TRANSPORT CONTROL IN HETEROGENEOUS REACTIONS

By L. L. BIRCUMSHAW, M.A., D.SC.
(THE UNIVERSITY, BIRMINGHAM)
and A. C. RIDDIFORD, PH.D.
(THE UNIVERSITY, SOUTHAMPTON)

I. Introduction

THE study of the kinetics of heterogeneous reactions covers a wide field. In one system the problem may be purely chemical in nature, but in another the characteristics which are of interest to the chemist may be entirely determined by non-chemical factors. In this Review an account will be given of systems in which the observed rate of reaction is either wholly or partly determined by the rate of a transport process, *i.e.*, by the rate of mass-transfer of a species by convection and diffusion. In general, attention will be confined to systems subject to forced convection, although many of the considerations apply also to mass-transfer under natural convection. The subject has been reviewed as a whole, or in part, by Centnerszwer,[1] Taylor,[2] Bowden and Agar,[3] Tovbin,[4] and by Moelwyn-Hughes.[5] Hixson and Crowell,[6] and Hixson,[7] have reviewed the topic from the standpoint of the study of agitation.

The general case of a reaction between a solid and a solution, resulting in soluble products, will be taken as a model. The overall process may comprise as many as five primary steps :

(*a*) Transport of solute molecules to the interface.
(*b*) Adsorption at the surface.
(*c*) Reaction at the surface.
(*d*) Desorption of the products.
(*e*) Recession of the products from the interface.

Of these, steps (*b*), (*c*), and (*d*) are characterised by an interaction between the solid and solute and, quite generally, will be termed chemical processes. Complications may arise in other systems ; for instance, the products may be gaseous, or may form an insoluble layer on the solid surface, or may undergo further reaction in the bulk of the solution. For a liquid–liquid system in which reaction takes place between two solute species, one in each phase, step (*a*) will comprise two transport processes, etc. By con-

---

[1] *Z. physikal. Chem.*, 1929, **141**, *A*, 297.

[2] " A Treatise on Physical Chemistry ", 2nd edn., Macmillan, 1931, Chap. XV.

[3] *Ann. Reports*, 1938, **35**, 90 ; see also Agar, *ibid.*, 1947, **44**, 5, and Hickling, *Quart. Reviews*, 1949, III, 95.

[4] *Bull. Sci. Univ. Kiev*, 1939, No. 4, 155.

[5] " The Kinetics of Reactions in Solution ", 2nd edn., Clarendon Press, 1947, p. 357.

[6] *Ind. Eng. Chem.*, 1931, **23**, 923.

[7] *Ibid.*, 1944, **36**, 488.

fining attention mainly to clear-cut examples, however, the modifications necessary for other systems will be obvious.

According to Nernst,[8] it is highly probable that the chemical processes at the interface are always very much faster than one or other of the transport processes, so that, unless there is a slow process occurring within the bulk of one of the phases, the observed rate is transport-controlled. This hypothesis caused considerable controversy. His theory, outlined in the next section, was supported by several workers who conducted investigations designed to test its validity, *e.g.*, Brunner,[9] Jablczynski and St. Jablonski,[10] and Van Name and his co-workers.[11] On the other hand, Ericson-Aurén and Palmaer,[12] Wildermann,[13] Gapon,[14] Miyamoto,[15] and Roller [16] are but a few of the workers who have criticised the theory, sometimes to the extent of denying that transport control ever occurs.

II. The Nernst Theory [5]

Noyes and Whitney [17] studied the dissolution of cylinders of benzoic acid and of lead chloride in water. The cylinders were rotated, and the process of dissolution was followed by analysing the solution at intervals. They expressed their results by the first-order equation

$$\mathrm{d}c/\mathrm{d}t = k(c_\mathrm{s} - c) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the concentration of the solute at time t, and c_s is the solubility of the compound in water at the experimental temperature. They suggested that a saturated layer is rapidly formed at the interface, and that the observed velocity is simply the rate at which solute molecules diffuse from this layer into the bulk of the solution. Their results were confirmed by Bruner and St. Tolloczko,[18] who showed that the rate of dissolution is proportional to the apparent surface area A.

Nernst,[8] in extending these views to heterogeneous reactions, assumed that equilibrium is established almost instantaneously at the interface between two phases. Thus for the dissolution of magnesium in acid, for example, the equilibrium concentration of hydrogen ion in contact with the metal is vanishingly small, and the dissolution velocity will be determined solely by the rate at which hydrogen ions arrive at the interface. Provided the solution is well stirred, the concentration in the bulk of the solution may be regarded as uniform and the hydrogen ions reach the surface by diffusing through a thin layer of solution, of thickness δ, adhering to the solid surface.

---

[8] *Z. physikal. Chem.*, 1904, **47**, 52; "Theoretical Chemistry", 5th English edn., Macmillan, 1923, p. 669.

[9] *Ibid.*, 1904, **47**, 56.

[10] *Ibid.*, 1911, **75**, 503.

[11] (*a*) Van Name and Edgar, *Amer. J. Sci.*, 1910, **29**, 237; *Z. physikal. Chem.*, 1910, **73**, 97; (*b*) Van Name and Bosworth, *Amer. J. Sci.*, 1911, **32**, 207; (*c*) Van Name and Hill, *ibid.*, 1913, **36**, 543; (*d*) Van Name, *ibid.*, 1917, **43**, 449.

[12] *Z. physikal. Chem.*, 1906, **56**, 689.

[13] *Ibid.*, 1909, **66**, 445; *Phil. Mag.*, 1909, **18**, 538.

[14] *Z. Elektrochem.*, 1928, **34**, 803.

[15] *Trans. Faraday Soc.*, 1933, **29**, 789.

[16] *J. Phys. Chem.*, 1935, **39**, 221.

[17] *Z. physikal. Chem.*, 1897, **23**, 689.

[18] *Ibid.*, 1900, **35**, 283.

Consider the solid, of surface area A, in contact with a volume V of solution of concentration c. Then by Fick's law

$$-\mathrm{d}c/\mathrm{d}t = (DA/V)\mathrm{d}c/\mathrm{d}y \quad . \quad . \quad . \quad . \quad (2)$$

where $\mathrm{d}c/\mathrm{d}y$ is the concentration gradient normal to the surface and D is the coefficient of diffusion of the solute. Nernst assumed that the concentration gradient can be expressed by $(c - c_i)/\delta$, where c_i is the concentration at the surface; by substitution in (2),

$$-\mathrm{d}c/\mathrm{d}t = DA(c - c_i)/V\delta \quad . \quad . \quad . \quad . \quad (3)$$

and the first-order constant is given by

$$k = DA/V\delta \quad . \quad . \quad . \quad . \quad (4)$$

It has the dimensions of a frequency. Equation (3) may be compared with equation (1). For the dissolution of a metal in acids, and for similar systems, he further assumed that the concentration of solute at the surface is practically zero. Equation (3) then reduces to

$$-\mathrm{d}c/\mathrm{d}t = cDA/V\delta \quad . \quad . \quad . \quad . \quad (5)$$

Tests of the Theory.—If the coefficient of diffusion of the solute is known, the thickness of the diffusion layer can be calculated from the observed velocity constant per unit area at unit volume k_T,* since

$$k_T = kV/A = D/\delta \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This unit constant has the dimensions of a velocity. Thus Brunner [9] gave the values listed in Table 1 (see also Table 3). He observed that these values are all of the same order of magnitude, and claimed that they are not unlikely values. Moelwyn-Hughes,[5] whilst pointing out that these values are physically improbable, draws attention to the significant fact that δ has roughly the same value for many reactions of quite different chemical character, consistent with the view that the rates are determined by a diffusion process.

TABLE 1. *Values of δ at 20°*

System	δ, mm.
Dissolution of benzoic acid in water	0·02–0·03
,, ,, magnesia in benzoic acid	0·029
,, ,, magnesia in acetic acid	0·028
,, ,, marble in HCl + $MgCl_2$	0·032–0·036
,, ,, magnesium in benzoic acid	0·022
,, ,, silver acetate in water	0·031–0·039

A second test of the theory concerns the effect of stirring. An increase in the rate of stirring should be accompanied by an increase in the observed velocity, since the thickness of the liquid layer adhering to the surface will decrease. For a given rate of stirring, moreover, the efficiency of the stirrer will be a function of the dimensions and shape of the system. These effects have been observed for some systems. For example, Nernst and

---

* Throughout this Review, quantities relating to a transport process and to a chemical process are denoted by the subscripts T and C, respectively.

Merriam[19] studied the electrolysis of acidified KI_3 solutions between platinum electrodes, one being rotated at constant, known, speeds. They found that the limiting current increases with increasing rate of stirring. Many investigators have confirmed this effect, usually expressing their results in a power relation of the form

$$k_T \propto (\text{r.p.m.})^a \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the power $a \leqslant 1$. Nernst and Merriam found $a = 0{\cdot}6$; some of the values reported by other workers are given in Table 2, together with the range of stirring speeds investigated. Hixson and Baum,[31] studying the rate of dissolution of benzoic acid pellets in sodium hydroxide solutions, calculated the value of δ for various rates of stirring (Table 3).* Over the range studied, δ is inversely proportional to the rate of stirring, *i.e.*, $a = 1$. Rather less attention has been paid to the influence of the

TABLE 2. *Values of* a, *the stirring coefficient*

System	R.p.m.	a	Ref.
Electrolysis of KI_3 solns.	120—400	0·42	20
Redn. of O_2 to H_2O_2 at Cu cathode	30—3600	0·5	21
Dissoln. of Zn in aq. iodine solns.	50—200	0·56	22
Electrolysis of HCl + KCl solns.	50—400	0·6	23
Dissoln. of magnesia in benzoic acid	135—182	0·66	9
Reaction of Na amalgam with dil. aq. acid . .	500—2450	0·7	24
Dissoln. of Hg in aq. iodine solns.	170—300	0·8	11*a*
Electrolytic oxidn. of chromous chloride . . .	300—350	0·85	25
Dissoln. of Mg in MeOH–H_2O solns. of HCl . .	350—700	< 1	26
	700—2730	1	
Concn. polarisation at a silver cathode . . .	< 300	< 1	27
	300—1500	1	
Dissoln. of Mg cylinders in HCl solns. . . .	0—1000	< 1	28
	1000—5600	~ 1	
Dissoln. of Na cylinders in liq. NH_3	116—834	1	29
Dissoln. of Zn cylinders in dil. acetic acid solns. .	450—26 400	1	30

---

[19] *Z. physikal Chem.*, 1905, **53**, 235.
[20] Sackur, *ibid.*, 1906, **54**, 641.
[21] Siver and Kabanov, *J. Phys. Chem.*, *U.S.S.R.*, 1948, **22**, 53; 1949, **23**, 428.
[22] Riddiford and Bircumshaw, *J.*, 1952, 698.
[23] Eucken, *Z. physikal. Chem.*, 1907, **59**, 72.
[24] Dunning and Kilpatrick, *J. Phys. Chem.*, 1938, **42**, 215.
[25] Jablczynski, *Z. physikal. Chem.*, 1908, **64**, 748.
[26] Garrett and Cooper, *J. Phys. Colloid Chem.*, 1950, **54**, 437.
[27] Nagel and Renner, *Z. Elektrochem.*, 1950, **54**, 547.
[28] King and Braverman, *J. Amer. Chem. Soc.*, 1932, **54**, 1744.
[29] Johnson and McDonald, *ibid.*, 1950, **72**, 666.
[30] King and Schack, *ibid.*, 1935, **57**, 1212. [31] *Ind. Eng. Chem.*, 1944, **36**, 528.

