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DETERMINATION OF THE ZINCATE DIFFUSION COEFFICIENT AND ITS APPLICATION TO ALKALINE BATTERY PROBLEMS

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ABSTRACT

The diffusion coefficient for the zincate ion at 24° C was found to be 9.9×10^{-7} cm^2/sec ±30 percent in 45 percent potassium hydroxide and 1.4×10^{-7} cm^2/sec ±25 percent in 40 percent sodium hydroxide. Comparison of these values with literature values at different potassium hydroxide concentrations show that the Stokes-Einstein equation is obeyed. The diffusion coefficient is characteristic of the zincate ion (not the cation) and independent of its concentration. Calculations with the measured value of the diffusion coefficient show that the zinc concentration in an alkaline zincate half cell becomes uniform throughout in tens of hours by diffusion alone. Diffusion equations are derived which are applicable to finite size chambers. Details and discussion of the experimental method are also given.

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SUMMARY

The diffusion coefficient for the zincate ion at 24° C was found to be 9.9×10^{-7} cm^2/sec ±30 percent in 45 percent potassium hydroxide and 1.4×10^{-7} cm^2/sec ±25 percent in 40 percent sodium hydroxide. Comparison of these values with literature values at different potassium hydroxide concentrations show that the Stokes-Einstein equation is obeyed. The diffusion coefficient is characteristic of the zincate ion (not the cation) and independent of its concentration. Calculations with the measured value of the diffusion coefficient show that the zinc concentration in an alkaline zincate half cell becomes uniform throughout in tens of hours by diffusion alone. Diffusion equations are derived which are applicable to finite size chambers. Details and discussion of the experimental method are also given.

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INTRODUCTION

A renewed interest in rechargeable batteries has led us to begin a study of the alkaline zinc electrode (Ref. 1). An important aspect of the investigation involves the transport of the zincate ion, $Zn(OH)_4^{=}$; two modes are possible: diffusive and convective. Measurements of the diffusion coefficient of the zincate ion, D, in alkaline media have been made (Refs. 2 and 3) but we desired to know D under specific experimental conditions, i.e., high zincate concentration. Note that although one speaks about the diffusion of zincate, it is the apparent diffusion coefficient of a metal (e.g., potassium) zincate that is measured. Equations have been derived that relate the measured value to that for the zincate ion (Ref. 4, pp. 119-121; and Ref. 5, pp. 124-126). Nevertheless, it is the apparent diffusion coefficient of potassium zincate as measured that should be applied to an actual problem.

Herein, we report the room temperature diffusion coefficient for both potassium and sodium zincates. The concentrations used during the measurements for potassium zincate approximated those used in the NASA silver/zinc and nickel/zinc batteries. The method used to determine the diffusion coefficients is described, and its applicability discussed. Finally, the diffusion coefficient for potassium zincate is used to answer some questions concerning the zinc-zincate half cell present in secondary batteries.

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EXPERIMENTAL DETAILS

Essence of Method

Various methods (Ref. 5, pp. 62-76) have been used to determine diffusion coefficients in hydrodiffusion systems. A popular method involves diffusion through a glass frit. Because the highly alkaline solutions with which we are involved are corrosive to glass frit, we designed a method which can make use of only materials that are resistant to the corrosive solutions. Our method is a modification of one used in solid state diffusion: a sample (a vertical column of solution) containing initially no zincate was butted against another sample (vertical column of solution) containing initially a uniform concentration of zincate, C_o, in moles per liter; the more dense sample was on the bottom. The concentration profile was then measured after certain times and D was calculated from Eq. [1] (Ref. 6, Eq. 2.14).

$$\frac{2C}{C_o} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad [1]$$

where C is the zincate concentration at time t and distance x from the butted interface. Equation (1) applies only for sufficiently long columns and when D is not a function of C. (See Appendix A for equations applicable to short columns.) Instead of sectioning the column to determine C, we adapted a technique that has been used to measure the zincate diffusion rate through battery separators (Refs. 7 and 8): the potential, E, was measured between an amalgamated zinc electrode at distance x and an amalgamated zinc electrode in a reference chamber of zincate concentration C_o. Eq. [2] was used to calculate C/C_o.

$$\frac{C}{C_o} = e^{-2EF/RT} = e^{-78.1E} \qquad [2]$$

where F is the Faraday; R, the gas constant; and T, absolute temperature. Eq. [2] should be applied only when the effect of gradients of the cation and hydroxide ion concentrations can be ignored (due to their high and nearly uniform concentrations). When Eqs. [1] and [2] both apply, they can be combined as follows:

$$2e^{-78.1E} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad [3]$$

Apparatus

Schematics of the cell are shown in Fig. 1 (a: disassembled; b: in filling configuration; and c: in running configuration). The cell consists of three chambers. The upper chamber is the one that contains aqueous solution of potassium or sodium hydroxide but initially no zincate. The middle one contains the aqueous solution of potassium or sodium hydroxide with

the initially uniform zincate concentration, C_o. The lower one is the reference chamber; it is separated from the middle chamber by a cellulose membrane (2.8 nm pore size, 90 μm dry thickness). The concentrations of the lower chamber are identical to the initial concentrations in the middle chamber. The zincate concentration in the lower chamber remains essentially constant during a $2\frac{1}{2}$ day experiment because of the relatively slow diffusion of the ions through the cellulose (Ref. 7) and the small concentration gradients existing across the cellulose in our experiments, indicated by negligible potentials between the reference electrode and lowest electrode in the middle chamber. Also, preliminary experiments indicated negligible gradients within the reference chamber.

