Correlation of Limiting Currents under Free Convection Conditions[1]

C. R. WILKE, M. EISENBERG, AND C. W. TOBIAS

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

ABSTRACT

Limiting currents were measured for deposition of copper on plane vertical cathodes from unstirred solutions. Electrolyte composition ranged from 0.01 to 0.7 molal $CuSO_4$, 1.38 to 1.57 molal H_2SO_4, and 0 to 6.38 molal glycerol. Cathode heights varied from 0.25 to 3.0 in. Limiting current densities were from 0.4 to 108 ma/cm². A general correlation of the data may be represented by the equation: $Nu' = 0.673 \ (ScGr)^{1/4}$, where Nu', Sc, and Gr are the mass transfer Nusselt, Schmidt, and Grashof numbers, respectively. This result is in good agreement with that predicted from the boundary layer theory for mass transfer by free convection.

INTRODUCTION

This paper is concerned with limiting rates of deposition of copper ions at a vertical cathode in an unstirred solution. In such a system, natural convection, or "spontaneous stirring," results from density changes which accompany concentration changes in the region of the electrode. The limiting process is controlled by the maximum rate of mass transfer of copper between bulk solution and the electrode surface. A more detailed discussion of mass transfer phenomena in electrochemical problems has been presented in an earlier paper (1).

Natural convection usually involves laminar motion of the fluid so that the over-all process requires consideration of the simultaneous action of molecular diffusion and convective flow. In steady-state free convection, the main resistance to mass transfer is associated with a relatively small region of fluid in the vicinity of the electrode, and the concentration of the bulk solution remains constant. It is convenient to describe the rate of transfer between any point on the electrode surface and the surrounding solution in terms of a mass transfer coefficient for free convection as given by the relation:

$$(N_D)_x = k_x(C_o - C_i) \qquad (I)$$

where: $(N_D)_x$ = local rate of mass transfer, gram moles/cm²-sec; k_x = local mass transfer coefficient at height x on the electrode surface; and C_o and C_i = concentration of reacting species in bulk solution and at electrode surface, respectively, gram moles/cm³.

The total local rate of mass transfer, excluding migration, is determined by the current density:

$$(N_D)_x = \frac{I_x(1 - t)}{nF} \qquad (II)$$

where: I_x = current density at height x; n = valence charge of reacting ion; F = the Faraday; and t = transference number of reacting ion averaged over the mass transfer path.

To describe the rate of mass transfer per unit area averaged over the entire electrode, an average mass transfer coefficient may be defined by the equation:

$$N_D = k_L(C_o - C_i) = \frac{I(1 - t)}{nF} \qquad (III)$$

where: N_D = average mass transfer rate, gram moles/cm²-sec; k_L = average mass transfer coefficient, cm/sec; and I = average current density, amp/cm², i.e., total current ÷ electrode surface area.

Limiting Current and Concentration Polarization

The mass transfer coefficient has a value characteristic of the system and current density under consideration, so that the average current density is given by rearrangement of equation (III):

$$I = \frac{nF(C_o - C_i)k_L}{(1 - t)}. \qquad (IV)$$

The theoretical maximum current density is that which would reduce C_i to zero. This theoretical limiting current density cannot be fully reached in practice because of the development of electrode polarization associated with depletion of the reacting ions in the region of the electrode. This polarization is approximately equal to the emf of a concentration cell formed between two solutions containing the reacting ion at concentrations C_o and C_i, respectively. Thus:

$$\Delta E = \frac{RT}{nF} \ln \frac{a_o}{a_i} \approx \frac{RT}{nF} \ln \frac{C_o}{C_i} \qquad (V)$$

where ΔE = concentration polarization, volts. As the current density is increased toward the theoretical limit, the applied potential must increase as a

result of the polarization, so that, in general, before the theoretical maximum current can be reached, some competing electrode reaction such as hydrogen evolution occurs. However, C_i often can be reduced in practice to an essentially negligible value before the onset of a successive reaction. For example, in the deposition of a copper ion at 25°C, a concentration polarization of 0.087 volt will require the ratio C_i/C_o to be 10^{-3}. In view of the possibility of successive reactions, it is necessary to define the limiting current density as the maximum current density which may be utilized exclusively for the production of a desired electrode reaction.

Equations for prediction of mass transfer coefficients and general correlation of data may be developed by analogy to solutions of the corresponding problem of heat transfer to vertical surfaces by free convection. In another paper (2), the authors have applied the boundary layer equations of Squires (3), as outlined by Eckert (4), to the present mass transfer problem. This procedure leads to the following results in the form of dimensionless groups:

$$(Nu')_x = 0.508Sc^{\frac{1}{2}}(0.952 + Sc)^{-1/4}Gr^{1/4} \quad \text{(VI)}$$

where: $(Nu')_x =$ local Nusselt number for mass transfer; $Sc =$ Schmidt number; and $Gr =$ Grashof number.

The Nusselt, Schmidt, and Grashof numbers are given by

$$(Nu')_x = \frac{k_x x X_f}{D} \quad \text{(VII)}$$

where: $k_x =$ mass transfer coefficient at height x, cm; $x =$ vertical height on electrode surface, cm; $D =$ effective diffusion coefficient of cupric ion, cm²/sec; $X_f =$ "film factor" for diffusion of cupric ion analogous to film pressure factor in gases (5, 6), equal to the log mean volume fraction of nondiffusing species in the present case.

$$Sc = \frac{\mu}{\rho D} \quad \text{(VIII)}$$

where: $\mu =$ average liquid viscosity, g/cm-sec, and $\rho =$ average liquid density, g/cm³.

$$Gr_x = \frac{g(\rho_o - \rho_i)\rho^2 x^3}{\rho_i \mu^2} \quad \text{(IX)}$$

where: ρ_o and $\rho_i =$ fluid densities in bulk solution and at the electrode surface, respectively, g/cm³, and $g =$ acceleration of gravity, cm/sec².

It is convenient to relate the density difference, $\rho_o - \rho_i$, to the concentration difference, $C_o - C_i$, by the specific densification coefficient, α, defined by the relation:

$$\alpha = \frac{\rho_o - \rho_i}{\rho_i(C_o - C_i)} \quad \text{(X)}$$

The specific densification coefficient does not vary greatly with concentration and, therefore, provides a convenient method for correlation of density data for use in these equations.

