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NATURAL CONVECTION MASS-TRANSFER MEASUREMENTS ON SPHERES AND HORIZONTAL CYLINDERS BY AN ELECTROCHEMICAL METHOD

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Abstract—In the electrolysis of cupric sulphate with sulphuric acid as supporting electrolyte the limiting current is directly proportional to the mass-transfer coefficient. Using spheres and horizontal cylinders as cathodes, limiting currents were measured for $(Gr \cdot Sc)$ numbers between $1{\cdot}22 \times 10^7$ and $1{\cdot}51 \times 10^{10}$. By insulating electrically a small area on the cathode local mass-transfer coefficients and also the transition laminar-turbulent of the hydrodynamic boundary layer could be determined. The accuracy of the method is estimated to be ±5 per cent with the instrumentation used.

NOMENCLATURE

c_o, concentration in bulk solution [kmol/m^3];
c_i, concentration at electrode surface [kmol/m^3];
D, diffusion coefficient, [m^2/s];
d, diameter, [m];
g, gravity constant, [m/s^2];
i, density of current, [A/m^2];
i_l, limiting current density, [A/m^2];
$\dot{n}$, rate of transfer per unit area [kmol/m^{2}s];
z, valence of reaction;
F, Faraday constant $= 96500 \,.\, 10^3$ As/kg equivalent;
Gr, Grashof number $= \dfrac{g \cdot d^3 \cdot \Delta\rho}{\nu^2 \rho}$;
Sc, Schmidt number $= \dfrac{\nu}{D}$;
Sh, Sherwood number $= \dfrac{\beta \cdot d}{D}$.

Greek symbols
β, mass-transfer coefficient [m/s];
ν, viscosity [m^2/s];
ρ, density [kg/m^3];
$\Delta\rho$, density difference between bulk solution and electrode interface.

INTRODUCTION

In an electrochemical process the rate of reaction is generally determined by the diffusion, the convection and the migration of the ions in the electrical field to the electrodes. The convection may be forced, by stirring the solution, or purely natural convection caused by density differences between bulk solution and electrode interface.

By adding a supporting electrolyte to the reacting electrolyte the migration is eliminated, and the transport is controlled only by diffusion and convection as in other mass-transfer problems, e.g. sulphuric acid can be added as supporting electrolyte to a solution of cupric sulphate; then the protons of the acid transport the current making the migration of cupric ions negligible, while at the cathode only the latter is discharged.

For the rate of transfer per unit area it is usual to write

$$\dot{n} = \beta(c_o - c_i). \tag{1}$$

As the current flowing between the two electrodes is proportional to the reaction rate the transport problem is reduced to the measurement of an electrical current:

$$\dot{n} = \frac{i}{zF}. \tag{2}$$

From (1) and (2) we get

$$\beta = \frac{i}{zF(c_o - c_t)}.$$

Since the concentration c_t is not known, we have to work at limiting current conditions, that is at the maximum current density which is allowed for the exclusive production of the desired electrode reaction. Here c_t is negligibly small and can be taken as zero, which means that every ion near the electrode is instantaneously removed by reaction. The limiting current can be found in a current vs. potential diagram and lies in the horizontal part of the curve where an increase of the potential difference between cathode and anode does not alter the current.

We obtain then

$$\beta = \frac{i_l}{zFc_o}.$$

The geometric form under investigation is usually used as the cathode. Local mass-transfer coefficients are determined by measuring the current only on a small, electrically insulated area of the surface (Fig. 1).

As Grassmann, Ibl and Trüb [1] have shown, this method applies very well to forced convection problems with potassium ferro- and ferricyanide as reacting electrolyte and sodium hydroxyde as supporting electrolyte. We shall now demonstrate its value under free convection conditions if another electrolyte is taken.

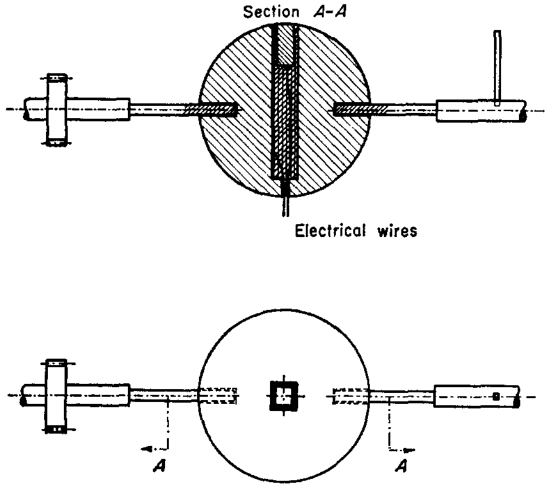

FIG. 1. View of a sphere with electrically insulated area. d = 24·9 mm, insulated area = 3 × 3 mm, width of insulation = 0·3 mm.