* For this system, the diffusion layer is composed of two regions: a layer adjacent to the solid surface wherein the concentration of benzoic acid decreases from the saturation concentration at the surface to zero at points distant δ_a from the surface, and a second layer in which the concentration of hydroxyl ions increases from zero at δ_a to the bulk concentration at points distant δ from the surface. The values recorded in Table 3 are for the total layer thickness.

TABLE 3. *Values of δ for the dissolution of benzoic acid in sodium hydroxide solutions*

R.p.m.	200	250	300	350	450
$\delta \times 10^3$, cm.	3·58	3·38	3·27	3·08	2·78

geometry of the system on the observed rate. In most investigations the effect is eliminated by maintaining the same geometry for all experiments. Some studies of the effect have been made, however ; these will be referred to in Section V.

Nernst considered that, if the thickness of the adhering layer is determined by experiment for one system with a given type and rate of stirring, the velocity constant k_T can be calculated for other reactions taking place under the same flow conditions. Thus Brunner [9] determined δ from measurements of the rate of dissolution of benzoic acid in water, and then calculated the rate of dissolution of magnesia in various acids, using the known coefficients of diffusion. The calculated values were in reasonable agreement with the experimentally determined rates. In this consideration, Nernst has introduced a further assumption, namely, that δ is a function of the type and rate of stirring only. This can be shown to be incorrect (see below). Without making this assumption, however, it is evident that the dissolution of a number of solids in the same solution under the same experimental conditions should proceed at the same rate, provided that in each case the observed rate is determined solely by the rate of transport of solute to the solid surface, the solids being insoluble in the pure solvent. Thus Van Name and Edgar [11a] and Van Name and Bosworth [11b] found that under the same conditions mercury, cadmium, zinc, copper, silver, iron, nickel, and cobalt dissolve in aqueous iodine solutions at the same rate, within the limits of experimental error. Their results have been confirmed.[22]

Again, from Nernst's assumption that δ is a function of the rate and type of stirring only, k_T should be proportional to the coefficient of diffusion of the solute, and hence inversely proportional to the viscosity of the solution. Results in qualitative agreement with these views were soon obtained, *e.g.*, Van Name and Edgar [11a] have shown that bromine attacks metals more rapidly than does iodine,[32] Jablczynski [25] found that an increase in the viscosity of the solution decreased the rate of oxidation of chromous chloride, Jablczynski and St. Jablonski [10] obtained similar results for the dissolution of magnesium and marble in hydrochloric acid, Van Name and Hill [11c] demonstrated that the addition of sucrose or alcohol to the solution decreased the rate of solution of cadmium in aqueous iodine solutions, whilst, in their earlier papers, King and his co-workers [33] published similar results for other systems.

Finally, if δ is a function of the rate and type of stirring only, it should

---

[32] See also Trotman-Dickenson and James, *J.*, 1947, 736.

[33] (*a*) King and Liu, *J. Amer. Chem. Soc.*, 1933, **55**, 1928 ; (*b*) King, *ibid.*, 1935, **57**, 828 ; see also ref. 28.

be temperature invariant: from eqn. (6), then, k_T and D should have the same temperature coefficient. At 25°, the value of the energy of activation for diffusion E_D ranges between about 2800 and 6500 cal./mole,[34] depending on the solute and on the solvent. For many electrolytes in aqueous solution $E_D \sim 4000—4500$ cal./mole. Many heterogeneous reactions do have values of E_A, the observed critical increment, of this order, *e.g.*, for the electrolysis of 0·66N-potassium chloride, $E_A = 4300$ cal./mole; [9] for the dissolution of cadmium in aqueous iodine solutions,[11d] $E_A = 4000$ cal./mole. It must be observed, however, that chemical reactions having a critical increment of this order, or less, are known.[5]

Defects of the Nernst Theory.[35]—As detailed above, Nernst, in formulating his theory, assumed: (1) that the chemical processes at the surface always proceed very much faster than one of the two transport processes; (2) that in a well-stirred system the concentration gradient is confined to a thin layer of solution adhering to the solid surface; (3) that within this layer the concentration varies linearly with distance, measured normal to the surface; and (4) that the thickness of this layer, whilst being a function of the rate of stirring and of the geometry of the system, is independent of the coefficient of diffusion of the solute, of the viscosity of the solution, and of the temperature. None of these assumptions is entirely correct.

Despite his support of the Nernst theory, Brunner [9] recognised the possibility of chemically-controlled reactions. That the chemical effect predominates in some systems is shown by the non-dependence of the observed rate on the rate of stirring, as in the case of the dissolution of certain metals in acid [36] and of glass in alkali.[37] Marc [38] found that the rate of crystallisation from aqueous solutions is independent of the rate of stirring, when this is sufficiently intensive.* Again, the large temperature coefficients of certain reactions rule out any possibility of transport-control. Moelwyn-Hughes [5] has discussed the kinetics of the decomposition of sodium hypochlorite in aqueous solutions catalysed by a cobalt peroxide suspension, studied by Howell.[39] For this reaction, E_A is 16,600 cal./mole, and the kinetics are satisfactorily explained on the assumption that the rate is controlled by activated collisions between the hypochlorite ions and the catalyst surface. Other cases of heterogeneous catalysis of this type, and of the type where the rate is governed by an adsorption process, are too well known to require mention. Lastly, if the

---

[34] Taylor, *J. Chem. Phys.*, 1938, **6**, 331.

[35] See also King, ref. 33*b*.

[36] *E.g.*, Centnerszwer and Zablocki, *Z. physikal. Chem.*, 1926, **122**, 455; Centnerszwer, *ibid.*, 1928, **137**, 352.

[37] Schmidt and Durau, *ibid.*, 1923, **108**, 128; but contrast Müller and Weinstein, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 465.

[38] *Z. physikal. Chem.*, 1908, **61**, 385; 1909, **67**, 470; 1909, **68**, 104; 1910, **73**, 685.

[39] *Proc. Roy. Soc.*, 1923, *A*, **104**, 134.

* At 0° the process is approximately of the second order, whereas at 25° the process is first-order. Since the rôle of diffusion in the mechanism of the crystallisation process, in certain circumstances, has been established beyond doubt (see, *e.g.*, the recent discussion of the Faraday Society on Crystal Growth; No. 5, 1949), one must conclude that, for some systems, a change in the experimental conditions may effect a change of control. This point is considered further in Section VII.

observed rate is transport-controlled, it should be independent of the particular crystal face exposed to attack. This has been shown to be the case for systems which, on other grounds, are known to be transport-controlled.[40] On the other hand, cases are known where the observed rate varies according to the face exposed to attack,[41] the effect sometimes being shown by the preferential development of certain crystal faces during the course of reaction.[42]

The assumption that the diffusion layer is stationary with respect to the surface must now be considered. As previously mentioned, concordant values of δ of the order of 0·03 mm. at 20° have been obtained for many reactions of very different types. Now such a value corresponds to a layer some 50,000 molecules thick, which, on general grounds, would appear to be improbably high. This conclusion is supported by experimental evidence. Roller,[16] for example, cites seemingly overwhelming evidence in favour of the view that fluid motion persists down to very short distances from the solid surface, if not to the surface itself. The most striking evidence is afforded by the work of Fage and Townend,[43] who, using the ultramicroscope, studied turbulent flow in pipes. Minute particles present in the tap-water used in the investigation were intensely illuminated, and these particles used to follow the motion of the fluid. In this way, they were enabled to measure the maximum values u_1, v_1, and w_1, of the three components u, v, and w, of the velocity disturbance at any point. The radial dependence of the mean velocity U was obtained by the same means. At the centre of the pipe, u_1, v_1, and w_1 are approximately equal. As the wall is approached, the ratio v_1/U, obtained from the velocity disturbance normal to the wall, decreases to zero, whilst the corresponding ratios u_1/U and w_1/U increase. At the wall itself, it was found that the flow tended to the laminar type (see next section), motions of the particles in the laminæ being observed to within a distance of $0{\cdot}6 \times 10^{-4}$ cm. from the wall.

If fluid motion persists up to points very close to the solid surface, the assumption that the concentration is a linear function of the distance y (measured normal to the surface) over the range $0 \leqslant y \leqslant \delta$ can be but an approximation. For the case of a plane disc electrode rotating about an axis perpendicular to the plane, Levich [44] has calculated values of c_y, the concentration at any point y. Fig. 1 shows the ratio c_y/c plotted against y/δ, where c is the concentration in the bulk of the solution.* The full line shows the calculated dependence of c_y on y ; the broken line

---

[40] (*a*) King and Appleton, *Trans. Electrochem. Soc.*, 1940, **77**, 219 ; (*b*) Glauner, *Chem. Zentr.*, 1934, II, 2129 ; see also ref. 22.

[41] *E.g.*, (*a*) Spring, *Z. physikal. Chem.*, 1888, **2**, 13 ; (*b*) Wildermann, *ibid.*, 1910, **71**, 401 ; (*c*) Glauner, *ibid.*, 1929, **142**, *A*, 67 ; (*d*) Gwathmey and Benton, *J. Chem Phys.*, 1940, **8**, 431, 569 ; see also ref. 40*a*.

[42] *E.g.*, Tovbin and Baram, *J. Phys. Chem., U.S.S.R.*, 1949, **23**, 406.

[43] *Proc. Roy. Soc.*, 1932, *A*, **135**, 656.

[44] *Acta Physicochim. U.R.S.S.*, 1942, **17**, 257 ; *J. Phys. Chem., U.S.S.R.*, 1944, **18**, 335.

* Fig. 1 has been adapted from Fig. 2 in Levich's paper (ref. 44). See also Levich, *Discuss. Faraday Soc.*, 1947, **1**, 37.

indicates the concentration gradient in the hypothetical Nernst layer. The calculated concentration gradient occurs over a distance δ', where δ' is related to δ by the expression (see Section IV)

$$\delta = 0{\cdot}893\delta' \qquad . \quad . \quad . \quad . \quad (8)$$

Finally, there is the question of the dependence of δ on the coefficient of diffusion of the solute, on the viscosity of the medium, and on the temperature. According to Nernst, δ is independent of the diffusion coefficient D, and hence k_T should be proportional to D. Experimentally, this is not the case. King and Cathcart [45] find the relation

$$k_T \propto D^{0{\cdot}70} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

for the dissolution of magnesium cylinders in acids, whilst King [46] suggests that the power on D should be 0·75 for dissolution under turbulent flow conditions. Eucken [47] found the power on D to be 0·66 for laminar flow. These results indicate that δ is a function of D, and this, together with the fluid flow within the Nernst layer discussed above, suggests that δ is probably also a function of the viscosity of the medium and of the temperature. Having regard to the similarity between the observed critical increment and the energy of activation for the diffusion process in certain transport-controlled systems, it is to be expected that the dependence of δ on temperature will be slight (see Section VII).

