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CONVECTION EFFECTS DURING ELECTRO-
TRANSPORT OF LIQUID METALS

Ph.D. Thesis Submitted to Iowa State University,
November, 1972

R. E. Shaw

Ames Laboratory, USAEC
Iowa State University
Ames, Iowa 50010

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Convection effects during electrotransport of liquid metals

by

Robert Eby Shaw

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major: Metallurgy

Approved:

John Verhoeven
In Charge of Major Work

Monroe S. Kechler
For the Major Department

Martin J. Ulmer
For the Graduate College

Iowa State University
Ames, Iowa

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Convection effects during electrotransport of liquid metals

Robert Eby Shaw

Under the supervision of J. D. Verhoeven
From the Department of Metallurgy
Iowa State University

Convection during electrotransport in liquid metals is a well known effect. Yet no satisfactory explanation of the convection mechanism is presently available. Caused by the presence of such convection are several deleterious results: 1) inability in reaching the high separations predicted; 2) inaccurate measurement of liquid metal diffusion coefficients; and 3) incomplete understanding of one aspect of the theory of liquid metals. Literature reviews are presented on several theoretically proposed convection mechanisms and on several attempts to experimentally determine the relationship between convection and the driving force for electrotransport. On the basis that no general agreement has been reached in the several experimental studies, a series of measurements using the four probe capillary reservoir resistivity technique are made of the effective diffusion coefficient of Cd in dilute amalgams. Numerous current densities, j , and capillary radii, a , are used and several statistical analyses of the data are carried out in order to check the parametric dependence of

x

convection on j and a . None of the proposed mechanisms, or combination of them, is as successful in explaining the results as is a model containing only a $j^2 a^4$ dependence. Since no mechanism containing this dependence is present in the literature, it can only be said that in order to minimize convection during electrotransport the smallest practical radius capillary should be used so that j may be large enough to lead to relatively rapid processes.

INTRODUCTION

The word electrotransport describes the phenomenon by which a direct current causes the transport of the components of an alloy with respect to each other. The effect is also called electromigration or electrodiffusion. A number of theories have been presented as to the mechanism of electrotransport. None is completely satisfactory. General reviews of this subject have been given by Schwarz,¹ Jost,² Seith,³ Verhoeven,⁴ Belashchenko,⁵ and Sellors and Pratt.⁶

This work does not concern itself with the mechanism by which electrotransport occurs in liquid metals but rather deals with a problem that must be overcome if electrotransport is to be used as a means of achieving one of three goals. These goals are: 1) understanding how to use electrotransport to achieve maximum purification of a liquid metal; 2) using electrotransport to measure mutual diffusion coefficients in liquid binary alloys; and 3) attaining more reliable values of the parameters used in the theoretical description of electrotransport in liquids in order to serve as an aid both to that description and to our understanding of the structure of liquid metals. With regard to the first goal Verhoeven⁷ has discussed electrotransport as a means of purifying both liquid and solid metals and Polovinkina et al.⁸ have recently designed a column for the semi-continuous purification of liquid metals at low temperatures.

The chief problem that must be overcome or at least understood in any electrotransport experiment is that of convective mixing. The most pronounced mixing effect is that due to the presence of the direct current used to drive the separation process. The magnitude of this effect is evidenced by the fact that "effective diffusion coefficients" measured using electrotransport may be one or two orders of magnitude higher than mutual diffusion coefficients determined by several other means. Thus the achievement of the goals set out above depends upon understanding the mechanism or mechanisms by which current related convective mixing arises. Convective mixing may also result from: 1) convection produced during solidification or cooling and heating as a result of volume change; 2) convection produced in the region of the mouth due to stirring used to prevent solute buildup in the reservoir at the capillary mouth; and 3) convection produced as a result of local density differences within the capillary liquid. Convection due to these effects can generally be avoided or at least minimized thru proper experimental design. These types of convective mixing have been discussed elsewhere.⁹⁻¹⁸

This study of current dependent convection mechanisms was done using the four-probe capillary reservoir resistivity technique in which a current was passed through a capillary containing liquid metal and the voltage drop across the capillary was measured as a function of time. The voltage drop was then related to the average composition of the alloy in the

capillary and from this the mobility and diffusion coefficient of the impurity were determined. The experiments were carried out with an amalgam of starting composition 1 atom % Cd using various capillary diameters and current densities. The results were analyzed using a multiple linear regression program to allow comparison with several theories concerning the mechanism of current dependent convection.

DISCUSSION OF THEORIES

Several theories have been presented concerning possible mechanisms of current related convection. The theoretical basis for relating these mechanisms to experimental observables and the development of the mechanisms will now be briefly developed. A parameter which measured convection is D_c , the so called convective diffusion coefficient. Table I summarizes the expressions given in the literature for D_c and points out the distinguishing features of each.

Theory of J. W. Westhaver

The groundwork for relating observations of convection effects during electromigration in liquid metals to theoretical models was advanced by Westhaver.¹⁹ He was considering the electromigration of the isotopes ^{39}K and ^{41}K with a superimposed counter flow. He assumed steady state conditions. A mass balance done for each species on a volume element at point r, z was based on the fact that the net accumulation thru the z faces due to all means must be balanced by the net accumulation by lateral diffusion. A second steady state condition was that the transport of each species integrated over the capillary cross section must be zero. Using these two conditions Westhaver showed that for an isotropic medium

$$\bar{C}_1 \int_0^a (v - v_b) r dr = \left\{ \int_0^a \left[\int_0^r (v - v_b) r dr \right]^2 \frac{dr}{Dr} + \frac{\bar{D} a^2}{2} \right\} \frac{\partial \bar{C}_1}{\partial z} . \quad [1]$$

In the work of this thesis there is no net bulk flow so $v_b = 0$.

$\bar{C}_1$ is the concentration of impurity averaged over the cross section at a given z and a is the radius of the capillary. On rearranging Eq. [1] one finds that the term in { } represents a diffusion coefficient which is in fact called the effective diffusion coefficient

$$D_e = D + \frac{2}{a^2} \int_0^a \left[\int_0^r v \, r dr \right]^2 \frac{dr}{Dr} . \quad [2]$$

Here v = velocity due to convection and D is the molecular diffusion coefficient.

Theory of G. E. Pikus and V. B. Fiks

Pikus and Fiks²⁰ considered the problem of electron scattering at the boundary of a liquid metal. If an electron undergoes inelastic (or diffuse) scattering at the capillary wall, the wall, or an immovable layer of liquid adjacent to the wall receives an additional impulse in the direction of electron motion. The remaining liquid receives an equal and opposite impulse. If the capillary is open there occurs liquid flow in the direction of the current. If the capillary is closed so that no net flow is allowed then a convective flow develops in the current direction at the walls and in the reverse direction in the bulk. The convection should reverse direction if the electric field is reversed. This mechanism is variously called the electro-osmotic or electrokinetic mechanism.

