reported slopes of the order of 60–70 mV on Au, Cu, and Co anodes, but an unambiguous discussion of these results is not possible as yet. Bardina[39] has obtained some interesting results in our laboratory on the anodic oxidation of high-temperature pyrolytic carbon below the equilibrium oxygen potential. We believe that these results can be most satisfactorily explained in terms of barrierless electrochemical desorption of CO_2 accompanying the discharge of OH^- ions.

A slope of ~ 60 mV has been frequently observed in the anodic evolution of nitrogen from azide solutions on anodes of different materials[40-42]. The variation of potential with azide concentration[40,41] corresponds exactly with the requirements of barrierless discharge (or electrochemical desorption). However, another explanation is possible, based on the shape of the adsorption isotherm of nitrogen[42]. A choice between these possibilities must await further experimental work.

In conclusion, we can state that the existence of barrierless discharge in the evolution of hydrogen on mercury is a firmly established fact. A barrierless process offers the most plausible explanation of the features of hydrogen evolution on silver and chlorine evolution on graphite: we may hope that current investigations will finally resolve this problem. Furthermore, there are numerous data which justify the belief that many other electrode reactions can occur by the barrierless mechanism.

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THEORY OF THE MACROSCOPIC KINETICS OF HETEROGENEOUS AND HOMOGENEOUS-HETEROGENEOUS SYSTEMS

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1. PRESENT STATE OF DEVELOPMENT OF MACROKINETICS

The term macroscopic kinetics usually denotes the kinetics of chemical changes in real systems in which the reaction rate is affected by mass-transfer and heat-transfer processes. Transfer processes take the form of molecular diffusion and thermal conduction, on the one hand, and of convective transfer phenomena, on the other hand. In the latter, substance (mass or energy) is transferred by the macroscopic motion of the medium.

Mass-transfer processes are especially important in heterogeneous chemical changes. It is often found that in heterogeneous changes the overall rate of the reaction is determined by the rate of access of the reactants to the reaction surface or by the rate of removal of the reaction products from the surface. In this case we say that the kinetics of the heterogeneous reaction are diffusion-controlled. Diffusional kinetics are most often rate-determining in fast heterogeneous reactions.

In processes attended by large absorption or evolution of heat the overall kinetics are determined by heat transfer. To simplify the terminology, we shall combine mass--transfer and heat-transfer processes under the term "transport phenomena", and we shall use the term macrokinetics to describe the kinetics of a reaction involving complicating transport phenomena.

To the chemist the supply or removal of reagents or heat to or from reaction surfaces, vessel walls, etc., is of little interest, and is merely an obstacle to an understanding of the true reaction mechanism. To the technologist these processes are the main barrier preventing the achievement of the optimum reaction conditions. This is why the mechanism of mass- and heat-transfer processes has long been ignored by chemists and technologists alike, who have confined their attention to ways of eliminating diffusional and thermal limitations. It soon became apparent that adequate convection of the liquid or gaseous medium was essential for this purpose. Hence, the problems of macrokinetics became tightly bound up with problems of hydrodynamics.

We can identify three stages in the development of the macroscopic kinetics of chemical reactions. The first goes back to the turn of the century, when the basic qualitative ideas underlying the transport of reacting species and of heat in reaction vessels and in mass-exchange apparatus were formulated. Nernst's hypothesis of the diffusion layer, Langmuir's film theory, etc., relate to this period.

In the 1930's to 1950's many workers (mostly chemical technologists and heat engineers) were forced to study transport phenomena in greater detail, because of the developments in the design of reactors and mass-exchange apparatus. Transport equations applicable to moving media were formulated. Since these could not be solved exactly, the methods of group similarity theory were applied with success to the description of mass and heat transport processes.

The development of the basic (distinguishing) similarity criteria and the numerical treatment of experimental results constitute the second stage of the development of macroscopic kinetics. This period is characterised by a large number of experimental studies. In some cases, a practical description of the transport phenomena in macrokinetics was achieved by establishing the numerical relationships.

However, it became clear in recent years that this partial description was inadequate and not always satisfactory. Furthermore, in many cases it was quite impossible to base a model on the equality of distinguishing criteria. This is particularly true of models of chemical reactors, in which the various criteria are often mutually incompatible.

With heterogeneous reactions, whose rates can vary over fairly wide limits, it is easily possible to cover the whole range of reaction rates (from the activation-controlled to the transport-controlled region) under constant conditions of stirring.

This case is most commonly met in electrochemistry. It is easy to vary the rate of an electronic reaction over quite wide limits by controlling the potential difference applied to an electrochemical cell.

It is usually found that the current–voltage characteristic has the form of a rising curve with a plateau, indicating that the rate of the process is independent of the applied e.m.f. Since the rate of the electrode reaction is essentially a function of the e.m.f., it follows that in the plateau region the process is controlled by mass transfer: the supply of ions to the electrode surface. This phenomenon has been called concentration polarisation.

A. N. Frumkin laid the foundations of the quantitative theory of concentration polarisation about 20 years ago[1,2]. A few years earlier, the quantitative theory of combustion processes in gases had begun to be developed intensively[3,4]. Lastly, the quantitative study of heat-transfer processes belongs to the same period[5]. The achievement of fast reactions and the enhancement of mass-transfer and heat--transfer processes in chemical engineering urgently need a formulation of the quantitative laws of macrokinetics, applicable to the complicated conditions which exist in chemical reactors and in mass-exchange apparatus. For this reason, disconnected investigations in these fields have begun to merge into a general theory of macrokinetics during the past ten years.

The third stage in the development of macroscopic kinetics is intimately concerned with the quantitative description of transport processes in moving media under conditions approaching those obtaining under realistic working conditions in chemical plant.

The mathematical calculation (or quantitative description) of the macroscopic kinetics under complicated conditions was made possible by two circumstances:

1. The study of the hydrodynamic, physicochemical, and kinetic processes which together characterise chemical change in real systems.

Important theoretical and experimental data have been obtained in recent years on the mechanism of convective mass and heat transfer. These apply to laminar and to turbulent flow, in liquids and in gases, at phase boundaries, under various geometries, and under stationary and non-stationary conditions.