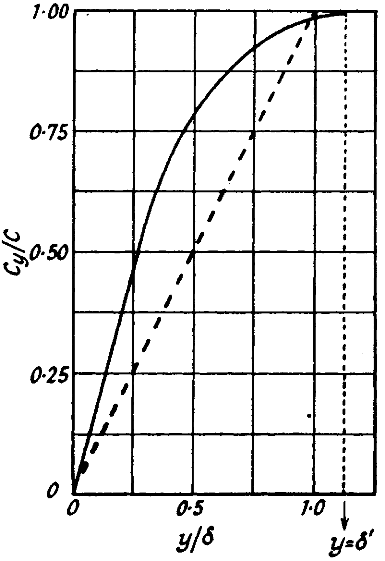

FIG. 1

Thus, whilst the experiments of Fage and Townend,[43] and of others, indicate that the concept of a stationary layer of liquid adjacent to the solid surface is wrong, there appear to be excellent grounds for the belief that in systems for which the observed rate is a function of the rate of stirring, and of the diffusion coefficient of the solute, etc., there is a concentration gradient existing between the solid surface and points in the liquid distant δ from the surface. Indeed, the existence of this region can be demonstrated very simply in certain cases,[48] and Antweiler [49] has photographed the diffusion layer at the dropping-mercury cathode. The properties, and extent, of this region in any given system will be determined

---

[45] *J. Amer. Chem. Soc.*, 1937, **59**, 63.

[46] *Trans. N.Y. Acad. Sci.*, 1948, II, **10**, 262. [47] *Z. Elektrochem.*, 1932, **38**, 341.

[48] *E.g.*, King and Brodie, *J. Amer. Chem. Soc.*, 1937, **59**, 1375; see also Hixson and Baum (ref. 31).

[49] *Z. Elektrochem.*, 1938, **44**, 719; some of the photographs have been reproduced by Kolthoff and Lingane, "Polarography", Interscience, 1941, p. 128.

by the value of the diffusion coefficient of the solute, by the viscosity of the solution, and by the nature of the flow of fluid in the system. Before dealing with the connection between the diffusion layer and the properties of the solute and solvent, it is instructive to consider certain qualitative aspects of the dynamics of fluid flow.

III. Qualitative Aspects of the Dynamics of Fluid Flow [50]

Consider the steady flow of fluid through a pipe. The nature of the flow may be investigated qualitatively by ejecting a coloured fluid from a capillary tube into the main body of fluid. Study of the forms assumed by such " flow-indicators " affords valuable evidence. For instance, for low velocities of fluid flow, the coloured filament flows parallel to the axis of the pipe and remains sharply defined, although its width increases very slowly owing to diffusive and convective transfer normal to the axis. For this type of flow, termed laminar (streamline, or viscous) flow, *u*, the velocity component parallel to the axis, depends only on the radial distance from the axis. The velocity component, *v*, normal to the axis is very small ; that it is not zero follows from the fact that at the solid surface there is no slip between the surface and the fluid in contact with it.* This stationary layer retards the fluid in contact with it, which in turn retards the next layer and so on, the thickness of the layer of retarded fluid increasing with distance along the solid surface. At a certain distance from the pipe inlet the retarded layer fills the whole cross-section of the pipe ; beyond this point the velocity distribution over any cross-section is parabolic, as indicated in Fig. 2*a*.

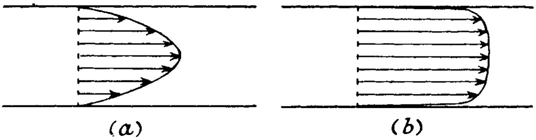

FIG. 2

As the rate of flow is increased, a velocity is reached at which the nature of the fluid flow alters abruptly ; the filament no longer flows parallel to the axis, but instead mixes rapidly with the main fluid body. On close examination it is seen that the mixing is due to very irregular fluid motions across the pipe. For this type of flow, termed turbulent flow, the velocity components *u* and *v* are now to be regarded as mean values taken over a sufficiently long interval of time. Their actual values at any given point fluctuate with time owing to the movement of turbulent eddies through the fluid body. The mean velocity component parallel to

---

[50] See Goldstein, " Modern Developments in Fluid Dynamics ", Clarendon Press, 1938.

* This postulate is of fundamental importance in the study of fluid dynamics (see ref. 50, p. 676). It must be noted, however, that it applies only to solid–fluid boundaries. Levich (*Discuss. Faraday Soc.*, 1947, **1**, 37) has pointed out that the tangential component of the velocity remains continuous at fluid–fluid boundaries, resulting in very much more favourable conditions for convective transfer.

the axis is zero at the wall, again owing to the absence of slip at the solid surface, but the distribution curve is now very much steeper near the wall and flatter near the axis (Fig. 2*b*).

The transition from laminar flow to turbulence is governed largely by the value of the dimensionless group $U\rho l/\eta$, where U is the mean rate of flow, ρ and η are respectively the density and viscosity of the fluid, and l is a length which characterises the system (in the present case, for example, the diameter of the pipe). This group is termed the Reynolds number *Re* and, if the fluid may be regarded as incompressible and η as independent of the rate of shear, is directly related to the mean velocity of the fluid. If the fluid entering the pipe is in laminar flow, the flow is laminar throughout the pipe for all Reynolds numbers below *ca.* 2100. Again, if the flow is turbulent at the inlet, the fluid reverts to laminar flow beyond a certain critical distance from the inlet for numbers below 2100 ; should the pipe be shorter than this critical length, which is a function of *Re* and of the diameter of the pipe, the flow remains turbulent. On the other hand, for Reynolds numbers greater than 2100, turbulence may develop. The onset of turbulence is favoured by sharp angles, roughness of the walls, constrictions in the pipe, etc. Once the character of the flow changes, the degree of turbulence increases with increasing *Re* until maximum turbulence results. Ideally, maximum turbulence should mean that the whole body of fluid is in turbulent flow. It appears, however, that this state is not realised in practice ; experiment (see, *e.g.*, Fage and Townend [43]) indicates that between the main fluid body in turbulent flow and the wall there is always a region of laminar flow. The thickness of this laminar boundary layer depends upon the mean velocity of the fluid and upon the degree of smoothness of the wall. The transition between the laminar boundary layer, in which the viscous forces predominate, and the turbulent main body, where the effect of the viscous forces is negligible, is continuous.

For kinetic studies of heterogeneous reactions, the system is usually of a different type. The liquid is contained in a vessel and is stirred, either with a stirrer (the propeller and paddle being the most common types), or with the solid itself, often in the form of a cylinder.* The same general considerations apply, subject to an important qualification. Unless the dimensions of the system are so large (or those of the solid so small) that the volume of fluid may be regarded as infinite, there are now other interfaces to consider, *i.e.*, between the stirrer and the fluid, and at the walls of the containing vessel. This necessarily must render the treatment more complex. Paddle-stirred systems are further complicated by the phenomenon of cavitation behind the trailing edges of the stirrer at high speeds of rotation. Hixson and his co-workers [51] have made a detailed

---

[51] (*a*) Hixson and Crowell, *Ind. Eng. Chem.*, 1931, **23,** 1002, 1160 ; (*b*) Hixson and Luedeke, *ibid.*, 1937, **29,** 927 ; (*c*) Hixson and Baum, *ibid.*, 1941, **33,** 478, 1433 ; (*d*) *idem, ibid.*, 1942, **34,** 120, 194 ; see also refs. 6 and 31.

* Levich [44] points out that the cylinder appears to have been chosen on grounds of simplicity of flow, although the system is, in fact, extremely complicated from a hydrodynamical point of view.

study of the characteristics of stirred systems. In particular, they have shown that there is a lower critical Reynolds number governing the transition from non-turbulent to turbulent flow, analogous to the case of pipe flow.

Although, for most systems, the quantitative treatment of fluid flow is difficult, if not impossible, the qualitative treatment is of significance in the study of mass-transfer rates. For laminar fluid flow parallel to the solid surface, the transport of matter must be governed partly by convection and partly by diffusion, the role of diffusion becoming more important as the surface is approached. Moreover, for turbulent flow, the state more often encountered in systems of chemical interest, the transport of matter to the surface can be broadly resolved into two processes : (*a*) the transport by forced convection from the body of the fluid to the boundary layer, and (*b*) the transport by diffusion and convection across the boundary layer to the solid surface. The important feature is that both for turbulent and for non-turbulent flow there is a region adjacent to the solid surface wherein the diffusive transport of matter is important. Thus we have a new, albeit approximate, interpretation of the physical nature of the layer of thickness δ determined from the simple Nernst theory.

For certain systems, a quantitative treatment of mass-transfer in terms of the fluid flow is possible (see next section) ; in general, however, the difficulties involved in the quantitative treatment are very great and one must resort to semi-empirical methods. Quite apart from the complex geometry of many systems of practical importance, the assumption that the entire resistance to mass-transfer lies within the boundary layer is sometimes incorrect. Thus Sherwood and Woertz [52] have shown that as much as 57% of the total resistance to mass-transfer may be due to the turbulent main body of the fluid.

IV. The Quantitative Treatment of Mass-transfer

If, at a given point in a solution, the velocity components parallel to the x, y, and z axes are u, v, and w, respectively, the rate of change of concentration at that point is given by the expression

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) - \left(u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z}\right) \qquad (10)$$

i.e., $\partial c/\partial t$ is the sum of the rate of change due to diffusion and of that due to convection. The velocity components are determined by the Navier–Stokes equations and by the equation of continuity, together with the appropriate boundary conditions. In general, a solution is possible only for those cases where the equations of fluid motion can be reduced to a simpler form.[53] Solutions have been obtained for certain systems, and in one case Levich [54]

---

[52] *Trans. Amer. Inst. Chem. Eng.*, 1939, **35**, 517.

[53] For a short account of the equations of fluid motion, and of mass-transfer, see Agar, *Discuss. Faraday Soc.*, 1947, **1**, 26.

[54] Ref. 44. See also the further papers by Levich : (*a*) *Acta Physicochim. U.R.S.S.*, 1944, **19**, 117, 133 ; (*b*) *J. Phys. Chem., U.S.S.R.*, 1948, **22**, 575, 711, 721 ; (*c*) *Discuss. Faraday Soc.*, 1947, **1**, 37.

has given a detailed treatment of mass-transfer under non-turbulent conditions. A brief account of the system is given below.

