fully polarised transducer operating under laminar diffusion layer conditions (when the ionic mass transfer is unaffected by turbulent pulsations in velocity and pressure) Eqn. (5) with the boundary conditions (6) takes the form of the well-known Leveque problem [109]

$$\frac{d^2\vartheta}{dY^2} + 3Y^2 \frac{d\vartheta}{dY} = 0; \quad \vartheta(\infty) = 0; \quad \vartheta(0) = 1. \tag{12}$$

The solution of this problem, in the form

$$\vartheta(Y) = 1 - \frac{3}{\Gamma(1/3)} \int_0^Y \exp(-x^3)\, dx, \tag{13}$$

allows us to establish the relationship between the ionic mass flow $j_w$ to the electrode, proportional to the electric current in the measuring cell, and the tangential stress $\tau_w$ at the wall:

$$j_w = 0.807\, c_0 \left(\frac{D^2 \tau_w}{\rho \nu l}\right)^{1/3}. \tag{14}$$

We should remember that the length $l$ of the transducer must be less than the quantity $l_1$ defined by Eqn. (8). (This equation imposes a limit on the range of dimensions for which the contribution of the turbulent mass transfer mechanism can be ignored.) At the same time, the length of the transducer should be large enough to justify neglecting edge effects, with the assumption that the transducer surface is fully polarised. According to the estimates made above, the condition is $l \geqslant \max(l_2, l_3)$, where $l_2$ and $l_3$ are the characteristic lengths defined by Eqns. (10) and (11).

The experimental conditions for the measurement of the mean wall friction, and the constructional details of the measuring cells, have been discussed by several workers [13-15,30,110-115]. These papers describe measurements of the tangential stress at the wall of a cylindrical tube, of a plane-parallel channel, and of a two-dimensional cavity in liquid and gas–liquid flows, and they deal with the interaction between a liquid (laminar, or turbulent) and a solid wall under thin-layer flow conditions. The electrochemical method has been used to study in detail the stabilisation of local friction in the initial portion of a plane-parallel channel [116], in flows under a longitudinal pressure gradient [117], and in flows involving complex vortex structures [30].

The correlation method of measuring the averaged characteristics of turbulent flows in boundary layers [30] has great conceptual and practical interest. One variant of this method involves monitoring the correlation between the random pulsations of the flows on two planar electrodes mounted on the experimental plate, mutually parallel and with their edges at right angles to the flow direction. The measured correlation function $R$ is related to the pulsations of the currents at the two electrodes ($i_1$ and $i_2$) by the expression

$$R(|x_1 - x_2|, \tau) = \frac{1}{T}\int_0^T i_1(x_1, t)\, i_2(x_2, t - \tau)\, \mathrm{d}t, \qquad (15)$$

where $\tau$ is the variable time-lag of the current $i_2$ with respect to $i_1$, $T$ is the measurement time ($T \gg \tau$), and $x_1$ and $x_2$ are the co-ordinates of the electrodes (the linear dimensions of the electrodes are assumed small in comparison with the distance $l = x_1 - x_2$). The function $R$ goes through a maximum at $\tau = \tau_m$, given by $\tau_m = l/V$ where $V$ is the mean velocity of the turbulent vortices in the disturbed region of the diffusion boundary layers at the electrodes. In this way we can measure the characteristic velocity $V$ of the turbulent vortices near the wall by noting the time $\tau_m$.

The correlation method can be used also to measure the tangential stresses in a laminar flow by introducing concentration markers from a third, auxiliary electrode a short distance in front of the first electrode.

The most characteristic feature of the correlation method is the lack of dependence of the measurement error on the diffuseness of the concentration wave in the region of the two electrodes, and on the presence of obstructions.

## 2. Measurement of the Spectral Characteristics of Wall Friction

The turbulent pulsations of the surface friction can be quantitatively characterised by the mean-square fluctuation of the friction $\overline{(\Delta\tau_W)^2}$, which is related to the distribution function of the spectral density $\epsilon_\tau(\omega)$ by the expression [118]

$$\overline{(\Delta\tau_w)^2} = \int_0^\infty \varepsilon_\tau(\omega)\, \mathrm{d}\omega, \qquad (16)$$

where the integration is carried out over the whole range of pulsation frequencies $\omega$. The spectral density function describing the pulsations of electric current $\epsilon_i(\omega)$ can be determined by analogy with the function $\epsilon_\tau(\omega)$. The functions $\epsilon_\tau(\omega)$ and $\epsilon_i(\omega)$ are interrelated by the expression

