

MASS TRANSFER IN THE ELECTROLYSIS OF CuSO_4 - H_2SO_4 IN AQUEOUS SOLUTIONS UNDER LIMITING CURRENT AND FORCED CONVECTION EMPLOYING A CYLINDRICAL CELL WITH ROTATING ELECTRODES*

A. J. ARVIA and J. S. W. CARROZZA

Instituto Superior de Investigaciones Facultad de Química y Farmacia,
Universidad Nacional de La Plata, La Plata, República Argentina

Abstract—The rate of mass transfer for the electrodeposition of copper ions has been investigated under different rates of stirring. The reaction occurs on the fixed cathode of a cylindrical cell where the anode is the stirring device.

The following correlation has been obtained,

$$j' = 0.0791 (Re)^{-0.30} (D_1/D_2)^{0.70},$$

which holds also for other transfer processes in cylindrical cells. The peripheral velocity of the anode, V , was the measure of the rate of stirring. The mass transfer rate constant, k , is a function of $V^{0.70}$. Figures for the effective diffusion layer under forced convection are also given.

The temperature dependence of the rate constant follows an equation of the Arrhenius type. The apparent energy of activation is 4500 ± 250 cal/mole, independent of the rate of stirring.

Résumé—La constante cinétique pour le transfert de masse dans l'électrodeposition des ions cuivre a été étudiée pour différents états d'agitation de la solution. La réaction d'électrodeposition a lieu sur une cathode stationnaire d'une cellule électrolytique cylindrique dans laquelle l'anode est le dispositif d'agitation. La relation obtenue est la suivante

$$j' = 0,0791 (Re)^{-0,30} (D_1/D_2)^{0,70},$$

laquelle s'applique aussi à d'autres processus de transfert de masse dans différents systèmes. L'état d'agitation est déterminé par la vitesse périphérique de l'anode, V . La constante cinétique, k , en ce cas, est une fonction de $V^{0.70}$. On montre les valeurs de l'épaisseur effective de la couche de diffusion.

La variation de k avec la température est représentée par une équation du type d'Arrhenius et l'énergie d'activation expérimentale est 4500 ± 250 cal/mole. Elle ne dépend pas du degré d'agitation de la solution.

Zusammenfassung—Die Stofftransportgeschwindigkeit bei der elektrolytischen Abscheidung von Kupfer ist für verschiedene Rührgeschwindigkeiten untersucht worden. Die Abscheidung erfolgte an einer feststehenden Kathode in einer zylindrischen Zelle. Gerührt wurde mit der Anode.

Es wurde die folgende Korrelation erhalten

$$j' = 0,0791 (Re)^{-0,30} (D_1/D_2)^{0,70}.$$

Als Mass für die Rührgeschwindigkeit wurde die Tangentialgeschwindigkeit V der Anode genommen. Die Stoffübergangszahl k ist proportional zu $V^{0.70}$. Die Werte der effektiven Diffusionschichtdicken werden in graphischer Darstellung gezeigt. Die Temperaturabhängigkeit der Stoffübergangszahl k gehorcht einer Gleichung des Arrhenius-Typus. Die scheinbare Aktivierungsenergie beträgt 4500 ± 250 cal/Mole und scheint von der Rührgeschwindigkeit unabhängig zu sein.

* Manuscript received 12 December 1960.