2. The general application to the solution of complicated problems of modern computational methods, relying on the use of high-speed computers.

Studies of macroscopic kinetics can be classified into three basic stages: (a) the study of "fundamental" processes in transport and macrokinetic phenomena; (b) the study of transport processes in statistical systems, including a large number of random fundamental transport steps; (c) the study of transport processes in chemical plant.

Each of these stages has its own special features, but they are all combined into a single complex. We can explain this by a simple example. Mass transfer to the surface of a single bubble, freely rising in a liquid, is a fundamental process according to our terminology. A column of bubbles executing a collective motion is an example of a statistical system with mass transport. In an absorption apparatus it is necessary to consider the motion of a column of bubbles, complicated by a large number of specific factors arising from the design of the column, e.g. non-uniform distribution of the bubbles over the cross-section.

Equations for matter and heat transport can be formulated on the most general assumptions concerning the properties of the medium.

When dealing with bulk or surface (catalytic) reactions involving the absorption or evolution of heat, we are faced with a system of interdependent equations for mass and heat transfer. The coupling between the equations of motion of the medium and the transfer equations arises from changes in viscosity and density of the medium with temperature or from volume changes in gas-phase reactions. The system of equations resulting from all these factors defies both analytical and numerical solution.

Nevertheless, in chemical kinetics and in chemical engineering the velocity, concentration, and temperature distribution in the reaction volume must be known. It is very important, therefore, to establish at least qualitatively the analytical dependence of these distributions on the basic external parameters of the system (prescribed flow rates, initial composition, etc.).

Indeed, the assignment of the velocity, concentration, and temperature distribution is essential both in order to establish the true kinetics of homogeneous and heterogeneous reactions and in order to establish the mode of operation of large-scale reactors and mass exchange apparatus. Therefore, the subdivision of real processes into similar phases or stages, susceptible to analytical or numerical study, is a very important aspect of this stage in the development of macrokinetics.

In the following Sections we shall discuss the realisation of this programme by considering various examples.

2. MACROKINETICS AT AN IMMOBILE PHASE BOUNDARY, LAMINAR FLOW

We shall begin the discussion with the fundamental process of transport to the surface of a solid body. The hydrodynamic behaviour of liquids and gases near a solid surface is known in fair detail both for laminar and for turbulent flow.

Consider the case of laminar motion. Analysis of the equations of momentum transfer (hydrodynamic equations), energy transfer (heat-transfer equations),and mass transfer indicates that all these transport processes show some definite similarities.

We know[6-8] that at high Reynolds numbers the total flow can be divided into a main region and a hydrodynamic (or Prandtl) boundary layer. In the main region the velocity of the liquid (or gas) has the constant value U_0 over the entire cross-section of the flow. The whole of the velocity change from U_0 to zero (at the solid surface) takes place in a thin boundary layer whose thickness is given by the formula

$$\delta_0 \sim \sqrt{\frac{\overline{vx}}{U_0}}, \qquad (1)$$

where x is the distance along the surface of a streamlined body. The shear stress under these conditions is of the order of magnitude

$$\tau \sim \mu \frac{U_0}{\delta_0}. \qquad (2)$$

In formulae (1) and (2) μ is the normal and $\nu = \mu/\rho$ is the kinematic viscosity.

A quantitative expression for the velocity distribution under steady-state flow can always be calculated for not too complicated geometries of the streamline surface.

In isothermal processes such as those associated with mass exchange the convective diffusion equation can always be solved if the velocity distribution is known.

For a planar or axially symmetrical interface, the convective diffusion equation can be written in the form[7]

$$\left(\frac{\partial c}{\partial x}\right)_{\psi} = D \frac{\partial}{\partial \psi}\left[v_x(x, \psi)\frac{\partial c}{\partial \psi}\right], \qquad (3)$$

where ψ is the hydrodynamic stream function, simply related to the velocity components, and v_x is the velocity component along the surface:

$$v_x = -\frac{\partial \psi}{\partial x}.$$

An entirely similar expression (with the diffusion constant replaced by the thermal diffusivity) applies to the temperature distribution if heat evolution resulting from viscous dissipation in the medium can be ignored. The usual boundary conditions are the given concentration c_0 or temperature T_0 at a point remote from the surface, the balance between the numbers of particles transported to the surface and of reacting particles, and also the temperature at or the heat flow to the reaction surface. From a mathematical point of view, Eqn. (3) is formally identical with the equation for non-stationary heat conduction in an immobile medium and with a thermal diffusivity depending on time and position:

$$\chi_{eff} = Dv_x. \qquad (4)$$

Eqn. (3) can be solved numerically in all cases for which the function $v_x(x, \psi)$ is known analytically or numerically.

Analytical solution of Eqn. (3) is possible for the case of a liquid phase. This is because of the very large value of the Prandtl number $Pr_D = \nu/D$, where ν is the kinetic viscosity of the medium. In liquids, where D is small

compared with ν, the Peclet number $Pe = RePr_D = U_0L/D$ (where U_0 is a characteristic flow velocity and L is a characteristic length) is large even at a relatively small Reynolds number Re (down to $Re \simeq 10^{-1}$). Therefore, a diffusion boundary layer (within which the main concentration changes occur) is formed near the surface of the streamlined body (Fig. 1). Outside the diffusion layer, in the main region, convective transport ensures that the concentration of material is constant, $c \simeq c_0$. In the diffusion layer the concentration changes from c_0 to the value c_S at the reaction surface. The thickness δ_{diff} of this layer is smaller than that of the characteristic region of velocity change. This allows the stream function in Eqn. (3) to be used directly in the neighbourhood of the surface. Thus, the ratio of the thicknesses of the diffusion and of the hydrodynamic boundary layers can be evaluated in the most general case:

$$\delta_{diff} \sim \delta_0 (Pr_D)^{-1/3}, \quad (5)$$

and there is a geometrical similarity between δ_{diff} and δ_0, as shown in Fig. 1. The thickness of the diffusion layer decreases with increasing flow velocity. The order of magnitude of δ_{diff} in liquids is $\sim 10\%$ of δ_0, and for normal velocities it lies between 10^{-2} and 10^{-4} cm. The whole of the diffusional resistance is confined within this narrow layer. In gases δ_{diff} is of the same order of magnitude as δ_0.

