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Limin Hsueh and John Newman

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The Role of Bisulfate Ions in Ionic Migration Effects

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July, 1970

Abstract

The limiting current and the surface concentration of supporting electrolyte are calculated for copper deposition from solutions of cupric sulfate and sulfuric acid, with emphasis on the effects of the incomplete dissociation of bisulfate ions. Results with a stagnant diffusion cell provide an experimental comparison.

Introduction

In an earlier paper,¹ the effect of ionic migration on limiting currents has been calculated for several electrolytic solutions. For the case of copper sulfate and sulfuric acid, the effect of migration was treated with the assumption that bisulfate ions were completely dissociated. In aqueous solution, sulfuric acid molecules ionize in two stages; the first and second ionization constants² at 25°C are 10^3 and 1.04×10^{-2} mole/l, respectively. Consequently, except at extreme dilution, the bisulfate ions will not dissociate completely.

For many discharge reactions, the concentration of supporting electrolyte is higher at the electrode surface than in the bulk solution. This concentration difference is of considerable interest in free-convection problems since the convective velocity is then due to the density differences in the solution produced by the electrode reaction, and these density differences are affected by the concentration of supporting electrolyte to roughly the same extent as by the concentration of the reactant.

Brenner³ has studied the concentration profiles near the electrode for deposition from copper sulfate-sulfuric acid solutions by freezing the solution and subsequent analysis of layers of the solidified solution.

Wilke, Eisenberg, and Tobias⁴ have measured limiting currents on plane, vertical cathodes from unstirred solutions. They have estimated the concentration of sulfuric acid at the electrode by equating the rate of migration of hydrogen ions toward the electrode to the rate of transport of the acid away from the electrode by diffusion and convection. Fenech and Tobias⁵ used a similar procedure to estimate the surface concentration

of sulfuric acid at horizontal electrodes in free convection at the limiting current. Recently, Ravoo⁶ has challenged the estimation procedure used by these authors.

Theoretical Analysis and Results

The theoretical analysis based on the dilute-solution theory is similar to that of the previous paper.¹ Material balance equations are written for the hydrogen, sulfate, bisulfate, and copper ions, the equations including where appropriate the rate of production in the homogeneous reaction.



The reaction was assumed to be fast, so that the concentrations also satisfy the relation

$$K' = \frac{c_{\text{H}^+} c_{\text{SO}_4^{2-}}}{c_{\text{HSO}_4^-}} \quad (2)$$

where K' was taken to be independent of position. The material balance equations could then be added to obtain three equations which do not include the reaction rate. These three equations, equation 2, and the electroneutrality relation are then used to determine the concentration distributions of the four ions and the potential distribution.

The ionic mobilities and diffusion coefficients were calculated from the ionic conductances at infinite dilution at 25°C. They were taken from Robinson and Stokes² and, for the bisulfate ion, from Owen and Gurry.⁷

The Nernst-Einstein relation was assumed to be valid in the calculation. See references 1 and 8 for the details of the analysis.

Let c_A^∞ and c_B^∞ be the bulk stoichiometric concentrations of copper sulfate and sulfuric acid, and let I be the bulk ionic strength based on a convention of complete dissociation:

$$I = 4c_A^\infty + 3c_B^\infty \quad (3)$$

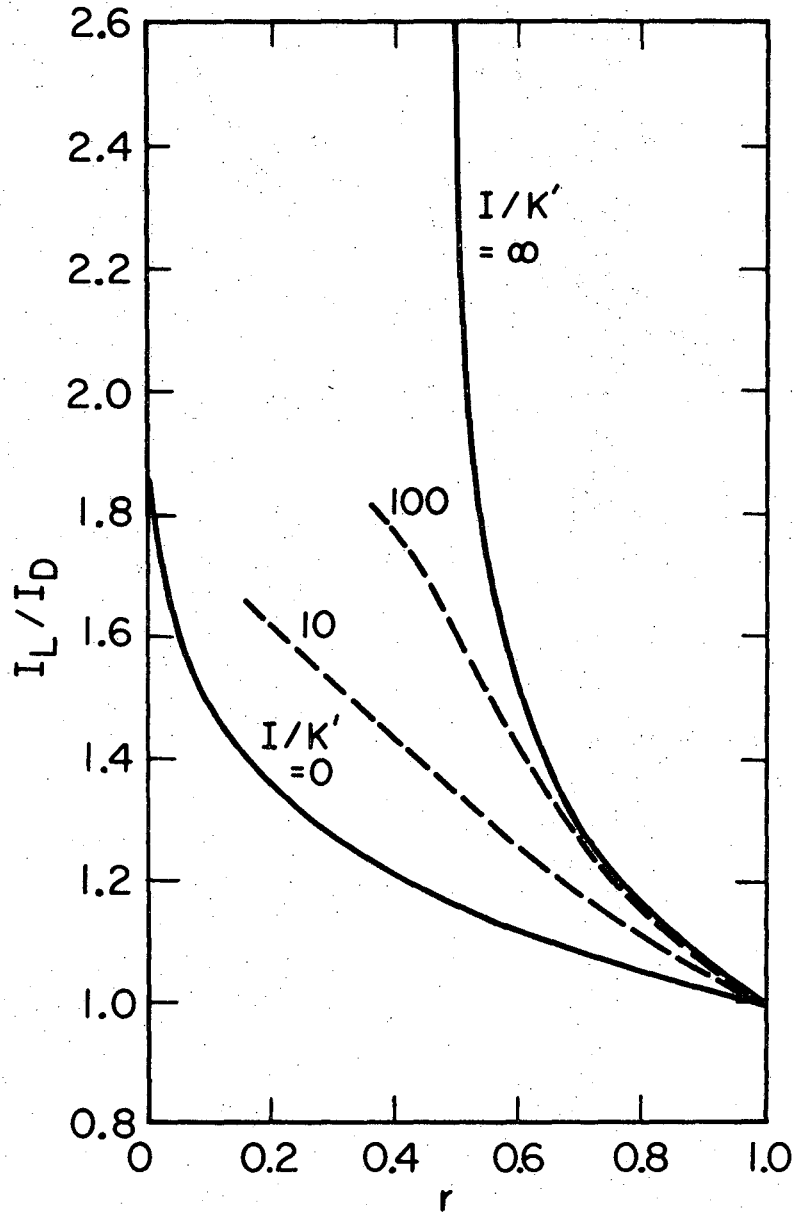
The two important parameters will then be the relative amounts of reactant and supporting electrolyte, expressed as

$$r = c_B^\infty / (c_A^\infty + c_B^\infty) \quad (4)$$

and the ratio I/K' of the ionic strength to the dissociation constant.