The authors give both rigorous and approximate expressions

for several quantities of interest. The approximate expressions are good to terms of the order λ/a where λ is the electron mean free path. In an open capillary the velocity is given by

$$v_c = .1(1-\epsilon) \frac{enE\lambda^2}{\eta} \quad [3]$$

except for a thin layer at the walls. Here n is the electron density at the Fermi surface, ϵ is the proportion of electrons undergoing elastic collisions at the capillary wall, and η is the viscosity. In a closed capillary

$$v(r) \approx v_c(2r^2/a^2 - 1). \quad [4]$$

To get the convective diffusion coefficient Fiks used an equation like that of Westhaver, Eq. [2], which he points out²¹ is the limiting case for the condition $\partial C/\partial t = 0$ of a more general formula given in an earlier paper by Pikus and Fiks.²⁰ Substituting he finds

$$D_c = \frac{10^{-4}}{.48D} (1-\epsilon)^2 \left(\frac{enE\lambda^2 a}{\eta} \right)^2, \quad [5]$$

or in terms of current density, j ,

$$D_c = \frac{2.08 \times 10^{-4}}{D} (1-\epsilon)^2 \left(\frac{en\lambda^2 \rho}{\eta} \right)^2 j^2 a^2. \quad [6]$$

They suggested one might check this theory by measuring the effective diffusion coefficient, D_e , where $D_e = D_c + D$ and D is the molecular diffusion coefficient. Their justification for this addition was that both D_c and D are proportional to mean square displacements which are independent of each other.

Pikus and Fiks estimated the magnitude of the quantities used in their analysis. Several problems arose. They assumed that the number of free electrons/atom does not change on melting so the product $\rho\lambda$ is the same for solid and liquid Hg. Measurements of λ were only available in solid Hg. Also they assumed $n=2$ feeling this to be somewhat high. Finally there was the problem of the $(1-\epsilon)$ term. In solid conductors reflection is almost entirely diffuse so $(1-\epsilon)=1$. However assuming diffuse reflection in liquid Hg gave theoretical values²² about one order of magnitude higher than those measured by Klemm.²³ Pikus and Fiks postulated that in liquids, especially those not wetting the surface, ϵ may be large. To match the experimental D_e results ϵ would have to be .9 to .95 in Eq. [6].

Theory of A. Klemm and A. Lodding

Lodding and Klemm²⁴ developed an expression for D_e equivalent to that of Westhaver.¹⁹ They then considered two convection mechanisms. One mechanism was that of electro-osmosis considered independently of Pikus and Fiks.²⁰ The only difference was that Lodding and Klemm introduced an empirical external mobility, b , and gave the convection velocity to be

$$v_z = v' [2(r/a)^2 - 1] \quad [7]$$

where

$$v' = bI/\pi a \sigma, \quad [8]$$

σ being the electrical conductivity. Using Eq. [2] they found that

$$D_e = D + \frac{I^2 b^2}{48\pi^2 a^2 q^2 D} \quad [9]$$

or in terms of current density j

$$D_c = \frac{2.08 \times 10^{-2}}{D} (b\rho)^2 j^2 a^2. \quad [10]$$

Comparing this with Eq. [6] one finds that

$$b = .1(1-\epsilon) \frac{en\lambda^2}{\eta}. \quad [11]$$

Lodding and Klemm also considered that convection might arise due to what they called a magnetohydrodynamic mechanism. This type of convection would appear only if irregularities are present in the capillary walls. Magnetohydrodynamic convection is not reversed on reversing current direction. Their theory considered that in a straight cylinder on the average all charge carriers have an axial velocity vector only. The induced magnetic field is perpendicular to the velocity vector so the axial Lorentz force is zero. However if there are irregularities in the wall then near this region charged particles will on the average have a nonaxial velocity component and thus will interact with the induced magnetic field. This interaction results in a convective velocity given by

$$v_z = \frac{I^2 \delta}{2400\pi\eta} \left[1 - 4\left(\frac{r}{a}\right)^2 + 3\left(\frac{r}{a}\right)^4 \right]. \quad [12]$$

Here δ is the conicity defined by

$$\delta = \frac{1}{a} \frac{\Delta a}{\Delta Z}. \quad [13]$$

Substituting Eq. [12] into Eq. [2]

$$D_e = D + \frac{I^4 \delta^2 a^2}{6.912 \times 10^8 \pi^2 \eta^2 D} \quad [14]$$

In terms of current density and using Eq. [13]

$$D_c = \frac{1.43 \times 10^{-8}}{D} \left(\frac{\Delta a / \Delta Z}{\eta} \right)^2 j^4 a^8. \quad [15]$$

The Eq. [26] of Lodding and Klemm²⁴ corresponding to Eq. [14] appears to be too large by a factor of one half.

Theory of R. L. Schmidt and J. D. Verhoeven

Schmidt and Verhoeven²⁵ proposed a convection mechanism related to the Joule heating produced in an electrotransport capillary. Assuming the heat flows radially out of the capillary, the metal in the capillary center will be slightly hotter than that near the walls. They have used the Stokes-Navier equation to calculate the convective velocity profile

$$V(r) = V_{\max} [1 - 4(r/a)^2 + 3(r/a)^4] \quad [16]$$

where

$$V_{\max} = \frac{\beta_e g d_e \rho j^2 a^4}{192 \eta k} \quad [17]$$

Here d_e is the density, β_e the volume expansion coefficient, g the acceleration due to gravity and k the thermal conductivity. Using Eq. [2] they obtained

$$D_c = \frac{2.26 \times 10^{-7}}{D} \left(\frac{\beta_e g \rho d_e}{\eta k} \right)^2 j^4 a^{10}. \quad [18]$$

Convection caused by this mechanism is not reversed on reversing the current. Regirer²⁶ has presented a similar proposal

as a special case of his more general consideration of convective processes in magnetic fields. Verhoeven¹⁶ has given a derivation leading to Eq. [2] also.

Theory of D. K. Belashchenko

Belashchenko²⁷ proposed a mechanism by which convection might arise. He considered the interaction of moving charge carriers with their own magnetic field. Assuming the current density to be uniform across the conductor he found that the resulting Lorentz force directed toward the capillary axis caused an uneven distribution of charge carriers across the capillary. In the case of a capillary sealed at both ends a pressure gradient will develop given by $\partial p / \partial z = j^2 v / c^2 \sigma$ where v is the velocity of the charge carriers. In the absence of a pressure gradient, as in an open ended capillary, a flow of liquid will occur. A force balance including viscous forces and the spatial electrical force led to an expression for the bulk velocity

$$v_z = \frac{j^2 v}{4\eta c^2 \sigma} (a^2 - r^2). \quad [19]$$

Belashchenko estimated that for a current density of 1000 amps/cm² in a 2 mm diameter cell $v_z = 1.7 \times 10^{-5}$ cm/sec at the capillary center. Using Eq. [19] in Eq. [2] one can find that

$$D_c = \frac{3.58 \times 10^{-3}}{D} \left(\frac{v \rho}{\eta c^2} \right)^2 j^4 a^6. \quad [20]$$

Table I. Summary of Theoretical Current Dependent Expressions for D_c

Mechanism	[Eq.]	D_c	Comments	Reference
Electro-osmotic	6	$\frac{2.08 \times 10^{-4}}{D} (1-\epsilon)^2 \left(\frac{en\lambda^2 \rho}{\eta} \right)^2 j^2 a^2$	2nd power dependence on j and a , reversible	20
Electro-kinetic	10	$\frac{2.08 \times 10^{-2}}{D} (b\rho)^2 j^2 a^2$	2nd power dependence on j and a , reversible	24
Magnetohydro-dynamic	15	$\frac{1.43 \times 10^{-8}}{D} \left(\frac{\Delta a / \Delta Z}{\eta} \right)^2 j^4 a^8$	4th power dependence on j , 8th power dependence on a , dependent on conductivity, non-reversible	24
Joule heating	18	$\frac{2.26 \times 10^{-7}}{D} \left(\frac{\beta_e g \rho d_e}{\eta k} \right)^2 j^4 a^{10}$	4th power dependence on j , 10th power dependence on a , should be present with alternating current, non-reversible	25, 26
Charge density	20	$\frac{3.58 \times 10^{-3}}{D} \left(\frac{v\rho}{\eta c^2} \right)^2 j^4 a^6$	4th power dependence on j , 6th power dependence on a , non-reversible	27