In laminar flow the thickness of the diffusion layer is inversely proportional to the viscous shear stress τ:

$$\delta_{diff} \sim \frac{|\operatorname{grad} \vec{v}|}{U_0} \sim \frac{\tau}{\mu U_0}. \quad (6)$$

If the surface has a small curvature the thickness of the diffusion boundary layer varies with the distance from the leading edge of the body according to the formula

$$\delta_{diff} \sim \sqrt{\frac{x}{U_0}} D^{1/3} \nu^{1/6}. \quad (7)$$

Thus the thickness δ_{diff} of the diffusional layer varies from point to point along the surface of the body. If the concentration at the surface is given (e.g. if the diffusing particles are used up by a fast reaction, or in the case of dissolution), the boundary condition at the reaction surface can be written in the form

$$c = c_S \text{ at the surface}, \quad (8)$$

where c_S is the constant concentration at the reaction surface itself (equal to zero in the special case of a fast reaction).

The equation for convective diffusion in liquids with boundary condition (8) at the reaction surface and the condition $c \to c_0$ in the main stream has been integrated for many solid reaction surfaces.

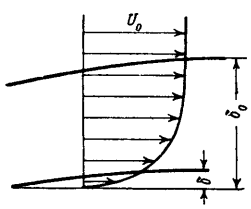


Fig. 1

Systems for which an analytical solution of the convective diffusion equation has been obtained are listed in the Table. Knowing the concentration distribution, we can find the diffusion flux accurately from the formula

$$j = D\left(\frac{\partial c}{\partial n}\right)_S, \quad (9)$$

where $\partial c/\partial n$ is the derivative along the normal to the surface S.

It has been shown that the diffusion flux is given, to the nearest order of magnitude, by the formula

$$j \simeq D\frac{\Delta c}{\delta_{diff}} = D\frac{c_0 - c_S}{\delta_{diff}}, \quad (10)$$

where Δc is the total (fixed) concentration difference.

The significance of this result is as follows. In liquids the thickness δ_{diff} of the layer is so small that the concentration change from c_0 to c_S can be satisfactorily approximated by a linear law. Formula (7) and the Table show that the diffusion flux varies along the reaction surface, increasing with velocity (for laminar flow) in proportion to U_0^n (where $n \leqslant 1/2$), in proportion to the diffusion coefficient D^m (where $m \leqslant 3/4$), and depending on the nature of the liquid. The dependence of j on the diffusion coefficient D is readily understood: molecular diffusion is a very slow process, and matter transport occurs mainly by convection. Under these conditions the slow stage of the transport process is the passage of matter through the thin layer of liquid adjacent to the solid surface, where its flux is determined by the viscosity.

The solution of the problem of convective diffusion in gases is somewhat more complicated than in liquids. In gases the diffusion coefficient is of the same order of magnitude as the kinematic viscosity, and therefore the thicknesses of the hydrodynamic and diffusion layers are of comparable magnitude. Consequently, we cannot use the approximate expression for the velocity close to the solid surface to solve the convective diffusion equation. The concentration distribution is best calculated numerically. However, the calculations have shown that in practice the concentration distribution can be again satisfactorily approximated by a linear law (over the thickness of the boundary diffusion layer).

The thickness of the diffusion layer in gases is given by the same expression as in the case of liquids, but with a different numerical coefficient (slightly dependent, strictly speaking, on the Prandtl number). The second difference between convective diffusion in gases and in liquids is that in the former the total pressure of the gaseous mixture can vary if the surface reaction is so fast that appreciable quantities of gas are generated (or consumed). The diffusion component of the gas mixture is also affected, since

TABLE.

Regime	Type of surface	Refs.	Regime	Type of surface	Refs.
Laminar	rotating disc	1, 7	Turbulent	semi-infinite plate	7
»	solid sphere	7, 9	»	disc	7
»	semi-infinite plate	7, 10–13	»	inner surface of a tube	7
»	semi-infinite, non-uniform plate	7, 14	»	rough surface	7
»	throttle	6, 7, 15	Natural convection	smooth vertical plate	7
»	inner surface of a tube	1, 7, 16	Turbulent	particle carried by a turbulent stream	7

the total pressure of the gas should remain constant. These features can readily be allowed for in two-component gas mixtures, but they seriously complicate the calculations in multicomponent systems. However, they do not bring any qualitative changes into the general picture.

We shall now consider the case of a chemical reaction proceeding at the surface. Its rate depends on surface concentration, usually according to a power law:

$$Q = f(c_1) = kc_S^n. \tag{11}$$

In these circumstances boundary condition (8) no longer applies.

The boundary condition now imposed on the surface concentration is of the form

$$D\left(\frac{\partial c}{\partial n}\right)_S = f(c_S). \tag{12}$$

The convective diffusion problem is not amenable to analytical solution with boundary condition (12) if $f(c_S)$ is a non-linear function of its argument and the reaction surface has a complicated shape.

A solution of this boundary problem was found[7,14] only for the simplest case of $f = \kappa c_S$ at the surface of a semi-infinite sheet. The effective thickness of the diffusional stream turns out to be a complicated function of the distance x, and also of the rate constant of the reaction k, of the diffusion coefficient D, and of the flow velocity U_0. The variation of the effective thickness of the boundary diffusion layer with the rate constant (k) of the reaction is a clear indication of the arbitrariness of this concept.

The quantity most commonly measured is the total flux $J = \int j\,dS$, where the integration is carried out over the whole of the reaction surface. It is evident that, having measured J, we can find the coefficients k and n in the kinetic law (11) only by solving the corresponding integral equation. The integral equations can be formulated, and their solutions presented in series form, for the surface of a plate and for the interior of a tube[17,18].

If the shape of the reaction surface exposed to the flow is more complicated, great difficulty is encountered not only in solving but even in obtaining the integral equation. Therefore, the kinetic law of the reaction must be determined either by carrying out the reaction under activation control or by making the measurements on "uniformly accessible" surfaces, for which the current density or the thickness of the diffusion layer have a constant value all over the surface.

