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MASS TRANSFER BY FREE CONVECTION AT HORIZONTAL ELECTRODES

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ABSTRACT

Limiting currents were measured in an unstirred cell at horizontal cathodes facing upward. Electrolyte composition ranged from 0.01 to 0.7 M $CuSO_4$ in 1.5 M H_2SO_4. Cathode sizes varied from 0.1 to 30 by 10 cm, and the free height above the electrode from 1 to 16 cm. Limiting currents for deposition of copper ranged from 0.68 to 129 mA/cm^2. For electrode width larger than 20 mm the data is well represented by the general correlation

$$Nu' = 0.19\ (Sc.Gr)^{1/3},$$

where Nu', Sc, and Gr are the Nusselt number for mass transfer, the Schmidt, and Grashof numbers, respectively. The experimental range used in the correlation included $10^8 < (Sc.Gr) < 1.4 \times 10^{12}$. The results indicate that the boundary layer is turbulent, as it is in the case of the analogous heat transfer model.

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INTRODUCTION

In recent years important advances have been made in the quantitative interpretation of mass transfer phenomena in electrode reactions. Through the definitive work of Levich,[1] Agar,[2] and others[3] the physical concept of the "Nernst diffusion layer" was replaced by the "mass transfer boundary layer", which allows for fluid motion to extend up to the solid-fluid interface.

Although exact solutions of the fundamental equations of hydrodynamics were obtained for a few models, in general the nonlinear partial differential equations representing convective mass transport and distribution of potential present insurmountable mathematical difficulties. The "Boundary Layer Theory" based on the asymptotic form of the exact differential equations of hydrodynamics yields analytic solutions for a restricted number of geometries and flow conditions.[4] By this method quantitative expressions were derived for limiting currents under free convection and forced convection conditions in cells of the simplest geometry, and for laminar flow.[5] When complex geometry or turbulent flow conditions do not allow formulation of an analytical approach the dimensional methods of analysis[6] proved to be quite as useful as in heat transfer studies. Even in the absence of clearcut concepts on detailed mechanism, the grouping of variables into dimensionless numbers greatly reduces the number of measurements necessary for obtaining coefficients and exponents, and development of qualitative theory is facilitated.[2,7,8]

Of the various models investigated, ionic mass transport in the absence of external stirring (free convection) at vertical electrodes received by far the most attention. Limiting currents[9] concentration gradients and velocity

profiles[10,11] have been measured over a rather wide range of solution properties and electrode sizes. Also, by means of the boundary layer technique various authors have developed theoretical solutions for this model. The agreement of experimental data with theoretical predictions is remarkably good.[10,12] When limiting current is reached over the entire surface of a vertical electrode and the fluid motion due to the buoyancy force is laminar, the following equation represents the interdependence of pertinent variables:

$$Nu' = 0.66\ (Sc.Gr)^{1/4} \qquad (I)$$

The proportionality constant 0.66 and the exponent of 1/4 was obtained by correlating results of hundreds of measurements of limiting currents.[7,9] [Numerical integration of the basic boundary layer equations by Ostrach[13] for heat transfer yields 0.67 for the constant when $Sc > 100$.] According to Eq. (I) the local limiting current density is proportional to the fourth root of the distance from the leading edge of the electrode, and approximately proportional to the 5/4 power of bulk concentration. As shown by Wagner,[14] when the applied current is substantially less than would correspond to the limiting current density, the current density distribution is essentially uniform over the electrode surface. While our understanding of free convection mass transport phenomena along vertical surfaces is rather well advanced, and close correspondence with the heat transfer analogue is clearly established, models of other geometry receive practically no attention. From theoretical and experimental results in heat transfer studies it may be expected that the mechanism of convective mass transport to a horizontal electrode should greatly differ from the vertical model. Since the use of horizontal electrodes in electrochemical practice is not uncommon, investigation of mass transport conditions for this model should be of interest not only to the student of mass transfer phenomena, but also to those involved in the design and operation of electrochemical processes.

In the present work only the case of horizontal electrodes facing upward will be considered. Spontaneous stirring, or free convection, results when the density of the electrolyte is reduced in the vicinity of the electrode relative to the density in the bulk solution. Such a density gradient is the

direct consequence of the concentration gradient of the reacting ionic species; the latter is caused by the fact that the transference number of the reacting ion is less than unity. The most convenient method for studying rates of mass transport by the free convection mechanism is by measuring the maximum rate of the electrode reaction (i.e., limiting current) which may be maintained in the steady state. This condition is reached when the steady state concentration of the reacting ions approaches zero on the solution side of the electric double layer.[5] An attempt to increase the current consequently results in a rapid increase of potential, until a consecutive electrode process becomes possible. The mass transfer coefficient k_L may be expressed in terms of the limiting current:

$$k_L = \frac{i_L(1 - t)}{nF\ C_b} \qquad \text{(II)}$$

It should be noted that k_L depends on hydrodynamic conditions and, therefore, when dealing with natural convection where stirring is generated by the electrode process itself, k_L is a function of current also. Therefore mass transfer coefficients measured at the limiting current do not apply at lower currents.[14]

Apparatus and Materials

The electrode reaction selected as a vehicle for this study was the cathodic reduction of cupric ion to copper from acid copper sulfate solutions. The obvious advantages of this choice are dominated by the fact that pertinent physical properties of these solutions have been measured previously.[15] Similarly to earlier studies,[9] the dissolution of a copper anode served as the anodic reaction.

The electrolyzing circuit (Fig. 1) corresponded to the usual arrangement employed in earlier studies, the only significant difference being in the use of a motor driven bank of rheostats. This feature allowed one to increase the applied potential across the cell terminals in a reproducible manner, and also permitted changing the rate of increase of current between rather broad limits.