At the limiting current, assuming C_i to be negligible over the entire electrode, k_x varies inversely as the $\frac{1}{4}$ power of x. By integration over the electrode, the average mass transfer coefficient over height 0 to x can be related to the local value at height x by the equation:

$$k_L = 4/3k_x \quad \text{(XI)}$$

Assuming $X_f = 1$ and the number 0.952 negligible compared to Sc, equations (VII), (VIII), and (XI) may be combined to give the general equation for correlation of mass transfer coefficients in liquid systems:

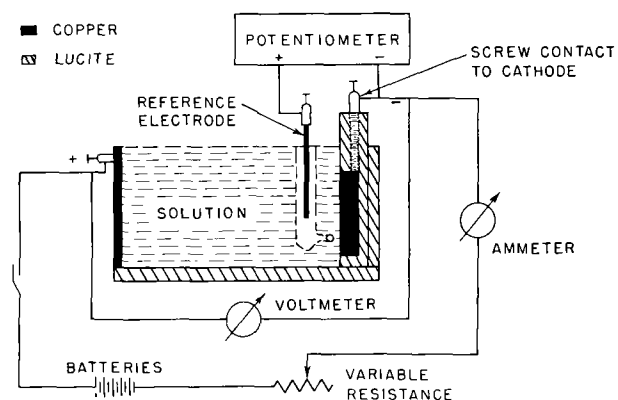$$Nu' = \frac{k_L x}{D} = 0.677 \, (Sc \, Gr)^{1/4} \quad \text{(XII)}$$

Fig. 1. Cell and circuit diagram

APPARATUS AND MATERIALS

The apparatus consisted essentially of an electrolytic cell for copper deposition and auxiliary equipment for measurement of total current and cathode potential relative to the bulk solution in the cell. Fig. 1 is a schematic diagram of the apparatus.

The cell was a rectangular container 7.6-cm wide and 10-cm high, formed of several sections of Lucite so that the distance could be varied between the cathode and anode located at opposite ends. Fig. 2 and 3 illustrate these features. A copper plate formed one of the end walls and served as anode. The copper cathodes were mounted in various Lucite holders as shown in Fig. 4. These holders permitted use of electrodes of four different heights: 0.634 cm, 2.54 cm, 3.75 cm, and 7.6 cm, and facilitated exchange of electrodes for repetition of the experiments. All cathodes were equal in width to the inner dimension of the cell, i.e., 7.6 cm. The sides of the cathodes were insulated with Glyptal lacquer so that only the side facing the anode conducted current. The cathode

circuit was completed by means of a contact screw, as indicated in Fig. 1. A fresh electrode was used for every limiting current determination, each electrode having been abrased and preplated by a standard procedure to assure uniformity of surface properties. Care was taken to obtain smooth alignment of the cathode surface with the vertical cell wall formed by the Lucite holder.

As reference electrode, a copper rod was immersed in a solution of the same composition as the bulk liquid in the cell and connected to the cell through a capillary of $\frac{1}{2}$-mm outside diameter, located in the corner of the cell at the centerline of the cathode at a distance of 1 mm from the surface. Data were not corrected for the small error in potential caused by ohmic resistance of the solution between the capillary tip and the electrode.

Potentials between the cathode and the reference electrode, i.e., total cathodic polarization, were measured with a type K-2 potentiometer, and current was measured with a range of calibrated ammeters.

Fifteen different solutions of $CuSO_4$ in approximately 1.5M sulfuric acid were investigated. $CuSO_4$ concentration varied from about 0.01M to 0.74M, and H_2SO_4 varied from 1.38M to 1.57M. The electrolyte composition remained essentially constant in any one experiment. The cell liquid was analyzed frequently during the course of the study; Cu^{++} by the iodine-thiosulfate method, and $SO_4^=$ by standard gravimetric procedure. C.P. chemicals were used for preparation of all solutions.

EXPERIMENTAL PROCEDURE FOR LIMITING CURRENT

The principal limiting current experiments are described below. Certain auxiliary experiments are discussed in a later section.

With the electrodes in place, the cell was filled with liquid to a depth of 10 cm, completely covering the cathode in all cases. Current was then passed through the cell and increased in small increments until the limiting current was attained, and usually increased further to the point of hydrogen evolution. Potential readings and new current settings were made at intervals of approximately 1 minute. These time intervals permitted the current and potential to reach essentially steady-state conditions at each rheostat setting, as demonstrated in preliminary experiments. Current-potential measurements were made with each electrode and electrolyte composition, and repeated three or four times, using freshly prepared cathodes. Reproducibility of successive limiting current determinations was within 1-2 per cent. The limiting current density for each experimental condition was determined by plotting the average current density over the electrode vs. potential, as determined by the reference elec-
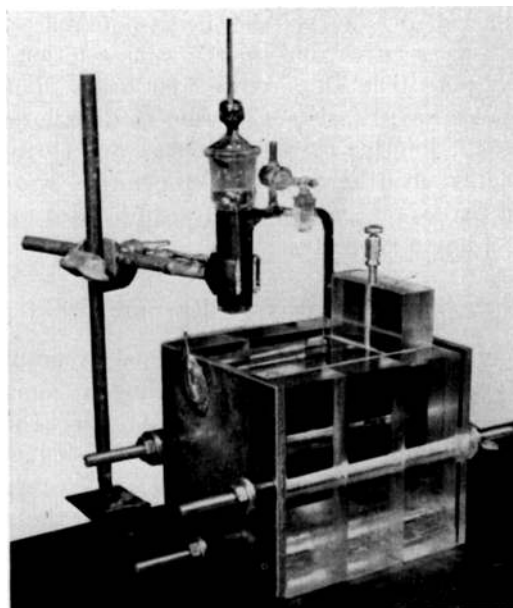

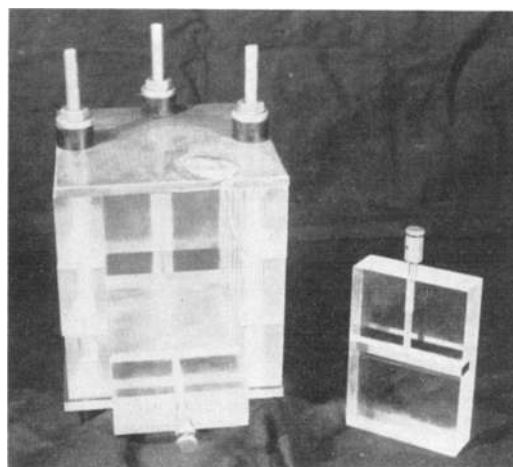Fig. 2. Assembled cell and reference electrode
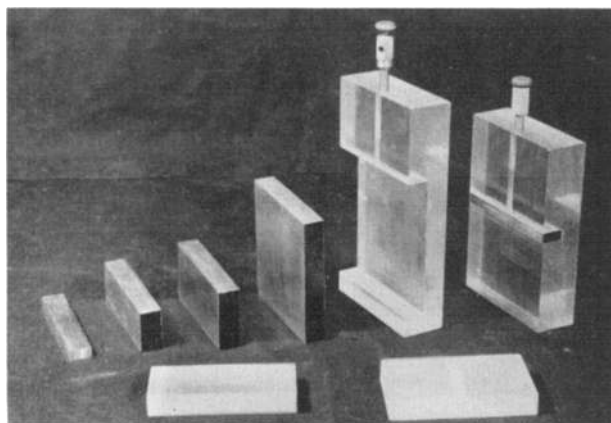

Fig. 3. Cell resting on end, anode at top

Fig. 4. Various cathodes and holders

trode, and observing the "plateau" where the current density became essentially independent of po-

tential. Fig. 5 is a typical current-potential curve for two consecutive runs on the same solution. Although potentials at currents well below limiting were not always consistent for runs on different electrodes, the limiting current plateaus were always in reasonably good agreement. Temperature was observed during the experiments for subsequent evaluation of liquid properties.