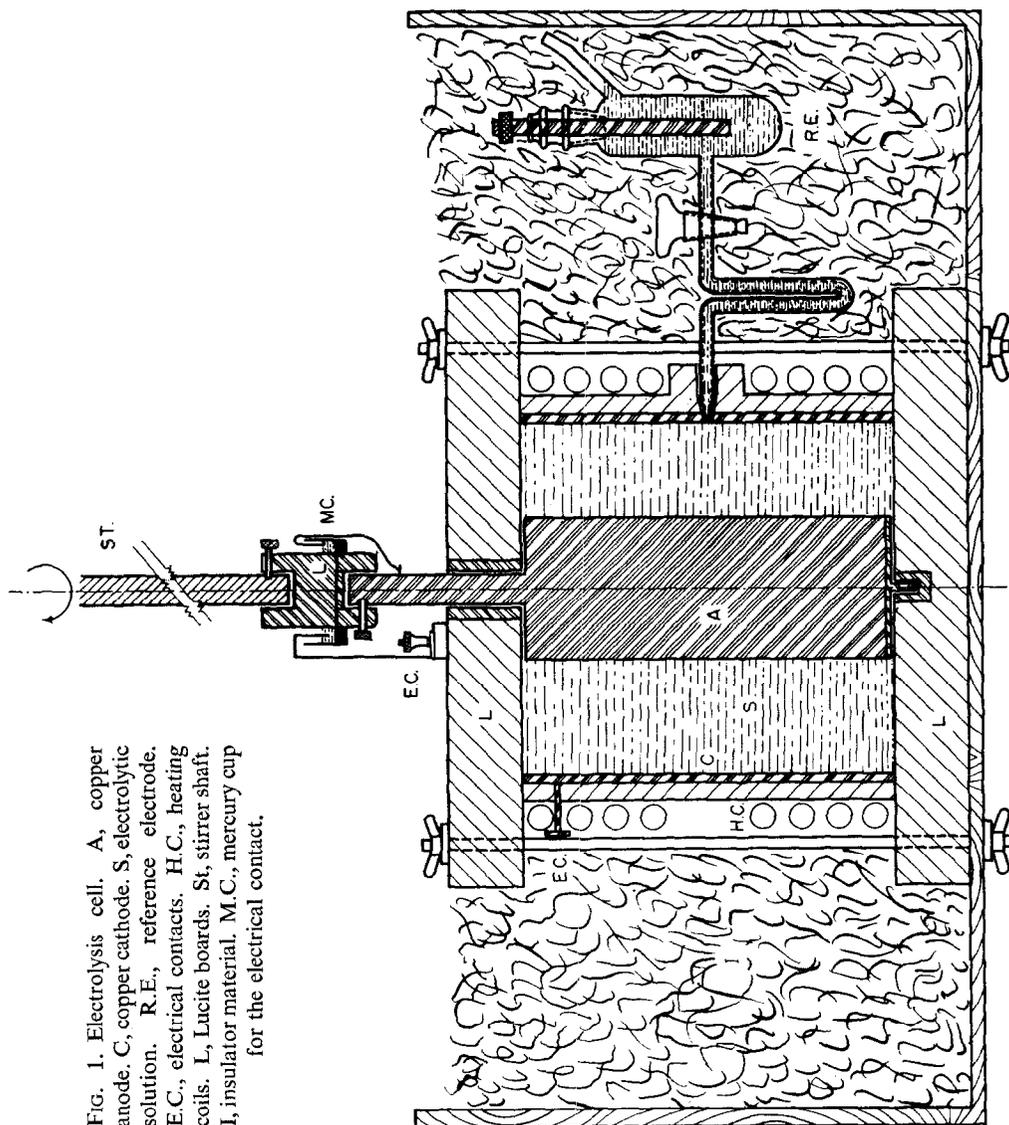


FIG. 1. Electrolysis cell. A, copper anode. C, copper cathode. S, electrolytic solution. R.E., reference electrode. E.C., electrical contacts. H.C., heating coils. L, Lucite boards. St, stirrer shaft. I, insulator material. M.C., mercury cup for the electrical contact.

INTRODUCTION

STIRRING is employed in many electrochemical reactions to increase the rate of mass transfer to the electrodes, a process which plays an important role in electrolysis. Several papers have been published on the subject in the last ten years. Mass transfer under forced convection was carefully studied in the dissolution of cylindrical rotors of benzoic acid and in the redox reaction of ferro- and ferricyanide ions on nickel electrodes.¹

In this paper the electrodeposition of copper ions was studied under conditions of mass-transfer control. The limiting current density was measured and from it the rate constant for mass transfer was calculated. The cell was a cylindrical one and the reaction was studied on the fixed cylindrical electrode. The anode was the stirring device and the rate of stirring was measured by its peripheral velocity.

The experimental results have shown that the rate constant for mass transfer of copper ions is a function of the peripheral velocity of the rotating electrode to the 0.70th power and from a plot of that relationship a deviation from linearity is observed for peripheral velocities lower than 13 cm/sec. The results could be correlated with the aid of dimensional analysis and the general equation obtained is in agreement with observations of other authors.^{1,2}

It has also been possible to obtain the temperature coefficient of the rate constant for mass transfer and it has been observed that its dependence with temperature keeps the usual form which is known for the rate constant of other chemical processes. The experimental activation energy for the mass-transfer-reaction studied here seems to be independent of the rate of stirring.

EXPERIMENTAL

1. *Description of the cell.* The electrolytic cell is shown in Fig. 1. The cathode is the inner surface of a copper tube and has been machined to a cylindrical shape and carefully polished. The anode is the exterior surface of another copper tubing and has been symmetrically placed at the centre of the cell. The space between them is filled with the electrolyte solution. The electrodes are kept in position with two flat square boards of Lucite and are held tightly by means of five bronze rods and screws. This electrolysis cell has a known geometry which was kept constant during each run. The distribution of the electrical field is a homogeneous one and the hydrodynamic flow is also constant for each rate of stirring. Vortex was carefully eliminated in the cell.

The cathode potential was measured against a reference electrode made with a pure copper rod dipped into a solution of the same composition as that used in the electrolysis cell. This electrode has a capillary tube tip which was introduced from the outside part of the cathode. This electrode has a pinhole and with this arrangement interference with the flowing of the liquid was avoided; this technique has been previously tested with good results^{3,4} in an electrolysis cell with vertical electrodes, under natural convection. The whole arrangement was mounted on a steel board under the stirring device.

The cathode surface was 274.6 cm² and its diameter was 9.70 cm. Three copper anodes have been employed in order to have three different gaps between the anode and the cathode. The diameter of the anodes were 2.17, 3.75 and 6.60 cm.

2. *The stirrer.* The stirrer could be employed at different programmed speeds of rotation in the range between zero and 350 rev/min. Its basic frame was made from a static bench driller. It was equipped with a d.c. electrical motor and a set of fixed pulleys which gave a ratio 1:10 between the rev/min of the anode and that of the motor. By means of variable electrical resistances placed in series with the electromagnetic field of the motor it was possible to adjust the speed of rotation of the anode in the cell. The rev/min was read on a special counter previously calibrated which was connected direct to the electrical motor.

The anode of the cell was fixed to the stirrer with an special Lucite holder. The whole arrangement was carefully centred before an experiment was started.

3. *Electrical measuring circuits.* The e.m.f. between the cathode and the reference electrode was measured with a Siemens-Halske precision potentiometer. An electrolysis circuit with accumulator as d.c. sources has been also employed. The electrical contact of the rotating anode was done with a metallic cup, centred in the shaft, filled with mercury and connected through a copper wire to the rest of the electrical circuit.