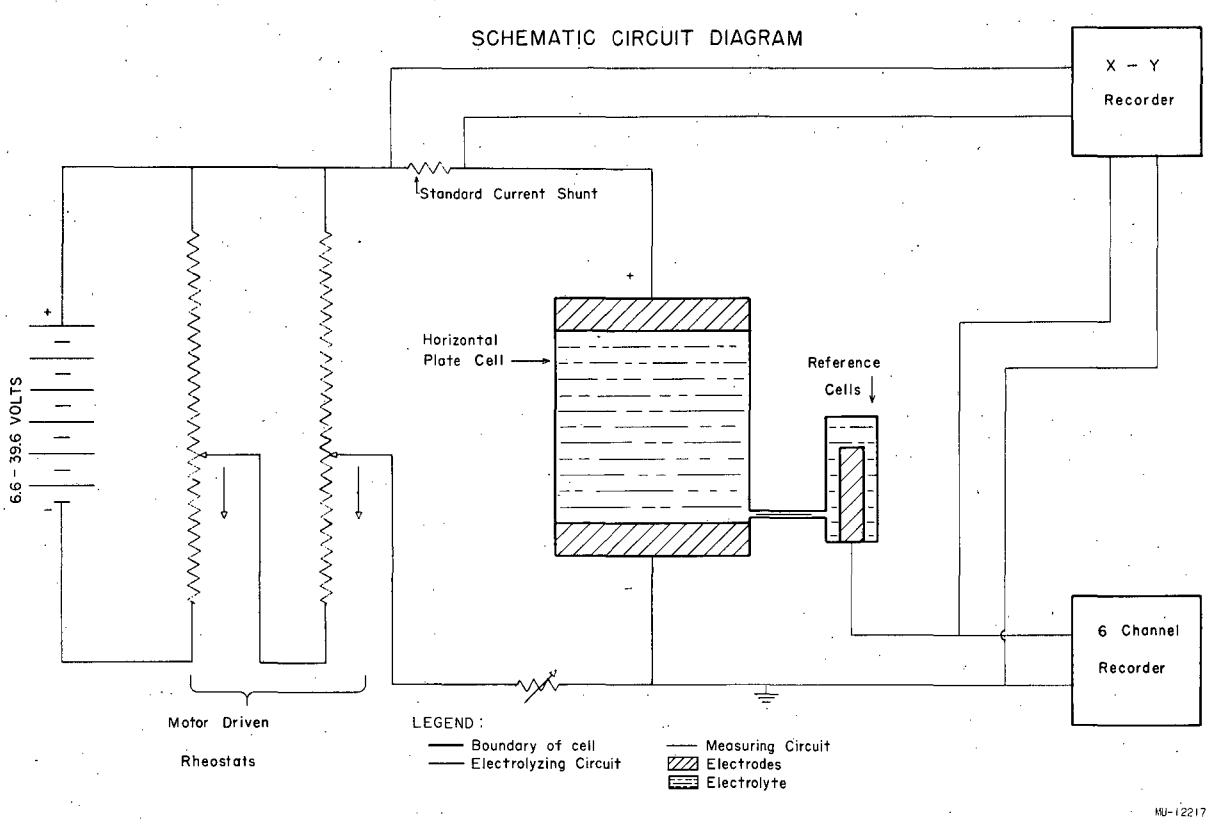

Fig. 1. Schematic diagram of experimental circuit.

To obtain the limiting current plateau, "identical reference" electrodes were used, which yielded the approximate concentration polarization directly.[9] The small amount of ohmic potential drop included in the measured potentials together with whatever activation polarization existed was of no consequence, because only the magnitude of limiting current needed to be asserted.

A cross sectional diagram taken through the long dimension of the lucite electrolysis cell built for these studies is shown in Fig. 2.

The anode was separated from the cathode compartment by a 1/8 inch thick acid proof ceramic diaphragm.* The use of this diaphragm was necessary to eliminate the influence of convection currents generated by the dissolving anode, and made use of more dilute solutions in the anode compartment feasible. Two mechanical stirrers served to prevent crystallization of copper sulfate on the anode. The cathode to diaphragm distance could be varied between 1 - 16 cm in 1 cm intervals by use of lucite spacers around the inner periphery of the cell.

Cathodes extended across the short inner dimension (10 cm) of the compartment; the widths used included 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 30 cm. The cathode holder was designed to hold each size electrode in such a manner that the cathode surface was in the plane of the surface of the lucite blocks on both sides. Thus, the entire cathode assembly formed a smooth horizontal plane.

For special studies, the blocks adjacent to the cathode could be replaced by tall lucite blocks which extended up to the diaphragm. This model permitted the study of the effect of limiting walls at the edges of electrodes.

Figure 3 represents a top view of the empty cell, with only the cathode holder in place. A copper rod served to make electrical contact with the cathode. Capillary holes (0.0135 inches i.d.) to which reference cells could be attached were located at the edge of each size electrode (0.1 mm over the plane of the cathode) and also at the exact center line of the cell. The reference cell unit which fitted the lucite adapter is shown in Fig. 4. Anolyte and catholyte were stored in 2 gallon glass bottles provided with a glass stopcock near the bottom, situated four feet overhead. Used electrolyte was

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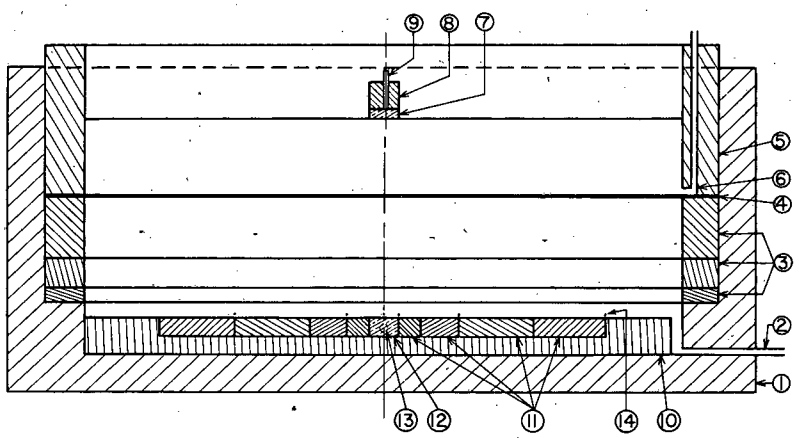
*"Filtros 35", Filtros Inc., East Rochester, New York.