It is convenient to use cylindrical polar co-ordinates, in which equation (10) becomes

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c}{\partial \phi^2} + \frac{\partial^2 c}{\partial y^2}\right) - \left(v_r\frac{\partial c}{\partial r} + \frac{v_\phi}{r}\frac{\partial c}{\partial \phi} + v_y\frac{\partial c}{\partial y}\right) \quad . \quad (11)$$

v_r, v_ϕ, and v_y are the velocity components at a point (r, ϕ, y). The system consists of a flat disc of very large area, the plane of which is taken as $y = 0$, rotating with a constant angular velocity ω about an axis $(r = 0)$ perpendicular to the plane of the disc in an infinite volume of solution. Under these conditions, the interface between the disc and the fluid is the only boundary surface in the system, *i.e.*, the shape of the containing vessel is without effect upon either the fluid flow or the rate of mass-transfer to the disc. The very large diameter of the disc means that any effects connected with the edge of the disc may be neglected. The solution of the equations of fluid motion, due to von Kármán,[55] leads to the following picture of the flow of fluid in the system, where we consider the side of the plane for which y is positive. At large values of y, v_y has a constant value $(-\,0{\cdot}886\sqrt{\nu\omega}$, where ν is the kinematic viscosity of the fluid) whilst the other velocity components are zero; *i.e.*, at points far distant from the disc the fluid moves towards the disc with a constant velocity. On the other hand, a thin layer of fluid at the surface is dragged by the disc and acquires rotational and radial motion. Finally, at $y = 0$, v_r and v_y are zero, and the rotational velocity at any point on the disc distant r from the axis is ωr. The flow is illustrated in Fig. 3 (after Levich [44]). Thus there is a transition from flow essentially normal to the surface to flow parallel to the surface, pointing to the existence of a viscous boundary layer. At a distance $y \sim 2{\cdot}8(\nu/\omega)^{\frac{1}{2}}$ the value of the component v_ϕ is one-tenth of the corresponding value at the solid surface, whereas the normal component v_y is about 80% of its maximum value. This distance, then, gives the approximate thickness of the layer of fluid dragged by the rotating disc. For water at room temperature, and for an angular velocity of 25 radians per second, the layer thickness is *ca.* 0·05 cm. All three components are functions of ν, ω, and y; v_r and v_ϕ are also dependent upon the radial distance from the axis, whereas the normal component is independent of r.

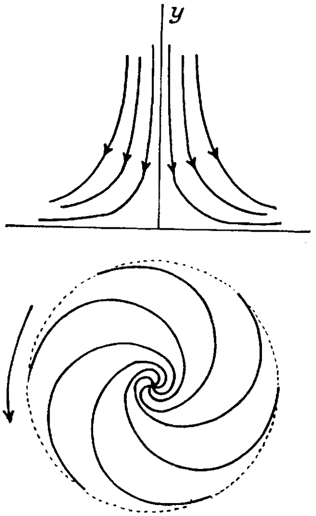

FIG. 3

Levich solved equation (11) for this system under non-turbulent flow

---

[55] See ref. 50, p. 110.

conditions.* A detailed account of his treatment is beyond the scope of this Review; it is of interest, however, to see how equation (11) was simplified, and to examine the solution, since Levich's conclusions stress the analogy between the fluid flow in the system (momentum-transfer) and mass-transfer.

The solution of the equations of fluid motion described above refers to the steady motion of the viscous fluid. For convective transfer, the condition for the steady state may be expressed $\partial c/\partial t = 0$. Moreover, from the axial symmetry of the system, it is evident that the concentration c must be independent of the angle ϕ; the terms in ϕ then disappear from (11). Finally, Levich assumed that c is independent of r, *i.e.*, that $c = c(y)$, so that equation (11) reduces to

$$D(\mathrm{d}^2c/\mathrm{d}y^2) = v_\mathrm{y}(\mathrm{d}c/\mathrm{d}y) \quad . \quad . \quad . \quad . \quad (12)$$

and we are dealing with one-dimensional transport. The form of equation (12) suggests the nature of the solution. At large values of y, v_y is constant, and provided this constant fluid velocity is sufficiently great (*i.e.*, reasonably high values of ω) the contribution of diffusion to the transport process will be small. This indicates a uniform concentration in the bulk of the solution. Very close to the disc, however, v_y decreases in magnitude, and the rate of mass-transfer is increasingly governed by diffusion.

The solution of equation (12) has already been given (see Fig. 1). Provided the volume of solution, V, is large enough to reduce the effects of the vessel walls to a minimum, and the diameter of the disc is very much larger than the thickness of the boundary layer, the solution may be applied to a system of finite size,

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{DA}{V}\cdot\frac{(c - c_\mathrm{i})}{0{\cdot}893\delta'} \quad . \quad . \quad . \quad . \quad (13)$$

where δ' is the thickness of the region over which the concentration differs significantly from the bulk concentration. From the integration of (12), $\delta' = 1{\cdot}805(D/\nu)^{\frac{1}{3}}(\nu/\omega)^{\frac{1}{2}}$. Comparison of equations (3) and (13) shows that the thickness of the Nernst layer is given by the expression

$$\delta = 0{\cdot}893\delta' = 1{\cdot}612D^{\frac{1}{3}}\nu^{\frac{1}{6}}\omega^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (14)\dagger$$

Levich's theory has been tested by Siver and Kabanov,[21] who studied the limiting currents ($c_\mathrm{i} = 0$) at an amalgamated copper disc cathode

---

* For this system the Reynolds number $Re = a^2\omega/\nu$, where a is the radius of the disc. Experiment (see, *e.g.*, ref. 50, p. 368) indicates that the lower critical Re is $\sim 10^5$.

† [*Added in proof* :] Wagner (*J. Appl. Phys.*, 1948, **19,** 837) has solved the equation corresponding to eqn. (11) for heat-transfer in this system. In a personal communication to King, he points out that his treatment, when applied to mass-transfer in the system, leads to the expression $\delta = 1{\cdot}78D^{\frac{1}{3}}\nu^{\frac{1}{6}}\omega^{-\frac{1}{2}}$. Wagner, however, has used the approximate solutions of the Navier–Stokes equations given by von Kármán (*Z. angew. Math. Mech.*, 1921, **1,** 244), whereas Levich employed the more exact solutions obtained by Cochran (*Proc. Camb. Phil. Soc.*, 1934, **30,** 365). The Reviewers are grateful to Professor C. V. King for drawing their attention to Wagner's paper, and for informing them of Wagner's communication to him.

rotating in various solutions ; in each case the limiting (diffusion) current was proportional to $\omega^{\frac{1}{2}}$. A more important test, however, consists in the comparison of values of δ calculated from equation (14) with those determined by experiment using the simple Nernst theory. Their results for the discharge of hydrogen ions from a solution 0·002N in hydrochloric acid and 0·1N in potassium chloride (added to eliminate ionic migration) are shown in Table 4.

TABLE 4

ω, radians/sec.	9·42	19·92	37·70	56·53	75·40
$10^3\delta$, cm., calc. from (6) . .	10·16	7·15	5·24	4·20	3·71
$10^3\delta$, cm., calc. from (14) . .	10·31	7·11	5·16	4·22	3·67

It appears that equation (14) also applies to a rotating paddle-type specimen.[22] In Table 5, the calculated values of δ for the dissolution of zinc specimens in aqueous iodine solutions are compared with the values derived from the Nernst theory. From Tables 4 and 5 it will be seen that the agreement between theory and experiment is satisfactory, particularly at the higher rates of stirring, as required by Levich's treatment. Thus for these two systems, the thickness of the conventional diffusion layer (and hence of the rate of mass-transfer) can be calculated without reference to the experimentally observed rate.

TABLE 5

ω, radians/sec.	5·23	7·85	10·5	15·7	20·9
$10^3\delta$, cm., calc. from (6) . .	7·36	6·01	5·20	4·25	3·68
$10^3\delta$, cm., calc. from (14) . .	7·98	6·40	5·61	4·37	3·72

From this, and the qualitative considerations advanced in Section III, it is reasonable to suppose that for any system, under turbulent or non-turbulent conditions, the thickness of the fictitious Nernst layer (and of δ' also) may be expressed as a function of D, ν, and the characteristic velocity of the system U. For non-turbulent flow, the form of the dependence will be similar to equation (14) ; thus, Levich has shown that for laminar flow along a flat plate (or a surface having a very large radius of curvature)

$$\delta = 3x^{\frac{1}{2}}D^{\frac{1}{3}}\nu^{\frac{1}{6}}U^{-\frac{1}{2}} \quad . \quad . \quad . \quad (15)$$

provided the dimensions of the system are such that other wall and edge effects are again negligible. For this case, δ increases as the square root of the distance x from the edge of the plate.* Since D is an inverse function of ν, the small values of the powers on D and ν explain why early workers assumed δ to be independent of these quantities, and why similar values of δ are often obtained for different reactions under the same flow condi-

---

* Eucken's treatment for mass-transfer to a plane surface from fluid in laminar flow parallel to the surface (ref. 47) has been criticised by Levich. Eucken's solution [$\delta = 1{\cdot}24(Dx/U_1)^{\frac{1}{3}}$, where U_1 is the fluid velocity at unit distance from the surface] may be compared with (15). Experimentally, Trümpler and Zeller (*Helv. Chim. Acta*, 1951, **34**, 952) find that $\delta \propto U^{-0{\cdot}43}$.

tions (see Table 1). Except for systems of very simple form, the constant of proportionality, which depends only upon the geometry of the system, must be determined by experiment.

The quantitative treatment of mass-transfer under conditions of turbulent fluid flow is very much more difficult. In addition to the problem of solving the equations of fluid motion, it is uncertain to what extent the analogy between mass- and momentum-transfer is valid in this region. For the allied problem of heat-transfer, Goldstein [56] regards the assumption of similarity in the velocity and temperature distributions as doubtful, whilst Levich,[57] from a theoretical study of mass-transfer to a smooth plate, asserts that the analogy definitely breaks down. On the other hand, Sherwood [58] has recently discussed the question of mass-, heat-, and momentum-transfer under turbulent flow conditions, and concludes that there is a good measure of experimental support for the analogy. The empirical approach described in the next section suffices for most practical purposes and, as will be seen, shows that the dependence of δ on D and ν is again such that one would expect δ to have approximately the same value for quite different reactions under the same flow conditions.

It is desirable that more extensive investigations be carried out on systems of simple geometric form, such as those described above, and pipe systems where a metal pipe reacts with a fluid flowing through it.* In practice, however, the geometry of the system is usually governed by other factors, with the result that a solution of the equations of convective transfer is not possible. For such systems, the use of dimensional analysis has proved to be of value.