4. *Thermostat.* The experiments were performed at temperatures between 15 and 40°C. To bring the electrolysis cell at the chosen temperature a heating copper coil was used. The coil was placed around the cathode with distilled water from the thermostat flowing through it. The whole arrangement was placed into a wooden box which had been filled with thermal insulator material. A sensitive thermocouple was attached to the exterior surface of the cathode to control its temperature.

During each run, the temperature tends to increase due to the Joule effect. The actual temperature of each run was taken when the limiting current density was flowing through the cell.

5. *Preparation and properties of the solutions.* The solutions chosen for these experiments were of the following approximate composition: CuSO_4 , 0.055–0.025 M, and H_2SO_4 1.5 M, in water. For each run the solution was prepared by dilution of a concentrated stock solution. A.R. chemicals and triple distilled water were employed for it.

The copper content of each solution was evaluated by the electrolytic method and its sulphuric acid content by titration with a standard sodium hydroxide solution; a correction for the copper-ion hydrolysis was made. The solution density and viscosity were determined at the temperature range of the experiments. A pycnometer method was employed for density and a Cannon-Fenske pipette for viscosity.

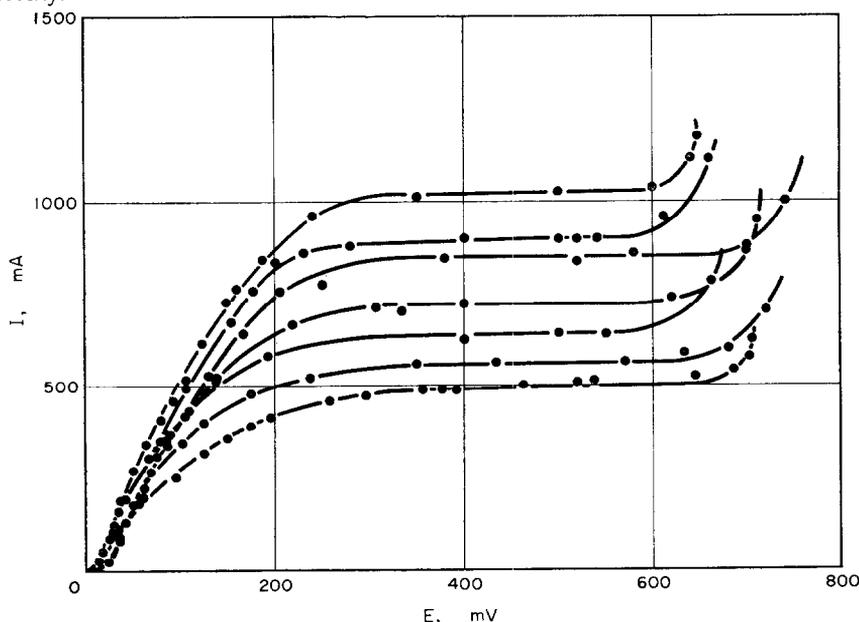


FIG. 2. Polarization curves obtained in one set of experiments with the smallest diameter anode, ($D_2 = 2.17$ cm).

6. *Experimental technique.* After the different parts of the cell had been assembled a stream of purified nitrogen passed through it. Before each run was started the electrodes were carefully polished on a lathe with the finest grained emery paper and then were degreased completely. Nitrogen was also bubbled through the solution at least for one hour. It had been previously purified from oxygen by bubbling through a sodium pyrogallate solution and passing over reduced copper shavings heated in an oven at 350°C.

The solution filled up the cell completely and bubble formation was not allowed to occur. While the cell was reaching the chosen temperature the stirrer was at its maximum speed and when this temperature was finally obtained, the speed was conveniently adjusted.

Electrolysis was started by increasing the voltage through the cell without interruption. For each 20–30 mV increase of potential a minute or so elapsed until a steady state was established in the electrolysis, and then the e.m.f., E , of the concentration cell formed between the cathode and the reference electrode was read on the potentiometer. The intensity, I , was also known from the ammeter.

Plotting E as a function of I , a polarization curve was obtained which gave the limiting current density, i_L , for the experiment (Fig. 2).

The accuracy of the stirring could be estimated to 2.5%. It was checked with an stroboscope in the case of the higher speeds and with a chronometer for the lower ones.

RESULTS

The experimental data are shown on Tables 1–6. The meaning of symbols and its units are the following: No. is the number of the experiment; T is the temperature in

TABLE 1. 0 REV/MIN.

No.	T	$i_L \times 10^2$	C_o	C_a	D_2	$k \times 10^4$
14	16.1	0.200	0.0565	1.498	3.75	1.82
21	18.2	0.188	0.0509	1.496	2.17	1.91
22	16.2	0.184	0.0507	1.506	6.60	1.88
200	27.8	0.226	0.0547	1.482	3.73	2.14
201	37.9	0.324	0.0547	1.482	3.73	3.07
202	30.7	0.280	0.0547	1.482	2.16	2.65
203	37.9	0.346	0.0547	1.482	2.16	3.28
204	38.9	0.364	0.0547	1.482	6.59	3.45
205	29.1	0.271	0.0547	1.482	6.59	2.57

TABLE 2. 55 REV/MIN.