EXPERIMENTAL

(a) *Apparatus*

The experiments were made at 25°C in a 15 × 15 × 25 dm Perspex cell which was fixed in a thermostated waterbath. According to Senftleben [2] there should be no interference between walls and electrode boundary layers in the range of our experiments.

The nickel cathodes were in the centre of the cell, surrounded by the copper anodes on the cell walls. For the measurement of the local mass transfer, the electrode including the insulated area could be turned to different positions with respect to the flow direction.

(b) *Electrolyte*

The electrolytic solution used was $CuSO_4$–H_2SO_4 in different concentrations as described by Wilke [3] and Fouad and Ibl [4]. After each experiment the concentration was checked by the thiosulphate-iodine method.

(c) *Physical properties*

The densities of the electrolytes were measured with a densitometer; for measuring the viscosities an Ubbelohde viscosimeter was used.

The diffusion coefficients of the cupric ion were determined electrolytically by the method of Stackelberg [5] and Cottrell [6]. The data corresponded very well with those of Wilke [3].

The density difference $\Delta\rho$ between bulk and electrodes interface was calculated as outlined by Fouad and Ibl [4]. For the densification coefficients of H_2SO_4, the value of Wilke *et al.* [3] was taken. The diffusion coefficients of H^+ was the same as in the works of Wagner [7] and Buob [8].

RESULTS

It is usual to bring the solutions of natural convection mass transfer problems on cylinders into the dimensionless form

$$Sh = k(Gr \cdot Sc)^{0{\cdot}25}.$$

This equation holds for very slow motion where the inertia forces are negligible compared to viscosity forces. The exponent 0·25 was found by theory and experiments for laminar flow. As Fouad and Ibl [4] and many others have shown, this exponent does not apply to turbulent conditions.

All of our results for the horizontal cylinder will be brought to the form of the equation above, while for spheres we will use the form

$$Sh = 2 + k(Gr \cdot Sc)^{0 \cdot 25}.$$

$Sh = 2$ is the limiting value for diffusion only to a sphere in an infinite medium.

(a) *Cylinder*

Fig. 2 shows the logarithmic graph of *Sh* vs. (*Gr*·*Sc*) (see also Table 1). All the points for

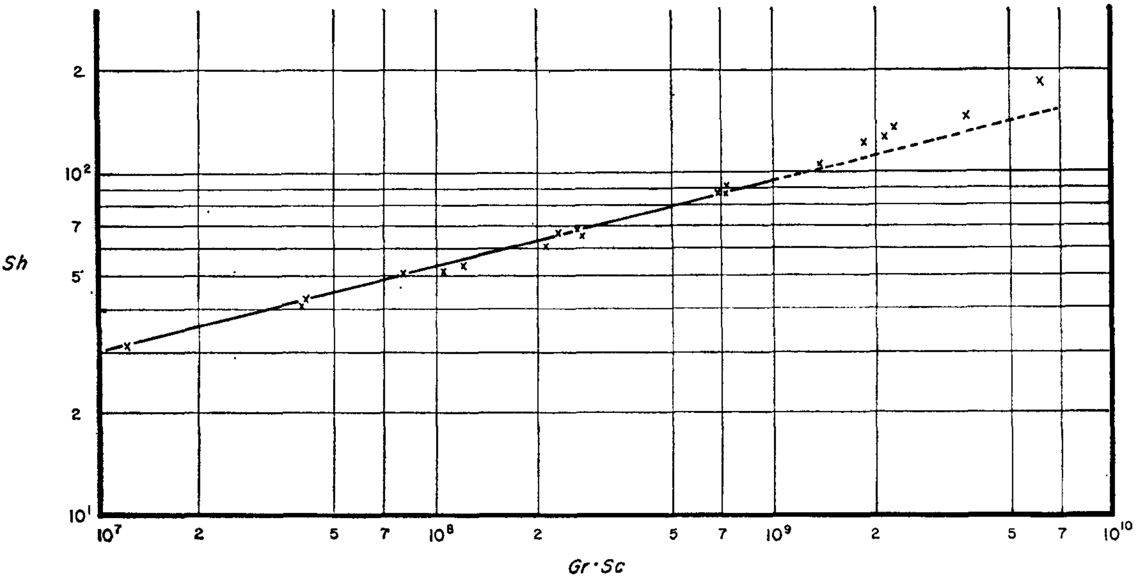

FIG. 2. Overall mass transfer on cylinder.

