

ON THE MECHANISM OF TURBULENT FLOW IN MASS-TRANSFER CONTROLLED ELECTROCHEMICAL REACTIONS*

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Abstract—The effect of turbulence on the rate of electrochemical reactions under diffusion control is considered. Cylindrical cells with rotating electrodes were employed.

Experimental results are interpreted in terms of Wranglén's treatment of turbulence recently given. Accordingly the limiting current density is proportional to the $3/5$ th power of fluid velocity and to the $1/3$ rd power of Schmidt number.

The dependence of the kinetic constant on viscosity and diffusivity indicates a mechanism of ionic mass transfer based on the penetration of eddies into the laminar sublayers.

Résumé—On a étudié l'influence de la turbulence sur la vitesse de réactions électrochimiques contrôlées par le transfert massique en employant des cellules cylindriques avec électrodes tournantes.

Les résultats expérimentaux sont interprétés à l'aide des considérations théoriques sur la turbulence récemment développées par Wranglén. Effectivement, on a trouvé que la densité de courant limite est proportionnelle à la vitesse du liquide élevée à la puissance $3/5$ et à racine cubique du nombre de Schmidt.

La variation de la constante cinétique avec la viscosité et le coefficient de diffusion indiquent certainement un mécanisme du transfert massique basé sur la pénétration des tourbillons dans la couche laminaire sous-jacente.

Zusammenfassung—Es wird der Einfluss der Turbulenz auf die Geschwindigkeit von durch den Stofftransport kontrollierten elektrochemischen Reaktionen untersucht. Es wurden dabei zylindrische Zellen mit rotierenden Elektroden verwendet.

Die experimentellen Ergebnisse werden anhand der vor kurzem von Wranglén entwickelten theoretischen Betrachtungen über die Turbulenz interpretiert. Dementsprechend ist die Grenzstromdichte proportional zur $0,6$ ten Potenz der Strömungsgeschwindigkeit und zur 3 . Wurzel der Schmidt'schen Zahl.

Die Abhängigkeit der kinetischen Konstante von der Zähigkeit und vom Diffusionskoeffizienten deutet sicher darauf hin, dass beim Mechanismus des Stofftransportes ein Eindringen der Wirbel in die laminaire Unterschicht im Spiel ist.

INTRODUCTION

THE effect of forced convection on the rate of electrochemical reactions has been studied in various particular cases under streamline and turbulent flow, with different types of cells. While in the first case the interpretation of results is clear, this is not the case for turbulent flow due to its complexity. Most of the work done on the subject is presented in the literature in the form of empirical equations which very often show discrepancies about the dependence of the limiting current density on other parameters.

One interesting approach to the problem of turbulence consists in the study of its effect on the rate of electrochemical reactions under mass-transfer control, with cylindrical electrodes concentrically arranged in such a way that the inner rotating one is the stirring device; the reactions are studied on the surfaces of both the rotating or the fixed electrode according to the circumstances. In this arrangement the regime of turbulence is easily achieved at relatively low values of the peripheral velocity of the rotating electrode.

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Eisenberg, Tobias and Wilke¹ have studied diffusion-controlled reactions in this type of cell using the rotating cylinder as the working surface. The same type of cell has been also employed in this laboratory² to study the electrodeposition of copper under diffusion rate control using the fixed electrode as the working one. In both cases the experimental data were given in terms of the Chilton-Colburn analogy.³ The empirical equation found in our previous work establishes a relationship among Sherwood, Schmidt and Reynolds numbers similar to the one earlier obtained by Eisenberg, Tobias and Wilke,¹ but including another term with the ratio of the diameters of the inner and outer electrodes. This empirical equation can correlate, within experimental error, the data obtained in both researches. Certainly, the Chilton-Colburn analogy for mass transfer can be approached assuming a certain relationship between the transfer coefficient and the friction factor for heat and mass transfer to liquids in pipes, as has been recently shown.⁴

In the present work additional experimental data have been obtained in the same type of cell covering a wider range of peripheral velocities of the rotating electrode and varying Schmidt number up to nearly 5×10^4 . The interpretation of results is based on the postulate of a laminar sub-layer which includes a diffusional sub-layer, as has been suggested by Eckert⁵ and Levich⁶ and recently applied by Wranglén and Nilsson.⁷

The results are approximated by an equation yielding a dependence of the kinetic constant with the diffusivity and viscosity of the system, which supports the theory of the effect of turbulence based on the penetration of eddies in the laminar sub-layers.