Clamping the polymethylmethacrylate spacers (Fig. 1(a)) to form the chambers (Fig. 1(b)) served to prevent leaking of the electrolyte at the zinc electrodes. Spacers were either 0.142 or 0.290 centimeter thick. The zinc electrodes were made from 0.005 centimeter thick zinc sheet of 5N purity. These were amalgamated in situ by contact with a saturated mercuric chloride solution for two minutes. Amalgamating only the portion of an electrode that contacted the electrolyte prevented the zinc tabs which were used for electrical contact from becoming too brittle. After amalgamation, the cell was washed with water, disassembled and dried before assembly for a diffusion experiment.

Chemicals

The zinc sheet was 5N pure. The stock potassium zincate solution was made by dissolving 50 grams of reagent grade zinc oxide, ZnO, in enough reagent grade nominally 45 percent potassium hydroxide, KOH (carbonate free) to make 500 milliliter. Typical analyses of such solutions have shown them to be 1.21 molar in potassium zincate and 9 molar in KOH. A lesser concentration of potassium zincate (0.30 M) was made by dilution of the stock solution with 45 percent KOH solution. The sodium zincate solution was made by dissolving 35 grams of the ZnO in enough (338 ml) 40 percent (14.3 M) certified A.C.S. grade sodium hydroxide, NaOH, aqueous solution to make 345 ml. The resultant solution was then 1.43 molar in sodium zincate and 11.2 molar in NaOH. Note that the concentrations need not be known to calculate D; see Eq. [3]. The solutions in the upper chamber were pure hydroxide solutions: 45 percent KOH for use with the potassium zincate and 40 percent NaOH for use with the sodium zincate.

In a preliminary experiment, in order to match more closely the concentration of hydroxide in the upper chamber with that in the middle chamber (which of course would mismatch the cation concentrations) 37 percent KOH was used in the upper chamber instead of 45 percent: in this case, the data were scattered with respect to Eq. [1] and deemed unreliable. This indicated to us that it was the cation concentrations that should be matched.

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Procedure

In preparation for a diffusion experiment, the cell was assembled in the filling position (Fig. 1(b)) so that the upper and middle chambers solutions could not mix. The chambers were filled with the proper solutions. The cell was positioned rigidly and then the run was begun (corresponding to $t = 0$) by carefully sliding the upper chamber into the running configuration (Fig. 1(c)). The potential between each electrode and the reference was fed sequentially into a digital voltmeter and printer. The temperature during the course of all experiments was 24°±1° C.

RESULTS AND DISCUSSION

The Diffusion Coefficient

Profile of zincate concentration. - The data for 1.21 molar potassium zincate butted against 45 percent KOH are shown in Fig. 2 (2 experiments); C/C_o is plotted against $x/\sqrt{t}$. In Fig. 2, an attempt was made to correct at least partially for any initial disturbance, i.e., convective mixing by the sliding of the upper chamber; this was done by subtracting values at 30 minutes from corresponding subsequent values as follows:

For upper chamber: $$\left(\frac{C}{C_o}\right)_{\text{corrected}} = \left(\frac{C}{C_o}\right)_{\text{measured}} - \left(\frac{C}{C_o}\right)_{\text{30 min. value}} \quad [4]$$

For middle chamber: $$E_{\text{corrected}} = E_{\text{measured}} - E_{\text{30 min. value}} \quad [5]$$

The solid line in Fig. 2 corresponds to a D of 9.9×10^{-7} cm^2/sec; its calculation is discussed later. The curve fits the general profile of the data points; thus the diffusion law for constant D (Eq.) appears to be applicable. The data points for electrodes with x values greater than one sixth of the chamber length should deviate from the curve near $C/C_o = 0.5$ (see Appendix A); this is not apparent in Fig. 2. All points near $C/C_o = 0$ and $C/C_o = 1$ do deviate from the curve; this may be due to convective transport effects and/or uncertainty in initial values of E arising in part from strains in the zinc metal collectors.

The profile of the 0.3 molar potassium zincate concentration is similar to that in Fig. 2. The profile of the sodium zincate concentration also approximates that predicted by Eq. [1] but with a D of about 1.4×10^{-7} cm^2/sec.