Table 1. Mass transfer on cylinder, $c_{H_2SO_4} = 1·5$ m; $T = 25$°C

No.	$d \times 10^2$ (m)	c_{CuSO_4} (kmol/m³)	$D \times 10^{10}$ (m²/s)	$\nu_0 \times 10^6$ (m²/s)	ρ_0 (kg/m³)	$\Delta\rho$ (kg/m³)	*Sc*	*Gr*	(*Gr*·*Sc*)	*Sh*
1	0·95	0·0113	6·27	1·0753	1090·1	1·04	1714	7·13 10^3	1·22 10^7	31·2
2	0·95	0·0325	6·14	1·0827	1093·0	3·36	1763	2·26 10^4	3·99 10^7	41·2
3	0·95	0·0245	6·22	1·0898	1092·9	3·54	1752	2·35 10^4	4·13 10^7	42·8
4	1·79	0·0112	6·27	1·0753	1090·1	1·04	1714	4·64 10^4	7·96 10^7	50·6
5	0·95	0·0750	5·95	1·1003	1099·5	8·69	1849	5·64 10^4	1·04 10^8	51·2
6	0·95	0·0815	6·02	1·1063	1101·1	10·15	1836	6·51 10^4	1·19 10^8	53·3
7	0·95	0·1465	6·09	1·1370	1111·5	18·68	1867	1·12 10^5	2·09 10^8	60·3
8	2·49	0·01246	6·27	1·0757	1090·2	1·11	1715	1·33 10^5	2·29 10^8	66·4
9	1·79	0·0325	6·14	1·0827	1093·0	3·36	1763	1·47 10^5	2·60 10^8	67·8
10	1·79	0·0245	6·22	1·0898	1092·9	3·54	1752	1·53 10^5	2·69 10^8	65·1
11	1·79	0·0750	5·95	1·1003	1099·5	8·69	1849	3·67 10^5	6·79 10^8	86·9
12	2·49	0·0332	6·14	1·0830	1093·1	3·44	1764	4·07 10^5	7·19 10^8	91·1
13	2·49	0·0245	6·22	1·0898	1092·9	3·54	1752	4·13 10^5	7·24 10^8	87·9
14	1·79	0·1466	6·09	1·1370	1111·5	18·68	1867	7·32 10^5	1·36 10^9	107·1
15	2·49	0·0750	5·95	1·1003	1099·5	8·69	1849	9·91 10^5	1·83 10^9	121·6
16	2·49	0·0815	6·02	1·1063	1101·1	10·15	1836	1·14 10^6	2·09 10^9	124·5
17	1·79	0·2500	5·43	1·1761	1126·0	30·24	2073	1·09 10^6	2·26 10^9	136·2
18	0·95	0·1466	6·09	1·1370	1111·5	18·68	1867	1·97 10^6	3·68 10^9	146·0
19	2·49	0·2500	5·43	1·1761	1126·0	30·24	2073	2·94 10^6	6·10 10^9	184·6

$Gr \cdot Sc < 10^9$ were used for the calculation of a regression line with the gradient 0·25, yielding

$$Sh = 0{\cdot}53(Gr \cdot Sc)^{0{\cdot}25}.$$

The same formula is recommended by McAdams [9] for natural convection heat transfer from horizontal cylinders to gases and liquids (Pr has to be replaced by Sc). The good correspondence can be taken as a proof of the usefulness of the electrochemical method.

For $Gr \cdot Sc > 10^9$ we are in the region where turbulence begins to influence mass transfer and the gradient of the curve increases.

The results of local mass-transfer measurements are represented by Fig. 3. As observed by Grassmann *et al.* [1] also for forced convection conditions, all the curves have a minimum at the flow stagnation point. This effect, however, has never been observed in experiments using other methods, although the curves otherwise have a similar shape. There are two possible explanations: either it is a real minimum which would point to an area of dead water around the stagnation point of this pole, or it is due to the nihomogenity of the surface caused by the electric insulation. By varying the width of the insulation stripe in further tests this problem will be cleared up.