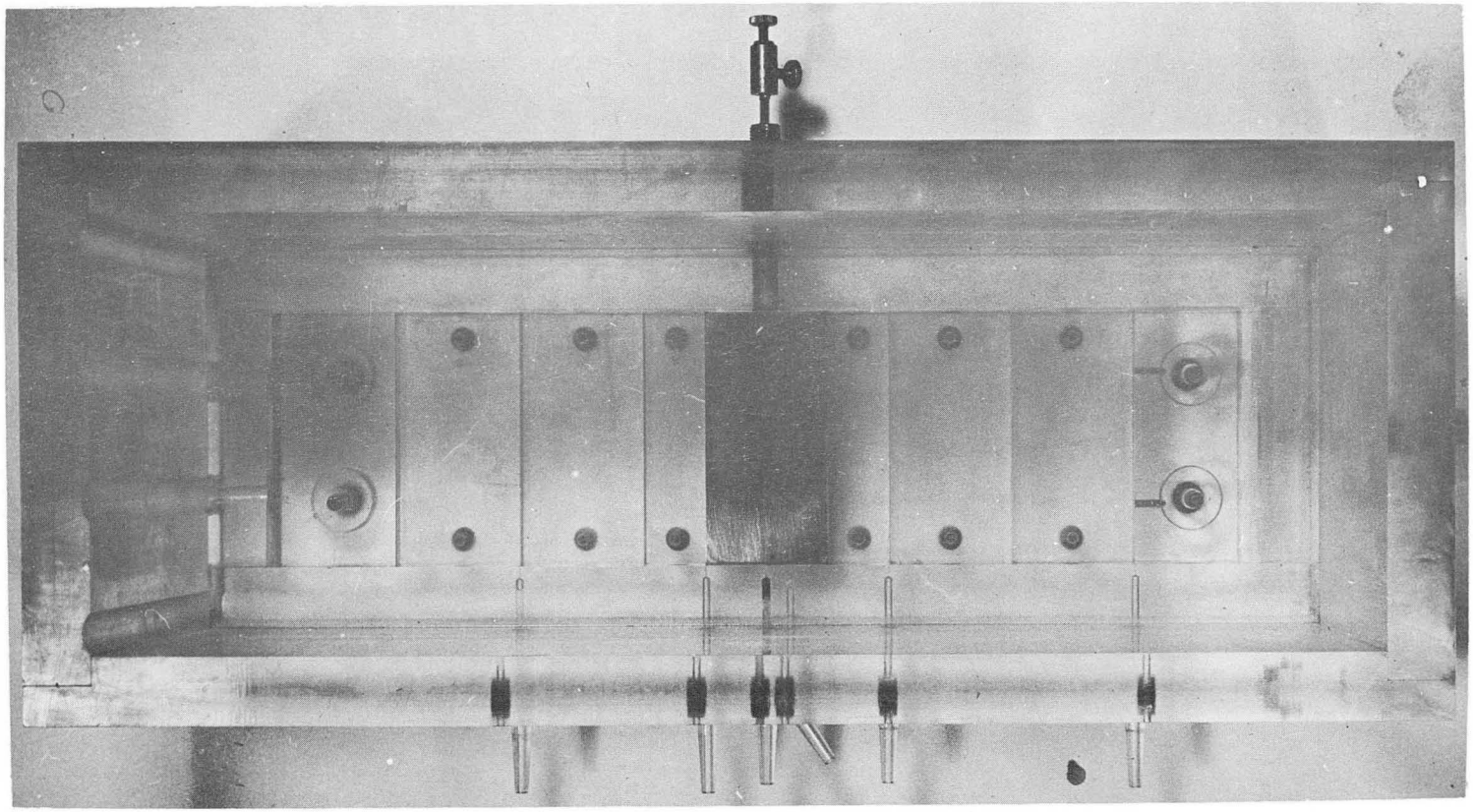
SIDE CELL ASSEMBLY

1 TANK
2 INLET-OUTLET CATHOLYTE
3 SPACERS
4 DIAPHRAM
5 ANODE COMPARTMENT
6 INLET-OUTLET ANOLYTE
7 ANODE
8 ANODE HOLDER
9 ANODE CONTACT
10 CATHODE HOLDER
11 SPACERS TO ACCOMODATE DIFFERENT SIZE ELECTRODES
12 CATHODE
13 CATHODE CONTACT
14 POINTS AT WHICH REFERENCE CELLS CAN BE ATTACHED

5 cm

MU-12202

Fig. 2. Section drawing of experimental cell.



ZN-1651

Fig. 3. Top view of cathode in place, showing cathode contact and points at thich reference cells could be attached.

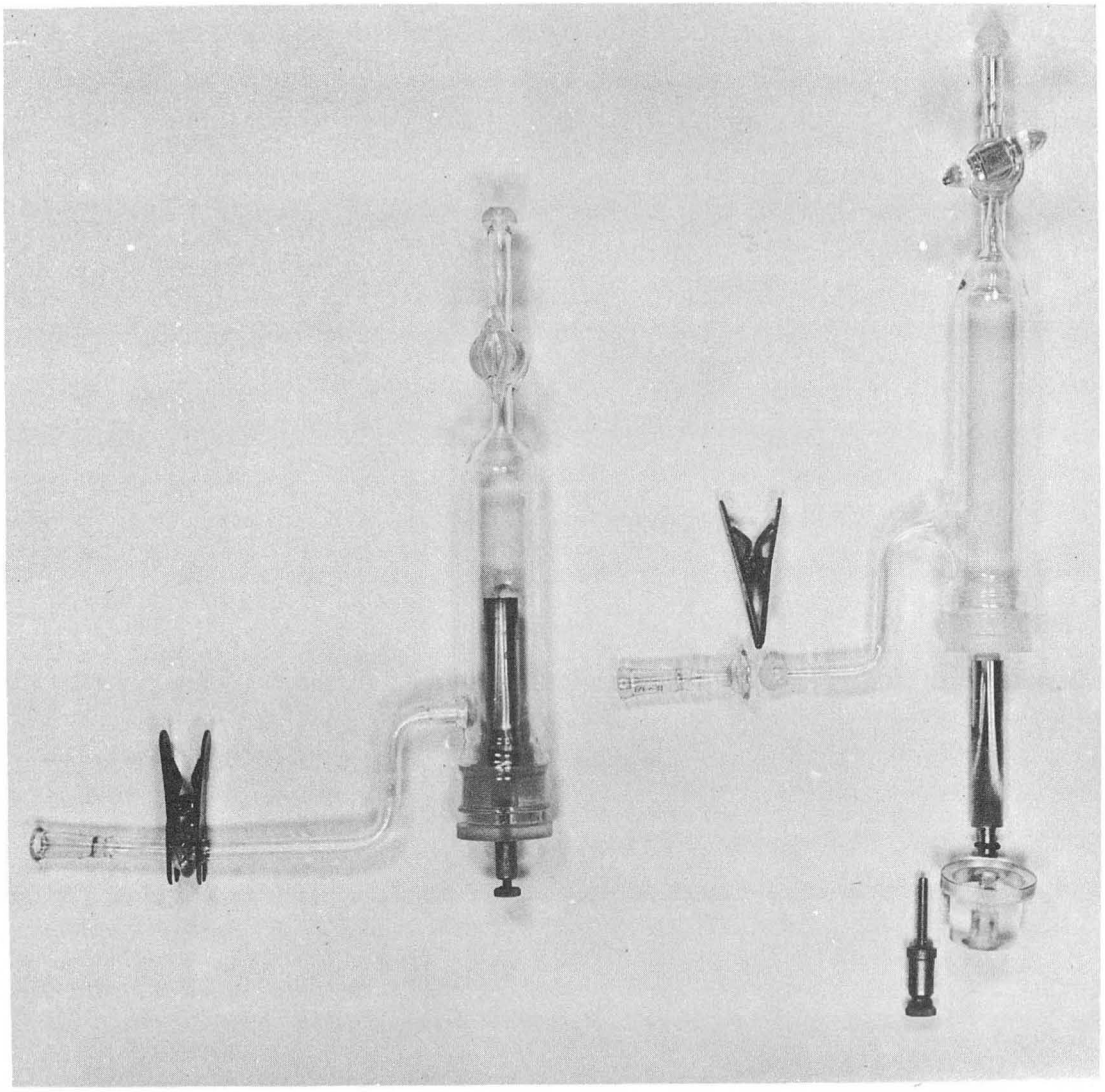


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Fig. 4. Reference electrodes.

drained into bottles below the cell. Cell compartments were filled by gravity flow from these bottles, through channels provided in the lucite wall of the cell. All chemicals used were of standard c.p. quality. Approximate molarities of catholytes were: 0.7, 0.23, 0.08, and 0.01 M Cu^{++} and 1.5 M H_2SO_4. Solutions containing glycerol were approximately 0.75 M H_2SO_4, 5.4 M glycerol, and 0.4 M Cu^{++}. Following preparation and then at suitable time intervals the solutions were analyzed: copper by the thiosulfate method,[16] acid by titration with NaOH, and glycerol by cerate oxidation.[17]

In order to insure reproducible surface quality after machining, the electrodes were polished by number 400 emery paper, subsequently washed and degreased. Reference electrodes were prepared in the same manner. Electrodes were used immediately after preparation.