No.	T	$i_L \times 10^3$	C_o	C_a	D_2	V	$k \times 10^4$
16	17.1	0.412	0.0565	1.498	3.75	9.82	3.78
18	21.2	0.296	0.0509	1.496	3.75	11.0	3.01
25	16.9	0.206	0.0507	1.506	2.17	6.36	2.10
29	20.4	0.580	0.0537	1.511	6.60	19.3	5.60
53	36.8	0.771	0.0503	1.487	6.60	19.3	7.94
56	26.8	0.628	0.0502	1.487	6.60	19.3	6.48
104	35.2	0.415	0.0530	1.479	3.74	11.0	4.06
106	28.2	0.364	0.0530	1.479	3.74	11.0	3.56
153	27.9	0.260	0.0517	1.492	2.17	6.36	2.61
157	34.6	0.300	0.0517	1.492	2.17	6.36	3.01

TABLE 3. 100 REV/MIN.

No.	T	$i_L \times 10^3$	C_o	C_a	D_2	V	$k \times 10^4$
15	16.4	0.372	0.0565	1.498	3.75	19.6	3.41
23	17.1	0.235	0.0507	1.506	2.17	11.9	2.40
26	17.8	0.845	0.0507	1.506	6.60	35.6	8.63
50	32.6	1.00	0.0537	1.491	6.60	36.6	9.71
52	35.9	1.03	0.0505	1.478	6.60	36.6	10.6
100	27.6	0.437	0.0530	1.479	3.74	20.6	4.27
102	36.1	0.532	0.0530	1.479	3.74	20.6	5.20
152	29.1	0.306	0.0517	1.492	2.17	12.2	3.07
156	33.6	0.346	0.0517	1.492	2.17	11.9	3.47

TABLE 4. 200 REV/MIN.

No.	T	$i_L \times 10^2$	C_o	C_a	D_2	V	$k \times 10^4$
13	18.8	0.540	0.0568	1.525	3.75	40.2	4.93
27	18.1	1.11	0.0507	1.506	6.60	69.1	11.3
51	37.6	1.53	0.0511	1.476	6.60	69.1	15.5
55	30.4	1.31	0.0504	1.480	6.60	69.1	13.5
101	29.6	0.637	0.0530	1.479	3.74	42.5	6.23
103	35.6	0.739	0.0530	1.479	3.74	39.2	7.22
151	29.6	0.382	0.0517	1.492	2.17	22.7	3.83
155	33.3	0.437	0.0517	1.492	2.17	22.7	4.38
207	20.0	0.310	0.0505	1.486	2.16	22.6	3.18

TABLE 5. 300 REV/MIN.

No.	T	$i_L \times 10^2$	C_o	C_a	D_2	V	$k \times 10^4$
28	20.6	1.28	0.0537	1.511	6.60	103.7	12.3
54	37.3	1.90	0.0506	1.481	6.60	103.7	19.5
57	27.6	1.51	0.0504	1.482	6.60	103.7	15.5
105	35.1	0.910	0.0530	1.479	3.74	58.8	8.90
107	28.9	0.805	0.0530	1.479	3.74	58.8	7.87
150	29.8	0.457	0.0517	1.492	2.17	34.1	4.58
154	38.0	0.553	0.0517	1.492	2.17	34.1	5.54
206	25.0	0.692	0.0505	1.486	3.73	58.5	7.10
208	16.3	0.328	0.0505	1.486	2.16	33.9	3.36

TABLE 6. OTHER SPEEDS

No.	T	$i_L \times 10^2$	C_o	C_a	D_2	V	$k \times 10^4$
11	19.2	0.610	0.0552	1.499	3.75	53.4	5.73
12	18.4	0.660	0.0554	1.492	3.75	63.8	6.17
17	17.2	0.460	0.0566	1.492	3.75	29.5	4.22
19	18.6	0.260	0.0509	1.496	2.17	17.0	2.71
20	19.2	0.320	0.0509	1.496	2.17	28.4	3.31
24	17.8	0.370	0.0507	1.506	2.17	39.2	3.81

$^{\circ}\text{C}$; i_L is the limiting current density in A/cm^2 ; C_o and C_a are the molar concentration of both electrolytes; k is the rate constant for the mass transfer in cm/sec ; D_2 is the anode diameter in cm , and V is its peripheral velocity in cm/sec .

INTERPRETATION

1. Calculation of the rate constant

The constant k as previously shown has been calculated from the limiting current density. When it has been reached, the rate of mass transfer becomes a diffusion controlled process and the following relationship is fulfilled,

$$i_L = k \cdot z \cdot F \cdot C_o, \quad (1)$$

where z is the copper ion valency and F the Faraday constant. Equation (1) has been employed in the calculation of k .

It is worth while to be mentioned here that the experimental values obtained for k and for i_L are average values for the whole electrode area⁵.

2. The rate constant and temperature

To study the influence of stirring upon the rate constant it is necessary to carry out all the calculations at a constant temperature. $T = 18^\circ\text{C}$ has been chosen and the properties of the solutions have been referred to this temperature.

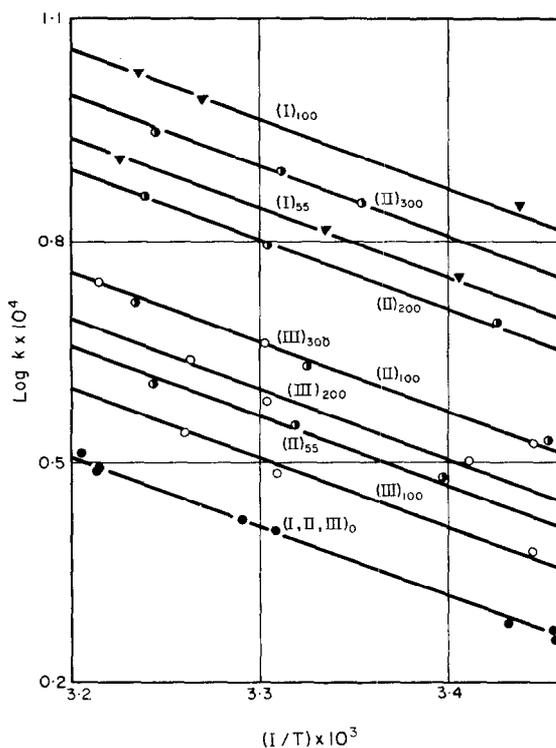


FIG. 3. Plot of $\log k$ as a function of $1/T$. Figures above the straight lines refers to the rev/min and I, II, and III refers to the 6.60 cm, 3.75 cm and 2.17 cm diameter rotating electrodes respectively.