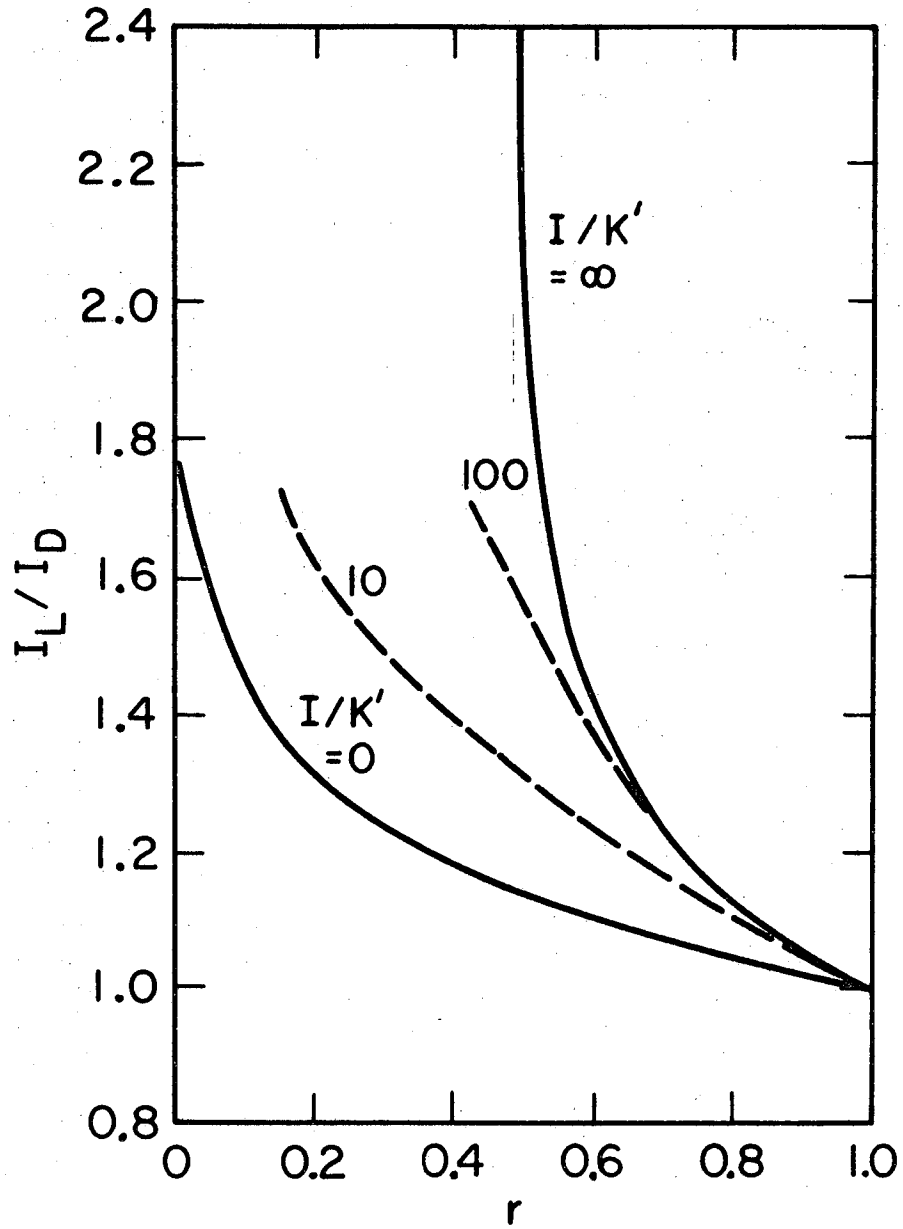
The effect of migration on limiting current is shown in figures 1 and 2 for the rotating-disk electrode and the stagnant diffusion cell. The ordinate, I_L/I_D , is the ratio of the limiting current to the limiting diffusion current of a well supported solution when the effect of viscosity variations is excluded. The abscissa is the ratio r of equation 4, and values of I/K' are given as a parameter. The two solid lines indicate the two extreme cases of complete ($I/K' = 0$) and no dissociation ($I/K' = \infty$) of bisulfate ions.

The concentration difference of sulfuric acid between the electrode surface and the bulk solution is shown in figures 3 and 4 for the two electrochemical systems. One may notice that the concentration



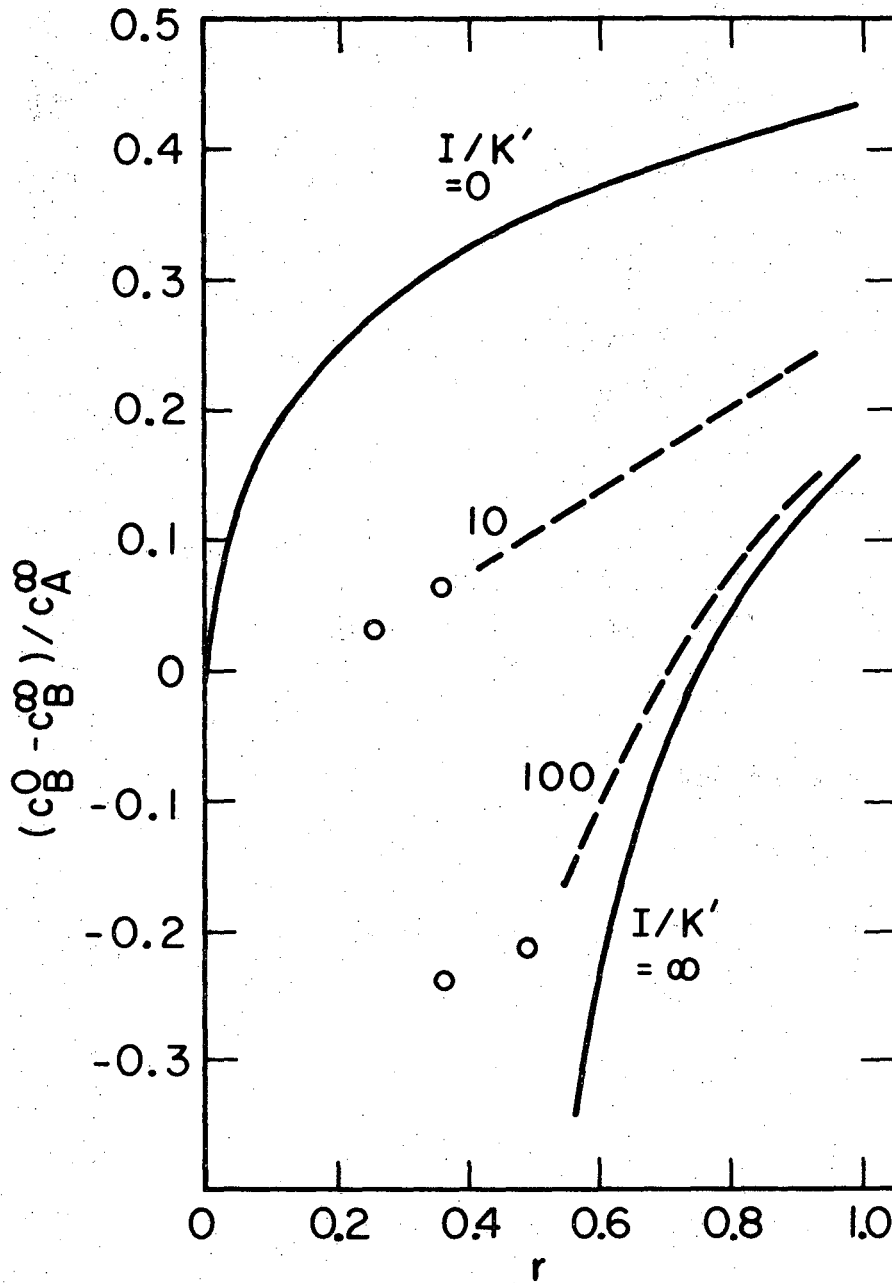
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Fig. 1. The effect of migration for a rotating disk electrode.