DISCUSSION OF PREVIOUS EXPERIMENTAL WORK

The work of several investigators who have looked into the mechanism of current related convection, or who have at least recognized that the problem does exist, will now be discussed. The often faulty experimental techniques and conclusions will be noted. One particularly questionable practice has been the use of horizontal diffusion paths. Verhoeven¹⁷ has pointed out that thresholdless convection should be expected in any horizontal or inclined capillary if there is present a horizontal density gradient due either to concentration or temperature variations. This effect will be magnified in an analysis that includes concentration changes at the capillary mouth where the horizontal temperature gradient would be especially large in an electrotransport experiment. In practice it appears thresholdless convection may in fact be insignificant if the diffusion path cross section is sufficiently small but the possibility of its existence certainly has clouded some of the studies of current related convection. Table II summarizes the results of various investigators.

Results of A. Klemm and A. Lodding

A. Klemm and A. Lodding have done perhaps the most extensive research into the problem of electroconvection. Klemm²³ studied electroendosmosis of mercury in a long glass capillary of 1.5 mm ID. The capillary was bent into a U-shape and filled with .1 mm diameter glass balls. Application of a current

resulted in a bulk motion of the mercury toward the cathode. Experimentally Klemm found the electrokinetic mobility of Hg, α , to be $2.5 \times 10^{-3} \text{ cm}^2/\text{v-sec}$. By considering electron and ion drift in the boundary layer near the walls he found that theoretically α should be $2.4 \times 10^{-2} \text{ cm}^2/\text{v-sec}$. In light of the approximations made in the theory this was said to be reasonably good agreement. Klemm concluded that though the electrokinetic effect may cause a counter-flow near the wall the effect is too small to be significant.

Lodding and Klemm²⁴ considered electro-osmosis and magnetohydrodynamic effects as causes of convection. They substituted values for D_e of K and In measured in .6 mm I.D. horizontal capillaries with $j=3500 \text{ amps/cm}^2$ along with the appropriate values for D , η , and ρ into Eqs. [9] and [14]. For the electro-osmosis equation to be true the external mobility, b , required would be about .42 for K and .071 for In, whereas measured values are usually of the order of $10^{-3} \text{ cm}^2/\text{v-sec}$. They concluded that electro-osmosis could not account for the large D_e values observed. However the magnetohydrodynamic equation would hold for a conicity, δ , of about $1 \times 10^{-2} \text{ cm}^{-1}$ which was felt to be at least possible so they concluded that MHD convection probably contributed significantly to D_e . No other mechanisms were considered. One must question the effect of their having used a horizontal capillary even if of small size.

Lodding²⁸ studied convective mixing in pure liquid gallium

as a function of current and temperature using mass spectroscopy to determine the $^{69}\text{Ga}/^{71}\text{Ga}$ ratio. His capillaries were of Pyrex, .6 mm ID and 1 mm wall. Again they were horizontal. Current densities were 2122, 3006 and 3537 amps/cm². The temperature at the outside cell wall was measured with a fine thermocouple and the temperature inside the cell estimated knowing the ohmic heat generated inside the cell, the heat conductivity of the glass and the cell dimensions. Lodding found the overall dependence of D_e on I to be nearly proportional to I^3 and thus suggested a combination of mechanisms, one proportional to I^4 and one less sensitive to current. Four possible convection mechanisms were considered. Thermal convection and thermal expansion mechanisms could only explain a few percent of the observed D_e . By considering the equation

$$D_e = D + AI^2 + BI^4 \quad [21]$$

Lodding found the dependence of D_e on I^2 and I^4 . His results can be summarized as follows: 1) at low I and highest T some 65% of D_c is given by the quadratic term and the value of b was in reasonable agreement with independent experimental values implying the electro-osmotic mechanism was present. The 4th power term explained from 80% of D_c at high I and low T to 35% of D_c at low I and high T . The value of δ calculated from Eq. [14] was somewhat large but this might have been due to experimental uncertainty in measuring δ . Thus Lodding concluded that the magnetohydrodynamic mechanism was possible but

that there may have been additional I^4 dependent mechanisms. Finally D values were close to those measured from self-diffusion experiments.

In a parallel work Norden and Lodding²⁹ studied isotope electrotransport in liquid rubidium. In this study the capillary diameter was .5 mm and current densities were 1513, 2674, and 4064 amps/cm². Mass spectrometry was used to determine the ⁸⁷Rb/⁸⁵Rb ratio. They state that liquid alkali metals are known to have a high electro-osmotic mobility and in fact they found the main convection mechanism to be quadratic in I but a secondary term in I^4 could not be ruled out. As for the more predominant electro-osmotic mechanism, using Eq. [9] they found $b = .18$ cm²/v-sec whereas direct measurements³⁰ give $b = .1$ cm²/v-sec in alkali metals. Thus as expected, the electro-osmosis mechanism appeared to predominate in Rb. The I^4 term accounted for about 20% of D_c at high I and low T but only 1% at low I and high T . Calculations showed that the Joule heating mechanism could only contribute about 1/2% of D_c . From Eq. [14] they found $\delta = .7\%$ /cm whereas measurements indicated $\delta = .2\%$ /cm for their cells. Again as in the Ga work this difference was not felt to be significant considering the uncertainty of the δ measurements. Thus the I^4 dependence was probably due to the magnetohydrodynamic mechanism. Finally they found that convection caused by thermal expansion and contraction during cooling and solidification could account for about 2% of D_e .

Results of A. R. Regal and S. I. Patyanin

Regal and Patyanin have not studied convection in electro-transport but they have made studies which bear on the electrokinetic mechanism. They have measured the electrokinetic mobility, α , of molten Ga and the K+Na eutectic,³⁰ and of liquid Hg.³¹ As part of these studies they determined the size of $(1-\epsilon)$, that is the proportion of charge carriers undergoing inelastic (diffuse) scattering at the capillary wall. Two methods were used. By observing the mobility of the level of Hg contained in a long tube they found that $\alpha = (2.5 \pm 1.2) \times 10^{-3}$ cm²/v-sec. But

$$\alpha = \frac{v}{E} = \frac{.1(1-\epsilon)en\lambda^2}{\eta} \quad [22]$$

according to Pikus and Fiks.²⁰ Solving for $(1-\epsilon)$ by assuming the product $\rho\lambda$ is the same for solid and liquid Hg and finding n from the Hall coefficient of Hg they determined that $(1-\epsilon) \approx 2.1 \times 10^{-2}$. By measuring $(1-\epsilon)$ from the difference in two levels they found a value of $2.4 \pm 1.4 \times 10^{-2}$.

Thus they concluded that for Hg at room temperature almost all scattering was elastic. However it was pointed out that one might also look at the phenomena by assuming diffuse scattering at the wall and a substantially increased viscosity in a thin layer of liquid of thickness about 3λ at the wall.