For $Gr \cdot Sc > 3 \times 10^8$ all the curves go through a minimum near the rear pole (for the range investigated this minimum lies between 130 and 180°). As can be shown in the current time plots (e.g. Fig. 4), turbulence sets in near this point with a corresponding rise in the rate of mass transfer. Thus it is easy to see from the local

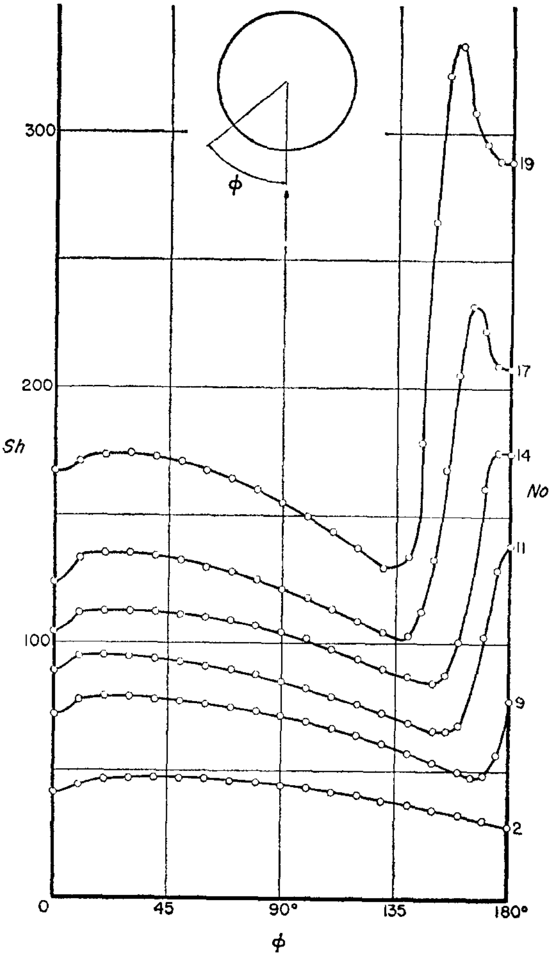

FIG. 3. Local mass transfer on cylinder for different ($Gr \cdot Sc$) numbers. The number of the curves corresponds with the number of experiments in Table 1.

Table 2. Mass transfer on sphere $c_{H_2SO_4} = 1{\cdot}5$ m $T = 25$°C

No.	$d \times 10^2$ (m)	c_{CuSO_4} (kmol/m^3)	$D \times 10^{10}$ (m^2/s)	$\nu_o \times 10^6$ (m^2/s)	ρ_o (kg/m^3)	$\Delta\rho$ (kg/m^3)	Sc	Gr	$(Gr \cdot Sc)$	Sh
1	2·49	0·0123	6·27	1·0755	1090·2	1·11	1715	1·33 10^5	2·29 10^8	68·2
2	3·17	0·0125	6·27	1·0757	1090·3	1·21	1715	3·02 10^5	5·18 10^8	89·1
3	2·49	0·0333	6·14	1·0830	1093·1	3·44	1764	4·07 10^5	7·19 10^8	90·7
4	3·98	0·0127	6·27	1·0759	1090·3	1·21	1716	5·97 10^5	1·02 10^9	106·7
5	3·17	0·0333	6·14	1·0830	1093·1	3·44	1764	8·45 10^5	1·49 10^9	117·1
6	2·49	0·0748	5·95	1·1003	1099·5	8·70	1849	9·92 10^5	1·84 10^9	113·4
7	3·98	0·0333	6·14	1·0830	1093·1	3·44	1764	1·67 10^6	2·94 10^9	143·7
8	2·49	0·1460	6·09	1·1370	1111·5	18·70	1867	1·97 10^6	3·69 10^9	137·3
9	3·17	0·0750	5·95	1·1003	1099·5	8·69	1849	2·05 10^6	3·80 10^9	150·2
10	3·98	0·0750	5·95	1·1003	1099·5	8·69	1849	4·06 10^6	7·51 10^9	184·3
11	3·17	0·1440	6·09	1·1370	1111·5	18·75	1867	4·11 10^6	7·68 10^9	180·8
12	3·98	0·1465	6·09	1·1370	1111·5	18·69	1867	8·09 10^6	1·51 10^{10}	216·5