From an examination of potassium zincate data as well as those for sodium zincate, we have drawn the following conclusions concerning the reliability of individual data points. Data points are more reliable when obtained from the upper chamber electrodes (those at which the zincate concentration builds up) and for electrode closer to the interface (butted surface). The electrode data close to the interface are also more reliable for mathematical reasons; see Appendix A. The most reliable values

of C/C_o are those between about 0.15 and 0.35. In order to prevent an interruption of our discussion of D and its implications, our evaluation of the general method is contained in Appendix B.

Calculation of D values. - To calculate D values, only the most reliable values of C/C_o were used; that is, those between 0.15 and 0.35. A value of D for each reliable data point was calculated from Eq. [3]. Corrections introduced by Eqs. [4] and [5] are very small for these data and were ignored. For potassium zincate we obtained the average D value (from 14 data points) of 9.9×10^{-7} $cm^2/sec\pm30$ percent mean deviation. For sodium zincate the average D (from 11 data points) was 1.4×10^{-7} $cm^2/sec\pm25$ percent. The average value of D for 0.3 molar potassium zincate was slightly higher than that for 1.21 molar, but was within the mean deviation; thus, indications are again that D is not a function of zincate concentration.

Agreement with other data. - In Fig. 3, the room temperature value of D for potassium zincate (Refs. 2 and 3) is plotted against potassium ion concentration. The D values in Ref. 2 appear to be due to a recalculation of data in Ref. 9. Our value of D falls on the curve defined by the other authors' data. The data other than ours was obtained via the Ilkovic equation at extremely low zincate concentration, about 10^{-3} molar. Our good agreement with their data emphasizes that D is constant over a wide range of zincate concentration.

Plotting D in terms of hydroxide concentration rather than potassium ion concentration would displace our data with respect to those of other investigators. Their hydroxide concentration essentially equals their potassium ion concentration while ours does not because of our high zincate concentration. With such a plot of D against hydroxide concentration our D would be about one third that predicted from these data. A logical inference would be that it is the potassium ion and not the hydroxide that is affecting the value of D.

To obtain a comparison for our sodium zincate data, we measured the permeation rate of both potassium zincate and sodium zincate through cellulose. (The method is described in Ref. 7.) Because cellulose is not an ion selective membrane, the ratio of the two permeation coefficients should equal the ratio of corresponding diffusion coefficients. Experimentally, we found 7.3 for the ratio of the permeation coefficient of potassium zincate to that for sodium zincate. This is good agreement with 7.1, the ratio of the corresponding diffusion coefficients. The low diffusion coefficient for sodium zincate with respect to that for potassium zincate is also in accord with the fact that the charging polarization is greater for the zinc electrode in NaOH than in KOH.

Theoretical effect of supporting electrolyte. - Experimentally, we have already seen a great effect of the supporting electrolyte on D. Let us now examine the phenomenological and widely used equation that relates the apparent value of D to the true D_z^* for the zincate ion.

$$D = D_z^* \left(1 + 2 \frac{\frac{D_M^* G_M}{G_z} - \frac{D_H^* G_H}{G_z} - D_z^*}{\frac{D_M^* C_M}{C_z} + \frac{D_H^* C_H}{C_z} + 2D_z^*} \right) \qquad [6]$$

where G refers to the gradients; C, the concentrations; D^* the true diffusion coefficients; z, the zincate ion; M, the cation; and H, the hydroxide ion (Ref. 5, pp. 124-126). The value of D should approach D_z^* at sufficiently high electrolyte (hydroxide) concentration (Ref. 5, p. 126). The value of D_z^* can then be related to η (viscosity coefficient) and r, the apparent radius of the zincate ion via the Stoke-Einstein equation (Ref. 2).

$$D = \frac{kT}{6\pi\eta r} \qquad [7]$$

where k is the Boltzmann constant; and T, the absolute temperature. Handbook values of η for the solvents (hydroxide solution, Ref. 10) can be used with little error for the η values of the solutions when the latter are not available.

Fig. 4 gives a plot of D against the reciprocal of η. The square points (Ref. 3) determine a good straight line through the origin in agreement with Eq. [7]. The other data, except for the bracketed point, fall reasonably close to the line. McBreen (Ref. 2) also plotted D against $1/\eta$ but concluded that there was nonlinear dependence due to the existence of the bracketed point.

The straightness of the line in Fig. 4 indicates an essentially constant r (Eq. [7]) independent of alkali concentration. This in turn indicates the same zincate species (i.e., $Zn(OH)_4^=$) at all alkali concentrations. The slope of the curve (Fig. 4) yields an r of about 1.9 Å.

Of much interest is the fact that our sodium zincate data point falls very near the straight line (Fig. 4). Thus the low diffusion coefficient for sodium zincate with respect to that for potassium zincate might be attributable solely to the high viscosity of the sodium hydroxide solution. This is additional evidence that the D measured corresponds to D_z^*, the diffusion coefficient for the zincate ion. Our results give no direct evidence as to the applicability of Eq. [6].