The experiments were done at different temperatures. A plot of $\log k$ as a function of $1/T_k$, where T_k is the temperature in degrees Kelvin, gives a set of parallel straight lines, each for a different rate of stirring. The values of k at 18°C were taken from these lines and they were employed in the following calculations (Fig. 3).

3. The rate constant and rate of stirring

The rate of stirring was measured by the peripheral velocity of the anode and it was assumed the state of a forced convection was determined by that velocity.

The whole arrangement of the electrolysis cell employed avoids the existence of a vortex component in the flowing of the liquid. In looking for a linear relationship between k and V , it was found that plotting k as a function of V to the exponent 0.70 led to a straight line, if the peripheral velocity was greater than 13 cm/sec, and this function works very well in the range of our experimental data, as shown in Fig. 4.

4. Application of dimensional analysis. Dimensionless correlation for the mass transfer under forced convection

Dimensional analysis is very useful to correlate experimental results in electrochemistry⁶ and it has been applied to our experimental data following the same notation Eisenberg, Tobias and Wilke have employed recently.¹

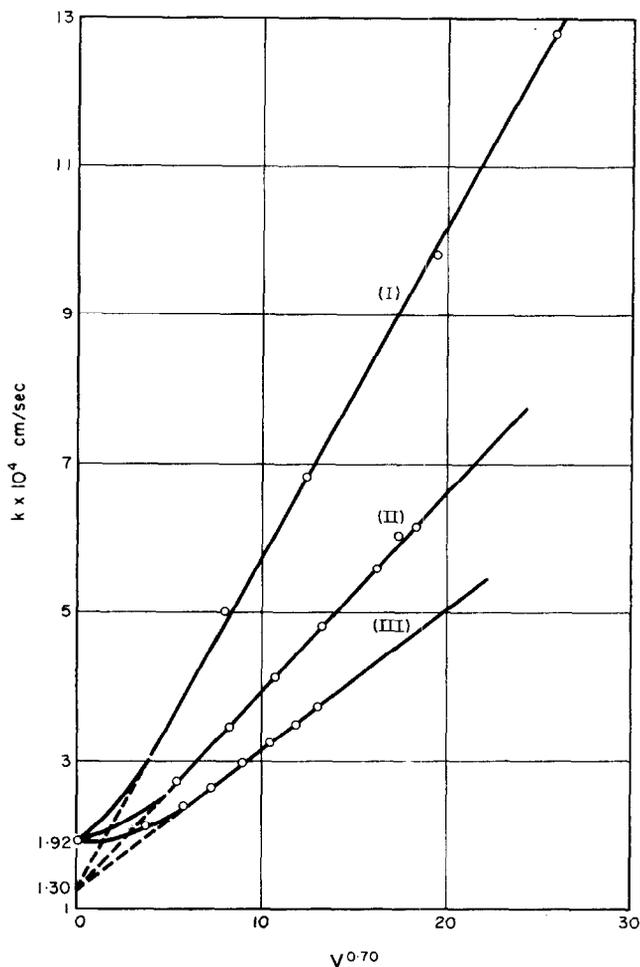


FIG. 4. Plot of k at 18°C as a function of $V^{0.70}$. The numbers I, II and III refer to the three copper anodes employed.

The experimental results of this study can thus be represented by the following relationship:

$$j' = \text{const. } Re^{-0.30} \cdot \left(\frac{D_1}{D_2}\right)^{-0.70} \quad (2)$$

In equation (2) j' is a dimensionless number which has been previously defined^{1,2} as

$$j' = \frac{k}{V} \cdot Sc^{0.644}, \quad (3)$$

and Re is Reynolds' number,

$$Re = \frac{V \cdot D_2}{\nu}, \quad (4)$$

where the rotating electrode diameter D_2 is the characteristic length, D_1 is the cathode diameter and Sc is the Schmidt's number. The experimental data to test equation (2) are shown in Table 7.

TABLE 7.

V	$k \times 10^4$	$j' \times 10^4$	Re	$(Re)^{0.30}$	$\frac{D_1}{D_2}$	$\left(\frac{D_1}{D_2}\right)^{0.70}$
6.36	2.13	51.0	1066	8.097	4.45	2.84
11.9	2.41	30.6	2012	9.797	4.45	2.84
22.7	2.99	20.0	3806	11.86	4.45	2.84
34.1	3.32	15.6	5700	13.36	4.45	2.84
17.0	2.65	23.7	2850	10.84	4.45	2.84
28.4	3.25	17.4	4760	12.80	4.45	2.84
39.2	3.73	14.1	6570	13.98	4.45	2.84
11.0	2.74	37.8	3179	11.24	2.58	1.94
20.3	3.46	25.9	5867	13.51	2.58	1.94
40.6	4.81	18.0	11730	16.63	2.58	1.94
58.7	6.05	15.7	16960	18.57	2.58	1.94
53.4	5.60	16.0	15470	18.06	2.58	1.94
63.8	6.16	14.7	18490	18.64	2.58	1.94
29.5	4.23	21.8	8548	15.12	2.58	1.94
19.3	5.15	40.6	9840	15.77	1.46	1.30
36.3	6.82	28.6	18513	19.06	1.46	1.30
69.1	9.82	21.6	35200	23.13	1.46	1.30
103.7	12.8	18.8	52880	26.12	1.46	1.30