They proposed that there is reason to believe that the scattering process may be dependent on the wetting of the glass surface by a liquid. Liquid Ga and the eutectic Na+K

wet clean glass while pure Hg does not. However experiments with Ga showed that $\epsilon \approx 0$ on the gallium glass interface while ϵ for the eutectic was close to that measured for Hg. These facts were said to support the idea that the molecular structure of the surface layer and the molecular interaction of the material at the interface markedly affect electrokinetic phenomena.

Results of P. C. Mangelsdorf

Mangelsdorf³² correctly pointed out that if a density gradient with a horizontal component exists in a liquid then convection will occur. Despite this knowledge he used a horizontal capillary. To avoid or at least minimize convection his typical cell was a thin ribbon-shaped capillary 2 mm wide and about .025 mm thick. The resultant high surface-to-volume ratio led to two desirable features in that both convection and the effect of solute buildup at the mouth were minimized. Convection due to thermal gradients was minimized by having essentially all heat produced within the cell removed thru the cell bottom. In practice he found that to eliminate all evidence of convective stirring the cell had to be tipped a few degrees from the horizontal to strike a balance between convective tendencies due to thermal gradients and those due to concentration gradients. When this was not done or when the cell was tipped the wrong way both mobility and diffusion coefficient data showed more scatter and the latter were in general

higher. The composition in segments along the length of the cell was determined by measuring the voltage drop between probes and converting this to composition. Since he measured concentration changes in segments within the cell, the horizontal temperature gradient at the cell mouth was not important.

Measurements of the mobility, U , of Cd in Hg were made with current densities of 600 to 1600 amps/cm². Results showed that U decreased slightly with increasing composition. He has reported³³ the value to be 3.80 cm²/v-hr or 10.6×10^{-4} cm²/v-sec at 27°C. Looking at Figure 6 of his earlier paper one might estimate U to be 10.27×10^{-4} cm²/v-sec at one atomic percent Cd in Hg and 27°C.

After the cell had reached steady state conditions with the electrotransport current on the following scheme was used to measure D . The electrotransport current was turned off and a very small measuring current turned on and used to determine the voltage drop across each segment of the cell as the impurity diffused back into the cell from the reservoir of known composition. The voltage drop was related to the mean composition of each segment. With the low measuring currents used current dependent convection should have been negligible. His results showed the D of Cd in Hg was not a function of composition up to 3 atomic percent Cd. He found that at 25°C $D = 1.53 \times 10^{-5}$ cm²/sec. At 148°C the value of D was about twice as large.

After a careful study of his work one must conclude that

his are the most reliable values for the mobility and the mutual diffusion coefficient measured to this time.

Results of F. Y. Lieu

Lieu³⁴ has studied the electrotransport of Bi in liquid Sn and the dependence of D_e on the current density. He used the four-probe capillary reservoir resistivity technique. The ratio of D_e/D was proportional to j^2 , thus pointing to the electrokinetic mechanisms. His data were however limited and U varied by about 17% with values measured at higher current densities generally being smaller than the low J value. Also he is wrong in his conclusion that 700 amps/cm² is the optimum current density to be used to attain maximum separation in this alloy system. This is because the ratio of the mean concentration in the capillary at steady state to the initial concentration, $\bar{C}/C_0$, is dependent on both capillary radius and length as well as on current density.

Results of S. I. Drakin

Drakin and coauthors have done extensive electrodiffusion work primarily with low melting alloys of Hg, Ga and alkali metals. They have recognized the importance of using capillaries with thin walls for good heat transfer. They have used various cell configurations to minimize convection effects: zig-zag shaped horizontal tubes;³⁵ spiral (or helical) tubes;³⁶ a two reservoir system with the connecting capillary

being a zig-zag shaped capillary of length 10 to 12 cm;³⁷ and most recently short vertical capillaries of typical size $L=1.2$ cm, $ID=.75$ mm and wall thickness of .9 mm.³⁸ Some of the problems they admit to having had with their earlier cells are bubble formation during filling and convection due to inverse density gradients. These problems were eliminated with the latter method and times to reach steady state were shorter. However the walls were thicker than desirable. In at least one case³⁸ they followed a procedure much like that of Verhoeven and Hucke.³⁹

In describing the results of their work Drakin and co-workers used the following terminology. The defining equation for the coefficient of electrodiffusion, K_ℓ was³⁶

$$\ln \frac{a_2'}{a_2''} - \ln \frac{a_1'}{a_1''} = K_\ell \frac{\Delta E_{1-2}}{T} \quad [23]$$

where a is the activity, ΔE_{1-2} the potential drop across a section of the cell, ' implies the first component, '' implies the second component. They introduced a transport number, n_t , and related it to D and K_ℓ by the relation³⁷

$$n_t = \frac{DK_\ell C \rho F}{T} \quad [24]$$

where C is the concentration of dissolved metal. They found U from the formula⁴⁰

$$U = \frac{M \Delta p}{p d_e I \rho \tau} \quad [25]$$

where M is the weight of the capillary contents, p and Δp the concentration of impurity in the reservoir and the change of impurity concentration in the cell, d_e the density of the alloy, and τ the experimental time. Finally they calculated a diffusion coefficient by using the Einstein relation $D=UT/K_g$. It is apparent that they did not really understand the physical meaning of U since to determine it they extrapolated back to zero time from a region where the apparent value of U was changing with time. But in fact U is a constant and can only be measured if no back diffusion is present at the point where the mass balance is being made. They were forced to estimate the value of U in this way because their experimental techniques did not generally permit determination of small changes in mean cell concentration.

In agreement with Belashchenko they only observed electrodiffusion when the resulting density gradient was such that the lighter alloy was on top.^{38,41}

They were not able to show a conclusive dependence of convection on current density or cell size. In much of their work the current density was low enough so that any convective effects were hidden by experimental scatter. In Sn-Ga experiments⁴⁰ in zig-zag cells they calculated $D_e=1.6, 2.8, \text{ and } 3.9 \times 10^{-3} \text{ cm}^2/\text{sec}$ at $j=640, 1300 \text{ and } 2150 \text{ amps/cm}^2$ respectively. But of course they had density inversion present with this cell configuration. In Sn-Ga experiments with vertical capil-

larities and j less than 250 amps/cm^2 they found no j dependence in K_ℓ values. However taking data for U , ρ , and the initial and final cell concentrations given in their paper and using our formalism one finds $D_e = 2.90, 4.04$ and $4.08 \times 10^{-5} \text{ cm}^2/\text{sec}$ at $j = 85, 126$ and 199 amps/cm^2 respectively. Thus it appears that the diffusion coefficient may be more sensitive to convection effects than is the electrodiffusion coefficient.

In their study of Bi diffusion in Ga⁴² they found that D_e had a first order dependence on j for six values of j ranging from 750 to 2500 amps/cm^2 . But this work was done with the two reservoir bent capillary system where density inversion was present. In a study of Hg diffusion in Na done in vertical cells³⁸ they observed a $\pm 9\%$ variation in K_ℓ for j values varied by a factor of 4. However in arriving at this conclusion they assumed E to be constant over the cell length whereas $E = j\rho$, thus changing as ρ does. In a study of electrodiffusion in indium alloys⁴¹ they concluded that K_ℓ and the apparent charge of the diffusing species showed no dependence on j . However looking at their values for D_e in Pb-In one can only conclude that the experimental scatter is so great that any j dependence would be masked. They claimed that the fact that all D_e values were of the order of magnitude of $10^{-5} \text{ cm}^2/\text{sec}$ was evidence that convection was not important.