CORRELATION OF RESULTS

Experimental data for the principal experiments are summarized in Table I. According to equation (XII) and related theory, the Nusselt number should be a unique function of the Schmidt-Grashof number product for all electrode heights and electrolyte compositions. The procedure for obtaining these dimensionless groups is outlined briefly.

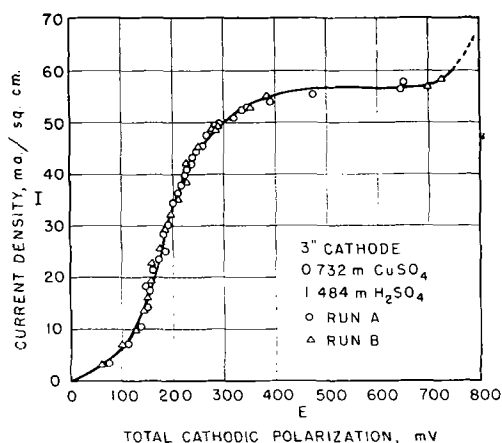*Mass transfer coefficients.*—Average mass transfer coefficients were calculated by substitution of ex-

FIG. 5. Typical current potential curve

perimental quantities in equation (III), assuming C_i to be negligible compared to C_o, and t for cupric ion to be zero. Estimates based on ionic mobilities at infinite dilution and corrected for concentration by comparison with similar systems indicated that the average value of t over the boundary layer probably did not exceed 0.015 for even the most concentrated $CuSO_4$ solutions. In absence of a rigorous theory for treating transference over the present concentration profiles further refinement of the analysis did not seem justified.

Film factor for cupric ion.—Due to the small volume of the cupric ion, (X_f) in equation (VII) was never less than 0.997 for the maximum concentrations and was, therefore, assumed unity in all calculations.

Diffusion coefficients.—The effective diffusion coefficient for cupric ion was assumed to be the value for $CuSO_4$ since sulfate was the only anion present.

Numerical values were based on the experimental data of Gordon and Cole (7) corrected for temperature, viscosity, and ionic strength of the solution. Hydrogen ion and sulfate ion were assumed to diffuse as sulfuric acid since the cupric ion concentration was relatively small in all cases. Sulfuric acid diffusivities were derived from data of Gordon (8) and Thovert (9), utilizing temperature and viscosity corrections in a similar manner to the procedure for $CuSO_4$. Diffusion coefficients and viscosities entering the final correlation were evaluated at the arithmetic mean composition between the bulk solution and electrode-solution interface. Numerical values are given in Table I.

Interfacial composition.—The cathode reaction and migration effects result in a net movement of sulfuric acid toward the interface. Eventually, a steady state is reached in which acid is transported away from the electrode by convective mass transfer at the same rate it is carried toward the electrode. The concentration difference thus developed between the electrode and bulk solution is expressed by the relation:

$$It_{H^+} = k_{H_2SO_4}(C_i - C_o)_{H_2SO_4} \qquad (XIII)$$

where t_{H^+} = transference number for hydrogen ion, and $k_{H_2SO_4}$ = mass transfer coefficient for sulfuric acid. According to equation (XII), the mass transfer coefficients for the various species vary as the $\frac{3}{4}$ power of the respective diffusion constants for any given electrode and solution. Therefore, the mass transfer coefficients for H_2SO_4 were calculated from the relation

$$k_{H_2SO_4} = \left[\frac{D_{H_2SO_4}}{D_{CuSO_4}}\right]^{3/4} \cdot k_{CuSO_4} \qquad (XIV)$$

From the known bulk solution sulfuric acid concentration, the electrolyte composition at the interface could be calculated for each experiment. Trial and error procedure was required in the solution of equations (XIII) and (XIV) since the average film composition, and, hence, the diffusion constant, was not known in advance.

Viscosities.—Viscosities were measured with an Ostwalt viscosimeter for sulfuric acid and copper sulfate solutions over the range of temperature and composition of interest. Results for pure sulfuric acid solutions were in agreement with the data of Vinal and Craig (10).

Densities.—Densities were measured with a special pycnometer of large volume for various solutions covering the range of compositions used in the experiments. A general correlation of α values for $CuSO_4$ and H_2SO_4 in water and aqueous glycerol solutions was developed which permitted the calcu-

lation of the density difference between bulk solution and the electrode-solution interface for each

General correlation.—Using the mass transfer coefficients and property values developed as discussed

TABLE I. *Experimental data and results for deposition of copper from* $CuSO_4$-H_2SO_4 *solutions on vertical electrodes*

