731. *Transport to the Surface of a Rotating Disc.*

By D. P. Gregory and A. C. Riddiford.

Hitherto, experimental investigations designed to check the validity of Levich's theory[5] for transport to the surface of a rotating disc have been confined to the measurement of limiting currents over a range of stirring speeds at one experimental temperature. It is shown that these published values are lower than those predicted by the theory.

The theory has been subjected to further experimental check by studying the rate of dissolution of zinc discs in aqueous iodine solutions as a function of temperature, and of the speed of rotation of the discs. The kinematic viscosity of the solution, and the coefficient of diffusion of iodine, have been measured at each temperature. The observed rate constants characterising the transport of iodine to the surface of the discs are significantly lower than those predicted by the theory. The discrepancy has been traced to an approximation made by Levich. It is shown how this approximation can be avoided, and good agreement is then found between theory and experiment, both for the zinc–iodine system and for the limiting current.

Many studies of the rates of heterogeneous reactions between solids and solutions have been reported. Very often, the observed rate is determined partly or wholly by the transport of a solute species to or from the reacting interface, and the study of these transport processes then becomes a matter of considerable theoretical and practical importance.[1]

In principle, the simplest method of determining the contribution of the transport process to the observed rate lies in the study of quiescent systems, wherein transport is purely diffusive. In practice, however, density gradients set up in the vicinity of the interface, sometimes coupled with fortuitous thermal gradients, can lead to relative motion between the solid and the fluid, with a resultant increase in the rate of transport.

One way of avoiding this difficulty is to impress a definite velocity of sufficient magnitude upon the fluid, whereby the effect of natural convection can be made entirely negligible. This method is attractive, for it permits the study of the process by simple experimental techniques over a wide range of temperatures; but the theoretical difficulties are such that, in general, transport under conditions of forced convection must be treated

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[1] Bircumshaw and Riddiford, *Quart. Reviews*, 1952, **6**, 157.

by semi-empirical methods.[2] The case where transport occurs to or from a rotating disc is of special interest since an exact solution of the equations governing mass transport has been achieved.

In 1921, von Kármán [3] showed that an exact solution of the Navier–Stokes equations governing viscous flow is possible for the case of an infinite plane lamina rotating with constant angular velocity in an infinite volume of fluid about an axis perpendicular to the lamina; the exact solution was obtained by Cochran.[4] In 1942, Levich [5] used the velocity distribution so obtained to solve the corresponding mass-transport equations for the case of fluids containing not more than three ionic species. For an electrode process when the critical solute species is uncharged or, if ionic, is present in a large excess of indifferent ions, his theory leads to the following equation for the limiting current:

$$i_{\text{lim}} = 0{\cdot}620zFAc_{\infty}D^{2/3}\nu^{-1/6}\omega^{1/2} \times 10^{-3}\ \text{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where z is the number of electrons involved in the electrochemical reaction, F is the faraday, A is the apparent area of the working surface (cm.^{2}), c_{∞} is the concentration of the critical solute species in the bulk of the solution (moles/l.), D is the diffusion coefficient of this solute species (cm.^{2}/sec.), ν is the kinematic viscosity of the solution (cm.^{2}/sec.), and ω is the angular velocity of the laminar electrode (rad./sec.). The corresponding unit rate constant, k_T, characterising the rate of transport of a solute species to the disc is given by the relation

$$k_T = 0{\cdot}620D^{2/3}\nu^{-1/6}\omega^{1/2}\ \text{cm./sec.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The first experimental check of this important theory was made by Siver and Kabanov,[6] who studied the limiting currents for the reduction of oxygen dissolved in dilute sulphuric acid at rotating silver and at amalgamated copper disc cathodes. They showed that i_{lim} is proportional to $\omega^{1/2}$, and by assuming a reasonable value for the diffusion coefficient of dissolved oxygen at the experimental temperature (20° ± 1°) they reported good agreement between the observed values of i_{lim} and those computed from the theory. Subsequently, they investigated the discharge of hydrogen ion at a rotating amalgamated copper disc cathode from a solution 2×10^{-3}N in hydrochloric acid, which was made 0·1N in potassium chloride to suppress ionic migration.[7] Using a value for the diffusion coefficient of hydrogen ion based upon mobility data, they reported agreement between theory and experiment to within 3% at the one temperature studied (18°).