Schmidt's number, which gives a ratio between the kinematic viscosity of the solution, ν , and the diffusion coefficient, D , for copper ions, changed very little in this work and it has been calculated as 2450. The diffusion coefficient was taken from Gordon and Cole⁷ and it is 5.22×10^{-6} cm²/sec. The kinematic viscosity has been determined and its average value is 1.279×10^{-2} cm²/sec.

When the gap between the cylindrical cathode and the rotating anode is nil, then $D_1 = D_2$ and equation (2) gives the relationship obtained by the above mentioned authors for their experiments on cylindrical rotors

$$j' = 0.0791 \cdot Re^{-0.30}. \quad (5)$$

We have plotted together the experimental data of the present paper with the ones found earlier for mass transfer on cylindrical rotors and have observed that all the data may be approximated with equation (2) if its constant is also 0.0791.

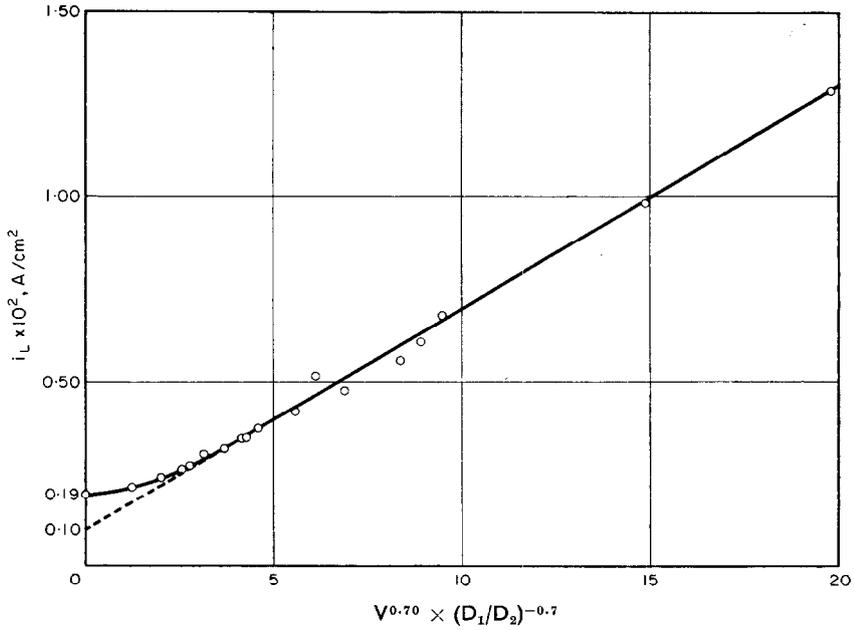


FIG. 5. Plot of the limiting current density, i_L , as a function of $V^{0.70} \cdot \left(\frac{D_1}{D_2}\right)^{-0.70}$ according to equation (6).

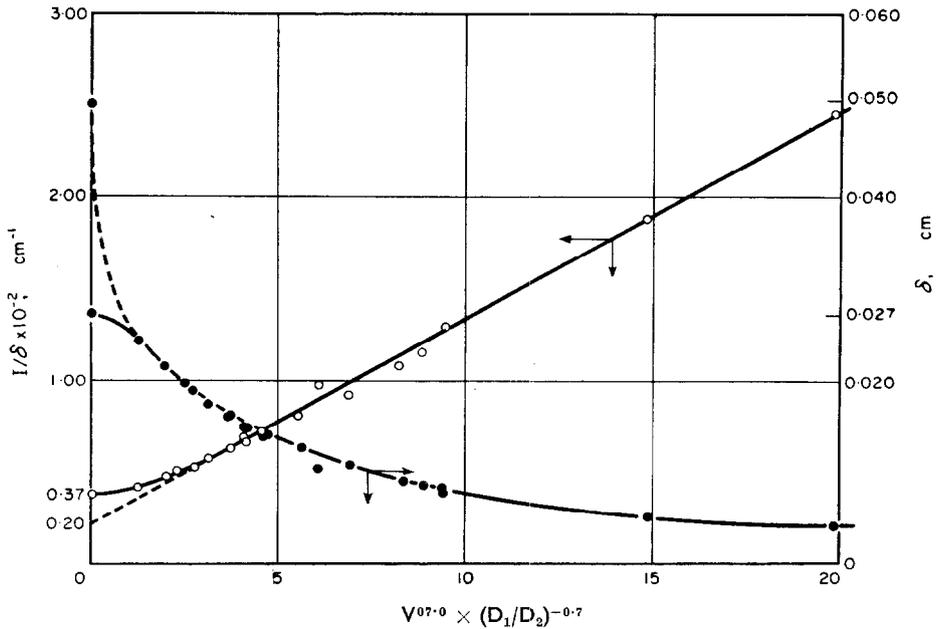


FIG. 6. Plot of “ δ ” as a function of $V^{0.70} \cdot \left(\frac{D_1}{D_2}\right)^{-0.70}$, according to equation (7). “ δ ” for a diffusion-natural convection process are shown.