Run No.	Electrode height, in.	CuSO₄ molarity	H₂SO₄ molarity	Lim. current density ma/cm²	Mass transfer coefficient × 10³ cm/sec	Temp, °C	Avg. viscosity centipoise	Avg. density g/cm³	Avg diffusion coefficient × 10⁵ cm²/sec	ΔC_H₂SO₄ moles/liter	ρo − ρi g/cm³	Nu'	Sc	Gr × 10⁻⁶
1	0.25	0.01002	1.530	0.602	0.3113	24.7	1.197	1.0898	0.628	0.0031	0.00139	31.43	1749	0.00264
2	0.25	0.0270	1.561	2.12	0.4068	23.7	1.220	1.0919	0.615	0.0083	0.00371	41.94	1817	0.00680
3	0.25	0.0498	1.498	4.20	0.4370	23.0	1.260	1.0933	0.593	0.0153	0.00675	46.72	1943	0.01167
4	0.25	0.0688	1.523	6.44	0.4850	23.7	1.242	1.0924	0.604	0.0209	0.00926	50.91	1882	0.01641
5	0.25	0.0813	1.501	7.67	0.4890	23.7	1.229	1.0918	0.610	0.0247	0.0109	50.82	1845	0.01969
6	0.25	0.0966	1.508	9.63	0.5010	23.7	1.263	1.0968	0.594	0.0301	0.0133	53.47	1939	0.22290
7	0.25	0.189	1.573	20.69	0.5671	23.7	1.300	1.1034	0.580	0.054	0.0248	62.00	2031	0.04078
8	0.25	0.247	1.465	27.55	0.5778	20.5	1.396	1.1056	0.533	0.071	0.0319	68.73	2369	0.04575
9	0.25	0.376	1.450	48.68	0.6710	22.5	1.400	1.1150	0.537	0.103	0.0478	79.25	2338	0.06936
10	0.25	0.467	1.471	66.45	0.7373	22.5	1.438	1.1282	0.525	0.123	0.0594	89.01	2428	0.08345
11	0.25	0.624	1.424	92.44	0.7675	26.0	1.385	1.1328	0.522	0.156	0.0791	88.13	2215	0.1211
12	0.25	0.660	1.502	94.65	0.7435	21.5	1.576	1.1406	0.480	0.160	0.0845	98.21	2878	0.1006
13	0.25	0.732	1.484	108.2	0.7658	23.7	1.559	1.1447	0.490	0.174	0.0938	99.09	2779	0.1151
14	0.25	0.739	1.384	105.3	0.7376	23.7	1.536	1.1397	0.495	0.177	0.0941	94.47	2773	0.1186
15	1.00	0.0113	1.522	0.495	0.2270	22.9	1.218	1.0906	0.613	0.0035	0.00157	94.06	1822	0.1852
16	1.00	0.0270	1.561	1.46	0.2802	24.9	1.186	1.0913	0.635	0.0083	0.00371	112.1	1711	0.4625
17	1.00	0.0498	1.498	2.76	0.2872	21.0	1.317	1.0942	0.536	0.0153	0.00675	129.6	2138	0.6867
18	1.00	0.0813	1.501	5.00	0.3187	20.4	1.320	1.034	0.561	0.0247	0.0109	144.3	2152	1.101
19	1.00	0.189	1.573	13.05	0.3578	20.5	1.392	1.1050	0.536	0.0540	0.0249	169.5	2350	2.295
20	1.00	0.247	1.465	17.58	0.3688	20.1	1.404	1.1058	0.528	0.071	0.0319	177.4	2405	2.910
21	1.00	0.376	1.450	28.8	0.3969	19.4	1.495	1.1168	0.498	0.103	0.0479	202.4	2688	3.924
22	1.00	0.467	1.471	44.9	0.4982	24.0	1.390	1.1272	0.546	0.123	0.0593	231.7	2258	5.733
23	1.00	0.660	1.502	66.3	0.5252	25.0	1.466	1.1375	0.523	0.160	0.0844	255.0	2464	7.437
24	1.00	0.732	1.484	74.65	0.5284	21.3	1.654	1.1465	0.458	0.174	0.0939	293.1	3150	6.597
25	1.50	0.0113	1.522	0.45	0.2063	22.4	1.231	1.0910	0.605	0.0035	0.00137	127.9	1865	0.5839
26	1.50	0.0270	1.561	1.29	0.2476	25.5	1.171	1.0911	0.645	0.0082	0.00371	143.9	1664	1.528
27	1.50	0.0305	1.522	1.53	0.2599	22.0	1.265	1.0920	0.588	0.0094	0.00418	165.8	1970	1.476
28	1.50	0.0498	1.498	2.60	0.2705	22.5	1.276	1.0936	0.584	0.0153	0.00675	173.7	1998	2.351
29	1.50	0.0813	1.501	4.58	0.2919	20.0	1.331	1.0936	0.556	0.0247	0.0109	196.9	2188	3.485
30	1.50	0.189	1.573	12.05	0.3304	20.4	1.395	1.1051	0.535	0.054	0.0249	231.6	2359	7.354
31	1.50	0.247	1.465	16.6	0.3486	22.3	1.345	1.1046	0.557	0.071	0.0319	234.7	2186	10.18
32	1.50	0.376	1.450	26.2	0.3610	20.0	1.474	1.1168	0.506	0.103	0.0478	267.6	2608	12.99
33	1.50	0.467	1.471	39.5	0.4383	22.7	1.432	1.1280	0.527	0.123	0.0594	311.9	2409	17.41
34	1.50	0.660	1.502	49.2	0.3863	19.0	1.700	1.1417	0.441	0.160	0.0846	328.5	3376	17.93
35	1.50	0.732	1.484	66.8	0.4728	23.7	1.558	1.1448	0.490	0.174	0.0937	361.8	2777	23.85
36	3.00	0.0113	1.522	0.397	0.1820	22.3	1.231	1.0909	0.605	0.0035	0.00157	228.7	1865	4.860
37	3.00	0.0270	1.561	1.07	0.2053	24.8	1.190	1.0914	0.633	0.0082	0.00371	246.5	1722	12.31
38	3.00	0.0305	1.522	1.24	0.2107	22.4	1.256	1.0918	0.593	0.0094	0.00418	270.0	1940	12.46
39	3.00	0.0498	1.498	2.09	0.2175	21.2	1.310	1.0942	0.567	0.0153	0.00675	291.5	2117	18.59
40	3.00	0.0813	1.501	3.55	0.2263	20.4	1.320	1.0934	0.561	0.0247	0.0109	306.5	2152	29.48
41	3.00	0.189	1.573	9.91	0.2717	20.4	1.395	1.1051	0.535	0.054	0.0249	385.9	2359	61.22
42	3.00	0.247	1.465	14.05	0.2947	22.1	1.351	1.1048	0.554	0.071	0.0319	404.3	2207	84.03
43	3.00	0.376	1.450	20.7	0.2853	19.0	1.504	1.1171	0.494	0.103	0.0478	438.8	2725	103.9
44	3.00	0.467	1.471	29.7	0.3295	18.0	1.612	1.1308	0.461	0.123	0.0595	543.2	3092	114.9
45	3.00	0.660	1.502	44.1	0.3462	22.8	1.546	1.1396	0.491	0.160	0.0844	535.9	2763	179.7
46	3.00	0.732	1.484	56.6	0.4003	27.2	1.429	1.1422	0.540	0.174	0.0937	563.3	2317	235.1

Note: Transference numbers of H^+ varied from 0.75 to 0.81.

experiment. This procedure is outlined in detail elsewhere (11). Density data based on these α values are presented in the data tables pertaining to the various experiments.