More recently, Hogge and Kraichman [8] have studied the limiting currents for the reduction of tri-iodide ion at a rotating platinum disc cathode. 0·1N-Potassium iodide was used as supporting electrolyte, and the effect of varying the angular velocity at different concentrations of tri-iodide ion was determined at 25·7°. A linear relationship was found between i_{lim} and $\omega^{1/2}$ for each concentration. They measured the kinematic viscosity of the solution and, from the theory, calculated the only undetermined quantity, *i.e.*, the diffusion coefficient of the tri-iodide ion. They claim that the value so obtained ($D = 1{\cdot}021 \times 10^{-5}$ cm.^{2}/sec. for the tri-iodide ion) compares favourably with those found by non-electrolytic methods, and cite a value of $D = 1{\cdot}08 \times 10^{-5}$ cm.^{2}/sec. at 25° obtained by Edgar and Diggs [9] for a solution 0·05N in iodine and 0·25N in potassium iodide. In this they are mistaken: the value actually reported by Edgar and Diggs is 1·08 cm.^{2}/day, or $1{\cdot}25 \times 10^{-5}$ cm.^{2}/sec., more than 20% higher than their value.

Finally, these authors have investigated the reduction of silver ion at a rotating silver disc cathode, a large excess of potassium nitrate being used as supporting electrolyte.[10] From their results, they have calculated the two values $D = 1{\cdot}416 \times 10^{-5}$ cm.^{2}/sec. at 25°

[2] Agar, *Discuss. Faraday Soc.*, 1947, **1**, 26.
[3] von Kármán, *Z. angew. Math. Mech.*, 1921, **1**, 244.
[4] Cochran, *Proc. Camb. Phil. Soc.*, 1934, **30**, 365.
[5] Levich, *Acta Physicochim. U.R.S.S.*, 1942, **17**, 257.
[6] Siver and Kabanov, *J. Phys. Chem., U.S.S.R.*, 1948, **22**, 53.
[7] *Idem, ibid.*, 1949, **23**, 428.
[8] Hogge and Kraichman, *J. Amer. Chem. Soc.*, 1954, **76**, 1431.
[9] Edgar and Diggs, *ibid.*, 1916, **38**, 253.
[10] Kraichman and Hogge, *J. Phys. Chem.*, 1955, **59**, 986.

and $1{\cdot}458 \times 10^{-5}$ cm.^{2}/sec. at 25·2° for silver ion at very low concentration in 0·2N-potassium nitrate solution. These values are significantly lower than the corresponding value $D = 1{\cdot}485 \times 10^{-5}$ cm.^{2}/sec. which they have computed from Onsager's limiting law for diffusion.[11]

It seemed desirable to subject Levich's theory to a more detailed experimental investigation, and since the earlier studies were all of limiting currents at one temperature, it was decided to check the validity of equation (2) over a range of temperatures by studying a reaction whereby the disc material is consumed during the process. The reaction between zinc and aqueous iodine solutions was chosen since the observed rate has been shown to be solely determined by the rate at which iodine can be transported to the zinc surface.[12] The published data for the diffusion coefficient of iodine in potassium iodide solutions are meagre,[13] so the appropriate values have been determined.

EXPERIMENTAL

Materials.—" AnalaR " iodine, potassium iodide, sodium thiosulphate, and sulphuric acid were used without further purification. The zinc foil was of electrolytic grade (99·9%).

FIG. 1.

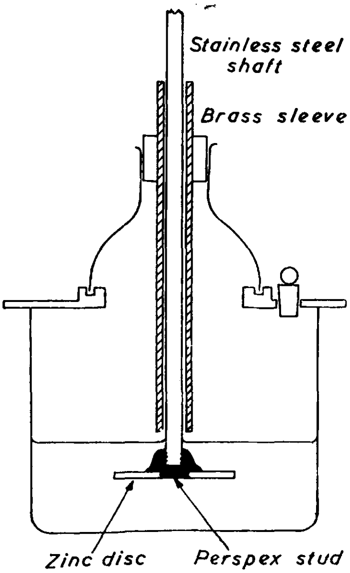
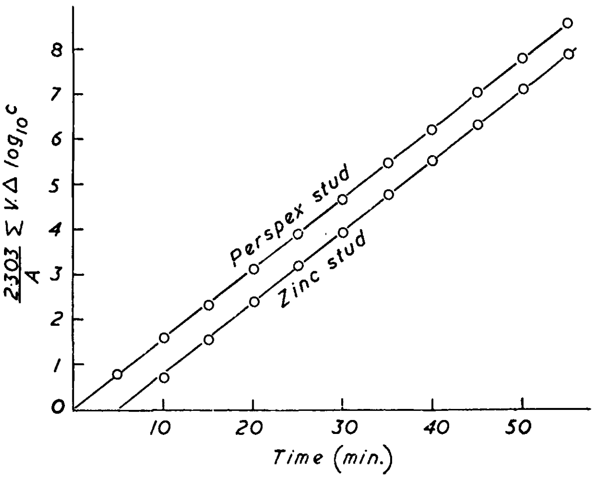


FIG. 2.