The first requirement is somewhat indeterminate. The value of the diffusion flux near the edge of the plate or at the mouth of the tube formally tends towards infinity. This means that in these regions the reaction is always activation-controlled. The relative contribution of activation control to the total diffusion flux over the entire surface depends on the size of the plate and on the kinetic law.

Conversely, the diffusion flux at the surface of a body of non-streamlined shape is always finite, and does not exceed the value $j \simeq \frac{D\Delta c}{\sqrt{\nu R/U_0}}$ if we take the leading part of a sphere as an example. (The trailing part is discussed below.) In any kind of stagnant region, such as depressions in the body, the diffusion flux is low, and the reaction can obey the laws of diffusion-controlled kinetics, whereas on the streamlined parts of the body activation control is possible. Hence, in order to find the true kinetic law of the surface reaction, it is advisable to carry out the measurements under conditions to which macrokinetic theory is applicable[19,20]. The work of Frumkin's school[21-23] on solid electrodes as well as on the dropping mercury electrode[24] offers a striking example of the successful use of developments in macrokinetic theory for the determination of the true kinetics of a surface reaction.

As was stated above, it is particularly desirable to carry out the kinetic measurements on a surface such that all points are equally accessible to diffusion.

For laminar flow of a liquid or a gas, only two surfaces of this type are available: (1) the surface of a rotating disc; (2) the inner surface of a pipe or crack, beyond the inlet section where diffusion occurs (whose length L is approximately equal to 50 RePr).

The rotating disc was first used to study the kinetics of electrochemical reactions by Frumkin's school[25], and is now very widely applied in electrochemistry[26,27] and in studies of the kinetics of the dissolution of solids[28,29]. The investigations in which the rotating disc has been used are numbered in hundreds.

The thickness of the diffusion layer (as well as the flux density) is constant over the surface of the disc, and is given by

$$\delta_{\text{diff}} \simeq 1.61 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}}, \tag{13}$$

where ω is the angular velocity of rotation.

To determine the kinetic law, we only need to solve the transcendental algebraic equation[8]

$$kc_S^n + \frac{D}{\delta_{\text{diff}}}(c_S - c_0) = 0. \tag{14}$$

The function $j(\omega)$ for reactions with $n = 1$ and $n \ll 1$ is presented graphically in Fig. 2. These curves enable us to assess the degree of selectivity of surface reactions, falling in the region of mixed kinetics on going over from $n = 1$ (curve *1*) to $n \ll 1$ (curve *2*).

However, this unique, uniformly accessible surface has not as yet been used to any appreciable extent in the study of catalytic reactions. We know of only two investigations in which a rotating disc was used for catalytic measurements[30,31]. Yet, nothing short of a complete plot of j against ω can provide a sufficiently accurate means of evaluating the constants k and n in the kinetic law (11). We believe that measurements of this type would be highly desirable.

Non-stationary processes can play an essential role in the study of the faster heterogeneous reactions. These processes have already found an extremely wide field of application in electrochemistry, where they can be very easily realised in practice by measurements of potential or current as a function of time[32]. In catalytic reactions meaningful measurements can be made on the surface of a disc by using pulsewise input of reactants or a variable surface temperature.

Kinetic studies on uniformly accessible surfaces are especially important when several competing or consecutive reactions take place. The theory of this type of process has also been worked out to a useful degree. In particular, the method of a disc with ring has been successfully applied by Frumkin and coworkers to reactions involving unstable intermediate products[22,23].

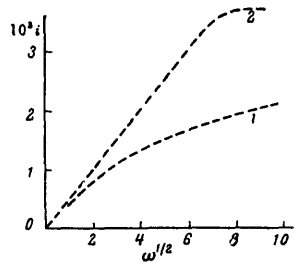


Fig.2.

The inner surface of a pipe cannot be used in liquid--phase processes, because the inlet section is very long in this case. It has been widely used, however, for reactions at the gas–liquid interface (see below).

In this context it is important to point out the relationship between the hydrodynamic theory of the boundary diffusion layer, discussed above, and the so-called "film theory", which has found very wide acceptance[33]. The underlying basis of this theory is the assumption that matter transport due to external convection is completely absent in a layer of thickness d, which is uniform over the reaction surface.

In liquids this is equivalent to assuming total absence of convective transport. Thus, the film theory in liquids coincides with Nernst's theory of the immobile diffusion layer.

In gases a somewhat different situation exists. In addition to convective transport, associated with the motion of the outer stream, we have a motion of the gas from (or towards) the reaction surface, due to the evolution (or absorption) of gas in the course of the reaction. The flow of gas arising from the removal or supply of particles from or to the surface is ignored in the film theory.

The main shortcoming of the film theory is the use of the arbitrary quantity d, which must be found by comparing the theory with measured mass fluxes. Yet, as the exact formula (7) shows, this thickness is in fact a function of the diffusion coefficient of the material (and therefore must be determined experimentally for each material), and also of the nature (viscosity) of the medium. Also, generally speaking, the thickness of the diffusion layer is variable from point to point along the reaction surface.

The attractions of the film theory are its relative simplicity and its ability to deal with complicated reaction kinetics. But these do not outweigh, in the writer's opinion, the drawbacks of this theory.

So far only mass transport phenomena have been considered. Heat transfer phenomena are no less important to the theory of macrokinetics. This is particularly true of gas reactions, which are frequently characterised by large heat changes.

The equations describing the transfer of energy (heat) in moving media are formally very similar to the corresponding equations for mass transfer. This circumstance, as already pointed out, justifies the use of the term transport phenomena.

Heat transfer phenomena have been studied in great detail in the physics of heat. However, as will be stressed below, heat-transfer problems in chemically reacting media have a number of specific features. In mobile media (liquids and gases) a thermal boundary layer, across which the main temperature drop occurs, is formed at the surface of a solid body maintained at a given temperature. This boundary layer is the analogue of the hydrodynamic and the diffusion layer.