above, the Nusselt, Schmidt, and Grashof groups were evaluated for each experiment as presented in Table I. Fig. 6 is a log-log plot of the Nusselt group vs. the Schmidt-Grashof product. All of the data

correlate very satisfactorily in the manner indicated by the theory to a straight line corresponding to the equation:

$$Nu' = 0.673(ScGr)^{1/4}. \qquad \text{(XV)}$$

The constant 0.673 was evaluated by averaging the constants calculated for individual experiments, assuming the Schmidt-Grashof product to enter as the $\frac{1}{4}$ power. Such close agreement between equation (XV) and equation (XII) is no doubt fortuitous, but, nevertheless, the result appears to be a very encouraging indication of the general validity of the methods employed.
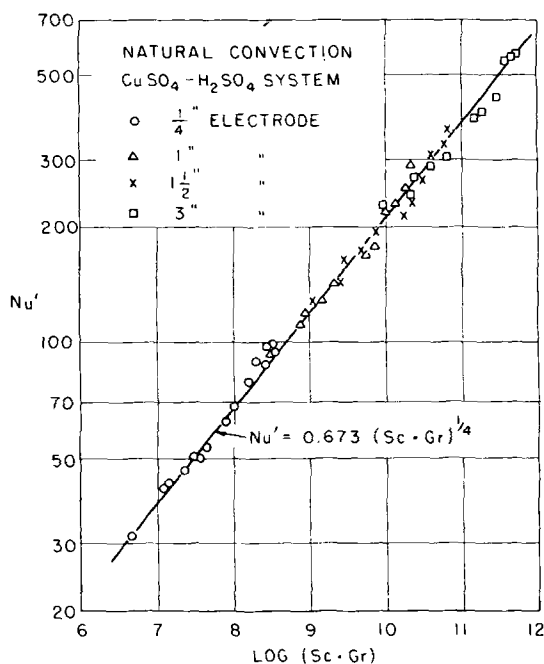
Fig. 6. General correlation of free convection data

Discussion

Comparison of Results with other Theories and Experiments

Diffusion layer theory.—As originated by Nernst (12), this theory assumes transfer of ions to occur by diffusion through a "diffusion layer" of thickness B' defined for dilute solutions by the relation:

$$N_D = \frac{C_o - C_i}{B'} D. \qquad \text{(XVI)}$$

The diffusion layer is thus a hypothetical layer of stagnant fluid by means of which the total rate of mass transfer by all mechanisms acting over the actual mass transfer path may be expressed by an equivalent rate equation for pure diffusion. This concept has been widely used in the chemical engineering literature, with B' usually designated as the "effective film thickness." From equations (III), (XV), and (XVI), the diffusion layer thickness is given by:

$$B' = 1.48x(ScGr)^{-1/4}. \qquad \text{(XVII)}$$

Equation (XVII) indicates that B' is not constant, but varies with electrode height, electrolyte composition, and other factors which influence the Schmidt-Grashof number product. For the experimental results obtained in this study, B' ranged, in agreement with the theory, from 0.0064 cm to 0.0332 cm. Some authors (13, 14) have recommended use of an average value of 0.05 cm for B' in unstirred systems, a procedure which is theoretically unsound and which may be very seriously in error, as indicated by the present results.

Analogy to the Schmidt-Pohlhausen-Beckmann development for heat transfer (15).—As recommended for electrochemical systems by Agar (16) this theory gives the result:[2]

$$Nu' = 0.525(ScGr)^{1/4}. \qquad \text{(XVIII)}$$

Although the numerical coefficient in this equation disagrees with that derived from more exact theories and the present experimental result, the essential form of the equation is the same for large values of Sc. The disagreement is to be expected since the original solution of the differential equations by Pohlhausen was based upon Beckmann's experimental result for heat transfer to air from vertical plates. The numerical coefficient of equation (XVIII) can be considered applicable only to systems with Schmidt or Prandtl numbers of numerical value near to the Prandtl number for air, i.e., about 0.73.

Equations of Levich.—Levich (17) has developed an approximate solution to the differential equations for the free convection boundary layer which may be put into the form of equation (XII) as follows:

$$Nu' = 0.51(ScGr)^{1/4}. \qquad \text{(XIX)}$$

Again, although the exact numerical coefficient differs, this theory leads to an equation of the same general form as those previously described.

Equations of Wagner.—A detailed treatment of the free convection problem in relation to electrode processes has been presented by Wagner (18). Wagner uses the method of the boundary layer, assuming that the boundary layers for velocity and for diffusion of the various ionic species do not necessarily coincide. By assuming certain functions for the distribution of velocity and concentration between the electrode and point of maximum velocity, equations are developed to apply specifically to the system $CuSO_4$-H_2SO_4-H_2O. This result may be expressed in the following form for comparison with equation (XII):

$$Nu' = 0.805(ScGr)^{1/4}. \qquad \text{(XX)}$$

[2] Inspection of the equations as presented by ten Bosch indicates that the coefficient of equation (XVIII) should be 0.518.

As a consequence of assuming the boundary layer thickness for diffusion of H^+ to be greater than for diffusion of Cu^{++}, Wagner obtains an expression for calculation of the density difference between bulk solution and the electrode surface which differs from the result obtained in this paper. Direct comparison of the methods is, therefore, complicated.

When α may be assumed constant at an average value for each species, equations (IV) and (XIII) to (XV) lead to the following result for the average limiting current density over an electrode of height x_o:

$$I = \frac{0.673 n \mathrm{F} \Delta C_o}{x_o (1 - t_{Cu^{++}})}$$
$$\cdot \left[\frac{g x_o{}^3 D^3 \Delta C_o (\alpha_{CuSO_4} - \alpha_{H_2SO_4} t_H + [D_{CuSO_4}/D_{H_2SO_4}]^{3/4})}{\mu^2} \right]^{1/4} . \quad \text{(XXI)}$$

Equation (XXI) may be compared directly with equation (XLVI) of Wagner's paper. Limiting cur-

TABLE II. *Limiting current densities at copper cathodes in* 0.1M $CuSO_4$ + 1.0M H_2SO_4 at 25°C

Electrode height, cm	Average limiting current density, amp/cm²			
	Experimental result (18)	Calculated[1] equation (XXI) (physical properties, this study)	Calculated[2] equation (XXI) (physical properties of Wagner)	Calculated, Wagner
1	0.0103	0.0099	0.0083	0.0094
4	0.0067	0.0070	0.0058	0.0066
16	0.0052	0.0050	0.0041	0.0047

[1] $D_{CuSO_4} = 0.657 \times 10^{-5}$ cm²/sec; $\alpha_{CuSO_4} = 143.6$ cm³/mole; $\alpha_{H_2SO_4} = 51.9$ cm³/mole.

[2] $D_{CuSO_4} = 0.5 \times 10^{-5}$ cm²/sec; $\alpha_{CuSO_4} = 166$ cm³/mole; $\alpha_{H_2SO_4} = 68$ cm³/mole.

rent data for deposition of copper from 0.1M $CuSO_4$ in 1.0M H_2SO_4 are presented by Wagner for three electrodes of heights 1, 4, and 16 cm. These observations are given in Table II, along with values calculated by the method of Wagner, and calculated by equation (XXI) above. Equation (XXI), in conjunction with physical properties evaluated by the correlations developed for this paper, gives a very satisfactory prediction of the measurements, with an average deviation of 3.9 per cent between calculated and observed values. Use of physical properties recommended by Wagner, however, leads to a much less satisfactory result. The principal disagreement with respect to physical data lies in the values of the diffusion coefficient for $CuSO_4$ and in the densification coefficients for $CuSO_4$ and H_2SO_4, as indicated in Table II.