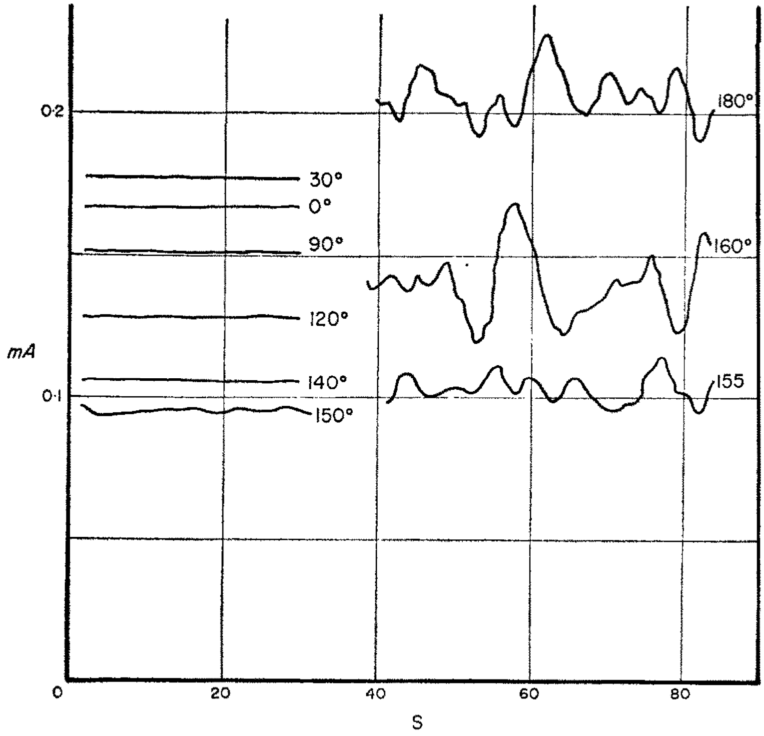

FIG. 4. Limiting current vs. time curve for experiment No. 5 in Table 2. Turbulence sets in at $\phi = 150°$. In the turbulent region the mean limiting current density was obtained by graphic integration.

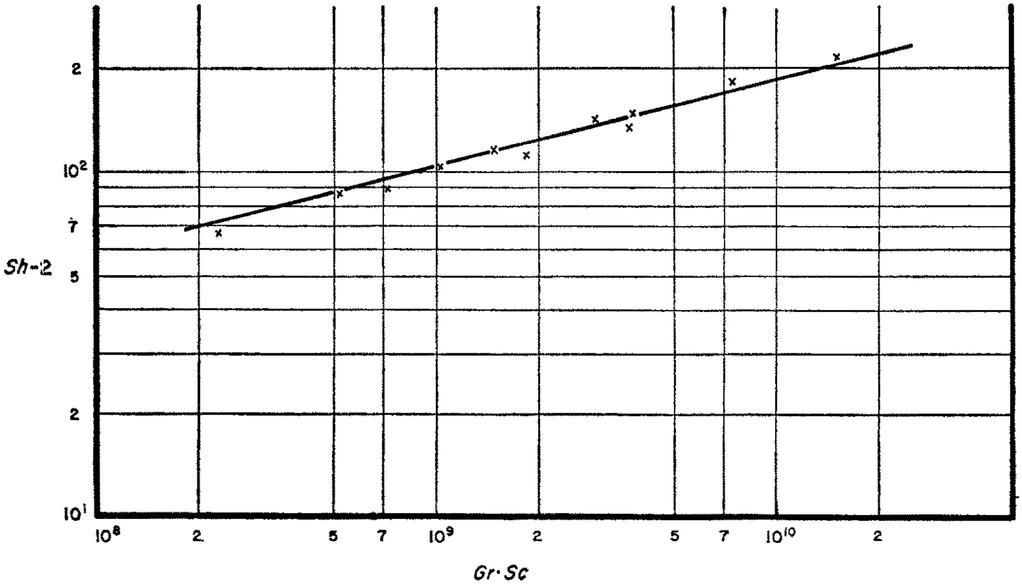

FIG. 5. Overall mass transfer on sphere.

curves where the laminar-turbulent transition begins.

(b) *Sphere*

Figs. 5 and 6 and Table 2 show the results for the spheres. The full line in Fig. 5 is represented by

$$Sh = 2+0{\cdot}59(Gr \cdot Sc)^{0{\cdot}25}.$$

This is still quite good compared with the theoretical line of Merk and Prins [10] ($k = 0{\cdot}55$). From the local mass-transfer curves it is observed that we are fully in the transition region, and it is questionable if this form of the equation is still applicable. To answer this question further experiments will be made extending to higher and to lower $Gr \cdot Sc$ numbers.