EXPERIMENTAL

Electrolysis cell

The type of electrolysis cell used in the present investigation resembles the one previously described in detail.² Essentially they were formed by rotating cylinders, diameters from 2.17 to 6.17 cm, and fixed cylinders of diameters from 9.66 to 9.80 cm. Those electrodes were made of copper tubing or nickel-plated copper tubing, according to the chosen electrochemical reactions. Electrodes of different heights and electrolysis cells of different volumes were used. They are shown in Fig. 1.

Solutions

The ionic mass-transfer process in the turbulent regime has been studied by employing three electrochemical reactions under different experimental conditions—the electrodeposition of copper on copper electrodes from copper-sulphate-sulphuric-acid solutions with glycerol added to change the Schmidt number, and the redox reactions involved in the electrolysis of potassium ferro- and ferricyanide with a large excess of sodium hydroxide. For the latter an activated nickel-plated copper-base electrode was used. The rest of the experimental set-up has been described previously.

The actual concentrations of the different components were determined by analysis. The viscosity and density of solutions were determined conventionally.

The electrical circuitry and measurements are given elsewhere.²

RESULTS

Experiments were performed in the range 16.1–38.9°C. Copper-ion concentration was changed from 0.0059 to 0.050 M in 1.5 M sulphuric acid, which was kept nearly

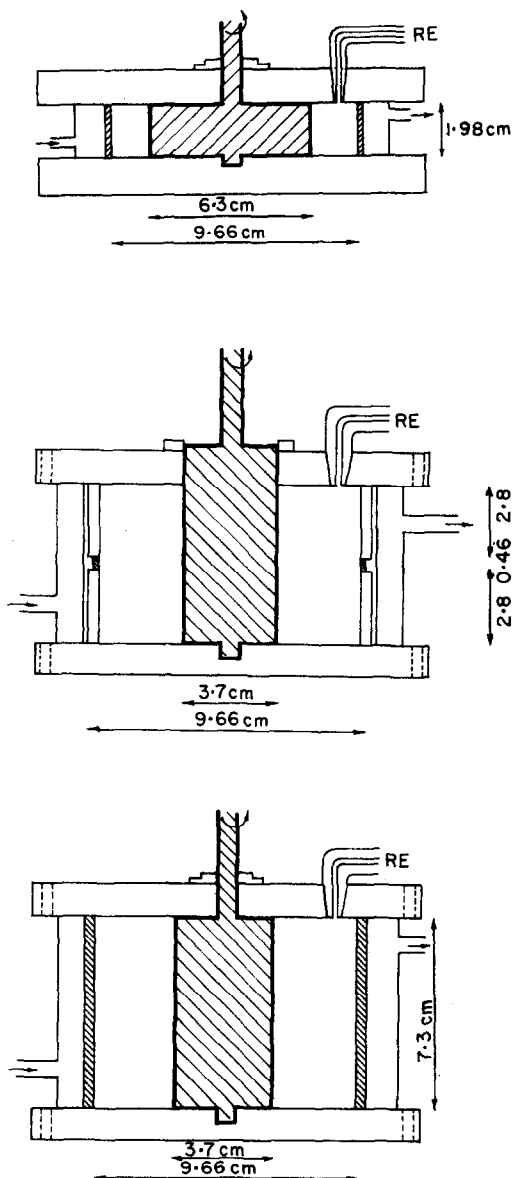


FIG. 1. Electrolytic cells with rotating electrodes.

constant. A 0.0128 M equimolecular concentration of potassium ferro- and ferricyanide in 2 M sodium hydroxide was used.

Working electrodes having areas from 14.18 to 274.6 cm² were employed. The peripheral velocity of the rotating electrode was varied from 6.36 to 264 cm/s. The kinematic viscosity of copper-sulphate-sulphuric-acid solutions was varied by adding glycerol to cover the range 1.391×10^{-2} to 5.089×10^{-2} cm²/s.