Recently (Ref. 1) we found that the transition from mossy to dendritic electrodeposited zinc appeared to be dependent on the hydroxide ion concentration; our present findings might indicate that this dependence is only a secondary one and that the primary dependence is on the viscosity of the solution. Moreover, the dependence of D on viscosity (applicability of the Stokes-Einstein equation) implies that the use of additives which lower the viscosity of the electrolyte in a battery can increase D, and thus lower concentration polarization.

Applications

Electrode boundary layer thickness. - In an earlier report (Ref. 1) we described the existence of a boundary layer during the electrodeposition of zinc from a potassium hydroxide solution (simulation of charging a silver/zinc or nickel/zinc battery). Not enough data were available at that time to calculate the thickness of the boundary layer. The concentrations involved in that work were the same as those described in this report. The boundary layer thickness, y, can be calculated from the following equation.

$$y = \frac{D}{P} \qquad [8]$$

where P, the permeation coefficient through the layer, is 4.7×10^{-4} cm/sec; it is the reciprocal of γ_1 given in Ref. 1. The boundary layer thickness, y, is thus found to be about 20 μm for a solution that is 9 molar in KOH and 1.21 molar in potassium zincate. One would of course expect y to be a function of KOH concentration.

Zincate distribution. - We now desire to see what effect a D of 9.9×10^{-7} cm^2/sec has on the zincate concentration profile in a secondary battery if ion transport occurs by diffusion alone. We have treated the subject in a manner to minimize assumptions; e.g., no charging or discharging rates have to be assumed. We start by assuming the most unfavorable starting situation for attaining a uniform zincate concentration; that is, at zero time all the zincate is present at the surface of the zinc metal collector. It may be present either in solution or as a precipitate. First, we will discuss the former case; the equations that are applicable are derived in Appendix C. Of importance to us is the time, t, required to attain a uniform concentration (within one percent).

$$t\ (\text{sec}) = \frac{0.5\ \ell^2}{D} \qquad [9]$$

A typical value for ℓ is about 0.15 centimeter (NASA silver/zinc alkaline battery); by using our experimental value for D, the time required is about 3 hours. Even if D is an order of magnitude less due to the separator present in the battery, the time required for essentially uniform zincate concentration is still quite short.

The situation where essentially all the zincate at the surface of the collector is present as a precipitate, appears to be an even less favorable situation for attaining a uniform zincate concentration. This is a possible situation though not probable because zincate will precipitate when saturation is grossly exceeded. According to our unpublished data, zincate precipitates readily from 45 percent KOH when it exceeds 2.5 times saturation (3 molar). The diffusion process starting with a precipitate is envisioned as follows: as dissolved zincate diffuses out from the electrode, the

zincate precipitate dissolves rapidly to keep the surface concentration at saturation (about 1.2 molar in 45 percent KOH) until the precipitate is exhausted. During this period, the following equation (Ref. 6, Eq. 4.18 is applicable.

$$\frac{M_t}{M_\infty} = 1 - \sum_{m=0}^{\infty} \frac{8}{(2m+1)^2} e^{-D(2m+1)^2\pi^2 t/4\ell^2} \qquad [10]$$

where ℓ is the length of the chamber and m is the number of the term. When M_t is the total mass available per unit area, M_∞ is the mass per unit area if the entire electrolyte could be at 1.2 molar, t becomes the time required for complete dissolution of the precipitate. M_t and M_∞ are respectively about 0.11 and 0.18 millimoles/cm^2 for the NASA silver/zinc battery. If $Dt/\ell^2 > 0.35$, omission of $m > 0$ causes only a 0.01 percent error in the sum. If this is true, we may write

$$t(\text{sec}) = \frac{-4\ell^2}{D} \ln\left[\frac{\left(1 - \frac{M_t}{M_\infty}\right)\pi^2}{8}\right] \qquad [11]$$

For the NASA silver/zinc battery, the time to attain complete dissolution would be 18 hours. Adding 3 hours (maximum time required for a uniform concentration starting from a completely soluble system) to this number, yields only 21 hours, which is still a relatively short time for attaining a very uniform concentration starting with a precipitate at the electrode.

The situation of course would be different if the dissolution of the precipitate were the rate-determining step. However, the NASA silver/zinc battery is regularly charged in 2 hours so that a precipitate if present must have a relatively fast rate of dissolution which could not be rate determining.

Without going into effects of ion selective membranes and complex formation (both are beyond the scope of our present report) we see no additional situations that might exist to affect the zinc concentration profile. We conclude that for a usual zinc alkaline half cell, the zincate concentration becomes uniform in a relatively short period of time (tens of hours) for any state of discharge. This means that prolonged standing cannot further affect the zincate profile and any detrimental effects caused by standing are not directly attributable to the concentration profile. In addition, the uniformity in concentration becomes an ideal starting condition in calculations of profile during various types of charging, e.g., pulse charging. Such calculations, however, should be performed with the functional D for the particular battery configuration (separator and electrolyte) under consideration.