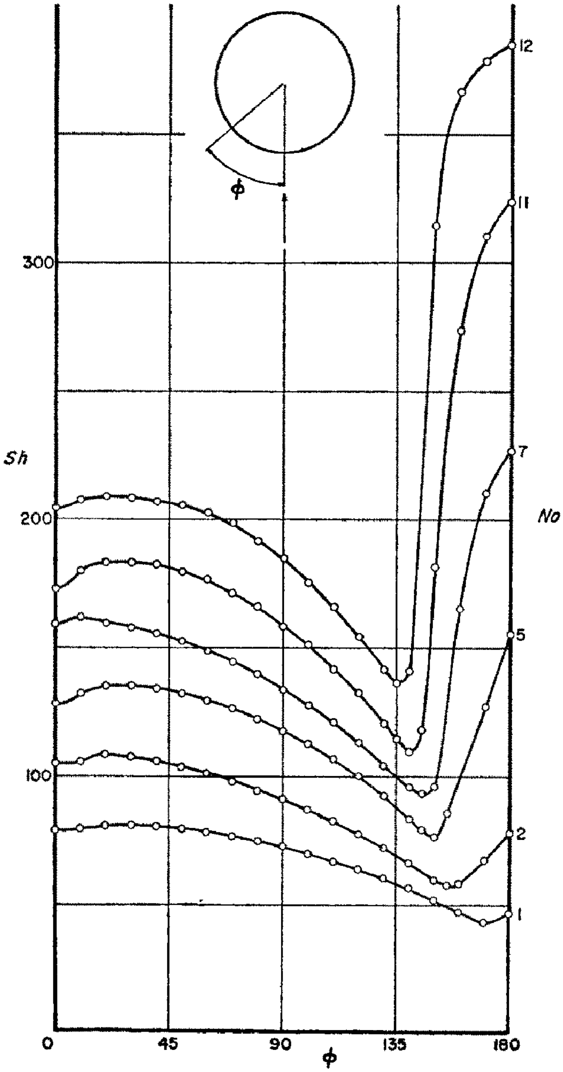

FIG. 6. Local mass transfer on sphere for different ($Gr \cdot Sc$) numbers. The number of the curves corresponds with the number of experiments in Table 2.

CONCLUSIONS

It has been shown that it is possible to solve mass-transfer problems with the aid of electrochemical experiments. Sherwood numbers were determined with an accuracy of ±5 per cent which could easily be improved by the use of more precise diffusion coefficients and more sensitive instrumentation.

ACKNOWLEDGEMENT

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Résumé—Dans l'électrolyse du sulfate de cuivre, l'acide sulfurique étant pris comme électrolyte support, le courant limite est directement proportionnel au coefficient de transport de masse. En utilisant pour cathodes des sphères et des cylindres horizontaux, on a mesuré les courants limites pour des nombres de *Gr* et de *Sc* compris entre $1{,}22 \cdot 10^7$ et $1{,}51 \cdot 10^{10}$. En isolant une petite surface sur la cathode on peut déterminer les coefficients de transport de masse locaux et la transition du laminaire au turbulent dans l'écoulement. On estime que la précision de la méthode est de ±5% avec l'instrumentation utilisée.

Zusammenfassung—Bei der Elektrolyse von Kupfersulfat mit Schwefelsäure als Leitelektrolyt ist der Grenzstrom direkt proportional dem Stoffübergangskoeffizienten. Unter Verwendung von Kugeln und horizontalen Zylindern als Kathoden wurden Grenzstrommessungen für $(Gr \cdot Sc)$-Zahlen zwischen $1{,}22 . 10^7$ und $1{,}51 . 10^{10}$ gemacht. Durch elektrisches Isolieren einer kleinen Fläche auf der Kathode konnte der lokale Stoffübergang und auch der Umschlag laminar-turbulent der hydrodynamischen Grenzschicht bestimmt werden. Bei der verwendeten Versuchsanordnung wird die Genauigkeit der Methode auf ±5% geschätzt.

Аннотация—При электролизе сульфата меди, когда в качестве несущего электролита используется серная кислота, предельный ток пропорционален коэффициенту массообмена. Применяя шары и горизонтальные цилиндры в качестве катодов, измеряли предельные токи для значений чисел $(Gr \cdot Sc)$ от $1{,}22 \times 10^7$ до $1{,}51 \times 10^{10}$. Изолируя небольшой участок на катоде, можно было определить локальные коэффициенты массообмена, а также переход ламинарнотурбулунтного течения в гидродинамическое.

Данный метод дает возможность с помощью примененной аппаратуры получить результаты с точностью до±5%.