$$\varepsilon_i(\omega) = |\xi(i\omega)|^2 \varepsilon_\tau(\omega), \qquad (17)$$

where $\xi(i\omega)$ is termed the response function of the diffusion layer to harmonic pulsations of the velocity of the liquid with frequency $\omega$ (the symbol $i$ denoting an imaginary quantity). If the time-average frictional stress at the wall is termed $\overline{\tau_W}$, we can obtain the following relationship between the mean square frictional stress fluctuation $\overline{(\Delta\tau_W)^2}$ and the mean square total current $\overline{(\Delta I)^2}$ by using expressions (16) and (17):

$$\frac{\sqrt{\overline{(\Delta\tau_w)^2}}}{\overline{\tau_w}} = \frac{\sqrt{\overline{(\Delta I)^2}}}{\overline{I}} \left(\int_0^\infty \frac{\varepsilon_i(\omega)\, \mathrm{d}\omega}{|\xi(i\omega)|^2}\right)^{1/2}, \qquad (18)$$

where $\overline{I}$ is the time-average current. In the case of a rectangular electrode of area $S$ and length $l$ the mean current can be expressed in terms of the mass flow of ions, given by formula (14), by introducing the simple relationship $\overline{I} = mFSj_W$ where $m$ is the number of electrons transferred across the metal–solution interface by the elementary electrochemical reaction and $F$ is the Faraday.

It follows from Eqns. (17) and (18) that the spectral and the averaged characteristics of the pulsation field of the tangential stresses can be determined simply from a knowledge of the response function of the diffusion layer $\xi(i\omega)$. The latter can be evaluated, in principle, by solving the equation for a non-stationary boundary diffusion layer with a velocity profile given by the first non-vanishing term of the expansion in powers of the distance from the wall:

$$u_x = \frac{\overline{\tau}_w y}{\rho\nu}(1 + \lambda f(t)), \quad u_y = 0, \qquad (19)$$

where $f(t)$ is a harmonic function of time and $\lambda$ is the dimensionless amplitude of the pulsating velocity field.

An analysis of the solution of the non-stationary convective diffusion equation in the velocity field given by formula (19) with $f(t) = \exp(i\omega t)$ has shown [85] that the response function $\xi(i\omega)$ can be expressed as follows to a second-order approximation in the terms of the dimensionless amplitude $\lambda$:

$$\xi(i\omega) = 1 + \lambda\xi_{1,1}e^{i\omega t} + \frac{\lambda^2}{2}(\xi_{2,0} + \xi_{2,2}e^{2i\omega t}) + 0(\lambda^3), \qquad (20)$$

where $\xi_{1,1}$, $\xi_{2,0}$, and $\xi_{2,2}$ are functions of the longitudinal co-ordinate $x$.

Several workers [15,30,119,120] have tried to calculate the functions $\xi_{1,1}$, $\xi_{2,0}$, and $\xi_{2,2}$ by introducing various simplifying assumptions. Analytic expressions were obtained for the function $\xi_{1,1}(x)$ with small or large values of the parameter $\epsilon = (\rho\nu l\omega^{3/2}/\tau_W D^{1/2})^{2/3}$. In physical terms, this parameter denotes the ratio of the squares of the thickness of the stationary diffusion boundary layer (in the absence of velocity pulsations) and the periodic diffusion boundary layer [30,120]. The contribution from second-order amplitude terms has also been estimated, and it was shown that both high-frequency and low-frequency pulsations can lower the time-averaged and the area-averaged mass transfer coefficient [119,120].

Methods of determining experimentally the pulsation characteristics of the turbulent velocity field in boundary layers close to the wall have been developed from the published analytic expressions for the response function [30].

An experimentally simple but effective method of measuring surface friction is based on non-stationary pulse measurements [121]. The method does not differ in principle from the method shown in Fig. 2. A pulse of electrically active material is injected into the hydrodynamic flow by an electrochemical reaction at the upstream "marker" electrode *1* (see Fig. 2). This pulse is carried by the flow to the measuring electrode *2* (arbitrarily called the "counting" or indicator electrode). A definite time elapses between the application of the pulse at the marker electrode and its arrival at the counting electrode. This time (called the time-lag $t_l$) depends on the hydrodynamic regime and can be used as a measure of its intensity.