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Because diffusion is so rapid, transport by convection in our present discussion would be a moot point.

CONCLUDING STATEMENTS

1. The diffusion coefficients for potassium zincate and sodium zincate have been determined at high zincate concentrations.

2. They are highly dependent on the viscosity of the solution, following the Stokes-Einstein equation.

3. The measured values of D are characteristic of the zincate ion (not the cation) and independent of its concentration.

4. Because of the magnitude of D, the zincate concentration in an alkaline battery can become uniform in tens of hours. Thus, in terms of zincate profile, prolonged standing of a discharged cell can cause no detrimental effects.

APPENDIX A

EQUATIONS FOR FINITE SIZE DIFFUSION CELLS

The purpose of this appendix is to determine if Eq. [1] for an infinite length diffusion cell can be used for our experimental setup. Crank (Ref. 6, Eq. 2.17) presents an equation which gives the concentration profile for the diffusion system consisting of two butted columns of finite length.

$$C = \frac{C_o}{2} \sum_{-\infty}^{\infty} \left(\operatorname{erf} \frac{h + 2m\ell - x'}{2\sqrt{Dt}} + \operatorname{erf} \frac{h - 2m\ell + x'}{2\sqrt{Dt}} \right) \qquad [A1]$$

where

ℓ is the total length of both columns

h the length of the "zincate rich" column

x' distance measured from the end of the "zincate rich" column

$C = C_o$ at $t = 0$ for $0 < x' < h$

$C = 0$ at $t = 0$ for $h < x' < \ell$

To use Eq. [A1] it must be converted to our spacial coordinate system. Thus we set

$$x' = h + x \qquad [A2]$$

and

$$\ell = 2h \qquad [A3]$$

We also define q to be the ratio of half the cell length to the distance (from the interface) at which the concentration is measured.

$$q = \frac{h}{x} \qquad [A4]$$

Combining Eqs. [A1] through [A4] yields

$$C = \frac{C_o}{2} \sum_{-\infty}^{\infty} \left\{ \operatorname{erf} \frac{(4mq - 1)x}{\sqrt{4Dt}} + \operatorname{erf} \frac{[2q(1 - 2m) + 1]x}{\sqrt{4Dt}} \right\} \qquad [A5]$$

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Because this equation [A5] is relatively difficult to handle, we derived the equation in simpler form by returning to the general form of the equation for planer diffusion (Ref. 6, Eq. 2.25).

$$C = \sum_{m=1}^{\infty} (A_m \sin \lambda_m x' + B_m \cos \lambda_m x') e^{-\lambda_m^2 Dt} \qquad [A6]$$

where the A_m's, B_m's, and λ_m's are constants. The coordinate system and the limits are the same as those for Eq. [A1] so that Eq. [A6] can be reflected at 0, ℓ, 2ℓ, etc. thereby one finds

$$\lambda_m = \frac{m\pi}{\ell} \qquad [A7]$$

$$A_m = 0 \qquad [A8]$$

Via the limits used for Eq. [A1], evaluation of the Fourier series constants (Ref. 11, p. 71), and Eqs. [A7] and [A8]; Eq. [A6] may be written for $t = 0$.

$$C = C_o \left[\frac{h}{\ell} + \sum_{m=1}^{\infty} \frac{2}{\pi m} \sin\left(\frac{m\pi h}{\ell}\right) \cos\left(\frac{m\pi x'}{\ell}\right) \right] \qquad [A9]$$

From Eq. [A9], the B_m's become known and Eq. [A6] for any time may be written as follows.

$$\frac{C}{C_o} = \frac{h}{\ell} + \sum_{m=1}^{\infty} \frac{2}{\pi m} \sin\left(\frac{m\pi h}{\ell}\right) \cos\left(\frac{m\pi x'}{\ell}\right) e^{-(m\pi)^2 Dt/\ell^2} \qquad [A10]$$

Transforming Eq. [A10] into our set of variables via Eqs. [A2] to [A4] gives:

$$\frac{C}{C_o} = \frac{1}{2} + \sum_{\text{odd } m} \frac{2}{\pi m} \sin\left(\frac{m\pi}{2}\right) \cos\left[\frac{m\pi}{2}\left(1 + \frac{1}{q}\right)\right] e^{-\left(\frac{m\pi}{4q}\right)^2 \Big/ \left(\frac{x}{2\sqrt{Dt}}\right)^2} \qquad [A11]$$

or

$$\frac{C}{C_o} = \frac{1}{2} - \sum_{\text{odd } m} \frac{2}{\pi m} \sin\left(\frac{m\pi}{2q}\right) e^{-\left(\frac{m\pi}{4q}\right)^2 \Big/ \left(\frac{x}{2\sqrt{Dt}}\right)^2} \qquad [A12]$$