In a study⁴³ of the removal of impurities from liquid Ga they found that $D \approx 10^{-3} \text{ cm}^2/\text{sec}$ for j values ranging from 1500

to 2300 amps/cm². They were unable to determine any clear evidence for the effect of j , L or r on D_e .

Results of P. P. Kuzmenko

Kuzmenko and coworkers have carried out extensive electrotransport work. Their standard technique⁴⁴ involved a quartz tube .4 to 1.0 mm ID, 4 to 20 cm in length which was filled with a nonradioactive metal, solidified and then broken in two equal length pieces. A radioactive insert of about one tenth the length of the non-active pieces was placed between the original pieces. The three pieces were then sealed inside a quartz tube and electrodes added. Measurements were done with the cell held horizontally. In analyzing the concentration profile following diffusion they have either used radioactive analysis techniques,^{44,45} relative hydrostatic weighings on a microanalytical balance,⁴⁶ or a method⁴⁷ similar to that of Verhoeven and Hucke.³⁹ In all three techniques there must have been diffusion during the process in which the inserts and non-active sections were sealed together. The first two techniques involved diffusion during the solidification process. The latter method involved turning off the electrotransport current for about ten minutes during which time the sample temperature was reduced to that of the cell surroundings. Measurements were then made with a current of .1 amp. A measurement was made every hour. Thus the system was drastically affected by the measurement process.

Studies⁴⁴ of Ag migration in Pb showed D_e to be two to two and one half times D and for Co in Sn D_e was four to eight times D . They felt that this was due to the interaction of the charged particles with the magnetic field and the shape (conicity) of the capillary. They found that the mobility was not influenced by convection.

In a study⁴⁸ of electrotransport of several impurities in liquid Sn they found that D_e increased with current but gave no analytical relationship. They did calculate D_c for their experimental conditions using the formula of Pikus and Fiks²⁰ for the electro-osmotic effect but found the maximum calculated D_c about one tenth that observed.

From the results of a study⁴⁵ of electroconvective diffusion in liquid Sn and Pb involving some 80 experiments they determined that

$$D_c = AI^2a = A'j^2a^5. \quad [26]$$

No theory has predicted a 5th power dependence on capillary radius. They could find no relationship between D_c and capillary taper. Again the electrokinetic theory of Pikus and Fiks predicted a D_c much smaller than they observed. Convection during electrotransport of ¹¹⁰Ag in Sn was reported to be the same whether direct or alternating current was used.

In a review paper⁴⁹ they repeated the conclusions reached earlier that neither the electrokinetic mechanism or the magnetohydrodynamic mechanism can explain more than a small

part of their observed D_c . They also mentioned Regirer's proposal²⁶ based on Joule heating but again this predicted only a small part of the experimental D_c and further predicted $D_c \propto j^4 a^{10}$ whereas their observations were that $D_c \propto j^2 a^5$.

The use of horizontal capillaries must be questioned. Their claim is that density gradients caused either by electrotransport or temperature gradients result in free or thermal convection which may be decreased or eliminated by putting the tube in the horizontal plane.

Results of D. K. Belashchenko

Belashchenko and coauthors recognized the importance of preventing convection in electrotransport experiments.^{5,50} They have generally characterized electrotransport by reporting an effective charge Z^* defined by

$$\left(\frac{d \ln a_1}{d x} \right) = \frac{eEZ^*}{k_b T} \quad [27]$$

where a_1 is the thermodynamic activity of the impurity. They related Z^* to the diffusion coefficients by

$$Z^*/Z_{app}^* = 1 + D_c/D \quad [28]$$

where Z_{app}^* is the effective charge measured in the presence of convection. They also determined Z^* of impurities in Hg at 25°C using the U and D reported by Schwarz¹ and the relationship

$$U(\text{cm/hr}) = 3600eZ^*D/300kT. \quad [29]$$

The criterion $\tau_{ss} \approx l^2/D$, where l is the diffusion path length and τ_{ss} the experimental time to reach steady state, was used to determine the time to the steady state condition.

Their typical experiments involved vertical capillaries of 1 mm ID, 4 to 6 cm lengths and 2 mm walls. The alloy was drawn into a capillary after which .8 mm molybdenum electrodes were sealed into each end. Determination of the concentration gradient was done either by chemical or radioactive tracer methods. Z^* was then found from Eq. [27] where for dilute solutions a equals the impurity concentration.

Belashchenko and Grigor'ev⁵⁰ showed that neither surface diffusion or free convection were important in their electrotransport experiments. In work with minute quantities of ^{60}Co in Sn they concluded that Z^*/Z_{app}^* was proportional to E^2 thus supporting the electroconvective theory of Pikus and Fiks. In this work current densities ranged from 30 to 525 amps/cm².

Belashchenko, Gushchina and Armyanov⁵¹ proposed that electroconvection can be overcome in concentrated solutions by establishment of a density gradient such that the lighter component moves upward. By measuring the slope of the log of Bi concentration vs position along a Bi-Sn alloy for four current densities ranging from 132 to 282 amps/cm² and using Eq. [27] they were able to conclude that convection was absent. One must question whether end effects may not have come into play in some of their slope determinations. No indication of the accuracy or reproducibility of this technique was given.

In a recent work Belashchenko and Gushchina⁵² determined Z^* of 1 atomic percent Bi and .02 atomic percent Pb in Cd at about 360°C. In these dilute alloys suppression of convection by the presence of a density gradient certainly can not be claimed. Their value of Z^* is -13.1 ± 1.1 compared with Belashchenko's⁵³ earlier values of -16.4. Respective values of j and τ for the two studies were 120 vs 180 amps/cm² and 2 to 3 days vs 15 days. The authors also compared their Z^* to that of Zhmudski et al.⁵⁴ who obtained a value of -6.20. They implied that Zhmudski's smaller value was the result of his having had convection since convection lowers the value of Z^* . On this basis one would expect their more recent value of -13.1 for Z^* also evidences the presence of convection when compared to their value of -16.4.

One must conclude that while the authors recognized the desirability of minimizing convective effects they probably usually had convection present but it was hidden by their large experimental scatter.

Table II. Summary of Experimental Observations of D_c

Method	Conclusions as to Mechanism	Empirical Form of Dependence	Ref.
Horizontal capillary	Possibly magnetohydrodynamic	---	24
Horizontal capillary	Electro-osmotic and magnetohydrodynamic with possible additional fourth power I dependence	$D_e = D + AI^2 + BI^4$, where 65% of D_c given by AI^2 at low I and high T , 80% by BI^4 at high I and low T .	28
Horizontal capillary	Electro-osmotic predominates but magnetohydrodynamic present; Joule heating contributes only 1/2% of D_c	$D_e = D + AI^2 + BI^4$, where quadratic term predominates; 20% of D_c at high I and low T , 1% at low I and high T given by BI^4	29
Vertical four-probe capillary reservoir	Electrokinetic	$D_c \propto j^2$	34
Two reservoir bent capillary	No explanation given	$D_e \propto j$	42
Horizontal, two semi-infinite rod	Magnetohydrodynamic, D_e two to eight times D	---	44
Horizontal, two semi-infinite rod	Electrokinetic, magnetohydrodynamic and Joule heating explain only a small part of D_c	$D_c \propto A' I^2 a$	45, 49

EXPERIMENTAL FORMALISM

The flux of the i th species may be defined as the mean velocity times the concentration of the i th species. The velocity will be taken with respect to a fixed observer. Typical units of flux are atoms/cm²-sec. If two or more independent forces each act on the i th species then the resultant fluxes are additive.