Apparatus.—The theory refers to an infinite plane lamina, *i.e.*, the diameter of the disc must be very much larger than the thickness of the transport boundary layer (*ca.* 10^{-3} cm.). Accordingly, discs 5·30 cm. in diameter were cut from zinc foil 0·5 mm. thick; later, this thickness was increased to *ca.* 3 mm. A threaded hole was cut in the centre of each disc to take a Perspex stud, which in turn was screwed to the stainless-steel stirring shaft (Fig. 1). A jig was made to ensure that each disc was cut to the same diameter, and that the thread was cut perpendicular to the plane of the disc. The end of the stud was turned flush with the lower face of the disc. The upper surface and edges of the disc were protected from attack by a thin coat of " Tufnol " lacquer, which was baked on to polymerise it. Preliminary tests, in which a disc was coated completely, showed that this lacquer was impervious to iodine solutions. These tests also served to show that the loss of iodine from the reaction vessel was negligible.

The stirring shaft was rotated at known speeds by means of a stroboscopic assembly similar to that previously described;[14] ball-races and a heavily lacquered brass sleeve (Fig. 1) ensured the absence of " whip."

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[11] Onsager, *Ann. N.Y. Acad. Sci.*, 1945, **46**, 241; Gosting and Harned, *J. Amer. Chem. Soc.*, 1951, **73**, 159.

[12] Bircumshaw and Riddiford, *J.*, 1952, 701.

[13] *Idem, J.*, 1951, 1490.

[14] *Idem, J.*, 1951, 598.

The size and shape of the reaction vessel are important since the theory specifies an infinite volume of solution, *i.e.*, the rotating disc must be the only boundary surface. Preliminary runs, with discs 5·30 cm. in diameter and rotating at 146 r.p.m. in beakers of different sizes, showed that the observed rate is independent of the vessel diameter when this is greater than *ca.* 11 cm. The rate is also independent of the height of the disc above the bottom of the vessel provided that this distance is greater than *ca.* 0·5 cm. The vessel finally used was *ca.* 12·5 cm. in diameter, and was closed by a flat Perspex lid. The disc and stirring shaft could be lowered into the solution through a hole cut in the Perspex lid until a glass dome mounted on the stirring assembly located in an annular groove, so sealing the vessel (Fig. 1). The thermostat maintained the temperature constant to within ±0·05°.

Method.—A solution which was 0·02N in iodine and 0·08N in potassium iodide was made approximately 0·001N in sulphuric acid to suppress the formation of a basic coating on the zinc surface;[14] 500 ml. of this solution were warmed to the thermostat temperature, degassed, and placed in the reaction vessel. The disc was cleaned with fine emery paper, washed with distilled water, and fitted to the stirring shaft. The joint between the Perspex stud and the shaft, and the exposed part of the shaft, were coated with paraffin wax. With the motor running, the disc was lowered into the solution. The joint between the dome and the groove in the Perspex lid was sealed with a little water. After some 5 min., when the motor had steadied to the required speed, a 5 ml. sample was withdrawn by pipette and titrated against 0·005N-sodium thiosulphate solution. Further samples were withdrawn at 5-min. intervals. After the run, the disc was removed from the solution, washed with distilled water, and stored under 0·001N-sulphuric acid. All the volumetric apparatus had been calibrated, and the appropriate corrections were applied. In evaluating the unit rate constant, k_T, allowance must be made for the decrease in volume each time a sample is removed. Bradley's method[5] was used, which avoids undue weighting of the first titration, k_T being evaluated graphically by using the first-order expression : $k_T t = (2{\cdot}303\ \Sigma\ V\ \Delta \log_{10}c)/A$, where t is the time in min., A is the *total* area of the underside of the disc and stud, and $\Delta \log_{10}c$ denotes the difference in the logarithm of the concentration at the beginning and end of an interval for which the volume is V. The initial volume of solution was varied over the range 400—600 ml. without effect on the observed rate constant, except for the highest speed studied (328 r.p.m.) at which a low result was obtained with 400 ml. of solution. For this reason, 500 ml. of solution were used in the later work, and the stirring speed was kept below 300 r.p.m. The results of early runs under seemingly identical conditions were of poor reproducibility. One fault was traced to the gassing of the solution, bubbles being formed on the underside of the disc : previous de-gassing of the solution eliminated this trouble. The presence of small bubbles increases the observed rate constant although the exposed area of zinc is decreased. These bubbles may promote turbulence, with a consequent increase in rate which is greater than any effect due to the blocking of part of the surface. A second fault was traced to the occasional trapping of a large bubble (*ca.* 1 cm. diam.) underneath on lowering the disc into the solution. Abnormally high results could usually be traced to a fault in the protective lacquer coating the upper, non-working surface. Experiments were performed at least in duplicate, and standard runs (25°, 146 r.p.m.) were conducted at frequent intervals as a check.