The time-lag can be evaluated from the following considerations. The total transfer time includes a term for the diffusion of the electrically active material to some distance $y$ at right angles to the flow, and a term for the hydrodynamic transport to the indicator electrode. The diffusion time includes diffusion from the marker electrode and diffusion to the counting electrode. To the accuracy of the numerical factor of the diffusion time we can write

$$t_{diff} \simeq \frac{y^2}{D}. \tag{21}$$

The hydrodynamic time is given by the expression

$$t_{hyd} \simeq \frac{\rho v x}{\tau_w y}, \tag{22}$$

where $x$ is the distance between the marker and the counting electrode. Thus the total transfer time is

$$t_{tot} \simeq \frac{y^2}{D} + \frac{\rho v x}{\tau_w y}. \tag{23}$$

It follows from Eqn. (23) that we can define a distance $y_{min}$ corresponding to the minimum transfer time. Evidently, the smallest transfer time is equal to the time-lag. Hence we conclude that the thickness of the diffusion layer within which the electrically active material is transported from one electrode to the other is given (to the nearest order of magnitude) by the expression

$$y_{min} \simeq \left(\frac{\rho v x D}{\tau_w}\right)^{1/3}, \tag{24}$$

i.e. it is equal to the thickness of the stationary diffusion layer. Hence the time-lag is of the same order of magnitude as the relaxation time of the diffusion layer:

$$t_l \simeq \left(\frac{\rho v x}{D^{1/2}\tau_w}\right)^{2/3}. \tag{25}$$

It follows that the time-lag is inversely proportional to the tangential frictional stress to the power 2/3. This analysis (which ignores the finite size of the electrodes themselves) provides a numerical value of the multiplier needed in Eqn. (25): a recent calculation [120] gives

$$t_l = 2\left(\frac{\rho v x}{D^{1/2}\tau_w}\right)^{2/3}. \tag{26}$$

The frequency method [121] is closely related to the pulse-time method. If the electrodes *1* and *2* are included in the negative feedback circuit of an amplifier, undamped oscillations will occur at some frequency. The oscillation condition is a phase shift of 180° between the signals at the marker and the counting electrode. Using Eqn. (26), the frequency of the resulting oscillations can be expressed as

$$f = \frac{1}{2t_l} = \frac{1}{4}\left(\frac{D^{1/2}\tau_w}{\rho v x}\right)^{2/3}. \tag{27}$$

Thus the frequency of the oscillations is directly proportional to the tangential stress arising from viscous friction to the power 2/3.

The analysis applies also to a turbulent boundary layer if the diffusional transport in the normal direction takes place within the thickness of the laminar diffusion layer. Since the thickness of the diffusion layer increases only as far as the edge of the indicator electrode, the permissible size $x$ of the electrode system [see formula (8)] should include the length of the marker electrode and the length of the inter-electrode gap. The length of the indicator electrode should have only a second-order effect on the sensitivity of the electrochemical measuring system.

Since the frequency of the electrical oscillations is linearly related to the tangential frictional stress to the power 2/3, the sensitivity $\eta$ of the electrochemical transducer can be conveniently defined as

$$\eta_{2/3} = f\bar{\tau}_w^{-2/3} = \frac{D^{1/3}}{4}(\rho v x)^{-2/3}, \tag{28}$$

where the subscript 2/3 indicates non-linearity of the transformation.

A very interesting situation arises for large values of the tangential stress, when the thickness of the turbulent diffusion layer becomes less than the thickness of the laminar diffusion layer. Whereas in the case of a laminar diffusion layer the time-lag of the pulse includes the diffusion time of the electrically active material in the normal direction and the time for hydrodynamic transport in the tangential direction, under the conditions of a turbulent diffusion layer the only slow transfer step is the transport through the turbulent diffusion layer. The electrically active material which has passed through the turbulent diffusion layer is rapidly carried through the required distance in the tangential direction. Leaving aside the problem of the sensitivity which the indicator electrode must have in order to detect the concentration pulse, we can state that undamped oscillations will be generated in a turbulent diffusion layer and that their frequency will be of the same order as the relaxation frequency of the turbulent diffusion layer.

Assuming an effective exponent ($n$) of 4 for the damping law of the turbulent pulsations near the solid wall, given by Eqn. (4), we can apply the expression $f \simeq D\delta_{hyd}^{-2}$ and estimate the frequency of the resulting oscillations as

$$f \simeq \frac{\bar{\tau}_w}{\rho v}\mathrm{Pr}^{-1/2}. \tag{29}$$

The frequency of the oscillations for a predominantly turbulent diffusion layer is proportional to the first power of the tangential frictional stress and is independent of the inter-electrode distance over a wide range.