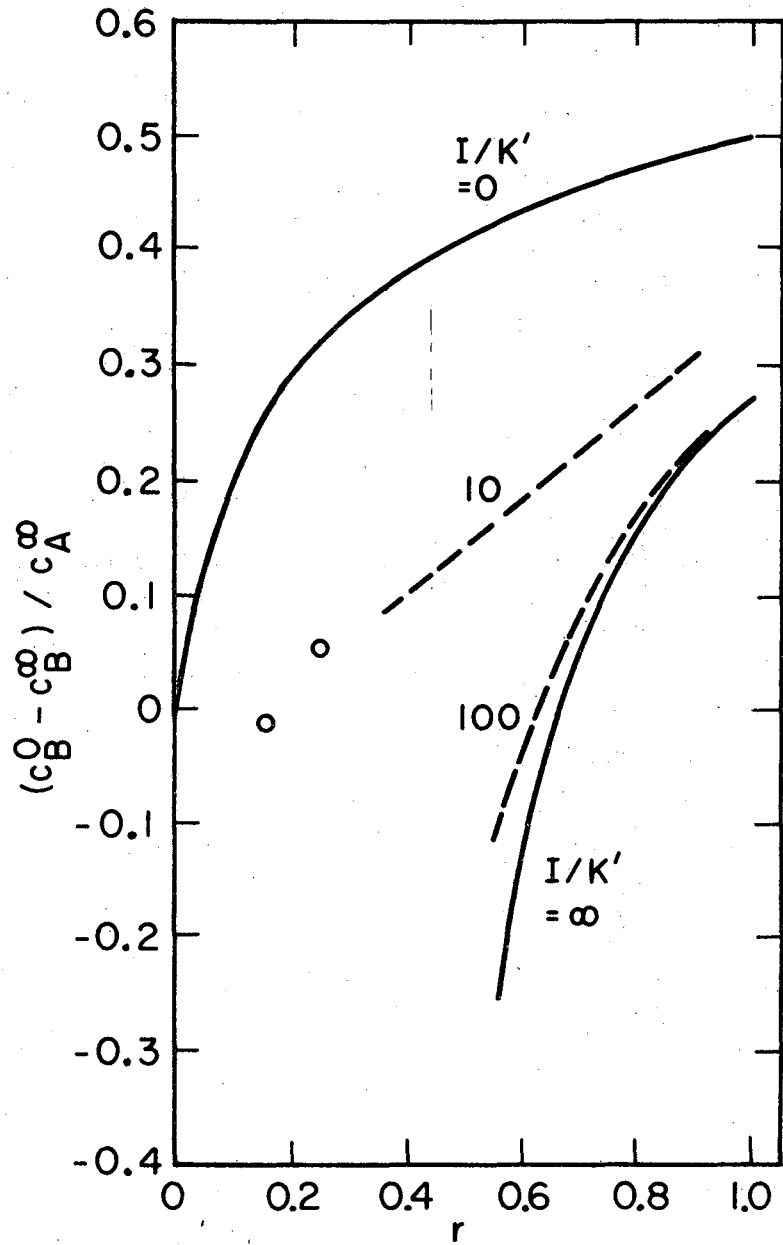
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Fig. 2. The effect of migration in a stagnant diffusion cell.



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Fig. 3. The surface concentration change for a rotating disk electrode.



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Fig. 4. The surface concentration change in a stagnant diffusion cell.

of sulfuric acid would even decrease near the electrode surface for some values of r when bisulfate ions are not completely dissociated. Qualitatively speaking, the bisulfate ions, containing hydrogen, are driven away from the electrode because of their negative charge. For no dissociation, $r = 0.5$ corresponds to a binary solution of copper bisulfate.

Theoretically, all the lines of figures 3 and 4 should go to $\Delta c_B / c_A^\infty = 0$ at $r = 0$, which means that the lines for high values of I/K' would pass through a minimum. However, the computer program does not converge at low values of r . The circles on figures 3 and 4 were calculated at a very slow convergence rate and are not considered completely reliable. An analytic solution can be obtained for a stagnant Nernst diffusion layer. Because this system is not of great physical interest, these results are put into the appendix.