Effect of Perspex and Zinc Centre Studs.—The observed values of k_T under the standard conditions (25°, 146 r.p.m.), and using Perspex centre studs, are shown in Table 1. The inert patch of Perspex at the centre of the working surface was *ca.* 1 cm. in diameter. Other runs were conducted with zinc centre studs, and the results are also shown in Table 1. Fig. 2 shows the plot of $(2{\cdot}303\ \Sigma\ V\ \Delta \log_{10}c)/A$ against t for one run with each type of centre stud. The origin for one run is displaced to distinguish the experimental points.

TABLE 1.

	k_T (obs.) (cm./min.)
Perspex stud	0·161, 0·159, 0·157, 0·156, 0·153, 0·158, 0·157, 0·160, 0·155; mean, 0·157
Zinc stud	0·152, 0·157, 0·157, 0·155, 0·157, 0·157, 0·160, 0·164; mean, 0·157

Rate of Stirring.—The effect of varying the rate of stirring was studied at 25° over the range 73—292 r.p.m., Perspex centre studs being used. In each case, the rate of stirring was maintained constant by means of the stroboscope and manual control described previously.[14] The observed values of k_T are recorded in Table 2.

Temperature Coefficient and Kinematic Viscosity.—The rate of reaction was studied at six temperatures over the range 20—45°, Perspex centre studs and stirring at 146 r.p.m. being used.

The kinematic viscosity of the solution was measured at each temperature by means of an Ostwald viscometer. The appropriate kinetic energy correction was applied by means of Barr's method.[16] The results are shown in Table 3.

TABLE 2.

Rate of stirring (r.p.m.)	k_T (obs.) (cm./min.)	Mean k_T (cm./min.)
73	0·116, 0·118	0·117
109	0·142, 0·141, 0·141, 0·136	0·140
146	(See Table 1)	0·157
219	0·193, 0·192	0·193
292	0·220, 0·224	0·222

TABLE 3.

Temp.	k_T (obs.) (cm./min.)	Mean k_T (cm./min.)	$10^3\nu$ (cm.^{2}/sec.)
20·0°	0·146, 0·142, 0·142, 0·143, 0·144	0·143	9·95
25·0	—	0·157	8·72
30·0	0·173, 0·169, 0·175, 0·173, 0·173	0·173	7·98
34·9	0·193, 0·195, 0·191, 0·189	0·192	7·15
39·9	0·209, 0·209, 0·204, 0·207	0·207	6·52
44·9	0·225, 0·224, 0·220, 0·220, 0·220	0·222	5·97

Coefficient of Diffusion.—Diffusion coefficients were determined by using Stokes's modification of the sintered-pad technique,[17] the only important difference being that cells with ground-glass joints were used since the rubber bungs used by Stokes would absorb iodine. The ground joints were lightly greased with a heavy lithium stearate wax, which proved quite satisfactory and did not penetrate into the pad. A solution of iodine dissolved in 0·08N-potassium iodide was placed in the lower compartment, and allowed to diffuse into potassium iodide of the same concentration. Duplicate determinations generally agreed to within 1%, and thus were sufficiently accurate for the purpose of this investigation. Within the limits of experimental error, no significant change in D was observed on varying the initial concentration of iodine over the range 0·01—0·07N. The observed values of D for solutions initially *ca.* 0·05N in iodine are recorded in Table 4.

TABLE 4.