From equation (2) we obtain

$$i_L = 0.0791 \cdot \left(\frac{D_2}{\nu}\right)^{-0.30} \cdot V^{0.70} \cdot \left(\frac{D_1}{D_2}\right)^{-0.70} \cdot Sc^{-0.644} \cdot z \cdot F \cdot C_o \quad (6)$$

This equation is presented in Fig. 5. From (6) and (1) we obtain

$$k = 0.0791 \cdot \left(\frac{D_2}{\nu}\right)^{-0.30} \cdot V^{0.70} \cdot \left(\frac{D_1}{D_2}\right)^{-0.70} \cdot Sc^{-0.644} \quad (7)$$

Fig. 6 indicates the way how the thickness of the effective diffusion layer, δ , changes with the rate of stirring. k is equal to D/δ .

DISCUSSION

1. The rate constant for the mass transfer under forced convection

The dependence of the rate constant, k , with the rate of stirring, ν , to the 0.70th power has been found by Roald and Beck⁸ in the dissolution of rotating magnesium electrodes and by Wilke, Eisenberg and Tobias^{1,2} for the mass transfer in the ferro-ferricyanide redox reaction on rotating electrodes and in the dissolution of benzoic acid cylinders.

This paper presents the data for an electrochemical system where a metal ion is deposited on the fixed cathode of a cylindrical shaped cell. The fact that equation (2) has the same form in the case of $D_1 = D_2$, as that obtained by Wilke, Eisenberg and Tobias from their results on other systems where the mass transfer process occurs on cylindrical rotors, shows that the same physical mechanism of diffusion and convection is involved. This fact is clearly indicated in Fig. 7. The mechanism of mass transfer seems to be independent of the type of electrochemical or chemical reaction under consideration.

The rate constant for the mass-transfer process keeps also in this case the expected dependence with the rate of stirring to the 0.70th power, within the range of velocities from 13 cm/sec up to the maximum one studied here.

King and Shack⁹ and Glicksman, Mouquin and King¹⁰ have considered the rate of dissolution of copper and zinc in acid solutions and the rate of displacement of silver from silver ions in solution with rotating cylinders of copper and zinc. These authors draw a linear relationship between k and V , but most of their figures for k could also be plotted as a function of $V^{0.70}$ yielding good straight lines.

Fig. 4, where k has been plotted as a function of $V^{0.70}$ shows a trend of the experimental data to deviate from the straight lines when V tends to zero. The rate constant for mass transfer under free convection—diffusion conditions, k_o , is the same for the three electrodes, 1.92×10^{-4} cm/sec. If the straight lines are extrapolated to zero velocity, the resultant rate constant is not zero, as it would be expected according to equation (7).

When this fact is compared to data in Fig. 7 it comes out that for the highest values for V , the largest are the deviations of k from equation (7); therefore, the j' values are placed under the line drawn according to the general correlation. This is also more evident when data obtained with the smallest diameter electrode is considered. This effect could be due to the fact that the stirring efficiency on the electrolyte