Experimental Procedure

After both the working cathode and reference electrode were mounted in place, the ceramic diaphragm was lowered into the cell and the anode inserted above it. The catholyte was then introduced from the overhead storage bottle and after flooding this compartment the anode compartment was filled. Following a 10 to 15 minute waiting period the current was switched on, and the motor driven rheostat set in motion gradually increasing the applied potential. When the limiting current plateau appeared on the x-y recorder which plotted current vs reference voltage directly, the experiment was terminated, the cell drained and disassembled. For each run fresh electrolyte and new cathodes were used.

The correct choice of rate of increase of applied potential presents an interesting problem. It is desirable to keep the electrolysis period as short as possible in order to avoid (a) appreciable depletion of bulk concentration, (b) excessive roughening of cathode surface. However, the rate of increase of current has to be low enough so as to allow natural convection to reach a quasi-steady state. A number of runs were made with the purpose of selecting the rate of change of applied potential and also to decide whether starting with a finite potential rather than zero would be of advantage. Figure 5 shows typical results when different initial voltages were applied and then rate of change of applied potential was kept the same. As illustrated the initial voltage and

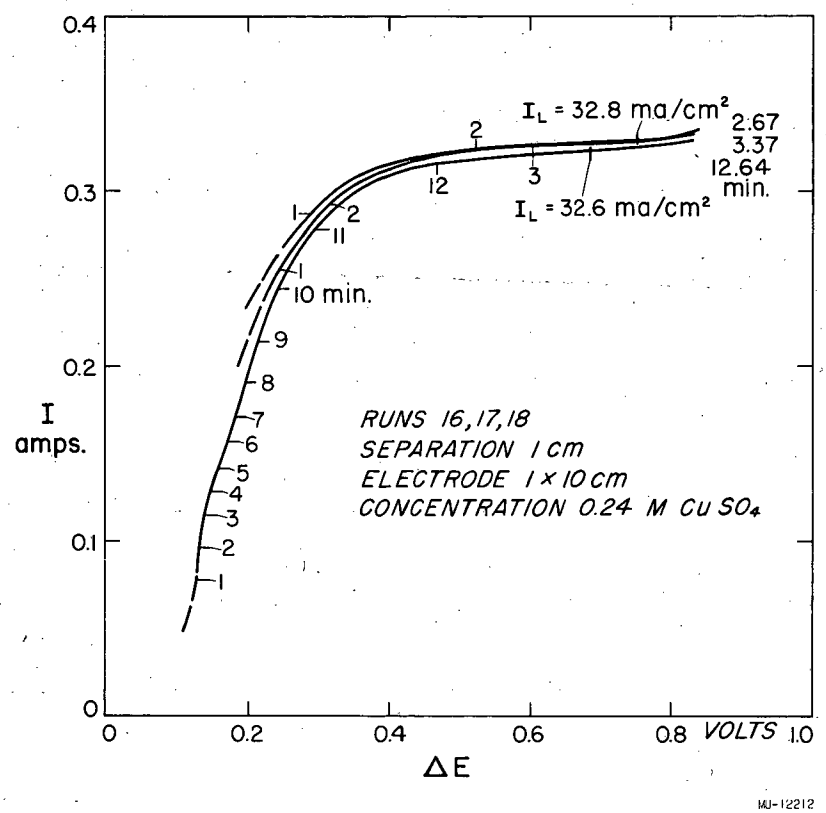

Fig. 5. Limiting current curves for different length runs with no other experimental variables changed.

the time required to reach the limiting current did not influence the limiting current observed, except when the duration of electrolysis was greatly increased. In these cases the bulk concentration has diminished already sufficiently to cause a lower limiting current. On the basis of these exploratory runs 3 to 5 minutes were used in subsequent runs for reaching the limiting region.

Serious difficulty was encountered however in the case of 0.01 M solutions. Because of the low bulk concentrations, extended periods could not be used for reaching limiting current. Employing the usual time interval however yielded i vs ΔE curves of the type illustrated in Fig. 6. An explanation for this behavior may be found if one considers the very low driving force for convection at these low concentrations. Undoubtedly in this case, when copper deposition is started unsteady state diffusion is the dominating mode of mass transport. The "true" steady state limiting current may be exceeded temporarily, but then, although the applied potential is increased, the current drops until hydrogen evolution starts. Thus the slow development of convection prevents one from observing a limiting current. The reproducibility of these "camelback" curves was extremely poor in contrast to the runs at higher concentrations. Since assignment of either the peak or the bottom of the camelback curve as the limiting current lacks justification, experiments with the 0.01 M Cu^{++} solutions were not included in the correlative work.

The effect of location of capillary junctions along the sides of electrodes proved to have negligible influence on the limiting currents observed. The time-voltage curves in Fig. 7 were obtained simultaneously by a multipoint recorder-potentiometer. In subsequent runs only the capillary junction located at the centerline was used.

Data

Approximately 400 individual limiting current measurements were performed in the frame of this study, of which over 100 were designed to obtain information about the effect of rate of increase of potential, location of capillaries, and in general as to the approximate values of limiting currents for a given set of variables. Using the procedures developed by these preliminary studies, 277 runs representing 99 different combinations of variables were subjected to evaluation. Ranges of variables investigated are given in Table I.

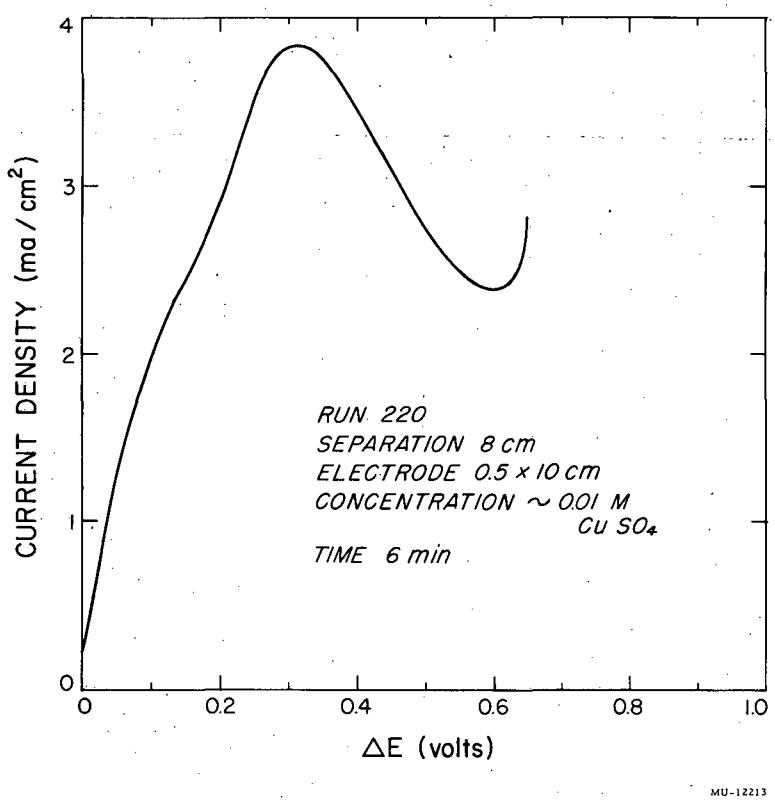

Fig. 6. Typical limiting current curve for 0.01 M $CuSO_4$ concentration.