Temp.	10^5D (obs.) (cm.^{2}/sec.)	10^5D (mean) (cm.^{2}/sec.)	Temp.	10^5D (obs.) (cm.^{2}/sec.)	10^5D (mean) (cm.^{2}/sec.)
25·0°	1·14, 1·15	1·15	40·0°	1·62, 1·63	1·63
30·0	1·31, 1·32	1·32	45·0	1·80, 1·78	1·79
35·0	1·47, 1·47	1·47			

DISCUSSION

The apparent area of the working surface, A, must be known before values of the unit rate constant, k_T, can be calculated from the experimental data. For the present system, the usual method of mounting the discs on the stirring shaft gave an inert patch of Perspex at the centre of the working surface. The exposed area of the centre stud was *ca.* 4% of the total area, whilst the experimental method is sensitive to changes in k_T of the order of 2%, so that it might at first sight appear necessary to subtract the area of the Perspex from the total apparent area of the surface. However, as shown by the results reported in Table 1, and by the two experimental plots shown in Fig. 2, there is no difference to be discerned in the observed rate when the Perspex centre stud is replaced by one of zinc. There can be little doubt that it is the total apparent area of the underside of the disc which must be used. All the reported values of k_T, including those in Table 1, have been computed on this basis.

There is an interesting explanation of this effect. Since the rate of reaction is solely determined by the rate at which iodine can be transported to the working surface, the zinc surface is capable of reducing iodine at a faster rate than that at which it is supplied. Iodine reaching the inert Perspex stud is thrown outwards along the surface of the disc,*

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* See ref. 1, Fig. 3.

[15] Bradley, *Trans. Faraday Soc.*, 1938, **34**, 278.

[16] Barr, " A Monograph of Viscometry," Clarendon Press, 1931.

[17] Stokes, *J. Amer. Chem. Soc.*, 1950, **72**, 763, 2243; 1951, **73**, 3527.

and is consumed in the surface reaction before reaching the outer edge of the disc. For a given solution, temperature, and rate of stirring, the maximum rate at which iodine can be transported to the disc is determined solely by the overall area of the disc, so that, provided the inert centre stud is relatively small, the rate of the surface reaction will nowhere reach the saturation value. As it would clearly be of interest to investigate the effect of progressively enlarging the inert centre patch, a study has been made for the reaction between copper and acidified dichromate solutions.[18]

The opposite effect was observed when a small pin-hole appeared in the lacquer protecting the upper surface of the disc. Although the increase in the exposed area was quite negligible, an appreciable increase in rate was observed. In normal circumstances, there is no concentration gradient set up at the upper, protected surface. Once a pin-hole appears in the lacquer, the exposed area of zinc is supplied with iodine at a very fast rate, and reaction becomes rapid. This argument is borne out in practice by the observation that a very deep pit is etched under such flaws in the lacquer, and it emphasises the need for extreme care when blocking off non-working areas.

FIG. 3.

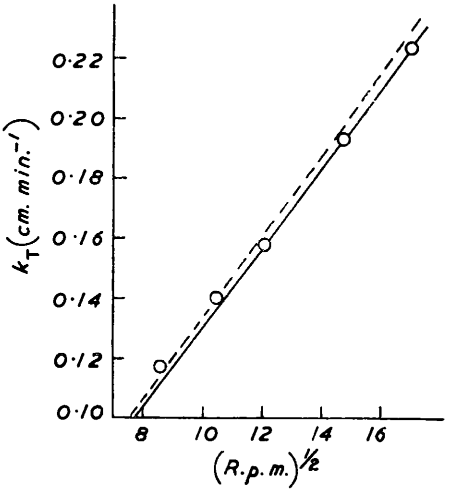
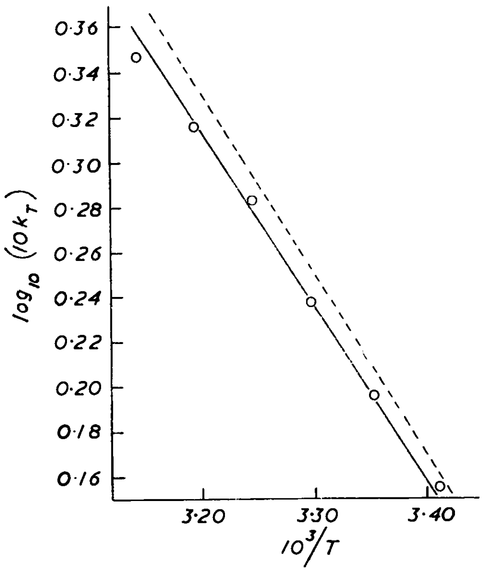


FIG. 4.