V. Application of Dimensional Analysis to Mass-transfer

In the preceding sections, attention has been confined to cases of forced convection. Although natural convection, arising from variations in density due to concentration changes and from temperature gradients within the system, must play some part in such cases, the effect is negligible for most systems. The following discussion will also be limited to cases of forced convection although the method is applicable, with modification in detail, to natural convection.†

Let $\bar{\jmath}$ represent the mean transfer rate per unit surface area, being defined by the relation

$$\bar{\jmath} = \frac{1}{A}\int_0^A \frac{\mathrm{d}m}{\mathrm{d}t}.\mathrm{d}A = \frac{D(c_i - c)}{\delta} \quad . \quad . \quad . \quad . \quad (16)$$

---

[56] *Op. cit.*, Chap. XV.

[57] Ref. 54*b*, p. 711.

[58] *Ind. Eng. Chem.*, 1950, **42**, 2077 ; see also Bedingfield and Drew, *ibid.*, p. 1164.

* *E.g.*, the dissolution of a copper pipe in ammonia solutions, studied by Uchida and Nakayama (*J. Soc. Chem. Ind., Japan*, 1933, *B*, **36**, 635), and in nitric acid and ferric chloride solutions, studied by Buben and Frank-Kamenetzkiĭ (*J. Phys. Chem., U.S.S.R.*, 1946, **20**, 225).

† For a more detailed account of both natural (free) and forced convection, and references to the literature, see Agar [53] and the recent study of mass-transfer under natural convection by Wagner (*J. Phys. Colloid Chem.*, 1949, **53**, 1030).

where A is the surface area and $\mathrm{d}m/\mathrm{d}t$ is the actual rate of mass-transfer per unit area at any point on the surface. Then for transport under forced convection in systems where the solid surface is the only boundary surface, we require to know the dependence of $\bar{j}$ upon the characteristic velocity of the fluid U, the kinematic viscosity ν ($= \eta/\rho$), the diffusion coefficient of the solute D, the concentration difference $(c - c_i) = \Delta c$, and upon the characteristic length of the system l. The dimensions and units of these quantities are given in Table 6, together with the corresponding details for the quantities involved in heat-transfer problems.[59]

The dependence may be expressed as

$$\bar{j} = \Phi(U,l,\nu,D,\Delta c) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where the form of the function depends only on the shape of the solid surface. For many purposes, the assumption that Φ is a power function of the form

$$\bar{j} = BU^{p_1}l^{p_2}\nu^{p_3}D^{p_4}\Delta c^{p_5} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

is satisfactory,* whence, by expressing the condition that the product of the dimensions of the quantities on the right-hand side (B being a number) must be the same as the dimensions of $\bar{j}$, the powers may be expressed in terms of any two of them, *e.g.*, in terms of p_1 and p_4,

$$\bar{j} = BU^{p_1}l^{(p_1-1)}\nu^{(1-p_1-p_4)}D^{p_4}\Delta c \quad . \quad . \quad . \quad (19)$$

This can be rearranged to form a relation between three dimensionless groups. Of the possible groups, the following are usually chosen, since it is convenient to have the velocity appearing in but one group :

TABLE 6

Mass-transfer			Heat-transfer		
$\bar{j}$	Mean transfer rate per unit area (mole/cm.^{2}-sec.)	$\mathrm{ML^{-2}T^{-1}}$	$\bar{q}$	Mean transfer rate per unit area (cal./cm.^{2}-sec.)	$\mathrm{Heat.L^{-2}T^{-1}}$
Δc	Concn. diff. (mole/cm.^{3})	$\mathrm{ML^{-3}}$	$\Delta\theta s\rho$	Heat difference (cal./cm.^{3})	$\mathrm{Heat.L^{-3}}$
D	Coeff. of diffusion (cm.^{2}/sec.)	$\mathrm{L^2T^{-1}}$	$\lambda/s\rho$	Thermal diffusivity (cm.^{2}/sec.)	$\mathrm{L^2T^{-1}}$
ν	Kinematic viscosity (cm.^{2}/sec.)	$\mathrm{L^2T^{-1}}$	ν	Kinematic viscosity (cm.^{2}/sec.)	$\mathrm{L^2T^{-1}}$
l	Characteristic length (cm.)	L	l	Characteristic length (cm.)	L
U	Characteristic velocity (cm./sec.)	$\mathrm{LT^{-1}}$	U	Characteristic velocity (cm./sec.)	$\mathrm{LT^{-1}}$

where, for heat-transfer : s is the specific heat at constant pressure (cal./g.-deg.),
ρ is the density of the fluid (g./cm.^{3}),
$\Delta\theta$ is the temperature difference (deg.),
and λ is the thermal conductivity of the fluid, (cal./cm.-sec.-deg.).

	Mass-transfer	Heat-transfer
The Nusselt number † . .	$Nu = \bar{j}l/D\Delta c$	$Nu = \bar{q}l/\lambda\Delta\theta$
The Prandtl number † . .	$Pr = \nu/D$	$Pr = \nu s\rho/\lambda$
The Reynolds number . .	$Re = Ul/\nu$	$Re = Ul/\nu$

Equation (19) may then be written

$$Nu = B(Re)^a(Pr)^b \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where p_1 and $(1 - p_4)$ have been replaced by a and b, respectively.

Since U appears only in Re, the power on Re is evidently the stirring coefficient (see Table 2). Thus a may be determined by studying the variation of Nu (or $\bar{j}$) with change of fluid velocity, all other factors being held constant. If the dependence of D on ν is known, b may similarly be determined from a study of the variation of Nu with change of fluid viscosity, and B can be evaluated. The advantage of the method lies in the fact that comparatively few measurements are required to establish the dependence of $\bar{j}$ on the other factors. Moreover, once the relationship has been established, it may be used to calculate the rate of mass-transfer for values of the individual variables lying outside the ranges covered by actual experiment, provided only that the values of the groups fall within the ranges studied.[60]

The physical significance of the dimensionless groups is of interest. For mass-transfer, the Nusselt number represents the ratio of the actual rate of mass-transfer per unit area $\bar{j}$, to the rate of mass-transfer by diffusion in the stationary fluid $\Delta cD/l$. The Prandtl number is the ratio of the fluid property governing the transfer of momentum by viscous effects due to a velocity gradient, to the fluid property governing mass-transfer by molecular diffusion due to a concentration gradient. The Reynolds number may be regarded as the ratio of fluid momentum per unit area per unit time ρU^2, to the viscous drag force per unit area $\eta U/l$ against which it is balanced. Evidently Re is the group which determines the velocity distribution (see Section III).

In practice, however, it is not always possible to design the system so that the solid reactant surface is the only effective boundary surface. If this cannot be done, $\bar{j}$ will also be a function of other lengths such as, *e.g.*, in stirred systems, the diameter of the containing vessel, the depth of the solid reactant below the liquid–air interface, etc. Provided all measurements are carried out upon the same system, or upon a series of geometrically similar systems, this dependence can be incorporated in the number B : but where, for example, it is desired to compare mass-transfer to the *same* reactant surface in a series of vessels of similar shape but differing dimensions, further dimensionless groups of the form (l'/l) must be included in equation (20). Comparatively little work has been done in this connection. The papers by Hixson and his co-workers [51] have

---

[59] See, *e.g.*, Fishenden and Saunders, " An Introduction to Heat Transfer ", Clarendon Press, 1950 ; Goldstein, *op. cit.*, Chapters XIV and XV ; Sherwood, ref. 58 ; Wicke, *Chem. Ing. Tech.*, 1951, **23**, 5.

[60] Fishenden and Saunders, *op. cit.*, ref. 59.

* Equations of another type have been proposed for presenting heat-transfer results over wide ranges (see, *e.g.*, Eckert, " Introduction to the Transfer of Heat and Mass ", McGraw-Hill, 1950, p. 140).

† For mass-transfer, the Nusselt and the Prandtl number are sometimes termed the Sherwood (Sh) and the Schmidt (Sc) number, respectively.

already been cited, and Pratt[61] has published an extensive study of the resolution of B for heat-transfer in a somewhat complicated paddle-stirred system.

Comparison of equations (16) and (20) shows that the relation between δ and the other variables can be expressed by

$$\delta = (l/B)(Re)^{-a}(Pr)^{-b} \qquad . \quad . \quad . \quad . \quad (21)$$

from which, since Δc does not appear in the equation, follows the important fact that the thickness of the Nernst diffusion layer must be independent of the concentration difference ;[53] the same holds true for δ', the thickness of the actual diffusion layer.

It is of interest to consider the values of a found for mass-transfer under non-turbulent and turbulent conditions, since the type of flow is largely governed by Re. Although very few investigations of mass-transfer in the non-turbulent region have been reported, it is known that $a = 0{\cdot}5$ for laminar flow along a plate, and for the rotating disc system (see Section IV) ; the same value is found for heat-transfer to a flat plate. On the other hand, a lower power ($a = 0{\cdot}33$) expresses the dependence for heat-transfer in pipes.[60] For turbulent flow, the dependence of δ on Re increases with the degree of turbulence until a reaches a maximum value, corresponding to fully developed turbulence. It appears that for most systems $a_{\text{max.}} \sim 1$ (see Table 2), although for both heat- and mass-transfer in pipes the value is again somewhat lower ($a_{\text{max.}} \sim 0{\cdot}8$).

The dependence of δ on Pr illustrates an important difference between heat-transfer in liquids and gases, mass-transfer in gases, and mass-transfer in liquids. The Prandtl numbers for heat-transfer, and for mass-transfer in gases, are usually of the order of unity, the highest numbers ($Pr \sim 300$) being observed in the study of heat-transfer in viscous oils. For these liquids, however, ν is markedly dependent on the temperature, with the result that the velocity distribution differs considerably from that obtaining under isothermal conditions. In particular, the distribution may vary according to the direction of heat flow so that the theoretical interpretation of the results is rendered very difficult. This difficulty does not arise for mass-transfer in liquids, however, and the process may be studied at Prandtl numbers of several thousands (*e.g.*, for aqueous solutions at room temperature, $Pr \sim 1000$).[62]

Several workers have postulated that the value of the power on the Prandtl group should be the same both for heat- and mass-transfer under comparable conditions.[63] The theoretical value of b is 0·33 for mass-transfer in the non-turbulent region, whilst the same value is suggested[64] for heat-transfer through a laminar boundary layer even when Pr is as low as 0·7. The postulate seems to be in accord with experiment, although the experimental determinations of b for mass-transfer are relatively few. Some of

---

[61] *Trans. Inst. Chem. Eng.*, 1947, **25,** 163.

[62] Buben and Frank-Kamenetzkii, *J. Phys. Chem., U.S.S.R.*, 1946, **20,** 225.

[63] See, *e.g.*, (*a*) Colburn, *Trans. Amer. Inst. Chem. Eng.*, 1933, **29,** 174 ; (*b*) Chilton and Colburn, *Ind. Eng. Chem.*, 1934, **26,** 1183.