While the dissociation constant K' is taken to be independent of position, it is not strictly a constant. It is related to the thermodynamic dissociation constant K by

$$K' = Kf_{\text{HSO}_4^-} / f_{\text{H}^+} f_{\text{SO}_4^{2-}}, \quad (5)$$

where f_i is the molar activity coefficient of the indicated ionic species. Consequently, K' was taken to be a function of the true ionic strength I_r of the bulk solution, where I_r is given by

$$I_r = \frac{1}{2} \sum_i z_i^2 c_i^\infty, \quad (6)$$

and where c_i is the concentration of the ionic species calculated with consideration of the dissociation equilibrium of bisulfate ions. The functional dependence of K' on I_r is based on the Raman-spectra investigation of sulfuric acid solutions by Young, Maranville, and Smith.⁹ The resulting correlation, covering the range of concentrations of sulfuric acid from 0 to 3 M, is plotted in figure 5 and given by

$$\ln(K'/K) = \frac{5.29\sqrt{I_r}}{1 + 0.56\sqrt{I_r}}, \quad (7)$$

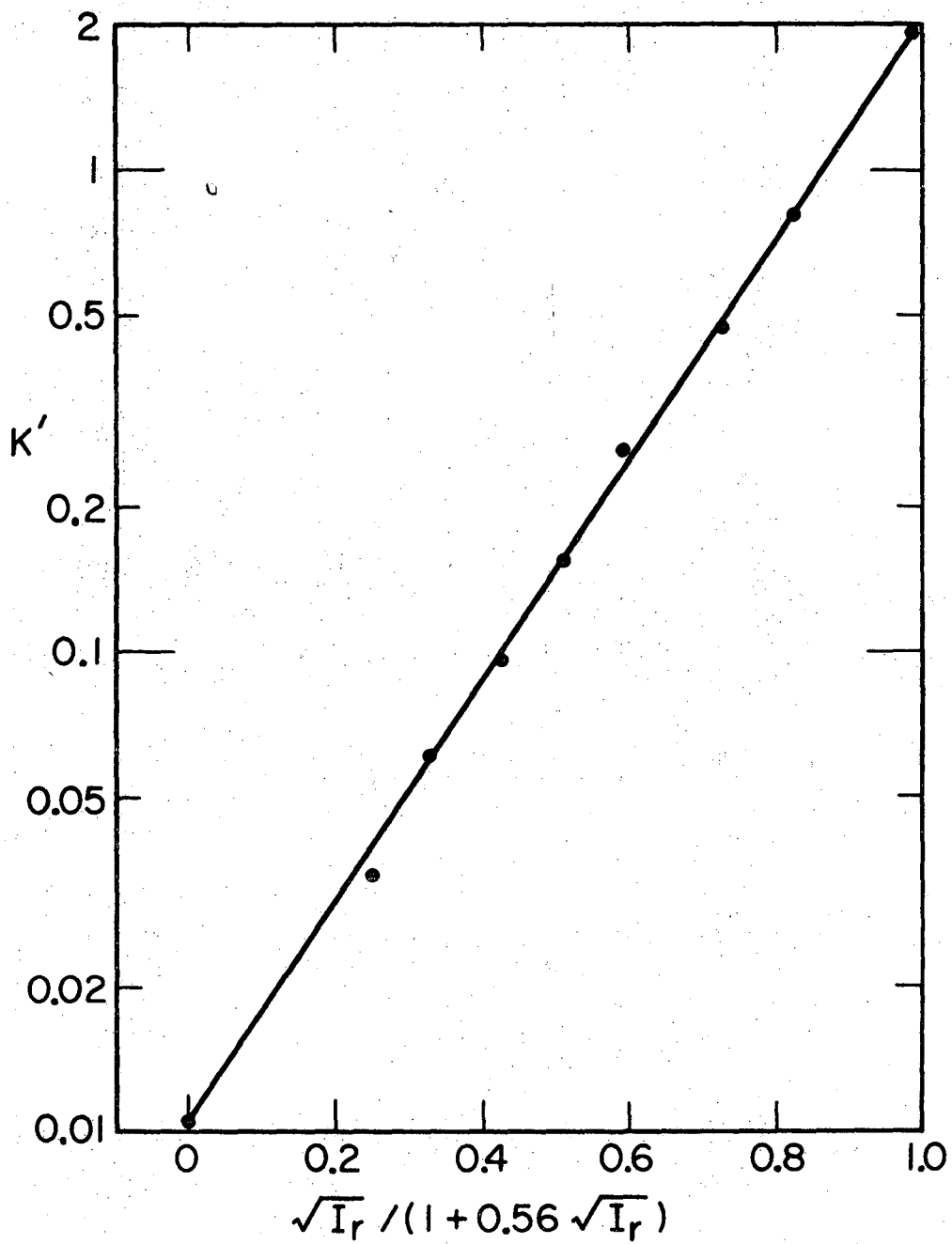
where $K = 0.0104$ mole/l and the true ionic strength I_r is expressed in mole/l.

Experimental Method and Results

Limiting currents in a stagnant diffusion cell

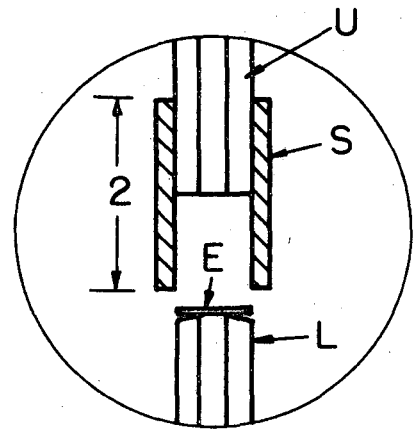
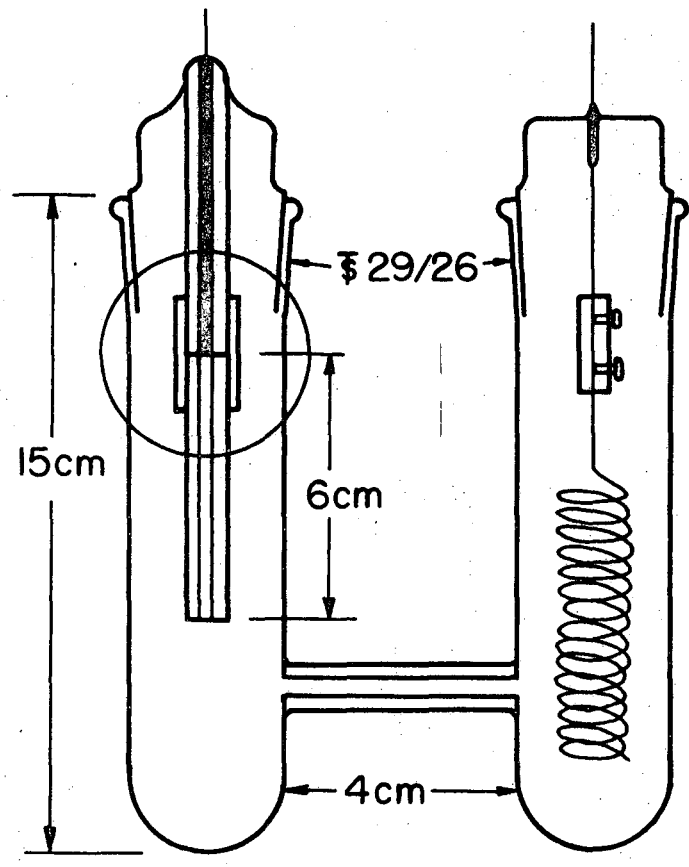
The cell was made of two pieces of precision-bore glass capillary tube. The glass capillary tube was chosen because of its good thermal conductivity and ease of cleaning in comparison with Lucite. To overcome the poor machinability of glass, the cell was assembled as shown in figure 6.