According to Eqn. (29) we can conveniently define the sensitivity of the transducer as

$$\eta_1 = f/\bar{\tau}_w = D^{1/2}/\rho v^{1/2}, \tag{30}$$

The subscript 1 denotes linearity of the transformation.

The electrochemical frequency method of measuring friction was tested experimentally using a model of the electrochemical tangential stress transducer [121] made of electrically insulating material. The electrode system was mounted flush with the surface exposed to the liquid flow, and consisted of three parallel linear electrodes made of platinum and oriented at right angles to the flow direction. The electrodes were connected in the following sequence along the flow: marker electrode, counting electrode, and common electrode. Sea-water was used as the electrolyte. The application of a positive potential to the

marker electrode induced an electrochemical reaction at the electrode surface, causing oxidation of chloride ions to chlorine atoms. The counting electrode was connected to a constant negative polarity of sufficient magnitude to draw the limiting current of the chlorine–chloride redox system. The amplifier input was connected to the counting circuit, and the output to the marker circuit. Self-oscillations were produced at some definite ratios of the current in the marker circuit and in the counting circuit. The phase-shift angle between the marker current and the counting current, and hence the self-oscillation frequency, is a function of the tangential frictional stress.

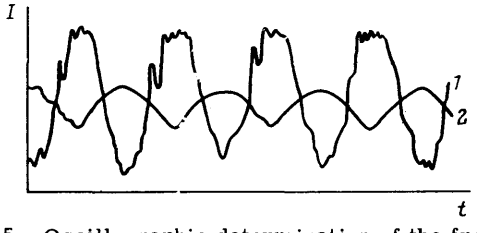



**Figure 5.** Oscillographic determination of the frequency of the electrical signals generated in experiments on the electrochemical measurement of tangential stress: *1*) marker current , *2*) counting current.

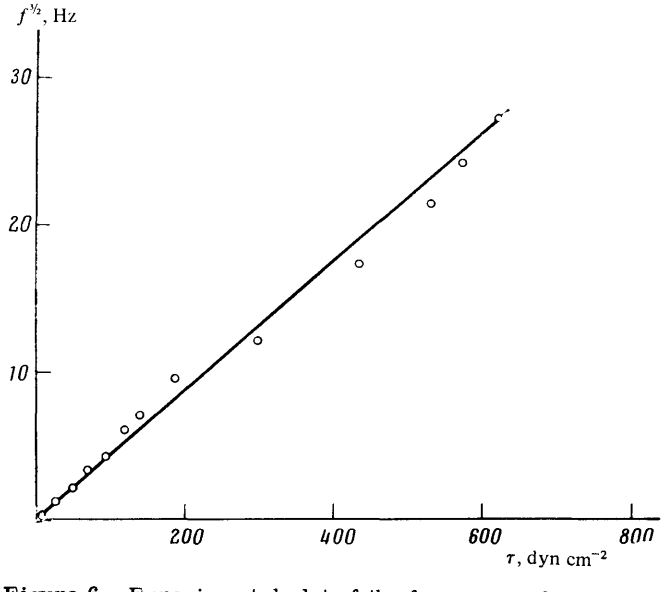



**Figure 6.** Experimental plot of the frequency of generated oscillations against the tangential stress at the solid wall ($f^{3/2}$ against $\tau$).

The experimental results are summarised in Figs. 5 and 6. The generation frequency was measured oscillographically (a typical trace is shown in Fig. 5). Fig. 6 shows an experimental plot of the generation frequency against the tangential frictional stress for a laminar flow regime. It can be seen that the power law of the experimental plot is close to the theoretical value.

Electrochemical transducers for the measurement of local velocity distributions in a flow have been widely used in recent years. These devices (wedge-shaped, spherical, or circular) are positioned in the flow of electrolyte at right angles to the flow, and they do not differ in principle from the wall-mounted electrodes described above.

## VII. STUDY OF THE STRUCTURE OF TURBULENT FLOW

The electrochemical method can be used to investigate the mechanism of momentum and mass transfer in liquid layers a few tens of microns thick. Hence it offers a unique and most effective means of probing the fine structure of the turbulence in the viscous sub-layer of a turbulent boundary layer. We have already referred to the work[41-44] on the limiting damping law of the turbulence at a solid wall. The structure of the turbulence has been investigated also by other workers[13-18,38,122-124], who studied vortex configurations, the rate of propagation of vortices by convection in the flow, and the microscopic and macroscopic features of turbulence.