The thermal Prandtl number $Pr_T = \nu/\chi$, where χ is the thermal diffusivity of the gas ($\chi = \varkappa/\rho c_p$, $\varkappa$ being the thermal conductivity), is of the order of 0.5–10 for gases and for most liquids alike. (The only exceptions appear to be some organic liquids and liquid metals[7].) The thicknesses of the boundary diffusion layer in a gas and of the thermal boundary layer in liquids are of the same order as the thickness of the hydrodynamic boundary layer. Therefore the equation for the temperature distribution must be solved by numerical methods.

Approximate methods of solution, such as Pohlhausen's method, have also found wide acceptance. In this method the distributions of velocity, concentration, or temperature in the boundary layer are described approximately by polynomials in powers of the distance from the surface[34]. There are also many other approximate methods, such as the method of integral moments[33]. The main disadvantage of these methods is that the error thereby introduced cannot be estimated quantitatively.

As regards the variation of concentration and temperature distribution in mobile media with the Prandtl number, the limitations of the analogy between mass transfer and heat (and also momentum) transfer must be borne in mind, particularly in the case of liquids. In gases the viscosity, thermal conductivity, and diffusion coefficients are relatively constant, so that the conditions under which the processes resemble each other are satisfied to a good approximation.

Non-isothermal reactions are very relevant to the study of the macrokinetics of heterogeneous chemical reactions. Non-isothermal processes are complicated by the interdependence of mass and heat transfer. In heterogeneous reactions this dependence is expressed not by the equations themselves, but by the boundary conditions, which take the following form at the reaction surface:

$$D\left(\frac{\partial c}{\partial n}\right)_S = kc_S^n e^{-\frac{E}{RT_S}} \quad \text{at the surface,}$$
$$\chi\left(\frac{\partial T}{\partial n}\right)_S = hkc_S^n e^{-\frac{E}{RT_S}} \quad \text{at the surface,} \qquad (15)$$

where T_S is the surface temperature, h is the heat of the heterogeneous reaction, and E is the activation energy.

The experimental and the theoretical study of such reactions is also most conveniently carried out on a uniformly accessible surface, such as the surface of a rotating disc. In this case the surface temperature T_S is constant along the surface, and simultaneous solution of the diffusion and thermal diffusivity equations involves the solution of a system of two transcendental algebraic equations.

By comparing the measured mass flux and surface temperature with experimental data, it is possible to determine the activation energy and the rate constant for a heterogeneous reaction.

Among other cases of diffusion-controlled kinetics at the boundary between a solid and a gas (or a liquid), diffusion to a porous catalyst particle deserves special mention.

Diffusion and heat transfer to a spherical particle from the external stream can be calculated. Departures from the spherical form merely introduce, in general, a different numerical coefficient.

In the case of isothermal reactions the problem of mass exchange in a pore can be solved for the general case. The main types of non-isothermal reaction, i.e. reactions of the first and of fractional orders, have been investigated in very recent years.

In this context, the so-called gradientless method of establishing the kinetics of catalytic reactions, which is now very widely applied, should be mentioned. In this method the main criterion of the presence of activation control is lack of dependence on the stirring rate. The method calls for three critical remarks.

1. Independence of the velocity of the external stream is a qualitative, but not a quantitative criterion of the transition to activation control.

2. The measured reaction rate is the combined result of the true chemical kinetics and of diffusional and thermal processes within the catalyst grains. The relation between these effects can be very complex, particularly in non-isothermal reactions. This can be demonstrated by calculations of non-isothermal reactions of zero, fractional[35], and first orders within the catalyst grain[36]. The presence of pores on whose surface the catalytic reaction proceeds is taken into account by introducing effective diffusion and thermal diffusivity coefficients for the particle. The effective activation energy E_{eff} is related to h, D, and χ and can be very appreciably different from the true activation energy E: it can be either smaller or greater than E. Therefore, the constants in the kinetic equations obtained by this method have a somewhat indeterminate meaning.

3. The method of measurement requires that the reaction products be removed from the reactor. No allowance is made for the possibility of build up, or for the effect of other non-catalytic reactions during removal of the products.

For these reasons, the writer believes measurements on a uniformly accessible surface to be essential.

3. MACROKINETICS AT A MOBILE PHASE BOUNDARY (LIQUID–LIQUID OR LIQUID–GAS)

The interface between mobile phases will now be considered. There are several cases of "fundamental" processes in mobile media: near the surface of drops, of bubbles, jets, and liquid films on solid surfaces. It must be stressed that the hydrodynamics of systems with mobile interfaces have been examined very much less fully than the hydrodynamics of flow in the neighbourhood of a solid surface.

With a mobile interface mass transport occurs by two independent transport processes in each of the phases. In particular, mass transfer at the liquid–gas interface involves processes occurring in phases of vastly different hydrodynamic behaviour.

Very often the mass-transfer process is complicated by chemical reactions between the diffusing species. Mass transport towards the simplest surface from the hydrodynamic point of view, a single bubble or drop moving in a quiescent medium, has been most fully investigated. The diffusion flux towards a growing, immobile drop was calculated several years ago[37,38]. The use of the formula for the diffusion flux towards a growing mercury drop provided the quantitative foundation of the polarographic method.

Frumkin and his coworkers[24] have developed the quantitative theory of the macrokinetics of reactions from the theory of the growing drop, and this has led to important results on the kinetics of hydrogen ion discharge. More recently, the theory of convective diffusion from the external phase to the surface of a moving drop or bubble has been worked out, and in very recent years the author has arrived at the general macrokinetic theory for the surface of small drops and bubbles[39], with allowance for transport in both the external and the internal phase. He has also arrived at the theory for the diffusion flux towards the surface of large drops[40], which are subject to periodic oscillations during their motion.

The diffusion flux in this case is expressed by relatively cumbersome formulae. Their main feature is that the flux is proportional to the square root of the velocity, and is also a function of the exchange (partition) coefficient of the diffusing species between the phases, and of parameters of both phases.