We turn now to the effect of varying the rate of stirring. Fig. 3 shows the mean value of k_T at each speed plotted against the square root of the rate of stirring. The three points corresponding to 146, 219, and 292 r.p.m. fall accurately on a straight line passing through the origin; the points for 73 and 109 r.p.m. are slightly higher. A possible explanation is that natural convection is making an appreciable contribution to the transport process under these conditions for, in practice, the limiting value of k_T as ω approaches zero is finite, not zero. The correct explanation, however, is thought to be the onset of an edge effect at low speeds due to the rather thick foils used in preparing the discs. In a similar study of the rate of transport of dichromate ion to copper discs only *ca.* 0·15 mm. thick, the experimental points all fall accurately on a straight line passing through the origin.[18]

Of more interest is the fact that the best straight line through the points is significantly lower than the broken line, which was computed from equation (2) by using the values for D and ν given in Tables 3 and 4. That Levich's theory predicts values which are too high is shown more clearly by Fig. 4, in which the logarithm of the mean value of k_T at each temperature is plotted against the reciprocal of the absolute temperature; again, the broken line was computed from equation (2) by using the data given in Tables 3 and 4.

Since the data reported in Tables 2—4 are accurately represented by the relation

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[18] Gregory and Riddiford, to be published.

$k_T \propto D^{2/3}\nu^{-1/6}\omega^{1/2}$ within the limits of experimental error,[19] the discrepancy lies in the number 0·620, and has been traced to an approximation made by Levich.

For the steady-state transport of mass in the system

$$D(\mathrm{d}^2c/\mathrm{d}y^2) = v_y(\mathrm{d}c/\mathrm{d}y) \qquad (3)$$

where c is the concentration of iodine at a distance y, measured normal to the plane of the disc ($y = 0$), and v_y is the normal component of the fluid velocity.[1] The boundary conditions are :

$$\left.\begin{array}{lll} y = 0, & c = 0, & v_y = 0 \\ y = \infty, & c = c_\infty, & v_y = -0{\cdot}886(\nu\omega)^{1/2} \end{array}\right\} \qquad (4)$$

The conditions for v_y are due to Cochran,[4] who has shown that for small values of y

$$v_y = (\nu\omega)^{1/2}[-0{\cdot}510(\omega/\nu)y^2 + 0{\cdot}333(\omega/\nu)^{3/2}y^3 - 0{\cdot}103(\omega/\nu)^2y^4 + 0{\cdot}0127(\omega/\nu)^{5/2}y^5 + 0{\cdot}00283(\omega/\nu)^3y^6 + \ldots] \qquad (5)$$

From the boundary conditions (4), transport at $y = 0$ is purely diffusive, so that the rate of mass transport to unit area of the surface is given by

$$-D(\mathrm{d}c/\mathrm{d}y)_{y=0} = -k_T c_\infty \qquad (6)$$

On the assumption that D is independent of c, integration of equation (3) yields

$$\mathrm{d}c/\mathrm{d}y = a\,.\exp\left(\int_0^y \frac{v_y}{D}\,.\,\mathrm{d}y\right) \qquad (7)$$

Substitution of $y = 0$ into (7) gives $a = (\mathrm{d}c/\mathrm{d}y)_{y=0} = (k_T c_\infty)/D$ from (6), hence

$$\frac{\mathrm{d}c}{\mathrm{d}y} = \frac{k_T}{D}\,.\,c_\infty\,.\exp\left(\int_0^y \frac{v_y}{D}\,.\,\mathrm{d}y\right)$$

or

$$\frac{c}{c_\infty} = \frac{k_T}{D}\int_0^y \exp\left(\int_0^y \frac{v_y}{D}\,.\,\mathrm{d}y\right).\,\mathrm{d}y \qquad (8)$$

The integral within the brackets can be obtained by substitution for v_y from (5), giving

$$c/c_\infty = (k_T\delta'/D)\,.\,\mathrm{I}(x) \qquad (9)$$

where $x = y/\delta'$, $\delta' = 1{\cdot}805(D/\nu)^{1/3}(\nu/\omega)^{1/2}$, c is now the concentration at a distance x from the interface, and

$$\mathrm{I}(x) = \int_0^x \exp[-x^3 + 0{\cdot}885(D/\nu)^{1/3}x^4 - 0{\cdot}394(D/\nu)^{2/3}x^5 + 0{\cdot}729(D/\nu)x^6 + \ldots]\mathrm{d}x$$

Then

$$k_T = D/[\delta'\,.\,\mathrm{I}(\infty)] = (0{\cdot}554D^{2/3}\nu^{-1/6}\omega^{1/2})\mathrm{I}(\infty) \qquad (10)$$

The problem therefore reduces to the evaluation of the integral $\mathrm{I}(\infty)$. Also, from equations (9) and (10),

$$c/c_\infty = \mathrm{I}(x)/\mathrm{I}(\infty) \qquad (11)$$

from which the distribution of concentration can be determined.