In the development that follows consider a capillary filled with a liquid alloy thru which a current is passed. At a given plane the total flux of the i th species is

$$J_i(\text{total}) = J_i(\text{electrotransport}) + J_i(\text{diffusion}) + J_i(\text{convection}). \quad [30]$$

In this development the three terms on the right will be considered in the order they appear as written above.

Electrotransport

The electric mobility is defined as the terminal velocity per unit electric field, $U_i = v_i/E$. The electric mobility is related to the absolute mobility, B_i , by $U_i = eB_i Z_i^*$ where Z_i^* is the effective valence of i . If no convection is present Eq. [30] becomes

$$J_i = U_i E C_i - D_i \frac{\partial C_i}{\partial Z}. \quad [31]$$

In a binary alloy there will be an equation of this type for both the solute, henceforth called component 1, and the solvent, component 2.

To find an expression involving only U_i consider application of Eq. [31] at a cross section of the capillary prior to the establishment of a concentration gradient at that point. Then combining Eq. [31] written in turn for 1 and 2

$$J_1 X_2 - J_2 X_1 = \frac{E}{\bar{V}} (U_1 - U_2) X_1 X_2 \quad [32]$$

where X_i is the mole fraction of i and $\bar{V}$ the total molar volume. For dilute solutions the partial molar volumes of 1 and 2 are constant. Then since the volume of metal in the capillary does not change during the electrotransport process if the partial molar volumes are assumed constant

$$J_1 \bar{V}_1 + J_2 \bar{V}_2 = 0. \quad [33]$$

Combining this with the relation between the partial and total molar volumes, Eq. [32] becomes

$$J_1 = \frac{X_1 X_2 E U_{12} \bar{V}_2}{\bar{V}^2} \quad [34]$$

where $U_{12} = U_1 - U_2$. Doing a material balance at the capillary mouth,

$$\int_{\text{area}} J_1 \cdot dA = - \frac{d}{dt} \int_{\text{volume}} N_1 dV. \quad [35]$$

Carrying out the integration

$$J_1 = -L \dot{N}_1 = -L \dot{X}_1 / \bar{V} \quad [36]$$

where a constant molar volume is assumed and

$$\dot{N}_1 = \frac{\dot{X}_1}{\bar{V}} = \frac{d}{dt} \left(\frac{1}{L} \int_0^L N_1 dz \right). \quad [37]$$

Combining Eqs. [34] and [36]

$$U_{12} = \frac{-L\dot{X}_1\bar{V}}{EX_1X_2\bar{V}_2} \quad [38]$$

For dilute solutions $\bar{V}_2 \approx \bar{V}$. If the alloy exhibits a first order dependence of resistivity on composition then

$$\rho_1 = \beta X_1 + \rho_0 \quad [39]$$

where ρ_0 is the resistivity of pure Hg. Equation [38] becomes

$$U_{12} = \frac{-L^2 K \dot{\rho}}{I \rho_m X_{1m} X_{2m} \beta} \quad [40]$$

where $K=A/L$ is the cell constant, $\dot{\rho} = \beta \dot{X}_1$, and ρ_m, X_{1m} and X_{2m} are the resistivity and mole fractions of the components of the alloy at the mouth. It can be shown that for dilute solutions

$$U_{12} \approx U_1 \quad [41]$$

since the volume of metal in the capillary is conserved and $\bar{V}_2 \approx \bar{V}$. Thus to a good approximation

$$U_1 = \frac{-L^2 K \dot{\rho}}{I \rho_m X_{1m} X_{2m} \beta} \quad [42]$$

gives the mobility of an impurity as a function of the time rate of change of the alloy resistivity, the cell dimensions and the initial alloy properties. In fact Eq. [42] will be used during the early stages of the electrotransport runs to measure U_{Cd} in a Cd-Hg alloy.

Diffusion

Now the formalism for determining the diffusion coefficient will be developed. Again assume no convection. Combining Eq. [31] written for the impurity with the continuity equation gives

$$\frac{\partial}{\partial Z} (U_1 E C_1) - \frac{\partial}{\partial Z} \left(D_1 \frac{\partial C_1}{\partial Z} \right) = - \frac{\partial C_1}{\partial t} . \quad [43]$$

Verhoeven et al.⁵⁵ wrote this equation in terms of dimensionless parameters. They assumed U_1 , E and D_1 to be independent of position and time and integrated over the capillary length to get the mean concentration variation with time

$$\frac{\bar{X}_1}{X_{10}} = \frac{1}{S'} [e^{S'} - 1] + \sum_{n=1}^{\infty} \frac{4\beta_n}{(S'^2 + 4\beta_n^2)} C_n e^{\lambda t} \quad [44]$$

for $S' < 2$ and where

$$S' = \frac{U_1 V}{D} . \quad [45]$$

They give expressions for determining β_n , λ and C_n . Considering only the steady state part of Eq. [44] the ratio of the mean steady state cell composition to the initial composition is

$$R' = \frac{\bar{X}_{1SS}}{X_{10}} = \frac{1}{S'} [e^{S'} - 1] . \quad [46]$$

As to the assumptions made: U_1 and D_1 should be quite constant especially over small concentration intervals. However $E^{\rho_{\text{alloy}}}$ which for Cd in Hg varies about 4% per atomic percent.

Packard⁵⁶ solved Eq. [43] for the steady state case assuming U_1 and D_1 to be constant but letting $E=j\rho=j(\beta X_1+\rho_o)$. He assumed as did Verhoeven that the composition at the capillary mouth remains constant during the diffusion process and found the steady state composition at the plane Z to be

$$X_{1SS} = \frac{-X_{1o}}{[Q - (Q+1)e^{-(S/L)Z}]} \quad [47]$$

where

$$Q = \frac{\beta X_{1o}}{\rho_o} \quad [48]$$

$$S = \frac{\rho_o U_1 j L}{D_1} \quad [49]$$

Then by integrating over the capillary length the ratio of the mean steady state cell composition to the initial composition was found to be given by

$$R = \frac{\bar{X}_{1SS}}{X_{1o}} = -\frac{1}{Q} \left[1 + \frac{1}{S} \log(-Q + (Q+1)e^{-S}) \right]. \quad [50]$$

Since U_1 can be independently measured this expression allows determination of D_1 by an iterative computer process provided that the initial and final alloy compositions can be measured, the resistivity-composition relationship is known, the cell geometry is known and the current density at steady state is measured.

Convection

So far this development of the formalism needed to determine measured values of the mobility and diffusion coeffi-

cients in liquid metals has not included convection. It will now be shown that when convection is present Eq. [31] can still be used to a good approximation except now D is replaced by $D_e = D + D_c$ where D_e is the so-called effective diffusion coefficient and D_c the convective diffusion coefficient.