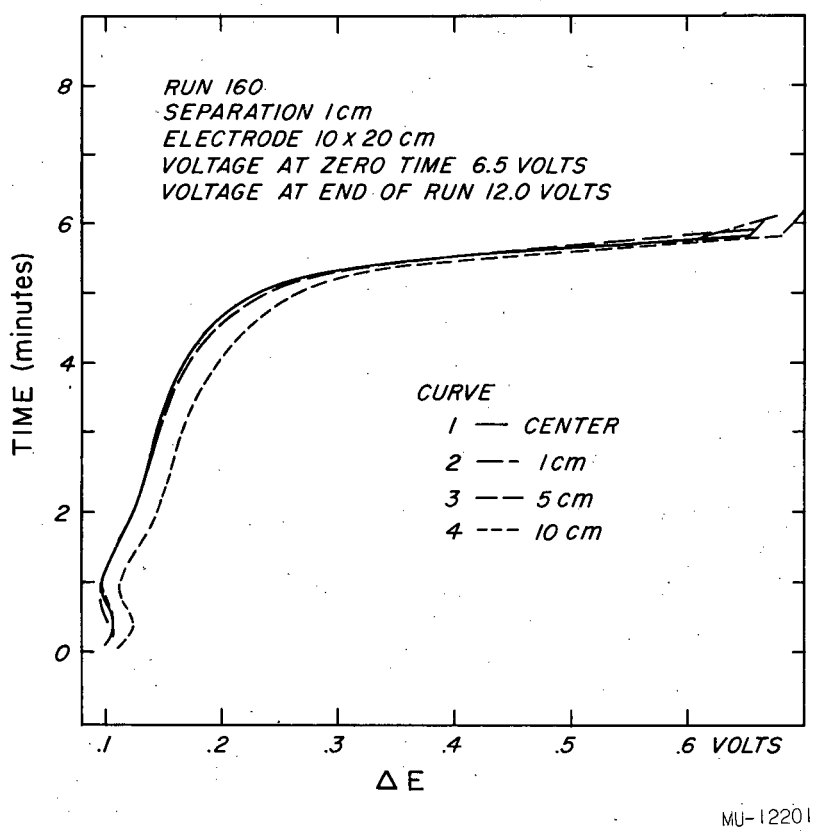

Fig. 7. Variation of polarization with time at four points along a 20 cm. electrode.

Table I

Ranges of variables included in experimental study and correlation

Variables	Experiments	Correlation
Cathode width, mm	1 - 300	20 - 300
Cathode diaphragm distance, cm	1 - 16	1 - 16
Electrolyte concentration; $CuSO_4$, moles/liter	0.011 - 0.692*	0.081 - 0.692*
Concentration difference (bulk-interface of H_2SO_4, moles/liter)	0.0045 - 0.236	0.032 - 0.228
Density (bulk) gr/cm^3	1.096 - 1.187	1.099 - 1.187
Density difference (bulk-interface) gr/cm^3	0.001 - 0.083	0.0084 - 0.079
Viscosity, average, cps	1.30 - 8.03	1.30 - 8.03
Diffusion, coefficient, average, cm^2/sec	$1.37 \times 10^{-6} - 5.74 \times 10^{-6}$	$1.37 \times 10^{-6} - 5.74 \times 10^{-6}$
Limiting current density mA/cm^2	0.68 - 129	6.9 - 125
Nusselt number	47 - 1,675	312 - 1,675
Grasshof number	$7,200 - 6.1 \times 10^8$	$5.4 \times 10^4 - 6.1 \cdot 10^9$
Schmidt number	$2.1 \times 10^3 - 5.2 \times 10^4$	$2.1 \times 10^3 - 5.2 \times 10^4$
Rayleigh number	$1.5 \times 10^7 - 1.4 \times 10^{12}$	$1.1 \times 10^8 - 1.4 \times 10^{12}$

*also 0.37m $CuSO_4$, 0.775 H_2SO_4, 5.4m Glycerol

Effect of cathode-diaphragm distance

Effect of depth of electrolyte over the cathode has been studied using all four concentration levels (0.1 M, 0.08 M, 0.24 M and 0.67 M $CuSO_4$). Depth was varied between 1 - 16 cm. Table II serves to illustrate results obtained. Within limits of reproducibility the cathode-diaphragm distance appears to have no effect on the measured limiting currents.

The absence of a height dependence of I_L indicates that the transport mechanism involves a thin turbulent boundary layer of the electrode-electrolyte interface and that velocity component of bulk motion of fluid in the horizontal plane must be negligibly small.

Effect of electrode width

Electrode widths were varied between 1 - 300 mm. When the electrolyte extended beyond the edges of the electrode, strong variation of limiting current with width was observed, (Fig. 8). The limiting current density is highest for the narrowest electrodes, but significantly, an increase of width beyond 20 mm causes only very slight drop in average limiting current. As a matter of fact I_L for 100 and 300 mm wide electrodes may be regarded as identical within experimental accuracy. This surprisingly strong dependence of I_L on electrode width may be explained if one considers the probable mechanism of transport. When Cu^{++} ions are removed from the solution in the region adjacent to the electrode, the resulting situation is unstable and any small disturbance will result in convective motion.[18,19] The stability criterion has been established by analytic methods by Lord Rayleigh[20] and heat transfer experiments by numerous workers have confirmed, that convective, "cellular" motion starts when the value of the product Ra = Gr·Sc exceeds approximately 1,700.[21] The character of this motion gradually changes as the Rayleigh number is increased, and somewhere between $20,000 < Ra < 45,000$ the boundary layer becomes fully turbulent.[22] This mechanism is characteristically independent of position, and there is a lack of dependence on interference with motion in the horizontal direction.