Levich pointed out that when $y \gg \delta'$, $x \gg 1$, so that, since $(D/\nu) \sim 10^{-3}$ for solutions at room temperature, the integral converges rapidly. He regards δ' as the thickness of the boundary layer over which a concentration gradient exists. He assumed that the convergence is so rapid that terms in x^4 and above may be neglected, *i.e.*, that

$$\mathrm{I}(\infty) = \int_0^\infty \exp(-x^3)\,.\,\mathrm{d}x = \Gamma(4/3) = 0{\cdot}8934$$

which, with equation (10), gives equation (2).

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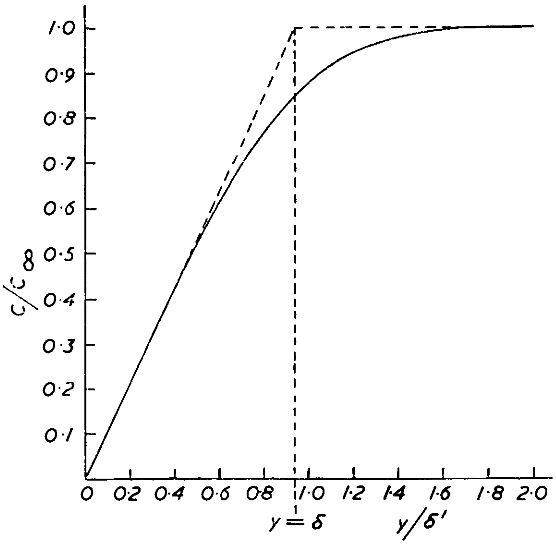
[19] Gregory, Ph.D. Thesis, Southampton, 1955.

FIG. 5.


1·0
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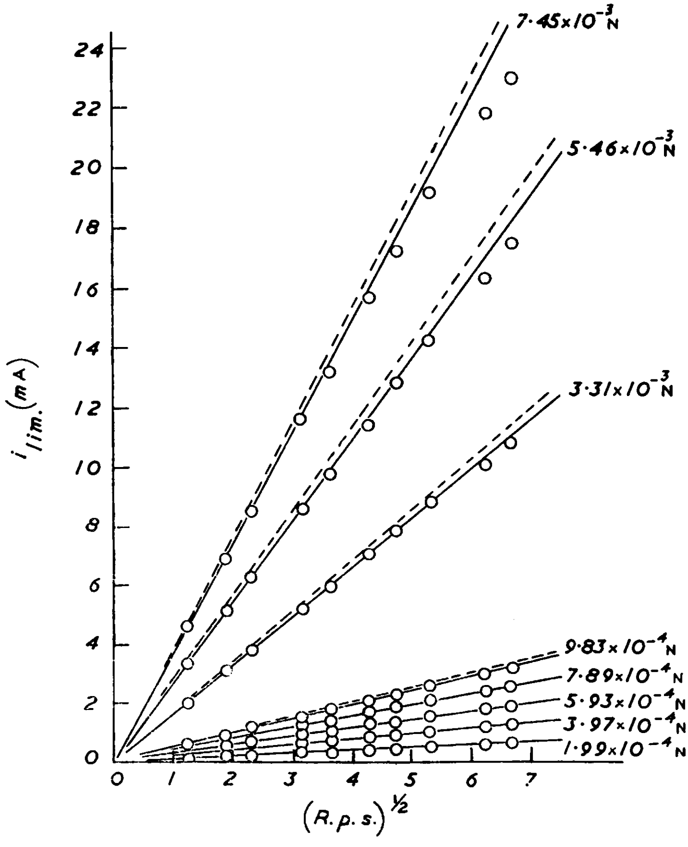
$y=\delta$
y/δ'