Experimental results are given in Tables 1-3. d_1 and d_2 are the diameters of the rotating and outer electrode respectively in cm; C_o , C_{o3} , C_{o4} , C_a , C_h and C_r the molar

TABLE 1

C_o	C_p	$k \times 10^4$	V	$D \times 10^6$	$\nu \times 10^8$	Re_{d_1}	Re_s	Sc	Sh_{d_2}	Sh_s
0.0267	2.50	3.88	58.9	4.59	1.917	11516	9144	4687	920	282
0.0242	1.25	5.60	58.9	5.30	1.391	15659	12430	2625	1025	314
0.0222	5.00	2.64	58.9	2.28	3.840	5749	4565	16842	1123	344
0.0053	1.25	9.18	161	4.96	1.643	36710	29150	3313	2795	858
0.0053	1.25	5.19	58.9	4.96	1.643	13436	10670	3313	1015	311
0.0066	1.25	5.73	58.9	4.88	1.657	13356	10650	3395	1139	349
				$d_1 = 6.30$		$d_2 = 9.66$	$C_a = 1.50$			
0.0066	1.25	12.5	99.0	4.88	1.657	37649	10050	3395	2480	431
0.0066	1.25	11.1	99.0	4.88	1.657	37649	10050	3395	2202	383
0.0104	2.00	16.5	197.0	4.46	1.761	70655	18665	3945	3580	623
0.0104	2.00	17.1	237	4.46	1.761	84790	22640	3945	3688	642
0.0059	2.00	13.5	163	4.74	1.622	63310	16900	3424	2760	480
0.0059	2.00	15.7	197	4.74	1.622	76710	20480	3424	2196	556
0.0059	2.00	18.0	237	4.74	1.622	92050	24580	3424	3670	639
0.0059	2.00	19.8	264	4.74	1.622	102505	27370	3424	4034	702
0.0059	2.00	16.8	197	4.74	1.622	76710	20480	3424	3422	595
0.0100	6.00	5.63	163	1.79	5.089	20180	5390	28493	3045	530
0.0100	6.00	7.46	237	1.79	5.089	29347	7840	28493	4034	702
0.0100	6.00	8.33	264	1.79	5.089	32680	8725	28493	4503	784
0.0100	6.00	5.96	163	1.79	5.089	20170	5385	28493	3222	555
0.0100	6.00	6.46	197	1.79	5.089	24440	6525	28493	3494	608
0.0100	6.00	7.08	237	1.79	5.089	29327	7830	28493	3832	667
0.0100	6.00	7.55	264	1.79	5.089	32670	8725	28493	4085	711
0.0100	4.00	9.65	163	3.28	2.526	40650	10850	7710	2845	495
0.0100	4.00	10.4	197	3.28	2.526	49260	13150	7710	3062	533
0.0100	4.00	12.6	264	3.28	2.526	65840	17580	7710	3703	644
0.0059	2.00	17.3	197	4.74	1.622	76710	20480	3424	3330	579
0.0059	2.00	19.6	237	4.74	1.622	92050	24580	3424	3990	694

concentrations of copper sulphate, potassium ferricyanide, potassium ferrocyanide, sulphuric acid, sodium hydroxide and glycerol respectively, V the peripheral velocity of the rotor in cm/s, D_i the diffusion coefficient of the reacting species i in cm^2/s ; ν the kinematic viscosity in cm^2/s of the electrolyte solution, k the kinetic constant for the ionic mass transfer process and Re , Sc , Sh , the Reynolds, Schmidt and Sherwood numbers respectively as defined below.

TABLE 2

$k \times 10^4$	V	Re_{a_1}	Re_s	Sh_{a_2}	Sh_s
$d_1 = 2.17$		$d_2 = 9.64$	$C_0 = 0.05$		$C_a = 1.5$
$\nu = 1.279 \times 10^{-2}$			$D = 5.22 \times 10^{-6}$		$Sc = 2450$
2.13	6.36	1079	1857	393	152
2.41	11.9	2019	3475	445	172
2.99	22.7	3899	6710	552	214
3.32	34.1	5783	9952	613	238
2.65	17.0	2884	4963	489	190
3.25	28.4	4818	8291	600	234
3.73	39.2	6650	11444	689	267
$d_1 = 3.75$					
2.74	11.0	3225	2532	506	155
3.46	20.3	5952	4684	539	165
4.81	40.6	11904	9348	888	271
6.05	58.7	17211	13516	1117	341
5.60	53.4	15656	12294	1034	316
6.16	63.8	18706	14689	1138	348
4.23	29.5	8649	6792	781	239
$d_1 = 6.60$					
5.15	19.3	9959	2293	951	150
6.82	36.3	18732	4314	1260	199
9.82	69.1	35657	8212	1813	286
11.98	103.7	53512	12323	2212	349

TABLE 3

$k \times 10^4$	V	Re_{a_1}	Re_s	Sh_{a_2}	Sh_s
$d_1 = 3.70$		$d_2 = 9.80$	$C_{0,3} = 0.0128$		$C_h = 2.00$
$\nu = 1.396 \times 10^{-2}$			$D = 5.17 \times 10^{-6}$		$Sc = 2698$
11.30	116	30745	25334	2140	666
13.30	139	36841	30357	2519	783
10.40	95.6	25338	20878	1969	612
13.20	139	36841	30357	2500	778

The experimental results assembled in the Tables are for the standard temperature of 25°C, except those in Table 2, which are for 18°C. Typical current/voltage curves are shown in Figs. 2-4.