The tip of the lower part of the capillary (L) was ground in a small angle, the diameter was measured on a platform microscope, and a platinum electrode (E) was then carefully glued to the tip by epoxy. A short sleeve of glass tubing (S) was fused to the upper part of the capillary (U). After the epoxy had completely set (24 hours), the lower part was glued into the sleeve. Heating was avoided to prevent any change of the size and shape of the glass tubing. The upper part of the capillary was then filled with mercury for electrical contact.



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Fig. 5. Correlation of the second dissociation constant of sulfuric acid with the true ionic strength.



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Fig. 6. Stagnant diffusion cell.

Reagent grade copper sulfate and sulfuric acid were used for making all the solutions. The copper sulfate concentrations were analyzed by the electrogravimetric method, and sulfuric acid was titrated with standardized NaOH solution.

Before each run, the capillary cathode was cleaned with dilute nitric acid to remove all previously deposited copper and rinsed with distilled water followed by the solution. The platinum electrode was then predeposited with copper. For filling and emptying the cell, the solutions and nitric acid were handled with a platinum needle and glass-tipped syringe. (The needle is made of 80% platinum, 20% iridium, Hamilton Company, Inc., Whittier, California.)

The helically shaped anode was made of oxygen-free, high-purity copper wire. All experiments were carried out in a constant-temperature bath, and the temperature was controlled at $25 \pm 0.02^\circ\text{C}$.

For this experiment, the limiting current should be inversely proportional to the square root of time.¹ The limiting current densities, measured at constant potentials in the range from 0.3 to 0.4 V, are tabulated as $i_L\sqrt{t}$ in table 1. After they are divided by the migration factors I_L/I_D , calculated for partial dissociation of bisulfate ions, the values of $i_D\sqrt{t}$ are fairly close to a constant and are more nearly so after a subsequent correction for the various viscosities of the solutions used.

Values of the assumed dissociation constant K' and the calculated increase of sulfuric acid concentration at the electrode,

$(c_B^0 - c_B^\infty)/c_A^\infty$, are also included in table 1.

Table 1. Limiting current densities measured in a stagnant diffusion cell.

CuSO ₄ mole/l	H ₂ SO ₄ mole/l	r	measured $i_L \sqrt{t}$ (mA/cm ²)√sec	calculated I_L/I_D	$i_D \sqrt{t}$ (mA/cm ²)√sec	K'	$\frac{c_B^0 - c_B^\infty}{c_A^\infty}$
0.0999	0.050	0.334	34.6	1.365	25.4	0.1410	0.182
0.0998	0.100	0.501	32.8	1.255	26.1	0.1609	0.230
0.1000	0.125	0.555	32.4	1.222	26.5	0.1716	0.245
0.1003	0.175	0.636	31.6	1.176	26.9	0.1938	0.266
0.1001	0.250	0.714	30.9	1.134	27.2	0.2281	0.287
0.1024	0.810	0.888	26.0	1.048	24.8	0.5394	0.337
0.1008	0.888	0.899	25.4	1.043	24.4	0.5855	0.340
0.0986	0.998	0.912	24.8	1.038	23.9	0.6524	0.344
0.1005	1.085	0.916	25.2	1.036	24.3	0.7121	0.346
0.1006	1.195	0.924	24.9	1.032	24.1	0.7859	0.349
0.1006	1.295	0.927	24.8	1.030	24.1	0.8544	0.351
0.0999	1.375	0.934	24.6	1.028	23.9	0.9090	0.352
0.0999	1.473	0.937	24.4	1.026	23.8	0.9783	0.354

Concentration of sulfuric acid at electrode surface

The surface concentration of sulfuric acid was measured interferometrically with a Perkin-Elmer model 238 electrophoresis apparatus. The optical cells were made of quartz and purchased from the same company. A slight modification was made to the cell and is shown in figure 7. Two electrodes were made of oxygen-free, high-purity copper and fit exactly into the channels, passing a water leak test when the sides of the electrodes are properly greased.

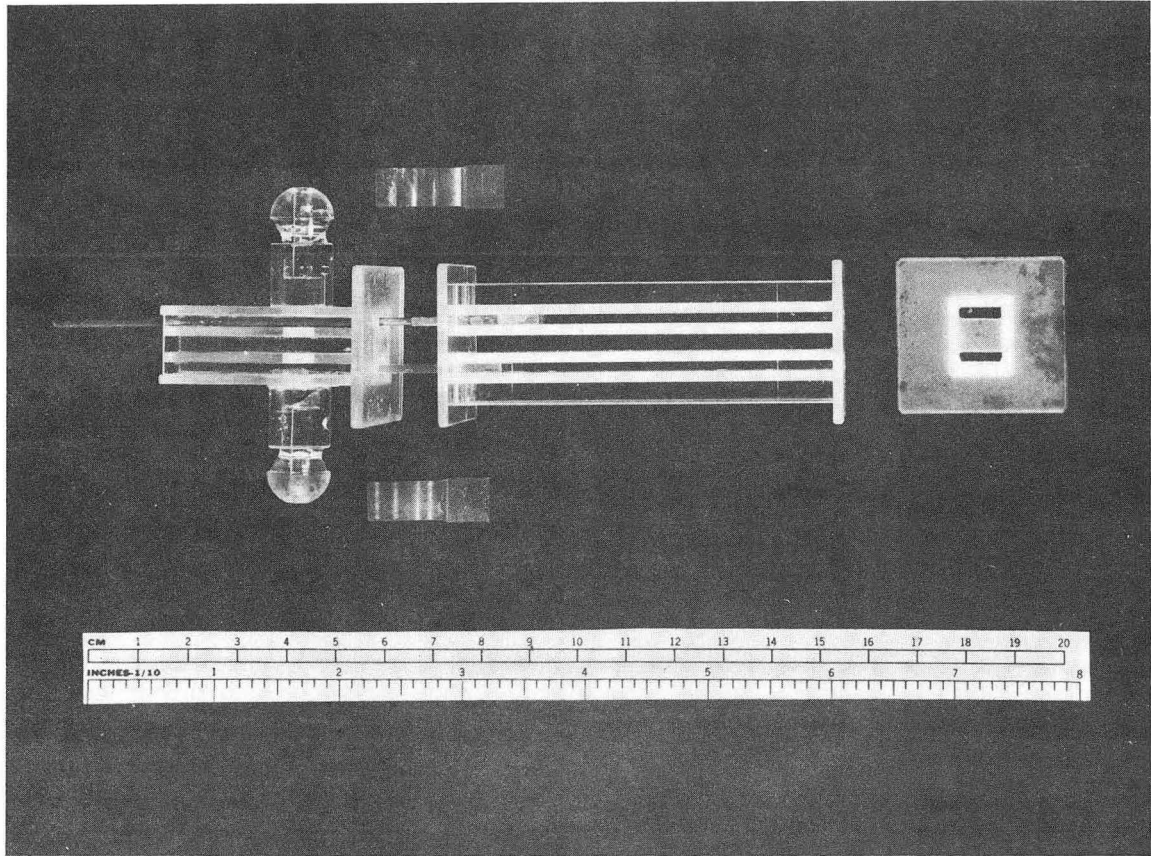
The basic principle in determining the surface concentration is that the number of fringe shifts m is proportional to the refractive index difference Δn :