[64] Lighthill, *Proc. Roy. Soc.*, 1950, *A*, **202,** 359.

the recorded values for heat- and mass-transfer are given in Table 7 ; the type of flow (turbulent T, or non-turbulent N.T.) is specified, where known. With the exception of the first value, the values fall within the range 0·3—0·5. So far as can be judged, b is the same for both turbulent and non-turbulent flow and, for most purposes, can be regarded as having the constant value 0·33.

TABLE 7. *Values of the Prandtl power*

System	Type of flow	b	Ref.
Dissolution of metal cylinders in acids, etc. . . .	T	0·17*	65
Dissolution of Zn foil in aq. iodine solutions . . .	N.T.	0·27	22
Dissolution of Zn, Cd in dil. HCl and HOAc, etc. .	T (?)	0·3* †	66
Heat-transfer in the same apparatus	T (?)	0·3	66
Dissolution of Mg cylinders in acids	T (?)	0·3*	45
Heat-transfer in paddle-stirred system	T	0·3	61
Reaction between wool and NaOCl solutions . .	T (?)	0·3—0·5	67
Dissolution of $Ph\cdot CO_2H$ in water, etc.	N.T & T	0·33—0·4‡	68*a*
Dissolution of $Ph\cdot CO_2H$ in aq. NaOH and NH_3 . .	N.T	0·33	68*b*
Dissolution of $Ph\cdot CO_2H$ in water flowing through pipe, etc.	T	0·33	69
Heat-transfer in conduits	T	0·4	70
Vaporisation of liquids from a wetted wall column into air	T	0·44	71
Dissolution of $Ph\cdot CO_2H$ in various solvents . . .	N.T & T	0·5	51*c*
Heat-transfer in same apparatus	N.T & T	0·5	51*c*
Dissolution of $Ph\cdot CO_2H$ in water, etc.	T (?)	0·5	51*d*

* King and his co-workers determine b from the relation : velocity constant $\propto D^{\text{const.}}$. Provided ν is constant (which will be approximately the case for the dilute solutions used), const. = $(1 - b)$.

† King and Howard's results have been recalculated by Hixson and Baum,[51c] who find the expression $Nu = B(Re)^{0\cdot41}(Pr)^{0\cdot4}$.

‡ The system consisted of granules of the solid packed into a tube, with the fluid flowing through it. For continuous fluid flow b = 0·4, whereas for film flow b = 0·33.

VI. A Classification of Heterogeneous Reactions

Since the publication of Nernst's theory, many experimental investigations of heterogeneous systems have been made. Some of the processes studied are properly to be interpreted in the light of the modified form of his theory, but there are numerous examples of reactions for which the observed rate is determined by the rate of chemical reaction at the interface. Van Name and Hill [72] were the first to propose a classification of heterogeneous reactions of the type considered in this Review. On the

[65] Ref. 33*b*. Results recalculated by King and Howard, ref. 66.

[66] King and Howard, *Ind. Eng. Chem.*, 1937, **29**, 75.

[67] Alexander, Gough, and Hudson, *Trans. Faraday Soc.*, 1949, **45**, 1058.

[68] Van Krevelen and Krekels, *Rec. Trav. chim.*, (*a*) 1948, **67**, 512 ; (*b*) 1950, **69**, 1519.

[69] Linton and Sherwood, *Chem. Eng. Progress*, 1950, **46**, 258.

[70] McAdams, " Heat Transmission ", 2nd edn., McGraw-Hill, 1942.

[71] Gilliland and Sherwood, *Ind. Eng. Chem.*, 1934, **26**, 516.

[72] *Amer. J. Sci.*, 1916, **42**, 301.

basis of the rate-determining step, they divided heterogeneous reactions into three types:

(i) The rate of chemical reaction at the interface is very much faster than the rate of transport of reactant to, or of products from, the surface. The observed rate is therefore determined solely by the rate of the slowest transport process. It seems preferable to term these "transport-controlled" processes rather than "diffusion-controlled", since mass-transfer occurs both by diffusion and by convection.

(ii) The rate of chemical reaction at the interface is much slower than the rate of either of the transport processes, and hence determines the observed rate. These may be termed "chemically-controlled" processes, although the term "activation-control" is sometimes used. (Since we are concerned with the rôle of transport in heterogeneous processes, it is convenient to term all steps in which transport plays no part, *e.g.*, the actual processes of solution or deposition at the solid surface, adsorption, etc., chemical processes.)

(iii) Both rates are of the same order of magnitude, and the observed rate is determined by some function of the two. These have been termed reactions of intermediate type.

From general kinetic principles, the distinction between the possible types of system will not be sharp: rather would one expect heterogeneous reactions to show a gradation between the limiting cases of chemical and transport control. Van Name and Hill's third class is evidently the general case.

It is noteworthy that, whereas the true rates of chemical reaction at interfaces vary over a very wide range, the overall rates range from extreme slowness to an upper limit determined solely by the rate of a transport process; [33b] the same is true, of course, for homogeneous reactions in the liquid phase.[73]

Chemically-controlled Reactions.—Since we are only incidentally concerned with reactions of this class, a brief treatment will suffice for our present purpose.

For chemically-controlled reactions we have the condition that the concentration of solute is uniform throughout the fluid body.* The solute molecules must collide with the surface before reaction can occur, hence the simplest case takes the form of a bimolecular process in which the "concentration" of the solid is represented by the surface area. For a given area, moreover, the rate will again be inversely proportional to the volume of solution, so that the rate may be expressed

$$-\mathrm{d}c/\mathrm{d}t = k_{\mathrm{C}}Ac^{n}/V \quad . \quad . \quad . \quad . \quad (22)$$

where k_{C} is the chemical velocity constant per unit area at unit volume

---

[73] Christiansen, *J. Colloid Sci.*, 1951, **6**, 213.

* This is not strictly true when adsorption occurs at the surface, but adsorbed layers are of negligible thickness compared with the usual thickness of the diffusion layer. Adsorption processes will not be considered, however, except for cases where the reaction products are adsorbed on the surface, so reducing the area of surface available for attack.

and n is a power expressing the order of the reaction. For many reactions of this type $n = 1$, reactions of higher order being uncommon. Centnerszwer[1] claimed that the reaction between tin and hydrochloric acid is of the fourth order, but the evidence on which the claim is based seems doubtful.[5]

The General Case. Reactions of Intermediate Type.—When the concentration of solute at the interface is neither the same as that in the bulk of the solution nor equal to the equilibrium concentration (where the latter implies the solute concentration after an infinite time of reaction, excess solid being present), the observed rate is a function both of the rate of chemical reaction at the interface and of the rate of a transport process. Many workers have proposed extensions of the Nernst theory to reactions of this type.[74] In essentials, these treatments are very similar.

The rate of the chemical process may be expressed as

$$-\mathrm{d}c_{\mathrm{i}}/\mathrm{d}t = k_{\mathrm{C}}Ac_{\mathrm{i}}^{n}/V \quad . \quad . \quad . \quad . \quad (23)$$

where c_{i} is the concentration of the solute at the interface. For the transport process,

$$-\mathrm{d}c/\mathrm{d}t = k_{\mathrm{T}}A(c - c_{\mathrm{i}})/V \quad . \quad . \quad . \quad . \quad (3')$$

Then for the steady state, $k_{\mathrm{C}}c_{\mathrm{i}}^{n} = k_{\mathrm{T}}(c - c_{\mathrm{i}})$, from which c_{i} may be expressed in terms of the remaining quantities. For first-order chemical reactions, $c_{\mathrm{i}} = ck_{\mathrm{T}}/(k_{\mathrm{C}} + k_{\mathrm{T}})$ and, substituting in equation (3′), we have

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \left(\frac{k_{\mathrm{C}}k_{\mathrm{T}}}{k_{\mathrm{C}} + k_{\mathrm{T}}}\right)\cdot\frac{A}{V}\cdot c \quad . \quad . \quad . \quad . \quad (24)^{*}$$

Then

$$k_{1} = k_{\mathrm{C}}k_{\mathrm{T}}/(k_{\mathrm{C}} + k_{\mathrm{T}}) \quad . \quad . \quad . \quad . \quad (25)$$

where k_1 is the observed velocity constant per unit area at unit volume, so that if the chemical process is of the first order with respect to the solute, other criteria must be used to diagnose the rate-determining step, as was pointed out by Van Name and Hill.[72] It will be evident that when $k_{\mathrm{T}} \gg k_{\mathrm{C}}$, the observed rate is determined solely by the chemical process at the interface. Similarly, the condition $k_{\mathrm{T}} \ll k_{\mathrm{C}}$ represents the case of transport control. The reported cases of " pure " systems are those in

---

[74] *E.g.*, (*a*) Heymann, *Z. physikal. Chem.*, 1913, **81**, 204 ; (*b*) Tu, Davis, and Hottel, *Ind. Eng. Chem.*, 1934, **26**, 749 ; (*c*) Damköhler, in " Der Chemie-Ingenieur ", Akademische Verlagsgesellschaft, Leipzig, 1937, Vol. III, p. 413 ; (*d*) Frank-Kamenetzkii, *J. Phys. Chem.*, *U.S.S.R.*, 1939, **13**, 756 ; *Acta Physicochim. U.R.S.S.*, 1940, **12**, 9 ; (*e*) Kimball, *J. Chem. Phys.*, 1940, **8**, 199 ; (*f*) Tovbin, *J. Phys. Chem.*, *U.S.S.R.*, 1946, **20**, 1435 ; (*g*) Zdanovskiĭ, *ibid.*, p. 869 ; (*h*) Tanaka and Tamamushi, *Bull. Chem. Soc. Japan*, 1949, **22**, 187 ; (*i*) Hochberg and King, *J. Electrochem. Soc.*, 1950, **97**, 191 ; see also refs. 16 and 72. The treatment of fast electrode processes when the current is subjected to a small alternating current relative to the solution (Randles, *Discuss. Faraday Soc.*, 1947, **1**, 11 ; Ershler, *ibid.*, p. 269) is essentially similar. The original suggestion that the concentration at the interface may not be the same as the equilibrium concentration was made by Berthoud, *J. Chim. phys.*, 1912, **10**, 624.

* When the chemical reaction at the interface is of higher order, the expressions are more complex ; for second-order reactions $-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{k_{\mathrm{T}}A}{V}c\left(1 + \frac{\beta}{2} - \sqrt{\beta + \frac{\beta^{2}}{4}}\right)$, where $\beta = (k_{\mathrm{T}}/k_{\mathrm{C}}c)$.[74d]

which one or other of these conditions is satisfied under the particular experimental conditions employed. In certain circumstances, a change in the experimental conditions effects a change of control; this is considered in the following section. There are, however, two further points to be considered in connection with the simple treatment given above.