Fig. 5 is a plot of C/C_o against $x/2\sqrt{Dt}$ for various values of q. The curves are compared with Eq. [1] (dashed line Fig. 5)

$$C = \frac{C_o}{2} \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad [1]$$

which is applicable for infinitely long columns. One can see immediately that it is the value of q that determines the validity of Eq. [1]. For $q > 10$, Eq. [A12] essentially coincides with Eq. [1]. As q decreases, deviation of Eq. [A12] from Eq. [1] is apparent at small values of $x/2\sqrt{Dt}$. As q decreases more, the deviation becomes greater and begins at larger values of $x/2\sqrt{Dt}$. At $q = 1$, there is no region of agreement between Eqs. [1] and [A12].

In this report, $q = 6$ for the electrodes closest to the butted interface. From Fig. 5, one can see that Eqs. [1] and [A12] are in excellent agreement except where $0.6 > C/C_o > 0.4$. And even in this region, agreement is reasonable. Therefore in this report, we have used Eq. [1] to approximate the behavior of the zincate concentration at the electrode close to the butted interface in our diffusion experiment.

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APPENDIX B

METHOD

A method such as we used is generally avoided by most investigators because possible convective transport might mask the diffusion or at least subject the value of D to considerable error in the positive direction. However, at least some convection cannot be ruled out of any method. Although convection can occur during the mere standing of the cell due to slight disturbances, most interference from convection would likely be produced by the initial butting or final sampling. We avoided a sampling effect by in situ measurement of a potential. The effect of initial butting was minimized by the sliding procedure used. The result was well behaved profiles (e.g., Fig. 2). Another contributing factor to the success of the method for the zincate species may have been the small (4 percent) density difference between the solutions in the upper and middle chambers (the denser being in the middle chamber).

Certain aspects of the use of E as a measure of zincate concentration should also be discussed. At zero time, the upper chamber has negligible zincate content so that the electrodes in that chamber are probably operating more as oxygen electrodes. This situation, however, gave no trouble in the present investigation because only large t values were used for the calculation of D. Another factor that could prevent E from being an ideal measure of the diffused zincate arises from the very slow chemical dissolution of (even amalgamated) zinc electrodes making such electrodes less negative due to build up of zincate at the surface. This would be a proportionally greater effect on the electrodes in the upper chamber and far from the butted interface and account for the greater reliability of electrodes close to the interface. Moreover, at lower values of C_o, the dissolution of zinc should have a proportionally greater effect on all values of C measured; this could result in an error in D in the positive direction in keeping with the slightly higher D we found for 0.3 molar potassium zincate.

Note that this general method can be applied to the determination of D for other ions. An example would be the Fe^{+3} ion in the presence of a constant Fe^{+2} ion concentration: the E for $Fe^{+3} - Fe^{+2}$ redox reaction could be used as a measure of the Fe^{+3} concentration.

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APPENDIX C

TIME REQUIRED TO ACHIEVE UNIFORM ZINCATE CONCENTRATION

In this report, we are interested in the time required to achieve a nearly uniform zincate concentration in a battery. The worst starting condition for achieving the situation is the presence of all the zincate at the collector surface at the start, either as a precipitate or in solution. An equation describing the former case has been derived elsewhere (Ref. 6, Eq. 2.7). However, for the latter case, only an equation for an infinitely long chamber is readily available.

$$C = \frac{M}{(\pi Dt)^{1/2}} e^{-x^2/4Dt} \qquad [C1]$$

The purpose of this appendix is to derive the corresponding equation for a finite long chamber and from it to derive the time required to achieve a uniform concentration profile. To start, we again turn to the general solution (Eq. A6) for planar diffusion. Because Eqs. [A7] to [A9] are valid, one may proceed to Eq. [A10].

$$\frac{C}{C_o} = \frac{h}{\ell} + \sum_{m=1}^{\infty} \frac{2}{\pi m} \sin\left(\frac{m\pi h}{\ell}\right) \cos\left(\frac{m\pi x'}{\ell}\right) e^{-(m\pi)^2 Dt/\ell^2} \qquad [A10]$$

No transformation of variables is needed because h is very small. M, the mass per unit cross section is given by the following two equations.

$$M = C_o h \qquad [C2]$$

and

$$M = C_\infty \ell \qquad [C3]$$

where C_∞ is C at infinite time. Thus,

$$\frac{C}{C_\infty} = 1 + 2 \sum_{m=1}^{\infty} \cos\left(\frac{m\pi x}{\ell}\right) e^{-(m\pi)^2 Dt/\ell^2} \qquad [C4]$$

In Fig. 6, C/C_∞ is plotted against x/ℓ for various values of Dt/ℓ^2. For large values of ℓ, Eqs. [C4] and [C1] are in agreement as is to be expected.