$$m = (l/\lambda)\Delta n, \quad (8)$$

where l is the length of the light path across the cell and λ is the wavelength of the light. When the refractive index difference is determined between the bulk solution and the electrode surface, it is then possible to calculate the concentration of sulfuric acid from a known correlation of concentrations and refractive index.

However, the direct use of this method of determining the surface concentration suffers the drawbacks of lack of accurate refractive index data for the copper sulfate and sulfuric acid system measured with a mercury lamp ($\lambda=5461 \text{ \AA}$) and uncertainty in the cell dimensions.

It is therefore desirable to assume that the number of fringe shifts is proportional to the concentration difference over a small



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Fig. 7. Optical cell and electrodes.

concentration range. For a multicomponent system

$$m = k_A \Delta c_A + k_B \Delta c_B \quad (9)$$

where Δc_A and Δc_B are the concentration differences of copper sulfate and sulfuric acid, respectively. No accurate refractive index data are needed, but the constants k_A and k_B have to be determined experimentally from solutions of known concentrations. This is done by counting the number of fringe shifts across two solutions of known composition with the less dense solution above the heavier solution in the optical cell. One may refer to the detailed experimental procedure in reference 8.

Two runs were carried out in copper sulfate concentrations of 0.1 and 0.05 M with a sulfuric acid concentration of 1.0 M. The total applied potential between the two electrodes was 0.15 V for both runs. The numbers of fringe shifts reached constant values after a certain amount of time. The concentration of sulfuric acid at the electrode surface is then calculated from equation 9 with the assumption that the copper sulfate concentration drops to zero at the limiting current. More runs were made with higher applied potentials. The experimental results are tabulated in table 2.

Table 2. Concentration of sulfuric acid at the electrode surface in a stagnant diffusion cell at 25°C.

Run	28	29	38	40	42
$\text{CuSO}_4, c_A^\infty$	0.1 <u>M</u>	0.05 <u>M</u>	0.0315 <u>M</u>	0.062 <u>M</u>	0.062 <u>M</u>
$\text{H}_2\text{SO}_4, c_B^\infty$	1.0 <u>M</u>	1.0 <u>M</u>	1.0 <u>M</u>	1.0 <u>M</u>	1.0 <u>M</u>
Applied potential	0.15V	0.15V	0.30V	0.395V	0.550V
Observed fringe shifts	60	30	17	38.5	38
$c_B^0 - c_B^\infty, \text{M}$	0.0569	0.0284	0.0236	0.0314	0.0330
r	0.91	0.95	0.97	0.94	0.94
$(c_B^0 - c_B^\infty)/c_A^\infty$	0.57	0.57	0.75	0.50	0.53

Discussion and Conclusions

The limiting current densities measured with various ratios of copper sulfate to sulfuric acid support the contention that this system should be treated with partial dissociation of bisulfate ions rather than complete dissociation.

The ratios $\Delta c_B / c_A^\infty$ of the experimental results did not fall within the theoretical predictions. However, the values can be compared favorably with the value $-\Delta c_B / \Delta c_A = 0.71$ deduced from the results of one of Brenner's experiments.³

The concentration at the electrode surface is certainly an important quantity in natural convection and in corrosion problems. An electrophoresis optical apparatus proves to be useful for the direct measurement of this quantity, for comparison with values calculated indirectly in the course of limiting-current measurements.^{4,5} It should also be more reliable than the freezing method,³ against which several objections can be raised.

Acknowledgments

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Notation

c_i	concentration of species i (mole/cm ³)
c_A	concentration of copper sulfate
c_B	concentration of sulfuric acid
D_i	diffusion coefficient of species i (cm ² /sec)
f_i	molar activity coefficient of species i
F	Faraday's constant (coul/equiv)
i	current density (amp/cm ²)
I	ionic strength (mole/l)
I_D	limiting diffusion current
I_L	limiting current
I_r	"true" ionic strength (mole/l)
k_A, k_B	constants in equation 9 (l/mole)
K	thermodynamic dissociation constant (mole/l)
K'	equilibrium concentration ratio (mole/l)
l	length of light path across the cell (cm)
m	number of fringe shifts
n	index of refraction
N_i	flux of species i (mole/cm ² -sec)
q	see equation 21
r	see equation 4
R	see equation 21
t	time (sec)
u_i	mobility of species i (cm ² -mole/joule-sec)
x	distance from electrode (cm)
z_i	charge number of species i

δ thickness of Nernst diffusion layer (cm)

λ wavelength of light (cm)

ϕ electrostatic potential (volt)

superscripts

0 adjacent to the electrode

∞ in the bulk solution

Appendix. The Nernst stagnant diffusion layer

The steady migration and diffusion of three univalent ions in a stagnant layer of thickness δ was treated by Eucken.¹⁰ His correction factor for the effect of ionic migration on limiting currents was rejected by Heyrovský because it did not agree with experimental results for polarography with hydrogen ions. Eucken's treatment can be extended to include three ions of arbitrary valence, thus covering the copper sulfate-sulfuric acid system with complete dissociation or no dissociation of bisulfate ions as special cases.