INTERPRETATION

A theoretical interpretation of turbulent mass transfer is a complex matter and consequently in most cases only empirical analysis has been advanced to deal with experimental results.

Taylor^{8,9} has studied the hydrodynamics of a cylindrical arrangement analogous to the one described in the present case. Recently Koshmarov^{10,11} has derived theoretical solutions of the transfer equations for the case of a newtonian fluid in steady turbulent flow in an annular space formed by two cylinders concentrically arranged, where the

inner one is the rotating device. The velocity equations worked out are not valid for the laminar sublayers formed near the surfaces. Taking account of the small thickness of laminar sublayers, von Karman's assumption of a linear relationship between velocity and distance for those sublayers is considered.

Levich and Landau⁶ have advanced a theory for mass transfer under turbulent convection which has been successfully applied to the rotating disk electrode.

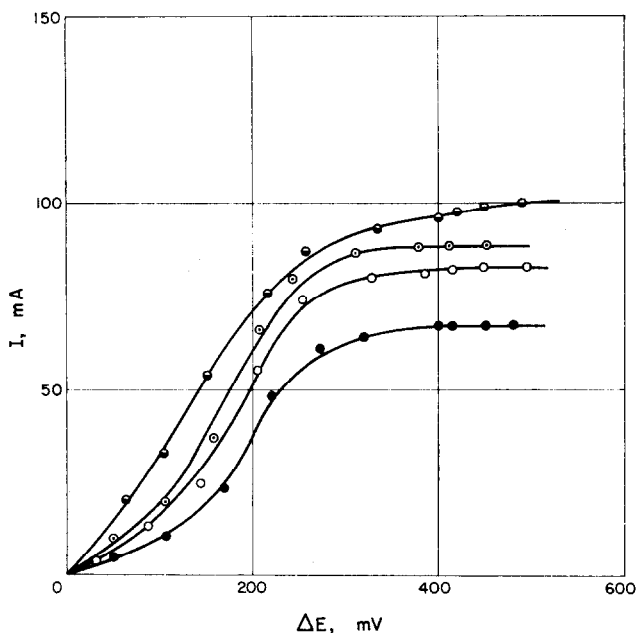


FIG. 2. Current/voltage curves for the electrodeposition of copper (6 M glycerol solutions).

● 163 cm/s; ○ 197 cm/s; ○ 237 cm/s; ● 264 cm/s.

The analysis of the effect of turbulence on mass-transfer rate has been usually condensed in different equations expressing the rate of the process as a function of the rate of stirring. According to those equations the kinetic constant is directly proportional to the rate of stirring to an exponent ranging from 0.6 to 1.¹⁴ Sometimes this fact has been used as a criterion of turbulence.

One of the approaches to the effect of turbulence on mass-transfer controlled electrochemical reactions on cylindrical rotors was made by Eisenberg, Tobias and Wilke.^{1,13} The equation they obtained indicated the limiting current density was proportional to the 0.7 power of the stirring rate, the latter being measured through the peripheral velocity' of the rotating device.

The interpretation of our experimental results is based on an equation derived recently by Wranglén and Nilsson⁷ for turbulent flow, considering distribution equations given by Eckert.⁵ This equation, obtained for the case of a flat plate, can be applied to the present case with certain reasonable assumptions.

Wranglén and Nilsson solved the momentum and mass-transfer equations taking into account the existence of a laminar boundary sublayer including the diffusion boundary layer within a rather thick turbulent layer. The diffusion layer has the

smallest thickness and is immediately adjacent to the electrode surface. In the laminar sublayer and the diffusion boundary layer, the velocity and concentration profiles, respectively, are assumed to be linear, while in the turbulent region the mean velocity is assumed to satisfy the 1/7th power law.¹² The final results are expressed by the dimensionless equation

$$Sh_x = 0.143 Sc^{1/3} Re_x^{3/5} [1 - (x_0/x)^{0.9}]^{-1/3}, \quad (1)$$

where Sh_x is Sherwood number defined with the characteristic length x , Sc and Re_x