It is assumed that the areas appearing in equations (23) and (3′) are the same, but, in general, this will not be true. As mentioned in Section II, the rate of a transport-controlled reaction is proportional to A, the apparent surface area.[75] For chemically-controlled reactions, however, the rate is a function of the true surface area A_C. If the fraction of this area available for attack is σ, the rate is proportional to σA_C. With these modifications equation (25) becomes

$$k_1 = k_C k_T/[k_C + k_T(A/\sigma A_C)] \quad . \quad . \quad . \quad . \quad (26)$$

where k_1 is now the observed unit constant based upon the apparent area. The conditions for the limiting cases are now (i) $k_C\sigma A_C \gg k_T A$ for transport control, and (ii) $k_C\sigma A_C \ll k_T A$ for chemical control, *i.e.*, the conditions are based upon the overall rate constants.* The distinction is of importance since, although the apparent area A will usually change so slowly during the course of reaction (particularly for the case of the massive solid) that it may be regarded as constant, yet the available surface σA_C may increase owing to progressive roughening of the surface.

Secondly, since the thickness of the Nernst diffusion layer is independent of the concentration difference at the surface (Section V), the modified Nernst theory may be applied to k_T for reactions of intermediate type. For the simple systems discussed in Section IV, k_T may be calculated and k_C then determined from the observed rate constant by means of equation (25). For other systems, k_T must be determined experimentally.

TABLE 8. *The dissolution of metal cylinders in acid solutions*

($3\cdot5 \times 10^{-3}$M-*p*-Benzoquinone; metal cylinders $2 \times 2\cdot54$ cm.; 25°; 3200 r.p.m.; 250 ml. of solution. Experiments conducted under nitrogen.)

Acid or buffer	Metal	k_1 (cm.min.$^{-1}$)
0·1M-HCl, 0·05M-glycine . . .	Cd	0·88
0·03M-HCl, 0·07M-KHPh* . . .	Cd	0·82
0·1M-HOAc,† 0·1M-NaOAc† . .	Cd	0·82‡
0·1M-HOAc, 0·1M-NaOAc . . .	Pb	0·86
0·1M-HCl	Sn	0·86‡
0·1M-HOAc, 0·1M-NaOAc . . .	Cu	0·244

* Phthalate. † Acetate. ‡ Estimated from initial rate.

---

[75] See ref. 18. Laitinen and Kolthoff (*J. Phys. Chem.*, 1941, **45**, 1061) find this also to hold for mass-transfer under natural convection.

* Equation (24) may be written $-\mathrm{d}c/\mathrm{d}t = K_C K_T c/V(K_C + K_T)$, where $K_T = k_T A$ and $K_C = k_C\sigma A_C$ are the overall transport and chemical constants, respectively. The use of the unit rate constants (being independent of area) seems preferable, however, although the separate evaluation of k_C, k_T, and $A/\sigma A_C$ may not be possible for a given system.

As an example of the latter, we may consider the dissolution of metal cylinders rotating in acid solutions in the presence of *p*-benzoquinone as a depolariser, studied by Hochberg and King.[74i] The experimental conditions and results are detailed in Table 8. The first five results suggest that the observed rate is determined solely by the rate of a transport process, hence $k_1 = k_T = 0{\cdot}85$ cm.min.$^{-1}$. For copper, however, the rate constant is smaller ($k_1 = 0{\cdot}244$ cm.min.$^{-1}$) ; from equation (25), the difference between A and σA_C being neglected, $k_C = 0{\cdot}34$ cm.min.$^{-1}$. The authors give further examples in their paper.

VII. Factors affecting the Observed Rate

To conclude this Review, the factors which affect the observed rate must be considered. With the exception of temperature and of the initial concentration of solute, which are considered separately at the end of this section, the factors may broadly be divided into those affecting the chemical rate and those affecting the rate of the transport process. King,[46] Kressman and Kitchener,[76] and Zimmerman [77] have discussed the question of suitable criteria for diagnosing reaction type.

A change in the rate-determining step will be described as a change of control : this may be from transport control to the intermediate type of control, for example, or from one form of transport control to another.[78] More generally, an alteration in the dependence of the observed rate constant on the rate constants of the primary processes, an alteration which may or may not result in a change of control, will be termed a shift of control.

Factors affecting the Rate of the Chemical Process.—If the true surface area A_C increases during the course of reaction, the overall chemical rate constant K_C will increase, with shift towards transport control. In fact, varying the method of preparation of the solid surface provides one test of whether the chemical rate exerts any control on the observed rate,* provided the critical value of *Re* corresponding to the surface roughness (see below) is not exceeded. It is known, moreover, that k_C is often dependent on the particular crystal face exposed to attack (see Section II). The preferential development of certain crystal faces during the course of reaction may result in an increase in the mean value of k_C, reinforcing the effect of the increase in A_C. As we have seen, k_T is independent of the crystal face under attack.

For certain systems, the observed rate is decreased by the addition of small quantities of other substances. This effect, in some instances, is due

---

[76] *Discuss. Faraday Soc.*, 1949, **7**, 90. [77] *J. Phys. Colloid Chem.*, 1949, **53**, 562.

[78] *E.g.*, (*a*) Boyd, Adamson, and Myers, *J. Amer. Chem. Soc.*, 1947, **69**, 2836 ; (*b*) Alexander, Gough, and Hudson, *Trans. Faraday Soc.*, 1949, **45**, 1058, 1109 ; Alexander and Hudson, *J. Phys. Colloid Chem.*, 1949, **53**, 733.

* This test is particularly useful in the case of metal surfaces (see, *e.g.*, Salzberg and King, *J. Electrochem. Soc.*, 1950, **97**, 290 ; Bircumshaw and Riddiford, *J.*, 1951, 598) ; for non-metallic solids, submicronic disintegration of the surface (see Traube and v. Behren, *Z. physikal. Chem.*, 1928, **138**, *A*, 85), when this occurs, is an added complication.

to complex formation between the solute and the foreign substance, as in the case of the depression of the polarographic diffusion current of cadmium by bovine serum albumin studied by Tanford.[79] The increased size of the solute species results in a decrease of the diffusion coefficient, and hence of k_T (see below). In other cases, the effect has been traced to the adsorption of the foreign substance on the surface with consequent decrease in σ, the fraction of the area available for attack, and hence in K_C. Thus Marc [38] found that the addition of small quantities of certain dyes, *e.g.*, quinoline-yellow, reduces the rate of crystallisation of salts; Paine and France [80] have reported similar effects for the growth of alum crystals from solutions containing diamine sky-blue. The inhibition of corrosion of metals has long been known, and Jenckel and Bräucker [81] have shown that β-naphthaquinoline effects a reduction in the rate of dissolution of aluminium in hydrochloric acid solutions.

The reduction in K_C will result in a shift towards chemical control provided that, at the surface, the rate of transport of solute parallel to the surface is too fast to influence the observed rate, *i.e.*, provided the apparent surface area is unaltered. Owing to the fact that fluid motion persists up to points very near to the surface (Sections II and III) such that convection parallel to the surface is still marked although convection normal to the surface is negligible, this assumption would appear reasonable for systems subject to forced convection. There seems little doubt that the assumption is generally valid. Thus Volmer [82] demonstrated the existence of an adsorbed layer on crystals grown from the vapour or from the melt, and showed that the molecules in this layer are very much more mobile than in the melt. Moreover, a lateral flow of solute along the surface of a crystal must be assumed to explain the two-dimensional growth of crystals from aqueous solutions,[83] for, whereas the normal concentration gradient at the surface of the growing crystal varies from a maximum at the face centre to a minimum at each edge, the crystal face has generally the same linear rate of growth all over the face.

It should be noted that the influence of such added substances in itself offers no proof that the undisturbed system is subject to any degree of chemical control, although this has sometimes been assumed; as we have seen, the effect is to be interpreted as a shift of control. The magnitude of the shift may, of course, be increased by coupling the use of such foreign matter with a suitable alteration of the experimental conditions, *e.g.*, Jenckel and Bräucker [81] found that the reduction in the rate of dissolution of aluminium in the presence of β-naphthaquinoline was enhanced by an increase in the concentration of hydrochloric acid, and by a decrease in temperature (see below).

---

[79] *J. Amer. Chem. Soc.*, 1951, **73**, 2066. [80] *J. Phys. Chem.*, 1935, **39**, 425.

[81] *Z. anorg. Chem.*, 1935, **221**, 249. [82] *Trans. Faraday Soc.*, 1932, **28**, 359.

[83] (*a*) Bunn, *Discuss. Faraday Soc.*, 1949, **5**, 132; (*b*) Berg, *Proc. Roy. Soc.*, 1938, *A*, **164**, 79; (*c*) Humphreys-Owen, *ibid.*, 1949, *A*, **197**, 218; *Discuss. Faraday Soc.*, 1949, **5**, 144. In this discussion, recent work on the effect of impurities, dyes, etc., on crystal growth is reported.

Closely related to this effect is the case where accumulation and/or adsorption of the products affects the observed velocity. The adsorption of a soluble product may be considered first.[84] It is assumed that adsorption and desorption are rapid compared with the rate of reaction. Then the available fraction of the surface may be expressed by

$$\sigma = 1/(1 + k'x) \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where k' is a constant, and x is the concentration of product at time t. The rate of reaction is then

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{A}{V}\left(\frac{k_1c}{1 + k''x}\right) \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where $k_1 = k_\mathrm{C}k_\mathrm{T}/(k_\mathrm{C} + k_\mathrm{T}A/A_\mathrm{C})$, and $k'' = k'/(1 + k_\mathrm{C}A_\mathrm{C}/k_\mathrm{T}A)$. If $x = 0$ at $t = 0$, k_1 has the same significance as in equation (26). For strong adsorption of the product, σ will decrease very rapidly and the observed effect will be a shift towards chemical control, as in the case of added foreign substance. On the other hand, if the product is less strongly adsorbed, σ will decrease more slowly, and the observed effect will be a progressive fall-off in the overall rate, *i.e.*, an apparent change of order. Salzberg and King[85] have considered the more complex case when both reactant and product are adsorbed on the surface, adsorption equilibrium not being maintained whilst dissolution is proceeding.

Secondly, there is the case when the product accumulates as an insoluble layer on the surface. If this layer is impermeable to the solvent, the mechanism will undergo a marked change ; diffusion of reactants either way through the film may or may not now influence the observed rate. This case differs so markedly from the type of system under review that it will not be further considered.[86] For the case when the coating is permeable to the solvent, it seems probable that both the chemical and the transport rates will be affected. There is no doubt that the film will modify the characteristics of the diffusion layer owing to immobilisation of the solvent within the layer of product, possibly to the extent that δ becomes independent of the fluid velocity.[87] Certainly it appears that for several systems of this type the film offers additional resistance to mass-transfer.[22]

Factors affecting the Rate of Transport.—As mentioned above, a change in the roughness of the solid surface will be expected to affect A_C, and hence the overall chemical rate constant, rather than the corresponding quantities A and $k_\mathrm{T}A$ for the transport process. Nevertheless, the magnitude of k_T may be affected in certain circumstances.