Improved modifications of the electrochemical method are currently being developed for studying the structure of hydrodynamic flows and for measuring average and local rates of mass transfer[125]. One of these modifications relies on electrochemiluminescence, whose intensity is proportional to the local rate of mass transfer. Interesting results can be obtained by exploiting the colour change of some electrolytes under the influence of local changes of pH. A procedure for visually observing and studying velocity fields is based on this phenomenon.

## VIII. SOME PRACTICAL PROBLEMS

In our opinion, the most important scientific and engineering problems still to be solved in order to ensure wider practical exploitation of electrochemical modelling are the following: 1) the choice of electrochemical systems with the required physical and transport properties; 2) the theoretical understanding and practical control of blocking effects at the transducer surface during operation, and of transducer activation; 3) a more detailed study of correlation and other measurements using transducers of very small dimensions (in particular, for the measurement of transverse velocity pulsations); 4) an appreciation of the role of turbulence on the response of physically large transducers. Some of these problems have been discussed repeatedly in the literature, and have been the object of special investigations. For example, Eisenberg and coworkers[52] have discussed the choice of the best electrolytes and electrode reactions for modelling mass transfer. No less important is the problem of transducer blocking, which we shall briefly review in the following paragraphs.

A common problem in electrochemical measurements extending over long periods of time is the possible contamination of the electrode surface (e.g. by adsorbed surface-active materials, insoluble products of the electrode reaction, oxide films, evolved gas bubbles, etc.). These contaminants can inhibit the access of the reacting species to the transducer surface, and thus lower the rate constant of the electrochemical indicator reaction. The parasitic resistance experienced by the ionic mass transport as a result of the presence of contaminating surface layers adds

to the difficulty of interpreting the electrochemical mass transport data and introduces a need for empirical correction factors. Partial surface blocking is the most likely explanation of the substantial differences (20–30%) between measurements of stabilised electrochemical mass transfer obtained by different methods under identical hydrodynamic conditions (see, for example, Refs. 54 and 55).

Since it is impossible in practice to achieve complete control over the surface conditions of the transducer, especially in large-scale apparatus containing large volumes of electrolyte, we must continue to search for theoretical methods of assessing (within the limits imposed by the unavoidable assumptions) the effect of surface blocking on the results of electrochemical measurements.

The methods used to describe convective heat and mass transfer processes in systems with non-uniform surface activity are highly relevant to our problem. One of the simplest yet fairly typical models of a heterogeneous surface consists of a rotating disk with one or more annular active regions isolated from the other regions by the disk[126,127]. Another typical model consists of a flat plate with alternating active and "lacquered" parallel bands at right angles to the direction of the flow[6,128]. The effect of surface contamination on the efficiency of electrochemical diffusion transducers can also be described in terms of a model assuming a continuous variation in activity along the phase boundary[33,129–131]. Kader and Gukhman[33] allowed for partial blocking of the transducer surface by assuming a thin, uniform layer offering a constant resistance to the ionic mass transfer. The mass flow of reacting ions through this layer was assumed proportional to the difference in concentration of the ions on the two sides of the layer. In this way the blocking effect could be allowed for by replacing (in the boundary condition) the true rate of the electrochemical reaction by some arbitrary quantity linearly related to the surface concentration of reactant.

The parameters of the model can often be optimised by comparing the results of model calculations with experimental data. However it is far preferable (though not always possible in practice) to seek information on the distribution of the blocking impurities on the electrode surface. If this information can be obtained the apparent rate of the electrochemical mass transfer process can be calculated, in principle, either analytically or by numerical methods. Approximate methods of calculating the rate of mass transport to isolated active regions of arbitrary shape on the surface of a rotating disk have very recently been proposed, assuming a laminar flow regime[132,133].

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We have attempted a general review of the theoretical foundations, practical applications, prospects, and outstanding problems of the electrochemical method of studying and modelling transport processes in liquids. The method is relatively new, but its effectiveness and generality have already been amply demonstrated in practice. The large effort currently being devoted by various research teams to further developments and improvements of the electrochemical method justifies the belief that many fundamental problems in the theory and practice of mass transfer and inter-phase exchange will be solved with the help of this method.

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