The diffusion flux in the system consisting of "gas bubbles in a liquid" can be obtained from these formulae for the limiting case in which the density of the inner phase is much smaller than the density of the outer phase. With large bubbles, which are deformed during motion, the diffusion and thermal fluxes can be calculated to the nearest order of magnitude. It is useful to note that surface-active substances, which influence the hydrodynamic behaviour of drops and bubbles very considerably, must also affect the diffusion flux. Theoretical formulae for the diffusion and thermal fluxes towards the surface of a drop or bubble are in satisfactory agreement with experiment in the particular case of negligible mass transfer in the inner phase. However, the more general expressions for the flow, allowing for diffusion in the inner phase, have not yet been compared with experimental data, and neither have the formulae for large vibrating drops. The macrokinetics of the process in which species diffusing from the drop undergo chemical reaction in solution have been recently worked out[41]. Because of its practical importance, this process has been examined in a number of papers concerned with the so-called penetration theory.

According to this theory[42], the time needed for the diffusing substance to penetrate into the external phase is much smaller than the time during which its concentration profile is significantly modified by the non-uniform distribution of velocities in the stream. In other words, the theory assumes that the velocity at all points of the external phase which the diffusing particle can reach is equal to the velocity of the interface.

In fact, such is not the case at high Peclet numbers. Even a relatively small point-to-point variation in the velocity distribution in the external phase has a powerful influence on the transport conditions, since at high Peclet numbers convective transfer predominates over transport by molecular diffusion. Calculations show that the formulae of the penetration theory can be applied only over times so short that formation of the diffusion boundary layer has not gone to completion. This time is much smaller than the times involved in the transfer process under the realistic conditions of drops moving in extraction apparatus. Formulae suitable for long times have been obtained: these

give the diffusion flux both in the absence and in the presence of chemical reaction in the external phase.

The second case of flow with a mobile interface concerns thin liquid films flowing on a solid surface. The flow of very thin films is laminar, and the calculation of convective flux presents no difficulty. At somewhat greater thicknesses the flow becomes wavelike, and calculation shows that the diffusion or thermal flux increases by about 25% as compared with a smooth surface. However, we have no theory for convective diffusion in a film covered with ripples of relatively large amplitude. The successful experimental studies of convective diffusion in liquid films exposed to fast countercurrents of gas[43] are a further stimulus to the development of a theory. We also lack a theory for convective transfer in liquid or gaseous jets issuing into a quiescent medium from an orifice or a packed column. This list of important problems relating to "fundamental" transport processes at a mobile interface is far from complete.

However, the main achievement is that theoretical and experimental studies in recent years have provided a general picture of transport processes at a mobile boundary, and have explained their basic features.

4. TURBULENT FLOW

The flow of liquids and gases in practically all chemical reactors and mass-exchange apparatus is turbulent. Hence, the theory of mass transfer and heat transfer in the turbulent regime of flow of liquids and gases is at least as interesting as the theory of transport in the laminar regime. Modern theories of turbulence enable us to arrive to certain quantitative conclusions regarding the transport of mass and heat in a turbulent stream.

The most fully developed theory is that of local isotropic turbulence; the theory of a turbulent stream in the vicinity of a solid surface has been developed to a lesser extent.

The theory of turbulence near a mobile interface is in its initial stages of development. In the region of free turbulence, far from the interface, all the turbulence eddies transfer passive materials (solute, gaseous impurity, or heat). Agitation of the liquid, moving in a region of dimensions L, is caused by all eddies with velocities up to ΔU_0 and characteristic length L. The effective turbulent diffusion coefficient $D_{\text{eff}} \simeq \chi_{\text{eff}} \simeq \Delta U_0 L$ is so large that the turbulence ensures concentration and temperature constancy over the whole of the volume except for a very thin turbulence boundary layer close to the interface.

Here the scale of the turbulence eddies l decreases according to the law $l \propto y$, and at quite small distances according to the law $l \propto y^2$, where y is the distance to the solid surface. At a distance δ_0 from the solid surface, called the viscous sublayer, the turbulence eddies become so weak that momentum transfer in the liquid occurs by the molecular viscosity mechanism, and turbulence subsides. Nevertheless, the damped turbulence eddies are still able to transport mass and heat. At Prandtl numbers in excess of unity the molecular transfer mechanism begins to predominate over the convective mechanism in a liquid layer of thickness $\delta' \simeq \delta_0/\text{Pr}^{1/4}$, amounting to 10^{-4}–10^{-5} cm. This extremely thin layer is the diffusion boundary layer, within which is concentrated the major diffusional resistance. The concentration (or temperature) distribution in this layer is effectively linear. Under these conditions the flux is given by the expression[7]

$$j_{\text{turb}} \sim \sqrt{k_f} U_0 \text{Pr}^{-1/4} \Delta\varphi. \tag{16}$$

At low Prandtl numbers the molecular transport mechanism takes over from the convective mechanism in a layer of thickness

$$\delta'' \sim \frac{\delta_0}{\text{Pr}} \gg \delta_0, \tag{17}$$

and therefore[7]

$$j_{\text{turb}} \sim \frac{\sqrt{k_f} U_0 \Delta\varphi}{\ln \frac{L U_0 \sqrt{k_f}}{\nu} + \ln\text{Pr} - A}. \tag{18}$$

Here $\Delta\varphi$ is the concentration or temperature difference between the bulk and the layer of liquid close to the reacting or cooled surface, k_f is the resistance coefficient, a slowly varying function of distance, and U_0 is the velocity.

For Prandtl numbers of the order of unity, we can write down interpolation formulae which combine both limiting laws, (16) and (18). These expressions agree satisfactorily with experiment[7,44].

It must be stressed that in a turbulent stream the exposed surface is not uniformly accessible owing to the dependence of k_f on the coordinates, mentioned above. This is true, in particular, for the surface of a disc. The only geometries in which the surface is uniformly accessible are the inner surface of a tube (in the region beyond the inlet section), and the surface of a cylinder rotating about its axis and remote from the walls of the vessel. The resistance coefficient is constant over the entire length of the tube and the entire height of the cylinder. Therefore, what was said above regarding the surface of a disc under laminar flow applies to turbulent flow towards the surface of a tube and of a rotating cylinder.

A theoretical expression for the flow at high Prandtl numbers was derived by the writer for a smooth and a rough tube[7], and more recently for a cylinder.