Equations of Keulegan.—Keulegan (19) presents the differential equations for motion and diffusion in the boundary layer for mass transfer in a manner similar to that used by Pohlhausen (15) for heat

transfer. An approximate solution is developed by assuming the distribution of velocity and concentration to be arbitrarily selected sine functions of distance through the boundary layer perpendicular to the electrode surface. The resulting solution may be extended into the general form corresponding to equation (XV) as follows:

$$Nu' = 0.628 (ScGr)^{1/4}. \quad \text{(XXII)}$$

Keulegan compares density reductions between bulk solution and the electrode for deposition of copper and nickel, calculated by equations based on this theory, with experimental results determined in freezing experiments by Brenner (18). The agreement obtained between calculation and theory is sufficient to constitute a strong indication of the correctness of the concepts which have been assumed in the boundary layer theory. Keulegan's presentation does not consider effects of migration and resultant increase in concentration of acid at the electrode on the developed density difference between the interface and bulk solution; however, the resultant error is not sufficient to alter the general agreement of the theory with the interpretation of Brenner's experiments.

Equations of Ostrach for heat transfer.—An excellent comprehensive treatment of heat transfer by free convection to vertical plates has been presented by Ostrach (19). The convection-diffusion equations are developed to give differential equations of the form used by Pohlhausen. By use of an IBM Card Programmed Electronic Calculator, solutions of these differential equations were obtained for various values of Prandtl number to give useful tabular functions from which Nusselt numbers, temperature, and velocity distributions can easily be obtained. These equations are adaptable to the mass transfer problem by substitution of Schmidt number for Prandtl number. For the average mass transfer Nusselt number over a plate of height x_o, the result of Ostrach may be expressed as follows:

$$\frac{Nu'}{(Gr)^{1/4}} = 0.943 \, f(Sc) \quad \text{(XXIII)}$$

where $f(Sc)$ is a function of the Schmidt number, tabulated by Ostrach as the function $-H'(0)$ of Prandtl number. Equations (VI) and (XI) give:

$$\frac{Nu'}{(Gr)^{1/4}} = \frac{0.677 (Sc)^{1/2}}{(0.952 + Sc)^{1/4}}. \quad \text{(XXIV)}$$

A comparison of numerical values of equations (XXIII) and (XXIV) for various Sc, using $f(Sc)$ from the tables of Ostrach, indicates that satisfactory agreement is over the range of Schmidt numbers above 0.73, with the two methods almost coinciding in the region of high Schmidt numbers such

as usually prevails in liquid systems. Both of these methods indicate equations of the simple form of equation (XVIII) to be theoretically inadequate over an extended range of Schmidt numbers for mass transfer or of Prandtl numbers for heat transfer.
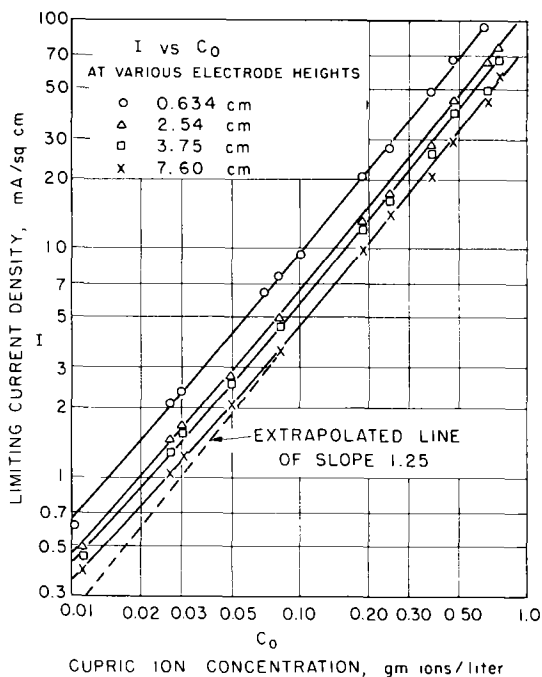

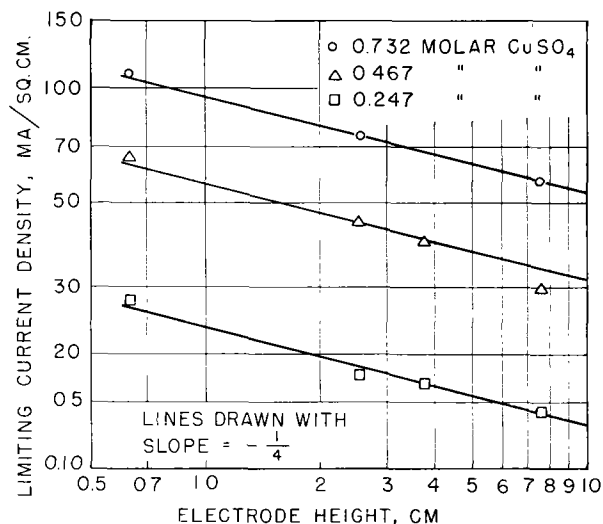Fig. 7. Variation of limiting current with bulk cupric ion concentration.

Fig. 8. Effect of electrode height on average limiting current density.

This limitation of equation (XVIII) has apparently been overlooked by ten Bosch, Agar, and others, who have postulated its application for all Prandtl and Schmidt numbers. A detailed discussion of these equations and comparisons with experimental heat transfer data is given by Ostrach.

Effect of Experimental Variables on Limiting Current Density

Bulk concentration of reacting species.—Equation (XXI) indicates the effect of all variables on the limiting current density when α may be assumed constant. If variation of other properties with electrolyte composition is not significant for a given system, the limiting current density should vary with the $\frac{5}{4}$ power of the bulk concentration of reacting species. In Fig. 7, limiting current densities for the present experiments are plotted against concentration of cupric ion in the bulk electrolyte. A straight line of slope $\frac{5}{4}$ passes through the data very well at concentrations greater than $0.1M$. However, at lower concentrations, the relationship breaks down, due to failure of the assumption of constancy of α and other properties. Thus it may be concluded that limiting current density may vary as the $\frac{5}{4}$ power of concentration in certain cases, but that the rule is not universal.

Electrode height.—According to equation (XXI), the average limiting current density over an entire electrode should vary inversely as the $\frac{1}{4}$ power of total electrode height. This relationship is substantiated in Fig. 8, which is a log-log plot of current density vs. electrode height for three different $CuSO_4$ concentrations. As a further consequence of this relationship, the total current passing to an electrode increases as the $\frac{3}{4}$ power of electrode height.