Our interest is in the value of Dt/ℓ^2 required for a uniform concentration profile; therefore let us calculate the average deviation, Y, of C/C_∞ from 1: this requires an integration over all values of x/ℓ. When $Dt/\ell^2 > 0.1$ (Fig. 6), the concentration is nearly uniform and

C/C_∞ crosses a value of 1 at about $x/\ell = 0.5$; thus, for the integration one may take twice the integral between $x/\ell = 0$ and $x/\ell = 0.5$.

$$\Upsilon = 2 \sum_{m=1}^{\infty} e^{-(m\pi)^2 Dt/\ell^2} \int_0^{0.5} 2 \cos\left(\frac{m\pi x}{\ell}\right) d\left(\frac{x}{\ell}\right) \qquad [C5]$$

that is,

$$\Upsilon = 4 \sum_{\text{odd } m} \frac{\sin\left(\frac{m\pi}{2}\right)}{m\pi} e^{-(m\pi)^2 Dt/\ell^2} \qquad [C6]$$

When $Dt/\ell^2 > 0.1$, omission of $m > 1$ causes less than a 0.01 percent error in Υ. Thus:

$$\Upsilon = \frac{4}{\pi} e^{-\pi^2 Dt/\ell^2} \qquad [C7]$$

or

$$\frac{Dt}{\ell^2} = - \frac{\ln\left(\frac{\pi\Upsilon}{4}\right)}{\pi^2} \qquad [C8]$$

The problem now becomes what should be meant by uniform concentration; we have arbitrarily chosen an average deviation of 1 percent which describes a far more uniform concentration than is required. In this case

$$t(\text{sec}) = \frac{0.5\ \ell^2}{D} \qquad [C9]$$

The concentration profile corresponding to this value of time is given by the curve for which $Dt/\ell^2 = 0.5$ (Fig. 6).

Note that Eq. [C9] has only the restriction of the starting condition: all of the ions (under study) are located in solution at the collector interface. We have applied this equation in the text of this report to the zincate ion. It is, however, applicable to all ions if their corresponding values of D are known.

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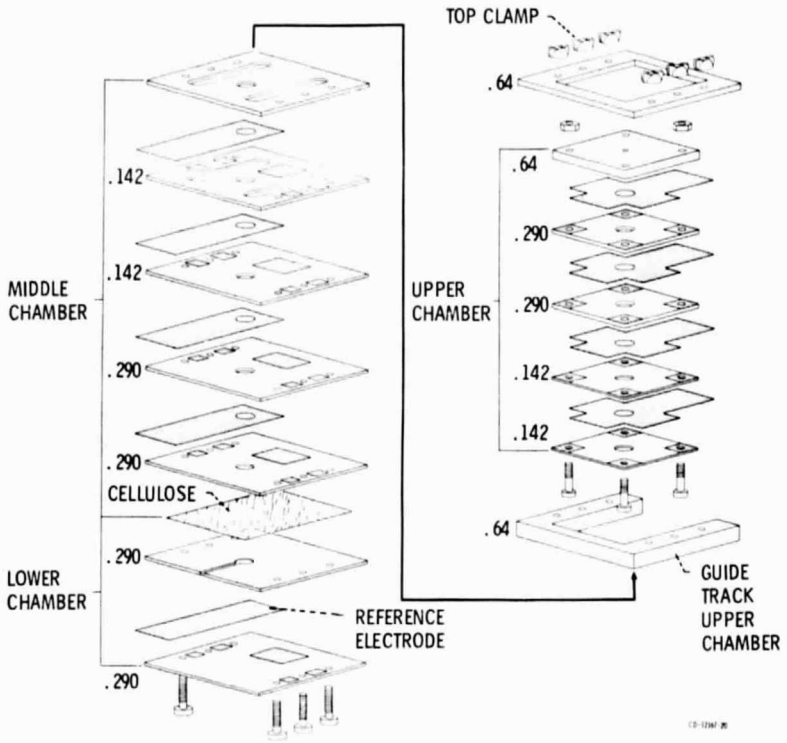
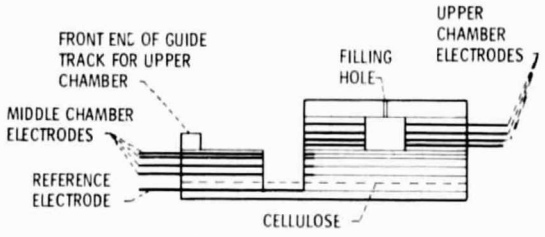
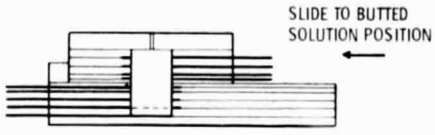


(a) DISASSEMBLED.

Figure 1. - Schematics of diffusion cell (thickness dimensions are in centimeters. Central hole in spacers and zinc sheet are 1.27 cm in diameter. Shaded pieces are zinc sheet; electrodes or shims. Clamping bolts are not shown in (b) and (c).).