Consider the case of a liquid metal contained in a cylindrical capillary of radius a . A mass balance on a cylindrical shell of height Δz may be based on the fact that the mass flux thru the sides due to diffusion plus the mass fluxes thru the ends due to diffusion, electrotransport and convection must equal the mass accumulation in the volume element per unit time. This can be written

$$\frac{D}{r} \frac{\partial(r \frac{\partial C}{\partial r})}{\partial r} + D \frac{\partial^2 C}{\partial z^2} - U \frac{\partial(EC)}{\partial z} - \frac{\partial vC}{\partial z} = \frac{\partial C}{\partial t} \quad [51]$$

where U and D have been assumed independent of position. Then integration over the cross section with the boundary conditions that $\partial C / \partial r = 0$ at $r = a$ and $\partial C / \partial r$ finite at $r = 0$ gives

$$D \frac{\partial^2 \bar{C}}{\partial z^2} - U \frac{\partial(E\bar{C})}{\partial z} - \frac{2}{a^2} \frac{\partial}{\partial z} (\int_0^a v C r dr) = \frac{\partial \bar{C}}{\partial t} \quad [52]$$

where

$$\bar{C} = \frac{2}{a^2} \int_0^a C r dr. \quad [53]$$

By using integration by parts it can be shown that

$$\int_0^a C v r dr = - \int_0^a [\int_0^r v r dr] \frac{dC}{dr} dr \quad [54]$$

provided that there is no net liquid flow as is the case when one end of the capillary is closed. Thus

$$D \frac{\partial^2 \bar{C}}{\partial z^2} - U \frac{\partial(\bar{E}\bar{C})}{\partial z} + \frac{2}{a^2} \frac{\partial}{\partial z} \left[\int_0^a \left\{ \int_0^r v r dr \right\} \frac{d\bar{C}}{dr} \right] = \frac{\partial \bar{C}}{\partial t}. \quad [55]$$

Going back to Eq. [51], multiplying by r/D and integrating over the radius

$$\frac{\partial \bar{C}}{\partial r} = \frac{1}{rD} \int_0^r \left[\frac{\partial \bar{C}}{\partial t} - D \frac{\partial^2 \bar{C}}{\partial z^2} + U \frac{\partial(\bar{E}\bar{C})}{\partial z} + v \frac{\partial \bar{C}}{\partial z} \right] r dr. \quad [56]$$

Then with the assumption that C is a very weak function of r so $C(r) \approx \bar{C}$ the result of putting Eq. [56] into Eq. [55] is that

$$\begin{aligned} \frac{\partial \bar{C}}{\partial t} = & \left[D + \frac{2}{a^2 D} \int_0^a \left\{ \int_0^r v r dr \right\}^2 \frac{dr}{r} \right] \frac{\partial^2 \bar{C}}{\partial z^2} - U \frac{\partial(\bar{E}\bar{C})}{\partial z} \\ & + \frac{1}{a^2 D} \int_0^a \left\{ \int_0^r v r dr \right\} r dr \left[\frac{\partial}{\partial z} \left\{ \frac{\partial \bar{C}}{\partial t} - D \frac{\partial^2 \bar{C}}{\partial z^2} + U \frac{\partial(\bar{E}\bar{C})}{\partial z} \right\} \right]. \end{aligned} \quad [57]$$

Now to a good approximation the assumption can be made that

$$\frac{\partial}{\partial z} \left\{ \frac{\partial \bar{C}}{\partial t} - D \frac{\partial^2 \bar{C}}{\partial z^2} + U \frac{\partial(\bar{E}\bar{C})}{\partial z} \right\} = 0. \quad [58]$$

The reason for this is that if there is no convection this term is identically zero and if convection is present then from Eq. [52] the term in $\{ \}$ is equal to

$$- \frac{2}{a^2} \frac{\partial^2}{\partial z^2} \left(\int_0^a v C r dr \right). \quad [59]$$

Neglecting the first derivative of this term is equivalent to assuming that the third derivative with respect to z of the convective flux averaged over the tube cross section is negligible. Writing Eq. [57] in terms of the total flux

$$J_i = UEC - \left[D + \frac{2}{a^2 D} \int_0^a \left\{ \int_0^r v r dr \right\}^2 \frac{dr}{r} \right] \frac{\partial \bar{C}}{\partial Z}. \quad [60]$$

Now it is seen that Eq. [60] has the form of Eq. [31] if the D in the latter equation is replaced by D_e ,

$$D_e = D + \frac{2}{a^2 D} \int_0^a \left\{ \int_0^r v r dr \right\}^2 \frac{dr}{r} = D + D_c. \quad [61]$$

Then both Eqs. [46] and [50], the expressions for the ratio of the mean steady state cell composition to the initial cell composition, should be expected to hold. The same conditions as applied in the derivations of Eqs. [46] and [50] hold. Additional conditions are that the only lateral flux is due to diffusion, the third derivative with respect to Z of the convective flux is negligible and that the concentration is a weak function of radius.

EXPERIMENTAL PROCEDURE

In order to carry out the study of convection in electrotransport several requirements must be met. First an alloy system is required which: is easy to work with; is easily separable by the electrotransport technique; and fits the assumptions used to develop the formalism. Secondly equipment is needed: a cell in which to make the measurements; an environment for that cell; a power source to drive the separation; and various measuring devices for determining such things as temperature and the composition of the material in the cell. Finally an experimental methodology is required by which certain fixed parameters may be measured and the interdependence of the several variables may be determined. These items will now be discussed.

Alloy System

For the sake of experimental convenience and confidence in the accuracy of measurements an alloy system was desired which was liquid at room temperature. Both temperature control and experimental operation would then be easier. This desire of course pointed to use of an amalgam. The amalgam of 1.0 atom % Cd was chosen. One disadvantage in using an amalgam is the strong oxide forming tendency of the impurity elements in amalgams. This tendency was partially overcome by repeated flushing of the system with high purity helium gas. The beneficial attributes of the Cd-Hg system outweighed this minor

inconvenience.

Two properties of significance to the separation of the components of an alloy and the measurement of that process are the size of the resistivity change with changing concentration and the size of the mobility of the impurity in the solvent. The values of $d\rho/dX_{Cd}$ and U_{Cd} are among the larger reported values for various amalgams.^{57,33} The first property insures that a small change in composition results in a sufficiently large resistivity change to allow measurement of the change in the voltage drop across a sample. The second property means that a separation will take place at a reasonable rate.

Does the Cd-Hg system obey the relevant assumptions used in the formalism? It has been found⁵⁸ that the partial molar volumes, $\bar{V}_{Cd}$ and $\bar{V}_{Hg}$ are nearly constant out to 9 atom % Cd and that the molar volumes of a one atom % Cd amalgam and pure Hg differ by only .03%. Using the data given in the International Critical Tables⁵⁷ the resistivity-composition relationship was found to fit the equation $\rho = \beta X_{Cd} + \rho_0$ with $\beta = -3.9954 \pm .0303 \text{ } \mu\Omega\text{cm/atom \%}$ at 22°C. For dilute solutions $U_{Cd-Hg} \approx U_{Cd}$ to better than 1%. The assumption that U is a constant independent of composition is somewhat weaker as a first order least squares fit of the data shown in Fig. 6 of Mangelsdorf's paper³² shows that for the composition range from .5 to 3.5 atom % Cd $U = [3.81 \pm .01 - (.088 \pm .007)X_{Cd}] \text{ cm}^2/\text{volt-sec}$ at 27°C. D has been shown not to be a function

of composition from 0 to 3 atom % Cd.³² Finally in the mass balance it was assumed that the amalgam density was constant. In fact $(d_{1 \text{ atom \% Cd}} - d_{\text{Hg}})/d_{\text{Hg}} = .53\%$.