In our case, however, the electrode receives a fresh supply of Cu^{++} ions also from a laminar fluid motion sweeping across the edges in a direction normal to the edges. The existence of such motion could be detected by direct

Table II

Effect of cathode-diaphragm distance on limiting current density

(Conc. 0.24 m $CuSO_4$ electrode width: 100 mm)

Run No.	$CuSO_4$ Conc. moles/liter	Cathode-diaphragm distance cm	I_L mA/cm
157	0.081	1	7.4
159	0.081	2	7.1
152	0.083	8	7.2
61	0.234	1	27.9
62	0.234	2	29.1
65	0.232	4	27.5
66	0.231	8	28.2
68	0.230	16	28.4
134	0.657	1	104.4
138	0.656	8	103.4

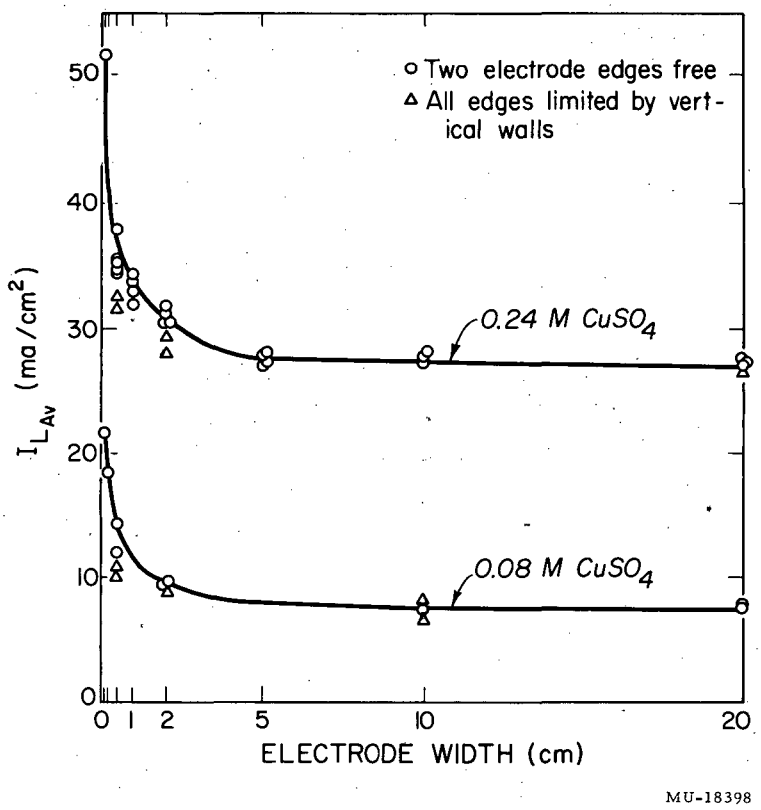

Fig. 8. Dependence of average limiting current density on electrode width.

visual observation. Since this mechanism contributes materially only to the mass transport near the edges, its effect is appreciable only on narrow electrodes, and for electrodes wider than 50 mm, the limiting current no longer decreases with increasing width. In further support of the above explanation, experiments with rigid boundaries around all four edges may be considered. In the case of electrodes wider than 50 mm, elimination of free edges caused no change in the measured limiting current density. With electrode narrower than 20 mm. I_L was always distinctly smaller with four walls than with two free edges. It should be mentioned, however, that the limiting currents over narrow electrodes even with four walls were larger than for wider electrodes. It is possible that between narrow vertical boundaries laminar bulk motion is generated sweeping down along one side, and ascending along the other. In such a manner vertical boundaries could contribute to the improved efficiency of mass exchange.

Reproducibility of results obtained on narrow electrodes (1, 2, 5, and 10 mm) was rather poor. For this reason, and because the mass transport on these is dominated by a secondary mechanism, these measurements were not used in the correlation proposed in a subsequent section.

Effect of concentration

In a given cell geometry, the limiting current density increases with bulk concentration of the reacting ion, Cu^{++}, far more rapidly than corresponding to a linear relationship between C_b and I_L. The exact dependence cannot be established without dimensionless grouping of variables because a change in concentration also affects viscosity, density, and diffusion coefficient. A Log-Log plot of limiting current vs concentration indicates the following approximate relation:

$$I_L \sim C_b^{4/3}$$

Effect of viscosity

To extend the range of viscosities in this investigation, limiting currents were also obtained in solutions containing 5.4 m/liter glycerol, 0.37 m/liter $CuSO_4$, and 0.77 m/liter H_2SO_4. Corresponding viscosity was approximately 8.2 centipoises. No evaluation of viscosity effect is presented here, because viscosity also affected the diffusion coefficient.

Correlation of Data:

On the basis of previous heat transfer studies[23,24] and also, considering the successful correlation obtained for vertical electrodes in laminar free convection, it was anticipated that the present data may be correlated in the form:

$$Nu' = a(Gr.Sc)^b \quad \text{or} \quad Nu' = c.Gr^d.Sc^e$$

As the characteristic dimension in the Nusselt and Grasshof numbers the vertical distance between cathode and diaphragm was chosen.* By this choice we restrict the validity of the proposed correlation to electrodes wider than 20 mm. In Fig. 9 all limiting current data within the range indicated in the second column of Table I (131 runs representing 56 different combinations of variables) has been plotted with Log(Nu') vs Log(Sc.Gr) as coordinates.** A sampling of data and calculated values of corresponding dimensionless groups is presented in Table III. Average percent deviation*** of limiting current values obtained under identical conditions were as follows: ± 4.2% for 0.08 M, 1.3% for 0.24 M, 0.4% for 0.69 M, and 2.6% for 0.37 M $CuSO_4$ solutions.

Least squares treatment in the form: Log Nu' = a + c Log (Sc.Gr) yields for the coefficient a : 0.190 with 95% confidence limits of 0.172 - 0.201; and for the exponent c : 0.329, where the 95% confidence limits are 0.325 - 0.333. The standard deviation in terms of Log Nu' is s : 0.0767. The coefficient of correlation is $r^2 = 0.994$. Instead of the optimal exponent, 0.329, one may

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*Average mass transport rate and local rate should not differ when extended surfaces are considered. Only when secondary effects, such as laminar flow from the sides - represent an appreciable part of the mechanism of transport should (and in effect does) the mass transfer coefficient depend on electrode width.

**For methods used to calculate values of dimensionless groups see Appendix.

***Percent deviation: $\left(\frac{I_L - I_{L\ \text{Ave. for identical runs}}}{I_{L\ \text{Ave. for identical runs}}}\right) 100$