FIG. 6.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$i_{lim.}$ (mA)
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4
5
6
7
$(R.p.s.)^{1/2}$
$7{\cdot}45\times10^{-3}$N
$5{\cdot}46\times10^{-3}$N
$3{\cdot}31\times10^{-3}$N
$9{\cdot}83\times10^{-4}$N
$7{\cdot}89\times10^{-4}$N
$5{\cdot}93\times10^{-4}$N
$3{\cdot}97\times10^{-4}$N
$1{\cdot}99\times10^{-4}$N

A closer examination shows, however, that the term in x^4 makes a significant contribution to the integral. The term in x^5 is very small, and the higher terms can be neglected. The present authors have computed $\mathrm{I}(\infty)$ graphically for several values of D/ν, and find that the results can be expressed to within 1% by the equation

$$\mathrm{I}(\infty) = 0{\cdot}8934 + 0{\cdot}316(D/\nu)^{0{\cdot}36} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

for values of D/ν falling within the range 0—4 × 10^{-3}. When $D/\nu = 10^{-3}$, $\mathrm{I}(\infty)$ is 3% higher than the value used by Levich.

By using the appropriate values of $\mathrm{I}(\infty)$, the solid lines shown in Figs. 3 and 4 were obtained, showing satisfactory agreement with the experimental data. For the values of D/ν investigated, the integral converges at $y = 2\delta'$, which is therefore the thickness of the transport boundary layer. This can be seen from Fig. 5, in which the variation of concentration with distance normal to the disc, computed graphically from equation (11), is shown for $D/\nu = 3{\cdot}08 \times 10^{-3}$, corresponding to a temperature of 45° in the present system. The broken line in Fig. 5 shows the Nernst slope (or " equivalent concentration profile " [20]) ; * δ, the thickness of the Nernst layer is given by

$$\delta = \delta' \, . \, \mathrm{I}(\infty) = 1{\cdot}805(D/\nu)^{1/3}(\nu/\omega)^{1/2}I(\infty)$$

It is of interest to see how far Hogge and Kraichman's data can be correlated by the extended theory, since their electrochemical investigations should be of greater precision than the corrosive study reported in the present paper. Their observed limiting currents for the reduction of tri-iodide ion at a rotating platinum disc cathode [8] are shown plotted against the square root of the speed of rotation in Fig. 6. The numbers shown on the plot refer to the concentrations of tri-iodide ion studied. Using their value for the kinematic viscosity of the solution, and the value $D = 1{\cdot}15 \times 10^{-5}$ cm.^{2}/sec. from Table 4, we have computed the theoretical slopes and these are shown as full lines in Fig. 6. The broken lines have been computed from equation (1) for the four concentrations indicated. The agreement between the extended theoretical equation and experiment is satisfactory, particularly at the lower concentrations of tri-iodide ion. The observed results at the higher concentrations are somewhat lower than the theoretical values. This is probably due to the fact that the concentration of tri-iodide ion is no longer negligible in comparison with the concentration of iodide ion (0·1N), so that ionic migration is causing a slight reduction in the rate of transport to the disc.

In their study of the $\mathrm{Ag^+}$–$\mathrm{KNO_3}$ system,[10] they used 0·2N-potassium nitrate as the supporting electrolyte. The highest concentration of silver ion used was $7{\cdot}47 \times 10^{-4}$N, so that ionic migration should play no part in the transport process. Their data can be used to check how rapidly values of D may be obtained from limiting-current measurements by cyclic approximation. From their results, the best value of $D^{2/3}/\mathrm{I}(\infty)$ is $6{\cdot}515 \times 10^{-4}$. Use of $\mathrm{I}(\infty) = 0{\cdot}8934$ as a first approximation gives $D = 1{\cdot}405 \times 10^{-5}$ cm.^{2}/sec. This, coupled with their determined value of the kinematic viscosity, and substituted into equation (12), gives $\mathrm{I}(\infty) = 0{\cdot}9255$ as a better approximation with $D = 1{\cdot}480 \times 10^{-5}$ cm.^{2}/sec. Repetition of the process gives $D = 1{\cdot}482 \times 10^{-5}$ cm.^{2}/sec., with no change thereafter. This value may be compared with the value $D = 1{\cdot}485 \times 10^{-5}$ cm.^{2}/sec. which they computed from Onsager's limiting law.

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* Ref. 1, Fig. 1, is wrong, and should be ignored.

[20] Tobias, Eisenberg, and Wilke, *J. Electrochem. Soc.*, 1952, **99**, 359c.