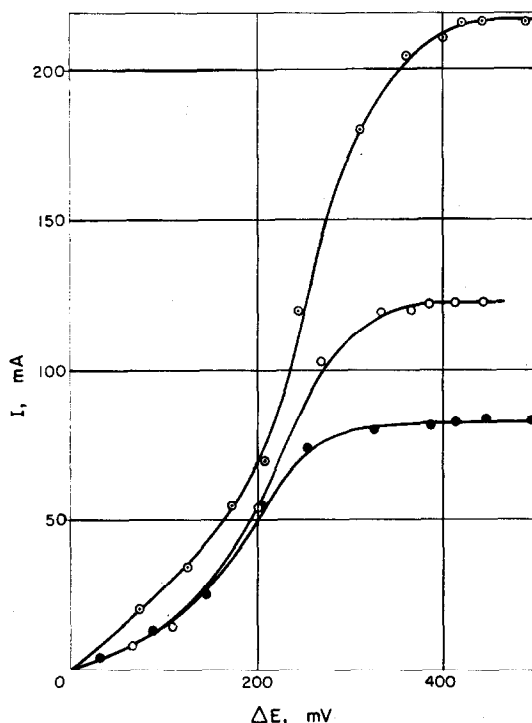


FIG. 3. Current/voltage curves for the electrodeposition of copper ($V = 197$ cm/s).
● 6 M glycerol; ○ 4 M glycerol; ○ 2 M glycerol.

are Schmidt and Reynolds numbers respectively and x_0 the length of the inlet channel. Equation (1), which has been worked out for local ionic mass transfer, is also obviously valid for the whole electrode area.

The application of (1) to our experimental results is reasonable because the radius of curvature of the cylindrical cell is much larger than the thickness of the boundary sublayers formed on the electrode area under forced convection.

In the experimental set-up described above the diffusion process takes place in the radial direction (the y -direction), while there is a turbulent convective effect produced by the rotating electrode. Therefore the situation can be interpreted as the case of the plane electrode under turbulent flow, extending to infinity, with no leading edge. In fact the results are also independent of the electrode height. Consequently the experimental results may be tested assuming that a function of the form

$$Sh = \text{const.} \times Re^{3/5} \times Sc^{1/3} \quad (2)$$

would be obeyed.

The characteristic length involved in the definition of Sh and Re must be properly selected in order to apply equation (2). In the first place, considering the meaning of x in (1), it was reasonable to fix the circumference of the working electrode as the x value entering Sherwood's number; it could be either the circumference of the inner rotating electrode or that of the outer cylindrical one, according to which was the working electrode. However, instead of the circumference it was more convenient to define Reynolds' number and Sherwood's number with the corresponding diameters

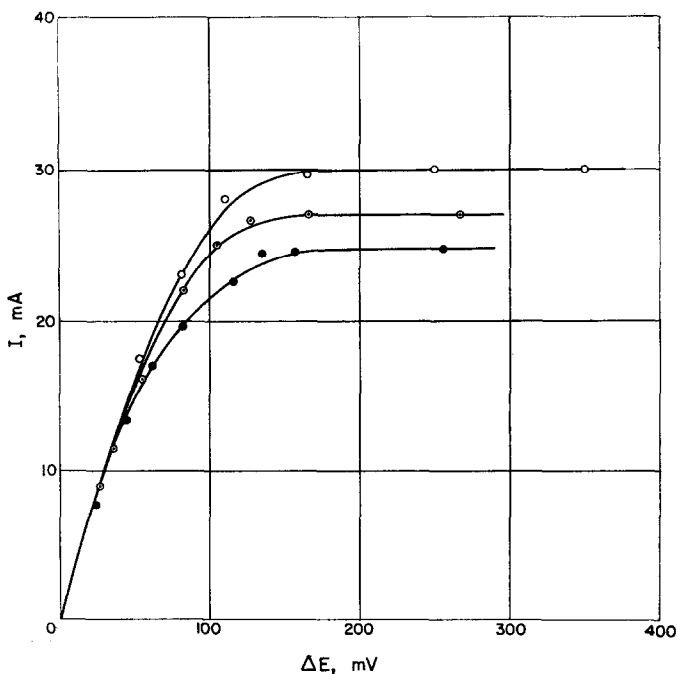


FIG. 4. Current/voltage curves for the reduction of ferricyanide ions.
● 95 cm/s; ○ 116 cm/s; ○ 139 cm/s.