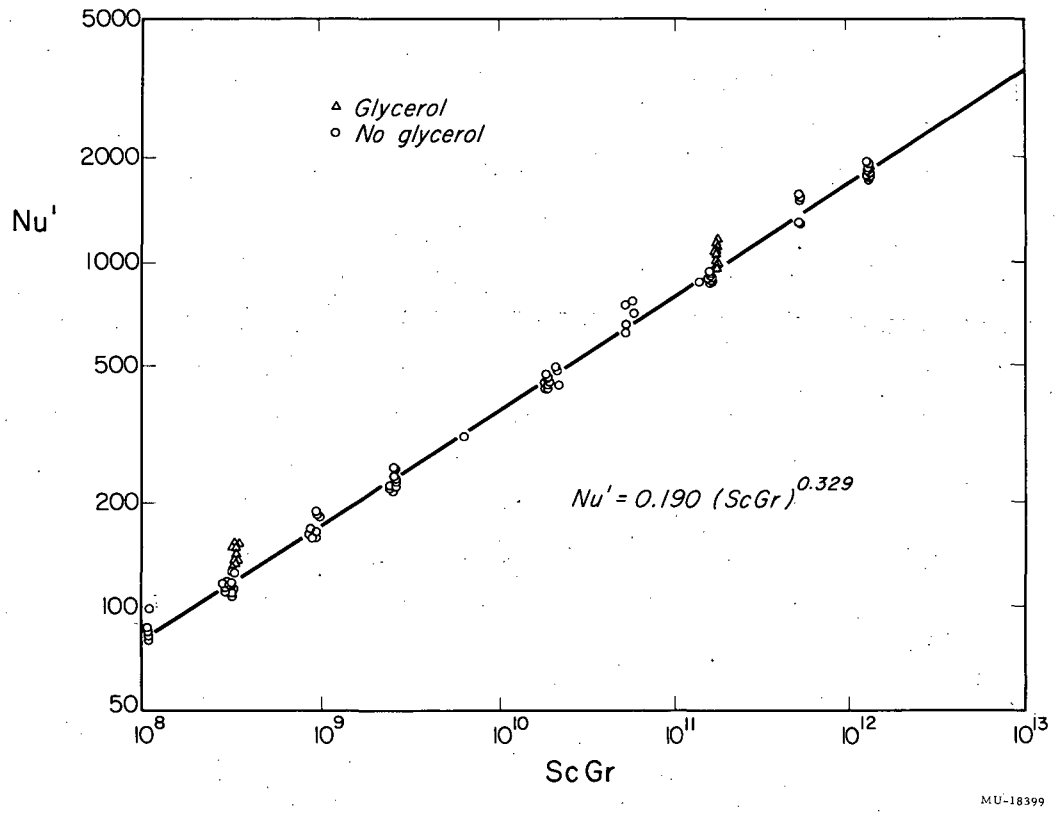

Fig. 9. General correlation of limiting current density at horizontal electrodes.

Table III

Sample data and corresponding dimensionless numbers

Run no.	161	162	45	61	71	82	233	239
$CuSO_4$ conc., moles/liter	0.082	0.082	0.239	0.234	0.220	0.220	0.373	0.370
H_2SO_4 conc., moles/liter	1.490	1.490	1.566	1.608	1.674	1.674	0.753	0.760
Glycerol conc., moles/liter	0	0	0	0	0	0	5.41	5.33
Electrode width, cm.	2.0	2.0	5.0	10.0	20.0	30.0	10.0	2.0
Free height, cm.	1	8	1	1	1	1	1	1
Limiting current density, mA/cm^2	8.99	8.50	27.3	27.9	25.0	25.6	14.5	14.3
H_2SO_4 conc. diff., moles/liter	0.033	0.033	0.093	0.091	0.085	0.085	9.174	0.173
Mass transfer coef., cm/sec x 10^4	5.65	5.35	5.86	6.12	5.84	5.98	1.95	1.94
Average viscosity, cps	1.31	1.31	1.39	1.40	1.45	1.41	7.98	7.79
Bulk density, gm/cm^3	1.100	1.100	1.125	1.127	1.129	1.129	1.186	1.183
Density dif., gm/cm^3	0.0086	0.0086	0.026	0.025	0.024	0.024	0.039	0.039
Average dif. coef., cm^2/sec x 10^6	5.69	5.69	5.38	5.34	5.28	5.28	1.38	1.40
Transference no. $CuSO_4$	0.045	0.045	0.0118	0.0111	0.0097	0.0097	0.0331	0.0327
Nu'	99	752	109	115	111	113	141	138
Sc x 10^{-2}	21.0	21.0	23.2	23.5	24.0	24.0	497.	477.
Gr x 10^{-5}	0.542	277.	1.49	1.44	1.32	1.32	0.0722	0.0748

conveniently use c = 1/3, in which case the proposed correlation is:

$$Nu' = 0.19\ (Sc.Gr)^{1/3} \qquad \text{(III)}$$

In view of the uncertainties involved in evaluating transference numbers, interfacial compositions and average properties, the degree of scatter of data about the line representing the proposed correlation is well within reasonable expectations.

Comparison with Heat Transfer Studies

An exact, or even an approximate theoretical treatment of our hydrodynamic model does not appear feasible. In the case of laminar cellular motion the necessity of considering the hydrodynamic equations for mass flux, along with those for force, present mathematical difficulties that are considered insurmountable by known techniques.[22] In the turbulent regime, where properties at any point are subject to random fluctuations, not even the mathematical formulation of the problem has been achieved.

Mass transfer studies on models related to the present one have not been reported in the literature. Comparison of the new correlation to results of heat transfer investigations should serve to give some enlightenment about the mechanism of the transport process under discussion.

Past work on rates of heat transfer across fluids confined between two horizontal plates, where the one at the bottom was heated was reviewed by Malkus,[22] and more recently by Globe and Dropkin.[23] The correlations proposed by Jakob[21] for air: $Nu = 0.068\ (Gr)$ and by Malkus on basis of work using water as the medium: $Nu = 0.085\ (Gr.Pr)^{.325}$ were based on work embracing rather narrow ranges of fluid properties. Globe and Dropkin expanded particularly the range of Prandtl numbers investigated, and found that the power on the Prandtl number should be different than on the Grasshof group:

$$Nu = 0.069\ (Gr.Pr)^{1/3}\ (Pr)^{0.74} \qquad \text{(IV)}$$

Data presented by Schmidt[24] also seem to indicate that a difference in exponents will more correctly represent the behavior of data.

A corresponding tendency has been detected in the present work also. The data points corresponding to high viscosity runs in Fig. 9 lie distinctly and consistently above the least squares line. These points may be shifted to coincide with the line, if one raises the Sc number to a power different than on the Grasshof number. The resulting equation

$$Nu' = 0.129\ Gr^{0.331} . Sc^{0.374} \qquad (V)$$

represents data slightly more accurately. However the viscosity range investigated was too narrow to suggest a definite preference between Eq. III and Eq. V. In aqueous electrolytes, and in molten salts, the viscosity range of practical interest is close enough to the range covered in the present work, hence the use of either correlation may be considered accurate enough for practical purposes.

The range of Rayleigh numbers covered in the present study, $10^8 - 10^{12}$, overlaps with the upper limit of the range studied by Globe and Dropkin. Although Smith and Saunders[19] and later Malkus[22] found evidence of distinct "transitions" from one mode of turbulence to another, the present results indicate that the mode of turbulent transport does not noticeably change between $10^8 < Ra < 10^{12}$.

Conclusions

Limiting current densities obtained on horizontal cathodes facing upward, when the sole electrode process was the deposition of copper plate from acid copper sulfate solutions, could be correlated according to:

$$\frac{I_L\ (1 - t_{Cu^{++}})x}{nFc_bD} = Nu' = 0.19\ (Gr.Sc)^{1/3}$$

The value of the exponent and also the fact that the depth of electrolyte had no noticeable influence on limiting current densities point to a mass exchange mechanism by turbulent eddies. The lack of dependence of limiting current densities on electrode width larger than 20 mm is consistent with such a mechanism. The rapid increase of limiting current densities found on successively narrower electrodes may be explained by the improvement of the supply

of ions provided by a laminar fluid motion sweeping in over the electrode edges.