From the standpoint of dimensional analysis, the roughness of the surface may be expressed as a dimensionless group termed the relative roughness, defined as the ratio of the mean height h of the surface irregu-

---

[84] Cf. Prutton and Day, *J. Phys. Colloid Chem.*, 1949, **53,** 1101, and ref. 74*i.*

[85] *J. Electrochem. Soc.*, 1950, **97,** 290.

[86] For a review of solid–gas systems of this type see Evans, *J. Corrosion*, 1948, **5,** No. 4, 15. For an interesting study of the change from transport control to control by diffusion through a compact layer of product, see Jaenicke, *Z. Elektrochem.*, 1951, **55,** 186.

[87] *E.g.*, Bircumshaw and Everdell, *J.*, 1942, 598.

larities to the characteristic length of the system. Equation (20) (Section V) then becomes

$$Nu = B(Re)^a(Pr)^b(h/l)^m \quad . \quad . \quad . \quad . \quad . \quad (29)$$

For fluid flow through pipes, the characteristic length being taken to be the radius of the pipe, Nikuradse[88] has shown that relative roughness over the range 1/507 to 1/15 is without effect on the friction factor in the region of laminar flow. For turbulent flow, however, the relative roughness effects a considerable increase in the friction factor, the effect becoming noticeable at a particular, critical Reynolds number: as the relative roughness increases, so the critical Re value becomes smaller whilst the increase in the friction factor becomes larger. Similar effects are to be expected in stirred systems. Thus we would expect the surface roughness, and hence the method of preparation of the solid surface, to be without effect on k_T in the region of non-turbulent flow (*i.e.*, $m = 0$). In the turbulent region, however, k_T may well depend on the method of preparation of the surface, may be unusually sensitive to the rate of fluid flow over a certain range of velocities, and, further, may alter during the course of reaction owing to progressive roughening of the surface. An increase in the friction factor may be regarded most simply as an increase in the characteristic velocity of the system; hence the effect of an increase in surface roughness, where apparent, will be to increase the value of k_T with consequent shift towards chemical control. Since many of the published investigations describe systems in turbulent flow, this effect clearly merits attention.

The remaining factors need little discussion. From the discussion in Sections IV and V, the dependence of k_T on the coefficient of diffusion of the solute D, the kinematic viscosity of the fluid ν, and the fluid velocity U, may be expressed by

$$k_T = \mathrm{F}(U,D,1/\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where D and ν are not independent variables.[89] Hence an increase in D (or decrease in ν) will increase k_T with a corresponding shift towards chemical control. The dissolution of magnesium in ethanol–water solutions of acetic acid,[90] and that of silver in mineral oil solutions of sulphur,[91] appear to be examples of this effect. Similarly, an increase in the fluid velocity will cause a shift towards chemical control. For some systems,[74c, 76] it is observed that as the rate of stirring is increased the observed velocity constant reaches a limiting value, and thereafter is independent of the fluid velocity. This may be due to a change to chemical control, or to the stirrer's having reached maximum efficiency;[76] for any given case, other criteria must be applied to distinguish between these possibilities. In particular, the use of baffles in stirred systems is a convenient way of promoting turbulence, and so increasing the efficiency of the stirrer.

---

[88] Forschungsheft No. 361, Suppl. to *Forschung auf dem Gebiete des Ingenieurwesens*, 1933, 4*B*, July/August.

[89] Bircumshaw and Riddiford, *J.*, 1951, 1490.

[90] Roehl, King, and Kipness, *J. Amer. Chem. Soc.*, 1941, **63**, 284.

[91] Foley, Morrill, and Winslow, *J. Phys. Colloid Chem.*, 1950, **54**, 1281.

Finally, since k_T may depend upon the geometry of the apparatus (Section V), it will sometimes be possible to vary k_T by using a different type of stirring, or by altering the dimensions of the apparatus.

The Initial Concentration of Reactant.—Since δ is independent of the concentration difference at the surface, and D, in comparison with the other variables, is but slightly dependent on concentration, an increase in the initial concentration of reactant will be accompanied by an increase in the maximum rate (corresponding to $c_i = 0$) at which reactant can be transported to the surface. Then if, for a transport-controlled reaction, the initial concentration is increased, a point may be reached at which the maximum transport rate exceeds the rate at which chemical reaction at the surface can deal with the supply. A change in the initial concentration might thus result in a change of control. A clear example of this effect is provided by the exchange adsorption of cations from aqueous solutions by phenol–formaldehyde resins ; [78a] for 0·001M-solutions the observed rate is determined by the rate of transport of cations to the resin surface, whereas at 0·1M-concentration diffusion through the resin is the rate-determining step. The reaction between wool and potassium permanganate solutions, between wool and chlorine solutions,[78b] and the exchange of ^{64}Cu between a single-phase copper amalgam and an aqueous solution of cupric ion,[92] are probably further examples of this effect.

The Temperature Coefficient.[93]—An increase in temperature will increase both the rate of chemical reaction at the interface and the rate of the transport process. It is convenient to begin, therefore, by considering the effect on the unit rate constants for each step, and then to consider the temperature coefficient of the observed unit rate constant.

For the chemical reaction at the interface, the dependence of k_C on temperature may be expressed by means of the Arrhenius equation

$$k_C = Z_C e^{-E_C/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where the pre-exponential factor is of the order of magnitude of the collision frequency per unit area for molecules colliding with the surface, E_C is the apparent critical increment for the chemical process,[94] and the remaining symbols have their usual significance. In practice, it is found that E_C varies from a lower limit of zero.

Similarly, it is found that the dependence of k_T on temperature may be expressed as

$$k_T = Z_T e^{-E_T/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

On the simple Nernst theory, $E_T = E_D$, the activation energy for diffusion : this conclusion, as we have seen, is based on the assumption that δ is temperature-invariant. For solid–liquid systems, however, we may write

$$\delta \propto U^{-a}\nu^{(a - b)}D^{b} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

---

[92] Kayas, *Compt. rend.*, 1948, **226**, 2144.

[93] Riddiford, *J. Phys. Chem.*, in the press.

[94] Cf. Hinshelwood, "The Kinetics of Chemical Change", Clarendon Press, 1945, p. 214.

(see Section V), *i.e.*, for constant fluid velocity,

$$\mathrm{d}(\ln\delta)/\mathrm{d}T = [bE_{\mathrm{D}} - (a - b)E_{\nu}]/\boldsymbol{R}T^2 \quad . \quad . \quad . \quad (34)$$

where E_{ν} is the activation energy for kinematic viscous flow. Since a and b are temperature-invariant, δ will vary exponentially with temperature: the dependence, however, will be slight in comparison with the variation of the other quantities.* From equation (34)

$$E_{\mathrm{T}} = (1 - b)E_{\mathrm{D}} + (a - b)E_{\nu} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

since $k_{\mathrm{T}} = D/\delta$. From the discussion in Section V, $b \sim 1/3$ and a varies from 0·5 for non-turbulent flow to 1 for strongly turbulent flow. Equation (35) may then be written

$$\left.\begin{aligned} E_{\mathrm{T}} &= (4E_{\mathrm{D}} + E_{\nu})/6, \text{ for non-turbulent flow} \\ &= 2(E_{\mathrm{D}} + E_{\nu})/3, \text{ for strongly turbulent flow} \end{aligned}\right\} \quad . \quad . \quad (36)$$

and, since E_{D} and E_{ν} are of the same order of magnitude, E_{T} will be somewhat smaller than E_{D} for non-turbulent or mildly turbulent flow. On the other hand, E_{T} may be larger than E_{D} under strongly turbulent conditions.[67] As a rough guide, $E_{\mathrm{T}} \sim E_{\mathrm{D}}$ when $a = 2/3$.

From equation (25), the dependence of the observed unit constant on temperature may be expressed by

$$\frac{\mathrm{d}(\ln k_1)}{\mathrm{d}T} = \frac{1}{\boldsymbol{R}T^2}\left[\left(\frac{k_{\mathrm{C}}}{k_{\mathrm{C}} + k_{\mathrm{T}}}\right)E_{\mathrm{T}} + \left(\frac{k_{\mathrm{T}}}{k_{\mathrm{C}} + k_{\mathrm{T}}}\right)E_{\mathrm{C}}\right] \quad . \quad . \quad . \quad (37)$$

If an experimental energy of activation, E_{A}, is defined by the relation

$$\mathrm{d}(\ln k_1)/\mathrm{d}T = E_{\mathrm{A}}/\boldsymbol{R}T^2$$

E_{A} may be determined at any value of T from the tangent to the curve of $\ln k_1$ plotted against $1/T$; then from equation (37)

$$E_{\mathrm{A}} = \left(\frac{k_{\mathrm{C}}/k_{\mathrm{T}}}{1 + k_{\mathrm{C}}/k_{\mathrm{T}}}\right)E_{\mathrm{T}} + \left(\frac{1}{1 + k_{\mathrm{C}}/k_{\mathrm{T}}}\right)E_{\mathrm{C}} \quad . \quad . \quad . \quad . \quad (38)$$

and in general the variation of E_{A} with temperature is governed by the variation of the ratio $k_{\mathrm{C}}/k_{\mathrm{T}}$. Since in practice $Z_{\mathrm{C}} \gg Z_{\mathrm{T}}$, we may distinguish three cases: (i) $E_{\mathrm{C}} = E_{\mathrm{T}} = E_{\mathrm{A}}$, for which case k_1 varies exponentially with T; (ii) $E_{\mathrm{C}} < E_{\mathrm{T}}$, which corresponds to the condition $k_{\mathrm{C}} \gg k_{\mathrm{T}}$ at all temperatures, *i.e.*, $E_{\mathrm{A}} = E_{\mathrm{T}}$ at all temperatures; (iii) $E_{\mathrm{C}} > E_{\mathrm{T}}$, when at low temperatures the observed rate will be chemically-controlled, whereas at high temperatures the process will be transport-controlled. For case (iii), then, an alteration of temperature will result in a shift of control; if a sufficiently wide temperature range is practicable, a change of control will be observed. The combustion of carbon spheres in a flowing air stream,[74b] the catalytic oxidation of sulphur dioxide on platinum pellets,[95] and the dissolution of very pure iron in acids,[96] are examples of systems conforming to case (iii).

[95] Olson, Schuler, and Smith, *Chem. Eng. Progress,* 1950, **46,** 614.

[96] Abramson and King, *J. Amer. Chem. Soc.*, 1939, **61,** 2290.

* No detailed study of the temperature coefficient of δ under forced convection appears to have been made. Laitinen and Kolthoff (*J. Phys. Chem.*, 1941, **45,** 1079) conclude that the effective thickness of the diffusion layer at a rotating platinum microelectrode remains practically constant for small temperature changes (see also Jaenicke, *Z. Elektrochem.*, 1951, **55,** 648).

The Reviewers wish to thank all the many authors who have so kindly sent them reprints of their publications, and they have pleasure in acknowledging their debt to Miss E. Koutaissoff for her kindness in translating several Russian papers. Figs. 1 and 3 are reproduced by kind permission of the Academy of Sciences of the U.S.S.R.