Effect of Free Convection on Limiting Current Distribution

Equation (XXI) gives the local value of limiting current density at height x on a given electrode when the total height x_o in the equation is replaced by local height x and the numerical constant is reduced to 0.508. According to this result, the local current density varies inversely as the $\frac{1}{4}$ power of distance from the bottom of the electrode. This effect has been demonstrated by Wagner (18), who measured the current distribution for deposition of copper. Fig. 9 shows the theoretical current distribution for one of the present experiments. To investigate the extent of nonuniformity of current distribution at current densities below the limiting value, two experiments were conducted in which copper was deposited at a steady state rate of 19.5 ma/cm² on an electrode of 7.6 cm height. After a given run, the fresh metal deposit was stripped off, and its weight per 1 cm² measured as a function of position on the electrode. This, in turn, permitted the calculation of local current density. At heights above 2 cm, the current distribution was fairly uniform. At lower heights, a significant distortion of current distribution is evident, indicating that the effect of free con-
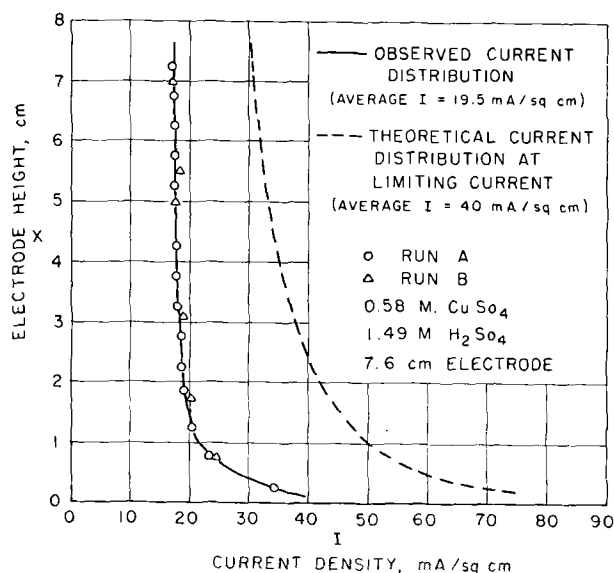
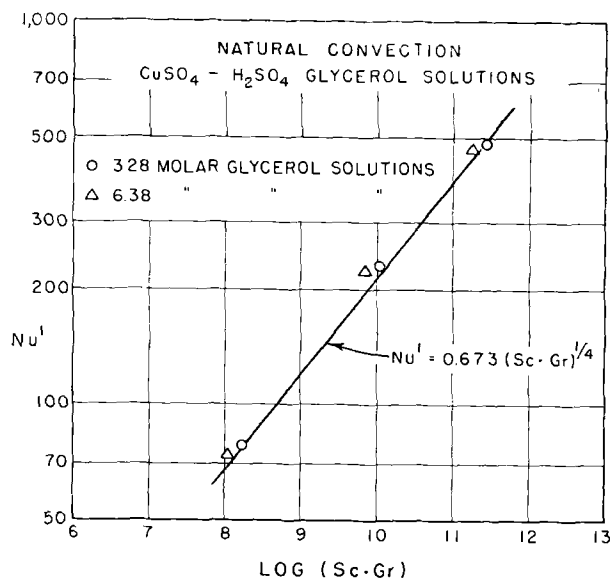Fig. 9. Current distribution in free convection

Fig 10. Comparison of data for glycerol solutions with general correlation.

Special Experiments

In order to illustrate certain additional features of the problem and to test further the general application of the correlation a number of special experiments were conducted as follows.

Copper Deposition from Aqueous Glycerol Solutions

In order to obtain a greater variation in properties of the electrolyte, particularly a variation in viscosity and diffusion coefficient, various H_2SO_4-H_2O solutions were prepared containing glycerol in amounts ranging from 3.28 to 6.38 moles/liter. This increased the viscosity of the liquid and reduced the diffusion constant, respectively, by a factor of ten. Limiting current data were obtained for $\frac{1}{4}$-in., 1-in., and 3-in. electrodes in the manner previously described. Table III presents the experimental results. Fig. 10 shows the comparison of Nu' as a function of $ScGr$ for these solutions with the line obtained in the general correlation, Fig. 6. This agreement is believed to be very satisfactory and an encouraging indication of the general validity of the correlation.

Study of Full-End Electrodes

In the preceding experiments, the electrodes were placed in Lucite holders and centered approximately midway between the floor of the cell and upper surface of the electrolyte. It seemed desirable, therefore, to study an electrode extending over the entire endwall of the cell, since this arrangement represents the opposite extreme in cell geometry. Accordingly, the entire Lucite end of the cell was replaced by a copper plate which served as the cathode. Limiting current measurements were made with liquid filling the cell at various levels from 2.5 cm to 10.0 cm. Experimental results are compared with the general correlation in Fig. 11. Although the best line through the data might be placed a few per cent below th-

TABLE III. *Data and results for copper deposition from* $CuSO_4$-H_2SO_4-*glycerol solutions on vertical electrodes*

Run No.	Electrode height, in.	$CuSO_4$ molarity	H_2SO_4 molarity	Glycerol molarity	Lim. C.D. ma/cm²	Mass transfer coeff. $\times 10^3$	Temp, °C	Avg viscosity centipoise	Avg density g/cm³	Avg diffusion coeff.[1] $\times 10^5$ cm²/sec	$\Delta C_{HS_2O_4}$ moles/l	$\rho_0 - \rho_i$ g/cm³	Nu'	Sc	$Gr \times 10^{-6}$
47	0.25	0.3679	0.751	6.38	9.32	0.1313	23.4	10.02	1.1983	0.113	0.153	0.0472	73.67	73,976	0.001437
48	0.25	0.5702	1.145	3.28	35.5	0.3226	22.5	4.254	1.1755	0.264	0.204	0.0719	77.47	13,708	0.01204
49	1.00	0.3679	0.751	6.38	7.12	0.1003	23.5	9.991	1.1983	0.114	0.153	0.0472	224.4	73,784	0.09284
50	1.00	0.5702	1.145	3.28	25.5	0.2317	21.5	4.392	1.1762	0.255	0.204	0.0719	230.8	14,643	0.7272
51	3.00	0.3679	0.751	6.38	4.58	0.0645	22.1	10.596	1.1992	0.106	0.153	0.0472	462.5	83,357	2.215
52	3.00	0.5702	1.145	3.28	18.65	0.1695	22.9	4.197	1.1752	0.268	0.204	0.0719	480.6	13,326	21.29

[1] Measured in diaphragm cell (23).

vection persists at current densities well below limiting in these systems.

line based on Fig. 6, the deviation is not very significant. It may, therefore, be concluded that the posi-

tion of the electrode with respect to the floor of the cell or with respect to the liquid surface is relatively unimportant insofar as limiting current is concerned.