The basic equations are three flux equations and the electro-neutrality relation:

$$N_1 = -z_1 u_1 F c_1 \frac{d\phi}{dx} - D_1 \frac{dc_1}{dx} = \frac{i}{z_1 F} \quad (10)$$

$$0 = -z_2 u_2 F c_2 \frac{d\phi}{dx} - D_2 \frac{dc_2}{dx} \quad (11)$$

$$0 = -z_3 u_3 F c_3 \frac{d\phi}{dx} - D_3 \frac{dc_3}{dx} \quad (12)$$

$$z_1 c_1 + z_2 c_2 + z_3 c_3 = 0 \quad (13)$$

These equations apply to steady processes in the diffusion layer in the absence of convection. Species 1 reacts at the electrode. Boundary conditions for these equations are

$$c_2 = c_2^\infty, c_3 = c_3^\infty, \phi = 0 \text{ at } x = \delta \quad (14)$$

$$c_1 = 0 \text{ at } x = 0 \text{ (at limiting current)}. \quad (15)$$

Integration of equations 11 and 12 gives

$$c_2 = c_2^\infty \exp \left\{ -\frac{z_2 u_2 F \Phi}{D_2} \right\}, \quad c_3 = c_3^\infty \exp \left\{ -\frac{z_3 u_3 F \Phi}{D_3} \right\}. \quad (16)$$

Substitution into the electroneutrality equation 13 gives

$$-z_1 c_1 = z_2 c_2^\infty \exp \left\{ -\frac{z_2 u_2 F \Phi}{D_2} \right\} + z_3 c_3^\infty \exp \left\{ -\frac{z_3 u_3 F \Phi}{D_3} \right\}, \quad (17)$$

and differentiation gives

$$z_1 \frac{dc_1}{dx} = F \frac{d\Phi}{dx} \left[\frac{z_2 u_2 c_2^\infty}{D_2} \exp \left\{ -\frac{z_2 u_2 F \Phi}{D_2} \right\} + \frac{z_3 u_3 c_3^\infty}{D_3} \exp \left\{ -\frac{z_3 u_3 F \Phi}{D_3} \right\} \right]. \quad (18)$$

These equations allow c_1 and dc_1/dx to be eliminated from equation 10, with the result

$$\begin{aligned} \frac{N_1}{D_1} = F \frac{d\Phi}{dx} & \left[z_2 c_2^\infty \left(\frac{u_1}{D_1} - \frac{z_2 u_2}{z_1 D_2} \right) \exp \left\{ -\frac{z_2 u_2 F \Phi}{D_2} \right\} \right. \\ & \left. + z_3 c_3^\infty \left(\frac{u_1}{D_1} - \frac{z_3 u_3}{z_1 D_3} \right) \exp \left\{ -\frac{z_3 u_3 F \Phi}{D_3} \right\} \right]. \end{aligned} \quad (19)$$

Integration gives

$$\frac{N_1 (x-\delta)}{D_1} = c_1^\infty - c_1 + \frac{u_1 D_2}{u_2 D_1} (c_2^\infty - c_2) + \frac{u_1 D_3}{u_3 D_1} (c_3^\infty - c_3). \quad (20)$$

Let

$$R = \frac{z_3 u_3 D_2}{z_3 u_3 D_2 - z_2 u_2 D_3} \text{ and } q = - \frac{z_2 c_2^\infty}{z_3 c_3^\infty} \quad (21)$$

At limiting current, equation 15 applies. Equation 17 then gives for the potential ϕ_0 at $x = 0$ the equivalent expressions

$$\exp \left\{ - \frac{z_2 u_2 F \phi_0}{D_2} \right\} = q^{R-1} \text{ and } \exp \left\{ - \frac{z_3 u_3 F \phi_0}{D_3} \right\} = q^R \quad (22)$$

Equation 20 can now be written at $x = 0$ as

$$\frac{I_L}{I_D} = - \frac{N_1 \delta}{D_1 c_1^\infty} = 1 + \frac{z_1 u_1 D_2}{z_2 u_2 D_1} \left[\frac{1-q^R}{1-q} \frac{1}{R} - 1 \right] \quad (23)$$

it being recognized that $-D_1 c_1^\infty / \delta$ is the limiting value of N_1 in the absence of a migration effect.

In the following special cases, we use the Nernst-Einstein relation throughout, and species 1 is the cupric ion.

Complete dissociation of bisulfate ion

Take species 2 to be hydrogen ions and species 3 to be sulfate ions. Now $R = 2/3$ and $q = r$, where r is defined by equation 4. The enhancement of the limiting current is expressed by

$$\frac{I_L}{I_D} = \frac{2+2r^{1/3}-r^{2/3}}{1+r^{1/3}+r^{2/3}} \quad (24)$$

and the excess concentration of sulfuric acid at the surface is given by

$$\frac{c_B^0 - c_B^\infty}{c_A^\infty} = \frac{r^{2/3}}{1+r^{1/3}+r^{2/3}} \quad (25)$$

No dissociation of bisulfate ion, $r > 0.5$

Take species 2 to be hydrogen ions and species 3 to be bisulfate ions. Now $q = 2r-1$ and $r = 1/2$. The enhancement of the limiting current is

$$\frac{I_L}{I_D} = \frac{3 - (2r-1)^{1/2}}{1 + (2r-1)^{1/2}}, \quad (26)$$

and the excess concentration of sulfuric acid at the surface is given by

$$\frac{c_B^0 - c_B^\infty}{c_A^\infty} = - \frac{1 - (2r-1)^{1/2}}{1 + (2r-1)^{1/2}} \quad (27)$$