of the electrodes. Therefore, for reactions taking place on the rotating device the following equation was obtained:

$$Sh_{a_1} = 0.217 \times Re_{a_1}^{3/5} \times Sc^{1/3}. \quad (3)$$

However, when the electrochemical reaction occurs on the fixed electrode Sherwood's number is defined with its diameter, and the mass-transfer rate depends on the diameters of both electrodes. Therefore (2) should have an additional dimensionless factor to describe the problem entirely, which can be defined as a ratio between diameters. The experimental results were correlated with the following equation:

$$Sh_{a_2} = 0.217 \times Re_{a_1}^{3/5} \times Sc^{1/3} \times (d_2/d_1)^{2/5}. \quad (4)$$

The numerical coefficient of equations (3) and (4) was obtained from the plot shown in Fig. 7. The average deviation of results is *ca* 10 per cent.

Considering the data obtained for the fixed electrode we may try an equation involving only one characteristic length in the definition of dimensionless terms.

The usual definition of Reynolds' number in the case of concentric rotating cylinders is with the spacing of the cylinders,

$$S = (d_2 - d_1)/2. \quad (5)$$

Sherwood's and Reynolds' numbers are also given in the Tables in terms of S . The dimensionless equation obtained in this case is

$$Sh_s = 0.10 \times Re_s^{3/5} \times Sc^{1/3}, \quad (6)$$

which is shown in Fig. 8. Equation (6) approximates the experimental results with a mean deviation of 11 per cent.

The above mentioned equations indicate a linear relationship between the limiting current density and the 0.6 power of the peripheral velocity of the rotating electrode. This dependence is satisfied by the different experimental results, as indicated in Fig. 5.

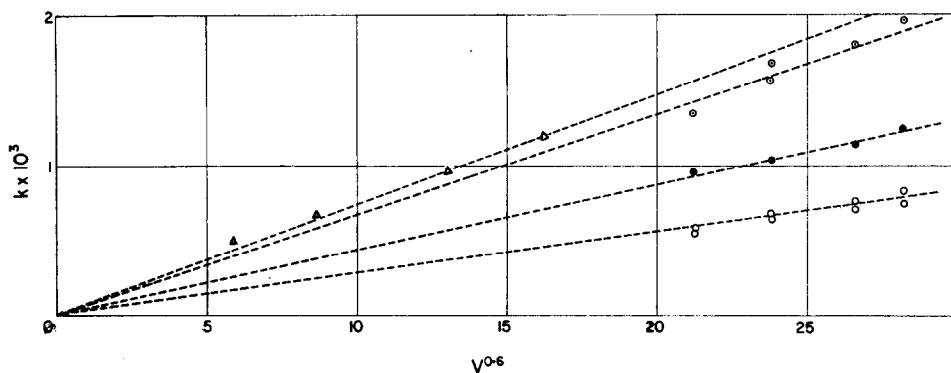


FIG. 5. Plot of k vs $V^{0.6}$; electrodeposition of copper ions.
 ○ 6 M glycerol; ● 4 M glycerol; ○ 2 M glycerol; △ without glycerol.

The exponent of the Schmidt number, which is an important term for the interpretation of turbulence, has been also verified from a log-log plot of Sherwood vs Schmidt numbers taken into account the experiments of copper ion deposition with solutions containing glycerol. These results appear in Fig. 6.

Corrections of viscosity and diffusivity due to the change of concentration of the supporting electrolyte near to the working electrode has not been taken into account in the calculations, because those corrections are much smaller than the experimental errors.

Finally, from (4) and (6), the following expressions may be derived for the limiting current density and the formal kinetic constant of mass-transfer controlled electrochemical reactions under turbulent regime on the cylindrical electrodes:

$$k = 0.217 \times V^{3/5} \times D^{2/3} \times \nu^{-4/15} \times d_1^{1/5} \times d_2^{-3/5}; \quad (12)$$

$$i_L = 0.217 \times Z \times F \times C_i \times V^{3/5} \times D^{2/3} \times \nu^{-4/15} \times d_1^{1/5} \times d_2^{-3/5}; \quad (13)$$

$$k = 0.10 \times V^{3/5} \times D^{2/3} \times \nu^{-4/15} \times S^{-2/5}; \quad (14)$$

$$i_L = 0.10 \times Z \times F \times C_i \times V^{3/5} \times D^{2/3} \times \nu^{-4/15} \times S^{-2/5}. \quad (15)$$

DISCUSSION

The experimental results obtained with the cylindrical electrolysis cell in the turbulent regime can evidently be approximated by an equation including a linear relationship between the limiting current density and the 0.6 power of the peripheral velocity of the rotating electrode. The difference between the exponents 0.6 and 0.7, the latter obtained earlier empirically, is within experimental error. The correlation obtained does not allow conclusions regarding the dependence of the mass-transfer rate upon the diameter of the stationary electrode since this was not varied.