(b) ASSEMBLED, FILLING POSITION.



(c) ASSEMBLED, RUNNING POSITION.

Figure 1. - Concluded.

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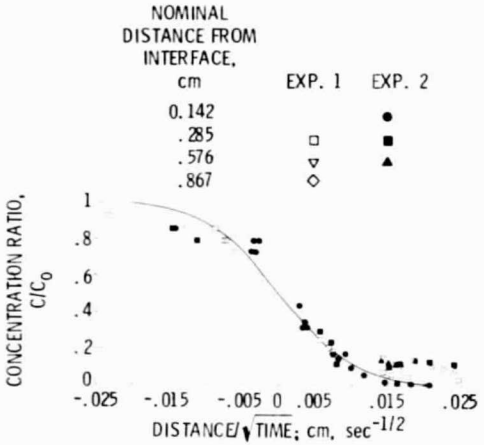

Figure 2. - Diffusion profile for potassium zincate.

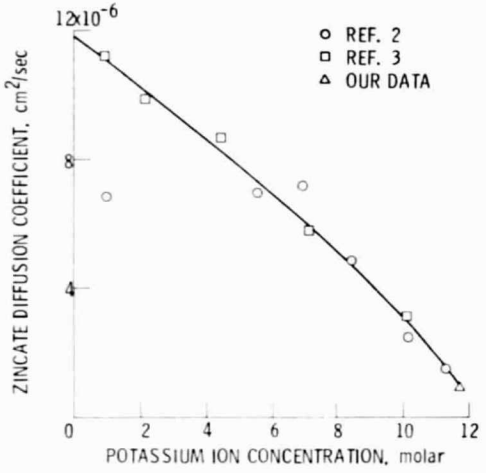

Figure 3. - Diffusion coefficients of zincate ion.

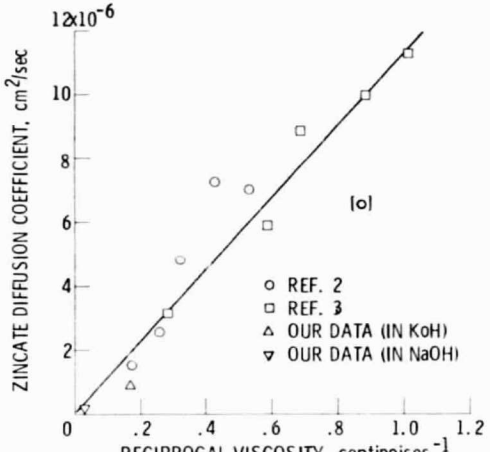

Figure 4. - Zincate diffusion coefficient as function of viscosity: $D = kT/6\pi\eta r$.

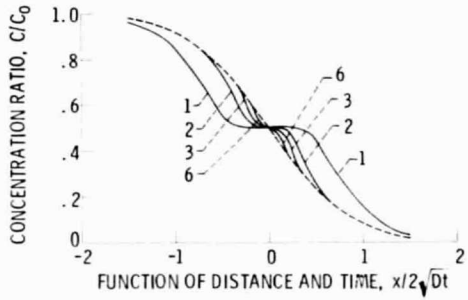

Figure 5. - Concentration profiles for finite size diffusion cells: $C/C_0 = 1/2 - \sum (2/\pi m)\sin(m\pi/2q)\exp(-m^2\pi^2 Dt/q^2x^2)$. [numbers on curves are q values, q = (cell length/2x); dashed line holds for infinite size cell.]

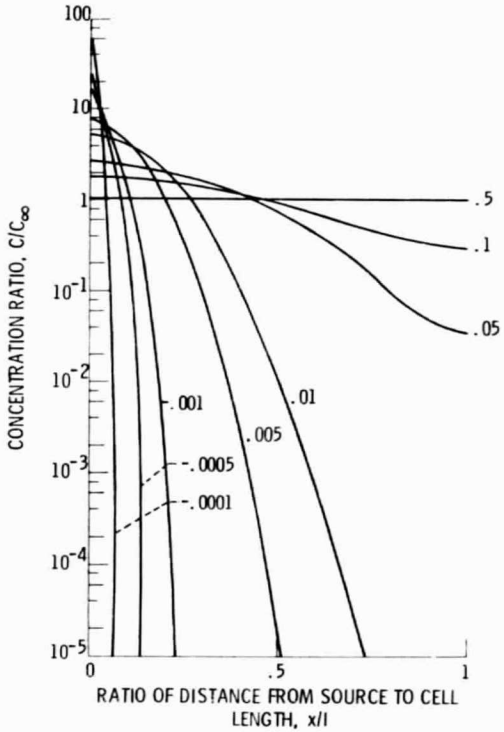

Figure 6. - Concentration profile starting with planar source [numbers on curves are Dt/l^2 values].