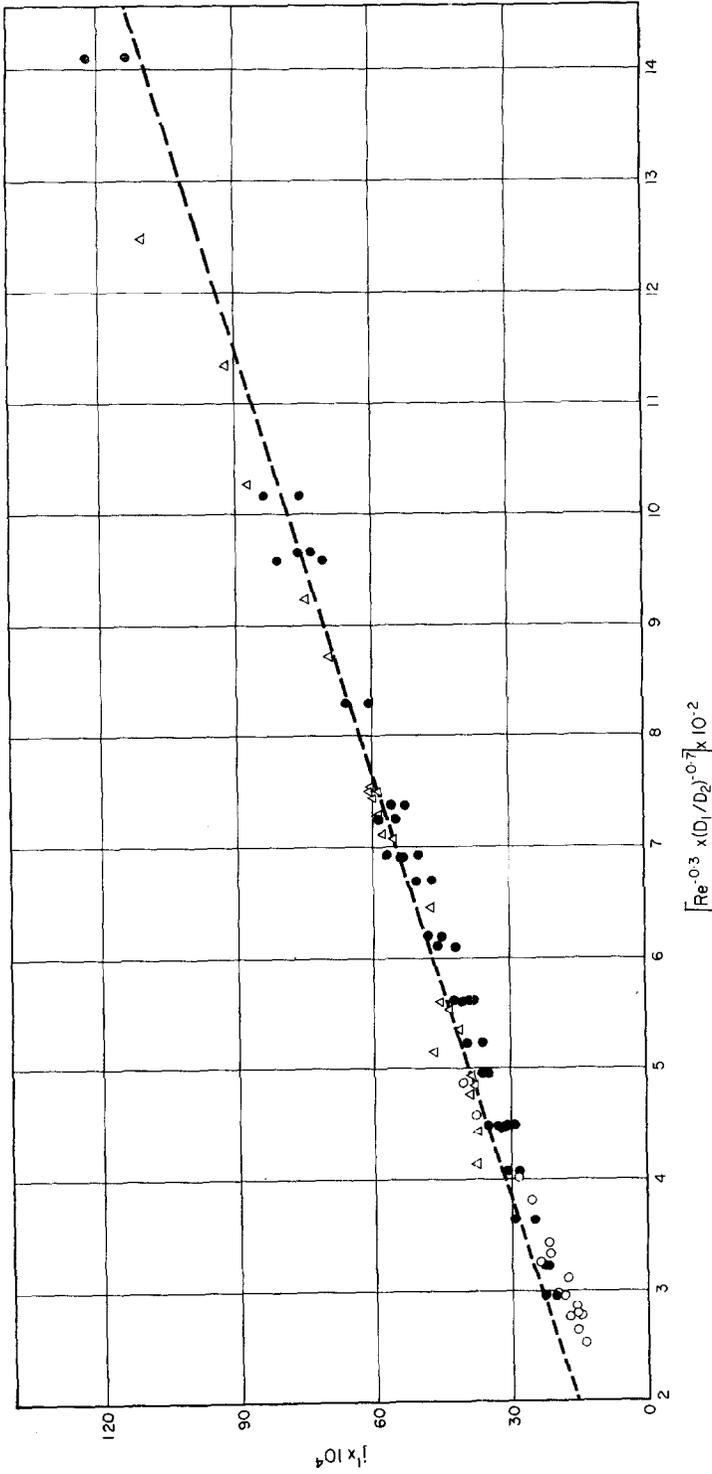


Fig. 7. The mass-transfer correlation. Data for the dissolution of benzoic acid rotors (Δ) and for the ferro-ferricyanide system (\bullet) are taken from Eisenberg, Wilke and Tobias^{1,2}. Results of our experiments are indicated with circles (\circ) and our figures are for experiments where the peripheral velocity was larger than 13 cm/sec.

placed in the cathode region is lower than the one measured through the speed of rotation of the anodes.

It is interesting also to emphasize that the straight lines drawn in Fig. 4 show the trend to curve for Reynolds numbers lower than 2300. Although these numbers are defined with an arbitrary length, that limiting value coincides with Reynolds numbers which indicate the transition between laminar and turbulent flow.

2. The effect of temperature on the rate constant for mass transfer

The rate constant for the mass-transfer process changes with temperature and its dependence fits into an equation of the Arrhenius type,

$$k = Z \cdot e^{-E_T/RT}, \quad (8)$$

where Z is the pre-exponential factor and E_T is the experimental activation energy for the mass-transfer process.

According to Nernst^{11,12,13} the activation energy for mass-transfer phenomena should be equal to the heat of activation for diffusion, E_D . The value obtained here for E_T is 4500 ± 250 cal/mole, which is close to the known value for the activation energy of the diffusion process of copper ions.¹⁴ Nevertheless, if E_T is equal to E_D it would mean that “ δ ” is temperature independent. Strictly speaking, this is not the case as can be deduced from equation (7). However, “ δ ” is proportional to $\nu^{0.344} \times D^{0.356}$, where as a first approximation, ν and D are inversely proportional to each other as temperature changes, so that the product νD remains nearly constant within the range of our experiments. This result is in accordance with the experimental observation of Kolthoff and Laitinen¹⁵ who found that “ δ ” is independent of the temperature at the rotating platinum microelectrode. The same experimental fact has been found by Jaenicke¹⁷ in his work on the dissolution of silver salts between 20 and 50°C.

The Arrhenius plot of Fig. 3 shows a set of parallel straight lines, each for a definite rate of stirring. Therefore, the apparent activation energy for these mass transfer processes are independent of the rate of stirring. This is clearly indicated by the fact that the zero rev/min experiments are given the same slope as the 300 rev/min ones. Although in the first case a general correlation for a free convection-diffusion process has to be applied¹⁵, the effect of the temperature on “ δ ” is not large enough to produce a measurable change on E_T .

Acknowledgement—The authors wish to thank the Director of the Institute, Dr. H. J. Schumacher, and the Head of the Technological Department, Dr. J. J. Ronco, for the interest shown on this work, and Dr. N. Ibl, for his helpful remarks. J.S.W.C. thanks the Consejo Nacional de Investigaciones Cientificas for the funds granted.

REFERENCES

1. M. EISENBERG, C. W. TOBIAS and C. R. WILKE, *J. Electrochem. Soc.* **101**, 306 (1954).
2. M. EISENBERG, C. W. TOBIAS and C. R. WILKE, *Chem. Engng. Prog. Symp. Series No. 16*, **51** (1955).
3. J. S. W. CARROZZA, Tesis doctoral, Fac. Quim. Farm. Univ. Nac., La Plata (1959).
4. J. S. W. CARROZZA, A. J. ARVIA and J. J. RONCO, *An. Asoc. Quim. Argent.* **47**, 69 (1959).
5. J. N. AGAR, *Disc. Faraday Soc.* **1**, 26 (1947).
6. N. IBL, *Electrochim. Acta* **1**, 117 (1959).
7. A. R. GORDON and A. COLE, *J. Phys. Chem.* **40**, 733 (1936).
8. B. ROALD and W. BECK, *J. Electrochem. Soc.* **98**, 277 (1951).

9. C. V. KING and M. SHACK, *J. Amer. Chem. Soc.* **57**, 1212 (1935).
10. R. GLICKSMAN, H. MOUQUIN and C. V. KING, *J. Electrochem. Soc.* **100**, 580 (1953).
11. W. NERNST, *Z. phys. Chem.* **47**, 52 (1904).
12. W. NERNST, *Z. phys. Chem.* **47**, 56 (1904).
13. W. NERNST, *Z. phys. Chem.* **75**, 503 (1911).
14. H. S. TAYLOR, *J. Chem. Phys.* **6**, 331 (1938).
15. C. W. TOBIAS, M. EISENBERG and C. R. WILKE, *J. Electrochem. Soc.* **99**, 359C (1952).
16. L. L. BIRCUMSHAW and A. C. RIDDIFORD, *Quart. Rev. Chem. Soc. Lond.* **6**, 157 (1952).
17. W. JAENICKE, *Z. Elektrochem.* **55**, 648 (1951).