The first interesting feature is the relatively simple equations for ionic mass-transfer processes at both the rotating and the fixed electrodes.

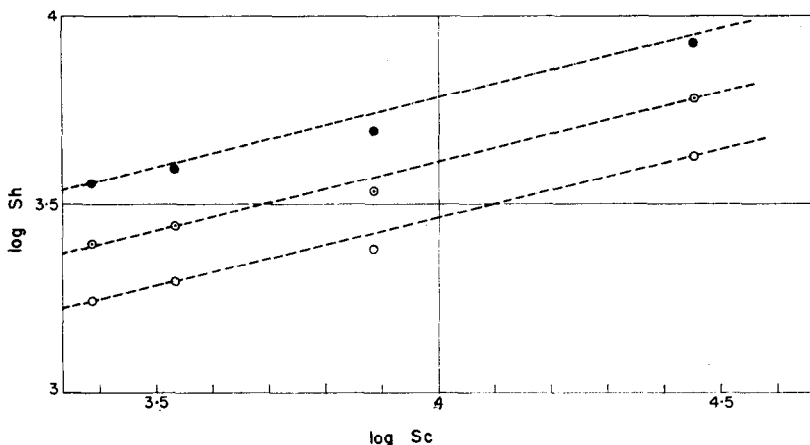


FIG. 6. Plot of $\log Sh$ vs $\log Sc$; slope of dotted lines is $1/3$.
 $\circ Re_d = 31,600$; $\odot Re_d = 56,200$; $\bullet Re_d = 100,000$.

The second feature, significant from the point of view of the mechanism of turbulence on the ionic mass-transfer rate, is the dependence of Sherwood number upon the 1/3rd power of the Schmidt number.

As reviewed earlier,¹⁵ the experimental dependence of the mass-transfer kinetic constant on the diffusion coefficient is in most cases not in agreement with the different theories; the kinetic constant has been found to be directly proportional to the diffusion coefficient of the reacting species to a power varying from 0.14 to nearly 1. Diffusion-controlled reactions in the turbulent regime were interpreted in terms of a simple stationary laminar sublayer associated with the transfer of mass and momentum. This theory, known as Prandtl-Taylor theory,⁵ predicts a dimensionless correlation independent of Schmidt number and, consequently, the kinetic constant for mass transfer is directly proportional to the diffusion coefficient of the reacting species. However, most of the experimental researches done in the turbulent regime lend no support to this theoretical prediction.

Landau and Levich⁶ have considered the problem of turbulence assuming a damping effect of turbulence on the laminar sublayer. Hence, when a steady state is reached a distinction between the diffusion laminar sublayer and the viscous laminar sublayer must be postulated. The thickness of the former sublayer is a small fraction of that of the latter. Assuming a smooth transition of velocity and concentration profiles from the complete turbulent region towards the laminar regions adjacent to the