Not included in the correlation were data obtained with dilute (0.01) molar solutions. The usual limiting current plateau could not be obtained in these cases because the time of electrolysis could not be extended sufficiently to allow the development of steady state convection.

APPENDIX

Calculation procedure used for obtaining values of the dimensionless groups: Nu', Gr, Sc

Data by Eisenberg, Tobias, and Wilke[15] were used to calculate densities and viscosities. Estimation of diffusivities were based on data by Gordon,[25] and Thovert.[26] Corrections were applied for temperature, viscosity, and ionic strength effects.[15]

Approximate values of the transference numbers were obtained by making the following assumptions:

(1) sulfuric acid is dissociated completely to H^+ and HSO_4^-

(2) the bisulfate ions dissociate to H^+ and $SO_4^=$ with $K = 2 \times 10^{-2}$ [27]

(3) $CuSO_4$ is completely dissociated.

Ionic mobilities were calculated by multiplying the conductance ratio with the ionic mobility at infinite dilution.[28] Using these approximations the transference number of species 1 is:

$$t_1 \simeq \frac{C_1 n_1 u_1}{\sum_i C_i n_i u_i}$$

To facilitate processing of data by digital computer,* dependence of density, viscosity, diffusion coefficient and transference number on composition were expressed in form of power series.**

$$\begin{aligned} \rho = 0.9978 &+ 0.06406\, M_{H_2SO_4} - 0.00167\, M^2_{H_2SO_4} \\ &+ 0.12755\, M_{CuSO_4} + 0.01820\, M^2_{CuSO_4} \\ &- 0.00235\, M_{Glycerol} + 0.00353\, M^2_{Glycerol} \end{aligned} \qquad \text{(VI)}$$

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*IBM 650.

**Equations are valid only for 22°C.

$$\mu = 0.974 + 0.1235\, M_{H_2SO_4} + 0.0556\, M^2_{H_2SO_4} + 0.5344\, M_{CuSO_4} + 0.5356\, M^2_{CuSO_4} + 0.1475\, M_{Glycerol} + 0.2029\, M^2_{Glycerol} \qquad \text{(VII)}$$

$$\mu . D_{CuSO_4} = (0.7363 + 0.00511\, M_{H_2SO_4} + 0.02044\, M_{CuSO_4} + 0.06530\, M_{Glycerol})10^{-5} \qquad \text{(VIII)}$$

$$\mu . D_{H_2SO_4} = (1.6691 + 0.24519\, M_{H_2SO_4} + 0.96637\, M_{CuSO_4} + 0.06530\, M_{Glycerol})\, 10^{-5} \qquad \text{(IX)}$$

$$t_{Cu^{++}} = (0.2633 - 0.1020\, M_{H_2SO_4})\, M_{Cu^{++}} \qquad \text{(X)}$$

$$t_{H^+} = 0.8156 - 0.2599\, M_{Cu^{++}} - 0.1089\, M^2_{Cu^{++}} \qquad \text{(XI)}$$

In the range of variables considered in this study, the maximum deviation of values calculated by these equations from curves representing data was ± 0.5%.

The calculation of average properties requires knowledge of interfacial composition. To estimate these, the following reasoning was employed: At the limiting current density concentration of Cu^{++} on the surface approaches zero. However due to migration, there is an increase in H_2SO_4 concentration. In the steady state the rate of movement of H_2SO_4 to the electrode must be balanced by an equal rate of transfer in the reversed direction by diffusion and convection:

$$\frac{I_L\, t_{H^+Av.}}{n.F} = k_{H_2SO_4}\, (C_i - C_o)_{H_2SO_4} \qquad \text{(XII)}$$

There are three unknowns in this equation: $t_{H^+Av.}$, $k_{H_2SO_4}$, and $C_{i_{H_2SO_4}}$. It is reasonable to assume, that the mass transfer coefficient for sulfuric acid bears the same relation to its diffusivity as in the case of $CuSO_4$. Thus if Nu' = a $(Gr.Sc)^{1/3}$ is approximately correct, one may write

$$k_{H_2SO_4} = (D_{H_2SO_4}/D_{CuSO_4})^{2/3}_{Av.} \cdot k_{CuSO_4} \qquad \text{(XIII)}$$

Using equations II, XIIIm and the equations expressing dependence of diffusivities and transference numbers on concentration (VIII - XI) all unknowns can be solved for by trial and error procedure. Subsequently, "average" properties were calculated by taking the arithmetic average between values in the bulk solution and at the interface. The procedures outlined above although not mathematically complex, are extremely time consuming. The use of digital computers for this purpose is well justified.

NOMENCLATURE

Symbol	Definition	Units
a	Constant coefficient	--
b	Constant exponent	--
c	Constant coefficient	--
c_p	Heat capacity	cal/gm ^{o}C
d	Constant exponent	--
D	Diffusion coefficient	cm^2/sec
e	Constant exponent	--
ΔE	Polarization	volts
F	Faraday	coulombs/equivalent
g	Acceleration of gravity	981 cm/sec^2
h	Heat transfer coefficient	cal/cm^2 ^{o}C sec
I	Current	amps
I_L	Limiting current density	amps/cm^2
k	Thermal conductivity	cal/cm^2 sec ^{o}C/cm
k_L	Overall mass transfer coefficient	cm/sec
$k_{Cu^{++}}$ or H^+	Mass transfer coefficient	cm/sec
M	Molarity concentration	moles/liter
n	Number of electrons exchanged in electrode reaction	equiv/mole
$t_{Cu^{++}}$ or H^+	Transference number	--
x	Characteristic dimension	cm

(Nomenclature cont'd)

Symbol	Definition	Units
Greek letters		
α	Thermal coefficient of expansion	$1/^{o}C$
β	Temperature gradient	$^{o}C/cm$
Δ	Signifies difference	--
$\kappa = k/\rho c_p$	Thermal diffusivity	cm^2/sec
μ	Viscosity	gm/cm sec
$\nu = \mu/\rho$	Kinematic viscosity	cm^2/sec
ρ	Density	gm/cm^3
Subscripts		
i	Interface	--
b	Bulk	--
Av.	Arithmetic average between bulk and interface	--

Dimensionless Groups

$Nu = hx/k$	Nusselt number for heat transfer
$Nu' = k_L x/D$	Nusselt number for mass transfer
$Pr = \frac{\mu \cdot C_p}{k}$	Prandtl number
$Sc = \nu/D$	Schmidt number
$Gr = \frac{g(\rho_o - \rho_i)\ \rho^2_{av} x^3}{\rho_i\ \mu^2}$	Grashof number
$Ra = \beta\ g\ \alpha\ x^4/\kappa\ \nu$	Rayleigh number for heat transfer.

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