Position of Electrode Relative to Floor of Cell

To observe further the effect of variation in electrode location, additional experiments were conducted with two electrodes 0.634 and 2.54 cm in height, respectively. In a series of runs, these electrodes were each placed at distances of 0, 1.3, 3.2,
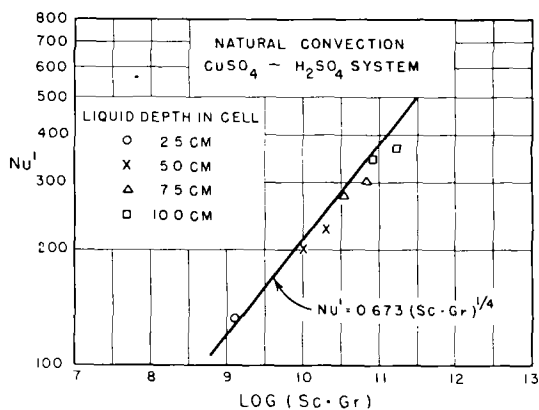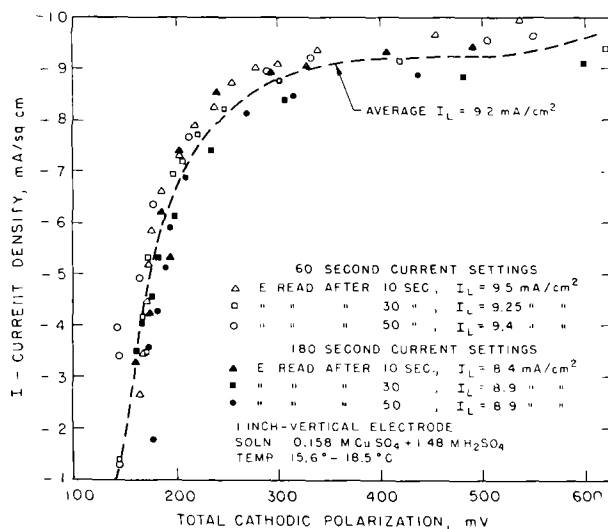

FIG. 11. Data for full-end electrodes

FIG. 12. Effect of time intervals between current settings and potential reading and between successive current settings upon the limiting current.

and 5.7 cm from the cell floor with the cell filled to a depth of 7.6 cm. Several solutions ranging from 0.042 to 0.732 in $CuSO_4$ molarity were used in these tests. For a given electrode and solution, variations in the observed limiting currents from the average for the series never exceeded 1.5 per cent over the range of electrode positions.

Effect of Window Baffles between Anode and Cathode

In the majority of experiments, the electrolyte between anode and cathode presented a larger cross

section perpendicular to the direction of current flow than did the cathode. Under these conditions, some nonuniformity of current distribution might be expected, particularly at the upper and lower edges of the cathode. To determine the extent to which such nonuniformity of current density might affect the limiting current data, several experiments were conducted using specially designed window-type Lucite baffles placed parallel to and near to the cathode. Two parallel baffles were used with windows of the same size as the electrode and located at the same elevation. Limiting current data were obtained for a 1-in. cathode at various elevations in the cell filled to a depth of 7.6 cm, with the baffles placed at distances of $\frac{1}{4}$ in. and 1 in., respectively, from the electrode. Limiting current results obtained with and without baffles were identical within limits of experimental accuracy.

Variation in Technique of Obtaining Current-Potential Curves

In order to establish the validity of the experimental techniques which was finally adopted, various ways of obtaining current-potential curves were studied. The objective of these studies was to determine any effect on the limiting current of altering the time intervals between successive current settings, and of altering the time at which the potential was measured following a given current setting. In one series of experiments, the time of electrolysis at each current setting was held constant at 60 seconds, and potentials were measured following each current setting at intervals of 10, 30, and 50 seconds, respectively, in successive runs. In another series of runs, the electrolysis time was held at 180 seconds between current settings, and the potentials were measured at the same intervals as in the preceding series. The data for these runs, giving six different current-potential curves for identical electrolyte compositions and electrodes, are shown in Fig. 12. The maximum deviation of the limiting currents from the average value of 9.22 ma/cm² is 3.2 per cent. Irreproducibility of polarization of copper cathodes should be expected in view of results of other studies (22). However, the limiting current density appears to be independent of the initial shape of the current-potential curve, in agreement with the concept of mass transfer being the controlling process at the limiting current point.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

REFERENCES

1. C. W. TOBIAS, M. EISENBERG, AND C. R. WILKE, *J. Electrochem. Soc.*, **99**, 359C (1952).
2. C. R. WILKE, M. EISENBERG, AND C. W. TOBIAS, To be published in *Chemical Engineering Progress*.
3. S. GOLDSTEIN, "Modern Developments in Fluid Dynamics," Squires' method, pp. 641-643, Oxford University Press, New York (1938).
4. E. R. G. ECKERT, "Introduction to Transfer of Heat and Mass," pp. 158-163, McGraw Hill Book Company, New York (1950).
5. C. R. WILKE, *Chem. Eng. Progr.*, **46**, 95 (1950).
6. O. A. HOUGEN AND K. M. WATSON, "Chemical Process Principles, III," 1st ed., p. 977, John Wiley and Sons, Inc., New York (1947).
7. A. R. GORDON AND A. COLE, *J. Phys. Chem.*, **40**, 733 (1936).
8. A. R. GORDON, *J. Chem. Phys.*, **7**, 89 (1939); **8**, 423 (1940).
9. G. THOVERT, Landolt-Boernstein Tabellen I, p. 248.
10. G. W. VINAL AND D. N. CRAIG, *Bur. Standards J. Research*, **10**, 781 (1933).
11. M. EISENBERG, C. W. TOBIAS, AND C. R. WILKE, To be published.
12. W. NERNST, *Z. physik. Chem.*, **47**, 52 (1904).
13. J. N. AGAR AND F. P. BOWDEN, *Proc. Roy. Soc. London*, **169A**, 206 (1938).
14. S. GLASSTONE, "An Introduction to Electrochemistry," pp. 448-52, D. Van Nostrand Company, New York (1942).
15. M. TEN BOSCH, "Die Wärmeübertragung," III Auflage, pp. 160-167, Julius Springer, Berlin (1936).
16. J. N. AGAR, *Discussions Faraday Soc.*, **1**, 31 (1947).
17. B. LEVICH, *Acta Physicochim. U.S.R.R.*, **19**, 125 (1944).
18. C. WAGNER, *J. (and Trans.) Electrochem. Soc.*, **95**, 161 (1949).
19. G. H. KEULEGAN, *J. Research Natl. Bur. Standards*, **47**, 156 (1951).
20. A. BRENNER, *Ann. Proc. Tech. Sessions, Am. Electroplaters' Soc.*, p. 28 (1941).
21. S. OSTRACH, *Natl. Advisory Comm. Aeronaut.*, Tech. Note 2635, Lewis Flight Propulsion Laboratory, Cleveland, Ohio, February 1952.
22. L. L. SHREIR AND J. W. SMITH, *J. Electrochem. Soc.*, **98**, 193 (1951).
23. PIN CHANG, Ph.D. Thesis, University of California (in preparation, 1953).