Turbulent motion at a mobile interface has been investigated in far lesser detail. For the turbulent motion of a gas stream over a liquid surface, we can expect turbulence of an entirely different character to be set up in the gas and in the liquid.

Since the density of the liquid is much greater than that of the gas, turbulence near the liquid interface will be damped in much the same way as near a rough solid surface. This statement is correct if the mean gas velocity is greater than the maximum rate of propagation of the waves (given by $\sqrt[4]{4\sigma g/\rho}$, where σ is the surface tension — 24 cm s^{-1} for water). However, we still lack experimental data on the distribution of velocities in the gas close to a liquid surface, and particularly measurements of the mean amplitude as a function of stream velocity. There have been few systematic measurements of resistance coefficients for a gas stream at different depths of liquid layer, surface tensions, etc. These measurements would be very valuable.

Turbulence near a free liquid surface has been studied in fair detail in the context of wind-generated waves in deep liquids. A similar approach is permissible under the conditions encountered in chemical hydrodynamics. By

using the ordinary theory of turbulent transfer in conjunction with the hypothesis as to the scale of the eddies near the free surface

$$l \sim \bar{a} \tag{19}$$

where $\bar{a}$ is the average amplitude of the surface waves, we can obtain an expression for the density of the diffusional flow near the surface:

$$j \sim v_0 \Delta c. \tag{20}$$

Here v_0 is the characteristic velocity of the turbulence eddies in the stream, related to the mean flow velocity by the familiar expression

$$v_0 \sim \bar{U} \sqrt{k_f}.$$

The total diffusional flow is of the order of magnitude

$$J = jS$$

where $S = S_0(1 + \bar{a}^2)$ is the true area, and S_0 is the nominal area of the liquid surface. Neither the turbulence in the gas phase nor the turbulence in the liquid phase have in fact been studied close to a free boundary by the powerful experimental tools of modern hydrodynamics.

On the subject of the difficulties presented by mass transfer problems near a mobile surface, it may be pertinent to point out that many authors[45,46] have been forced by the complications and lack of understanding of these problems to put forward views not in keeping with modern developments in hydrodynamics. The surface renewal theory is typical of this approach.

In the surface renewal theory the concept of turbulent eddies used in the turbulence theory is replaced by unsubstantiated ideas involving the time of renewal of surface elements with an entirely arbitrary distribution function for these times. These quasi-hydrodynamic theories are almost valueless.

5. HOMOGENEOUS–HETEROGENEOUS SYSTEMS

In the study of radical reactions occurring in cracking, pyrolysis, and other reactions in fast moving liquids and gases the most important problem is that of the relations between reactions in the bulk and at the surface. The macrokinetics of such systems have been discussed for the idealised case of an immobile medium[47] or of a medium undergoing laminar flow in a tube[19,48].

The last few years have witnessed the development of a general hydrodynamic theory of the macrokinetics of systems comprising both homogeneous and heterogeneous reactions at very high flow rates (more precisely, streaming at high Reynolds numbers), as is almost invariably the case in practice[49].

Consider a tube in which a turbulent stream of a chemically active medium (liquid or gas) is moving, and assume that chemical reactions accompanied by absorption or evolution of heat are taking place in the bulk. The kinetics of homogeneous reactions are usually described by an expression of the type

$$Q_i = k_i c_i^{n_i} c_j^{n_j} \ldots e^{-E_i/RT}$$

where Q_i is the rate of reaction of the ith component in the bulk phase, c_i and c_j are the bulk concentrations of the components, and E_i is the activation energy.

In the presence of homogeneous reactions the convective transport equation becomes non-linear, and accurate analytical solutions cannot be obtained. At the surface of the tube heterogeneous reactions take place, and under steady-state conditions the number of species arriving at the surface from the bulk equals the rate of heterogeneous reactions. Since the kinetics of heterogeneous reactions are also expressed by non-linear laws, the boundary conditions at the surface of the tube are non-linear. At first sight it would appear that a system of non-linear partial differential equations with non-linear boundary conditions is too complex to permit analytical or numerical solution. However, in practice it is possible to apply the ideas of the boundary diffusion layer to this system.

The total flow can be subdivided into the main region and a thin diffusion (or thermal) layer adjacent to the surface. In the main region the turbulent mixing ensures that the distribution of velocities, concentrations, and temperature is close to the average over the cross-section. A significant change in concentration along the tube axis, resulting from chemical reactions, occurs on a scale comparable to the length L of the reactor. If the change occurred over a shorter length one would simply shorten the reactor.

Surface reactions cause an appreciable change in concentration, from c_S at the surface to c_0 in the bulk, over the very thin boundary layer δ'.

It is clear, however, that in this thin layer we may ignore longitudinal changes in concentration of the main component at the outer limit of the boundary layer, and therefore we can also ignore the bulk reaction. The concentration change arising from the bulk reaction is significant at distances of the order of L, but not of the order of δ'.

By coupling the solutions for the main region and for the boundary layer, we can arrive at the distribution of concentration, temperature, and reaction rate along the reactor.

In two real systems — the pyrolysis of ethane to ethylene and the radical–chain oxidation of hydrocarbons — the overall macrokinetics have been calculated. The rate of the characteristic deposition of side-products has been obtained for the former reaction, and the effect of the surface-to-volume ratio of the reactor has been obtained for the latter reaction.

6. STATISTICAL SYSTEMS

In the previous sections we have dealt with some simple "fundamental" mass- and heat-transfer processes. Their main characteristic is a simple and well defined set of geometrical conditions. Furthermore, the flow regimes were assumed to be fixed and uniform over the whole of the system, and random time-changes of regime or spatial variations in the properties of the system were not considered. In practice, one attempts to stir as intensively as possible in order to obtain high rates of transfer. In real situations the process usually occurs in a statistical system, composed of a set of "elementary" objects, rather than on a single object such as a solid reaction surface, a drop, etc. Therefore, in order to construct a physicochemical model of a real process we must, on the one hand, analyse the complex process into its individual stages (or fundamental steps), and, on the other hand, we

must make a particularly careful study of the simple stages, uncomplicated by incidental and random phenomena. We shall illustrate these statements by two examples.