No dissociation of bisulfate ion, $r < 0.5$

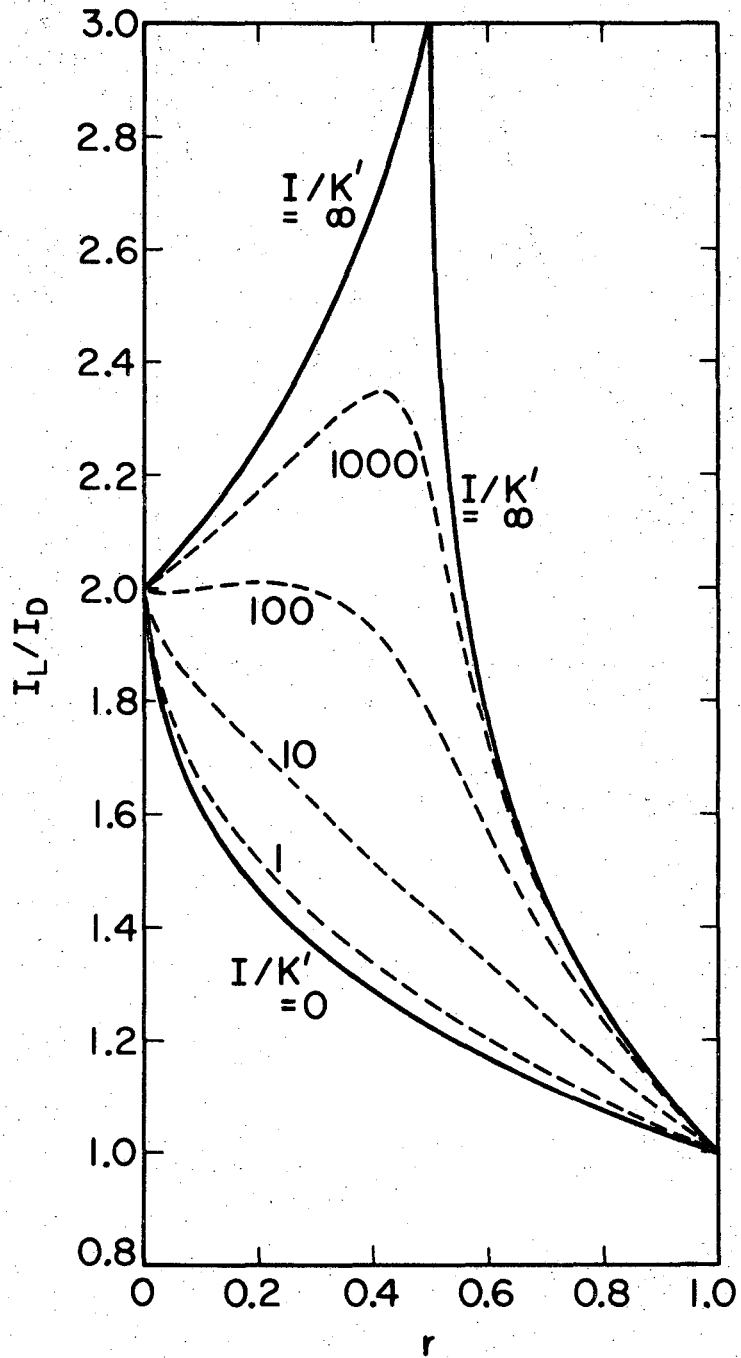
Take species 2 to be bisulfate ions and species 3 to be sulfate ions. In this case, the copper ion is the only cation; when its concentration drops to zero at the electrode surface, the remaining two anions have to be zero too, so that electroneutrality will be preserved. Equation 20 at $x = 0$ gives, with the Nernst-Einstein relation,

$$-\frac{N_1 \delta}{D_1 c_1^\infty} = \frac{I_L}{I_D} = 1 + \frac{c_2^\infty}{c_1^\infty} + \frac{c_3^\infty}{c_1^\infty} = \frac{2-r}{1-r}, \quad (28)$$

and the excess concentration of sulfuric acid at the surface is given by

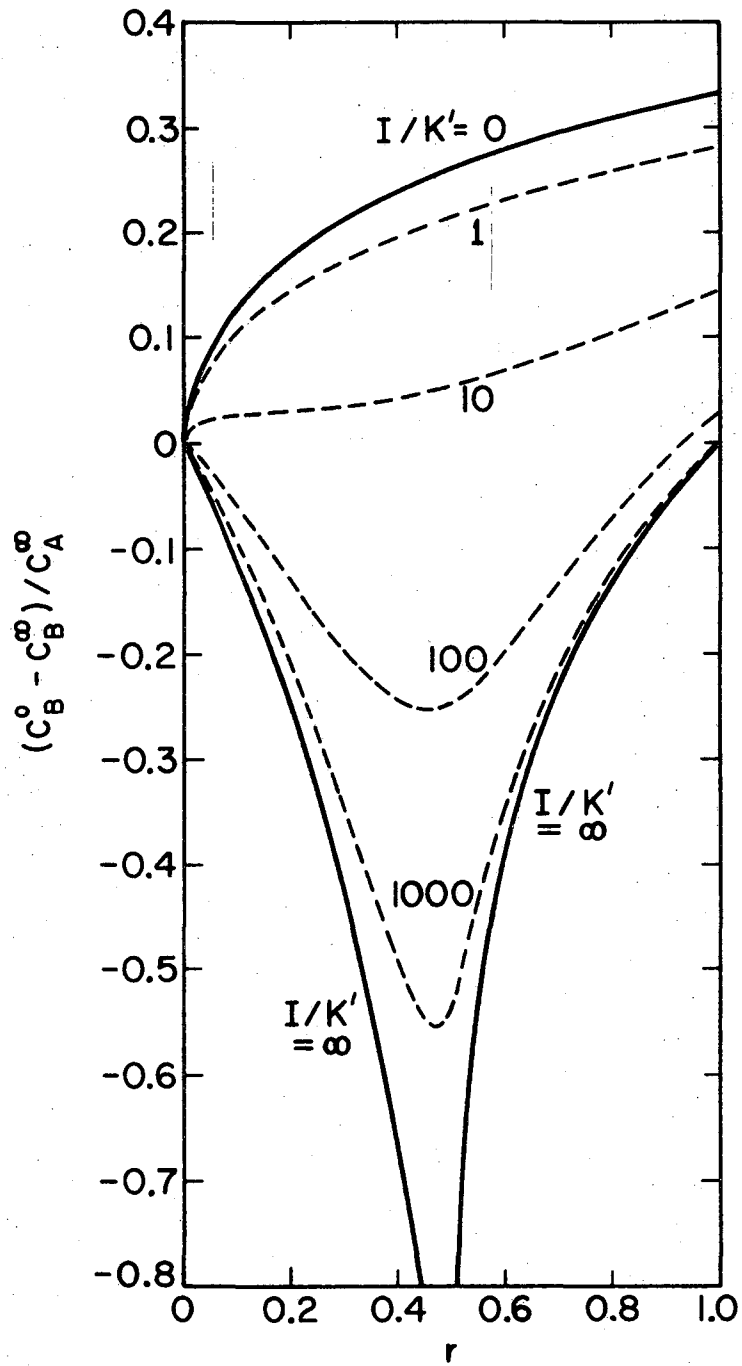
$$\frac{c_B^O - c_B^\infty}{c_A^\infty} = -\frac{c_B^\infty}{c_A^\infty} = \frac{-r}{1-r}. \quad (29)$$

These results are presented in figures 8 and 9. When the Nernst-Einstein equation is obeyed, equations 16 reduce to Boltzmann distributions. Under this same restriction, the nonreacting ions follow a Boltzmann distribution even when there is partial dissociation. This fact allows us to calculate the dashed curves on figures 8 and 9 without having to solve numerically any differential equations.



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Fig. 8. The effect of migration in a Nernst diffusion layer.



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Fig. 9. The surface concentration change in a Nernst diffusion layer.

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