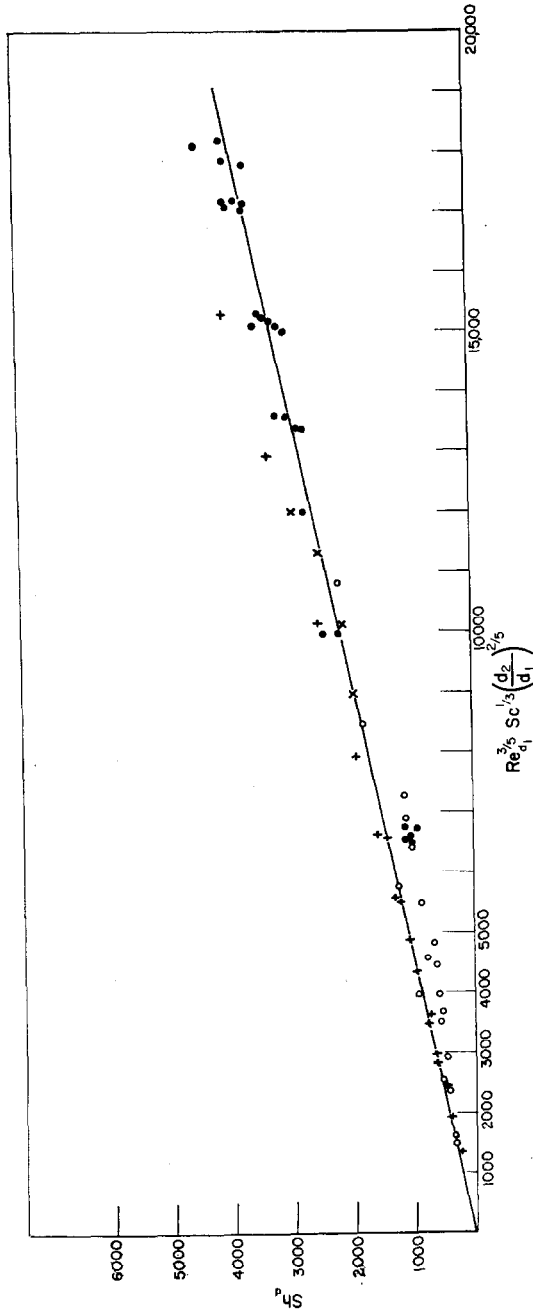


Fig. 7. Plot of equation (4). ○ Electrodeposition of copper from aqueous solutions on the fixed electrode; ● electrodeposition of copper from aqueous glycerol solutions on the fixed electrode; × reduction of ferricyanide ions on the fixed electrode; + reduction of ferricyanide ions on the rotating electrode (from Eisenberg, Tobias and Wilke^{1,13}).

surface, this treatment yields expressions relating the kinetic constant linearly to the 2/3rd power of the diffusion coefficient and to the velocity to the power of 0.5–0.9, the former for the case of rough surfaces and the second for flat plates. Bagotskaya¹⁶ and Fedorova and Vidovich¹⁷ have found experimentally that the kinetic constant is directly proportional to the 0.9 power of the velocity for the rotating disk electrode.

Higbie¹⁸, and later Danckwerts,¹⁹ working on other problems of mass transfer in the turbulent regime, have postulated other theoretical interpretations of the kinetic constant, deriving a linear relationship between the constant k and the 0.5 power of the diffusion coefficient of the reacting species. The second author modifies Higbie's

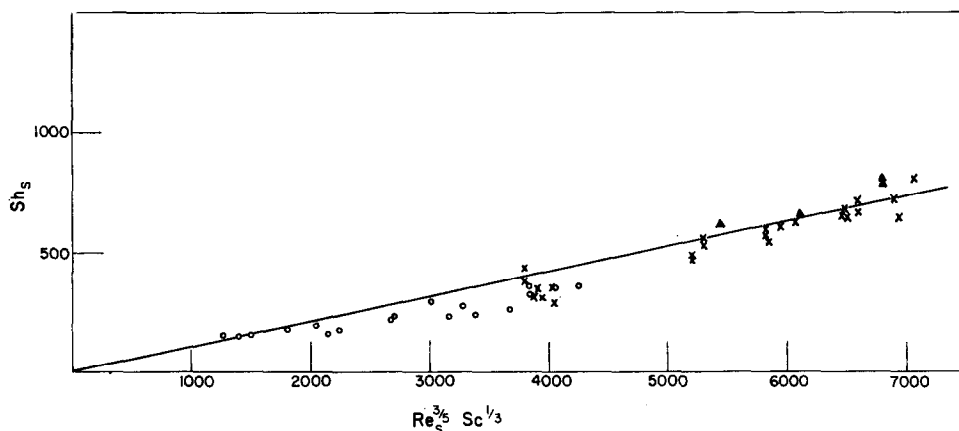


FIG. 8. Plot of equation (6).

×, ○ Electrodeposition of copper from aqueous solutions with and without the addition of glycerol, respectively; Δ reduction of ferricyanide ions on the fixed electrode.

penetration theory by assuming that the surface is continually replaced by fresh liquid.

Eisenberg, Tobias and Wilke, working on the dissolution of cylinders of benzoic acid in aqueous systems¹³ of different viscosities, obtained the experimental exponent of 0.63 for the Schmidt number, writing an equation in terms of Chilton–Colburn analogy. This exponent becomes close to $\frac{1}{3}$ when their results are expressed in the form of (2). Therefore this coincidence is also certainly remarkable.

Considering Levich's discussion of turbulent mass transfer, the results are a clear indication that the penetration of eddies into the laminar sublayers play an important role in the mechanism of the ionic mass transfer in cylindrical cells in the turbulent regime.

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