Absorption is a very complicated phenomenon. Yet, it can be separated into a number of stages whose relative contributions to the overall process depend on the particular conditions. We can distinguish the following stages: (1) the gas jet emerges from the nozzle and breaks up; (2) the resulting bubbles are further broken down, or coalesce; (3) motion of individual bubbles; (4) motion of the system of bubbles; (5) mass transfer to a single bubble, taking account of external and internal diffusional resistance; (6) exhaustion of the solution with time; (7) non-uniform radial distribution of gas and liquid; (8) foaming; (9) mass transfer in the bubble walls of the foam.

Some of these stages are adequately characterised at the present time, others are insufficiently understood.

However, some of the stages play an insignificant part under actual process conditions. Thus, the overall process becomes very much simpler if the liquid layer is deep enough, if the proportion of gas is not too large, and if conditions are constant over the cross-section.

The bubbles of different sizes formed by the breaking up of gas jets are further comminuted (if they are coarse) and coalesce (if they are fine) relatively quickly. The main body of bubbles achieves an almost uniform size, and rises at a uniform rate. Their mutual effect can be estimated, and the speed at which they rise can be found[50].

The mass transport for bubbles of a given size and velocity is known; thus, all the above stages can be evaluated, and the operation of a gas bubbler under these conditions can also be evaluated. Obviously, however, the calculation has no meaning for bubblers of different design, which fail to satisfy the above assumptions.

A detailed experimental and theoretical study of all the stages listed above would give an indication of their relative importance in various types of apparatus.

For our second example, we shall consider a tubular reactor containing a granular, immobile layer of catalyst. In this case the fundamental stages are as follows.

1. The kinetics of the process. It is essential to know the overall mechanism, and sometimes also the true, detailed kinetic mechanism of the process, including true kinetic data such as the rate constant, the activation energy, the order of the reaction with respect to concentration, the heat of the reaction.

2. Diffusion and heat-transfer processes within the catalyst particles (as a function of catalyst structure, thermal conductivity, etc.). The effect of these processes on the kinetics.

3. Motion of a liquid or gas through the granular medium, convective diffusion and heat transfer in a porous medium, heat transfer in the catalyst skeleton. The influence of these processes on the kinetics has already been discussed. Convective transfer in a granular medium has not been adequately investigated. The longitudinal diffusion coefficient in a granular medium with stagnant regions has been recently calculated[51] on the basis of quite general assumptions as to the actual properties of the medium.

The radial convective diffusion and thermal conductivity coefficients must be very much smaller than the longitudinal coefficients; their dependence on velocity has been calculated from an unsatisfactory model[52]. Experimental results for $D_{\parallel}$ in porous media are in satisfactory agreement with theory, but $D_{\perp}$ is often found (experimentally) to be slightly dependent on velocity. Other results suggest that $D_{\perp}$ is proportional to U_0. The vast majority of the experiments refer to a porous, but not coarse-grained, structure. The large scatter of the values of $D_{\parallel}$ and $D_{\perp}$ obtained from experimental data indicates a dependence on the actual structure, packing density, etc. It must not be forgotten that the overall thermal conductivity of a granular medium includes the convective thermal conductivity and the thermal conductivity of the skeleton. Under these conditions the concentration and temperature distributions will show significant differences. The calculations which have been made up to now make no allowance for the difference between $D_{\parallel}$ and $D_{\perp}$ or for their dependence on velocity. The resulting error is not easy to assess.

4. Transition from a granular structure to a continuous medium. Many workers treat the granular medium filling the reactor as a continuous, porous medium.

In practice, very wide variations in the ratio of grain diameter to tube diameter are encountered. There is a need for more detailed studies as to the nature of the approximations made on going from a granular to a continuous medium: this is particularly important when a laboratory-scale process is transferred to industrial plant. Various models of a granular medium in a reactor with an immobile layer have been put forward: the cellular model[53], the cellular model with stagnant regions[54], the quasi-homogeneous model[55], etc. This in itself is a clear indication of the lack of a universal model applicable to real systems.

5. Simplification of the basic equations for mass and heat transfer in a porous medium within the framework of the quasi-homogeneous model.

6. Calculation of the average temperature distribution along the reactor.

7. Calculation of the stability of the operating conditions of the reactor.

8. Allowance for non-uniform gas flow over the cross-section of the reactor.

As in the previous example, we see that some of these stages have been investigated to a sufficient extent, whilst others are inadequately understood.

In conclusion it should be stressed that the complications of hydrodynamics and of mass- and heat-transfer processes in chemical reactors and mass-exchange apparatus are such that mathematical and experimental studies must be brought to bear on them jointly. The common aim of these studies should be to produce sound physicochemical approximations (models) which would serve as a basis for calculations on processes and apparatus. Calculations on reactors which allow for major factors but ignore second-order factors (usually called mathematical modelling) should always be compared with experiment in order to confirm that the approximations made are compatible with real processes in chemical plant.

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THE ELECTROCHEMICAL EFFECT OF HIGH COVERAGE

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The inhibition of electrochemical reactions by adsorbed extraneous substances or reaction products is well recognised[1-8]. The basic causes underlying this phenomenon include blocking of the surface by an adsorption film, and the generation of an energy barrier opposing the reduction, through the adsorption of ions or polar molecules. In recent years, the inhibition of an electrochemical reaction by adsorbed reactant has been demonstrated by refined experimental techniques. This effect has been termed[9,10] the high-coverage effect.

Frumkin et al.[9] and Tedoradze and Dzhaparidze[10,11] were the first to compare the degree of coverage of the electrode surface by reactants, determined experimentally, with the rate of the electrochemical process, measured at the same potentials. They reported a decrease in current density with increase in coverage for the catalytic evolution of hydrogen from diphenylamine solutions. A qualitative explanation of the inhibition of the reduction of diphenylammonium ions at coverages of the electrode approaching unity has been given[9].

This article will describe the outward experimental symptoms of the high-coverage effect, and some possible causes. The reduction of organic substances at a mercury electrode, being the simplest case, will be treated in detail.

As long as the coverage of the surface by molecules of a reducible substance is not large, and interactions between these molecules (as well as the effect of adsorbed molecules of the product) can be ignored, the rate i of an