Thus the system 1 atom % Cd in Hg appeared to be a satisfactory system to work with. Perhaps the biggest drawback was the fact that U changes by about 2.4% from infinite dilution to 1 atom % Cd.

The mercury used in this work was triply distilled by Ames Lab personel. The cadmium was 99.999% pure and was obtained from Cominco Products, Spokane, Washington. Results of two analyses for impurities in the cadmium are given in Table III.

Table III. Analyses of Impurity Content of Cominco Cd

Element	Cominco ^a	Ames ^b	Element	Cominco ^a	Ames ^b
Ag	0.1	ft	Mg	1.0	vft
Al		vft	Mn		vft
As		-	Ni		-
B		-	Os		-
Bi	0.1	-	Pb	0.2	ft
Ca	0.2	ft	Sb		-
Cr		vft	Se		-
Cu	0.2	ft	Si	2.0	-
Fe	0.3	ft	Sn		ft
Ge		-	Ta		-
Hg		-	Te		-
In		-	Tl		ft
Ir		-	Zn		-

^aImpurity content in ppm.

^bft = faint trace, vft = very faint trace, - = tested for but none found. Ames Lab testing by conventional spectrographic qualitative analysis using the DC arc method.

Equipment

The study of electrotransport connected phenomena in the Cd-Hg system is particularly amenable to the four probe resistivity capillary reservoir technique.³⁹ Figure 1 shows the cell used in this technique. A cell was constructed which had a current electrode and a potential probe sealed into one end of a Pyrex capillary.^a The other end of the capillary opened into a reservoir which also contained an electrode and a potential probe. The electrodes and probes were tungsten. A current passed between the electrodes drove the separation process. The potential probes allowed measurement of the emf across the cell since the voltage drop between the reservoir probe and the open end of the capillary was negligible.

The cell environment is shown in Fig. 2. The cell was contained in an apparatus that allowed a vacuum to be pumped or purified He gas to be introduced. The helium gas obtained from Air Reduction Co., Inc. was reported to contain as significant impurities .31 ppm H₂O, .16 ppm N₂ and .03 ppm O₂. Provision was made for both rotational and translational motion of the cell as needed in the experimental procedure. The cell was placed in a reservoir of the alloy to be studied. The volume ratio of reservoir metal to cell metal was from 300 to 8000. The reservoir was contained in a thin wall

^aSpecifications on materials and equipment used during this work are given in Appendix I.

Figure 1. Electrotransport cell

Figure 2. Electrotransport cell environment

stainless steel crucible. This gave good thermal contact with the surrounding water bath. The bath was held at approximately 22°C by a temperature control system consisting of a cooling coil thru which cool tap water continuously flowed, an electrical heater controlled by a temperature regulator, and a stirrer which provided for mixing of the bath. With this system the temperature in the reservoir near the cell usually fluctuated by ± 0.05 to $\pm 0.2^{\circ}\text{C}$ over a period of one hour.

The DC power supply used was programmable in the constant current regulated mode to supply a direct current of from 0 to 15 amps at 0 to 36 volts. The current as measured across a 0.1 ohm shunt fluctuated by less than $\pm 0.01\%$ over the period of one hour. A schematic of the power supply and associated equipment is shown in Fig. 3. The five resistors R_s ranging in size from .032 ohms to 10 ohms were required so that programmed load currents of from several milliamps to 15 amps could be obtained. For good regulation it was necessary that R_s had a low temperature coefficient and that it be rated at a wattage at least 10 times the maximum power loss across it. The size of R_s was picked to give a 0.5 volt drop across it at the maximum current desired. The current control resistor R_{cc} was chosen on the basis of the control ratio of the comparison bridge, 1000 ohms/volt, and the voltage across R_s at maximum current. Thus $R_{cc}(\text{max}) = 0.5 \text{ volt} \times 1000 \text{ ohms/volt} = 500 \text{ ohms}$. In practice two 500 ohm Helipot wirewound potentiometers were used so that R_{cc} could be immediately switched to a new value

Figure 3. Schematic of power supply and associated equipment

when it was necessary to switch to a new R_s . R_{load} of Fig. 3 in reality consists of a standard shunt, R_{st} , of approximately 0.1 ohm; the cell itself, R_c ; and a switching device which allowed either R_{st} alone or both R_{st} and R_c to be in the circuit. The current direction could be reversed also. All switches used were of the shorting type so that the power supply would not be unloaded. This led to better current stability. The current circuit between the power supply terminals and the cell lead rods was designed for 15 amps.

The measuring devices are shown in Fig. 4. The potential across R_{st} , across R_c and that developed by a chromel-alumel thermocouple located in the crucible near the cell were all measured with a standard Leeds and Northrup type K-5 potentiometer facility. The switch shown in Fig. 4 is a rotary selector switch of the shorting type. The thermocouple was constructed by Mr. Ed Gibson of Ames Laboratory. It consists of 0.004" wires sheathed in a 0.020" OD stainless steel tube which was bent so that the tip was about 1 mm from the capillary and equidistant from its ends. A 0.095" OD stainless steel tube was crimped around the 0.020" sheath about 1.5" from the thermocouple tip. The outer tube provided mechanical stability. This thermocouple was calibrated against a Beckman Differential Thermometer which in turn had been calibrated in a 'standard' water bath maintained at $25.00 \pm 0.02^\circ\text{C}$. The latter temperature was determined using a platinum resistance

Figure 4. Schematic of voltage and thermocouple circuits

thermometer. Fifteen comparisons of the thermocouple and the differential thermometer were made over a 10°C temperature range. A least squares fit gave the equation $T_{tc} = 24.55775 V_{tc} + 0.1570$ where V_{tc} is the emf produced by the thermocouple. This equation fit the data with a standard deviation of $\pm 0.026^\circ\text{C}$.

Experimental Methodology

Necessary to this study was the construction of a number of electrotransport cells. Figure 1 shows the general cell construction. Several factors entered into the construction. The cell had the open end up to avoid density inversion as Cd was transported out of the cell. It was also important that the sealed end of the cell was constructed such that current did not pass thru the potential probe nor did the potential probe measure the emf developed at the tungsten electrode-liquid metal interface.³⁹ The actual construction procedure was patterned after that of Verhoeven and Hucke. Four pieces of tungsten wire of 5, 10, or 20 mil diameter were cut. One end of each piece was squared off using 600 grit silicon carbide paper. The current lead alone or both leads if the capillary diameter allowed were coated with Pyrex 2 to 5 mils thick. Small diameter tungsten wires readily form a glass to metal seal with Pyrex No. 7740 glass. The coating was put on by first drawing a larger Pyrex tube down so that the ID of the tube was just sufficient for the lead to be passed thru it.

The lead had been heated and then dipped in trichloro-ethylene to remove grease from it. A small torch using a methane-oxygen fuel mixture was then applied and the tungsten-Pyrex interface became a dark brown as the Pyrex collapsed around the tungsten.

The electrode and potential probe were then inserted into the desired size of capillary and the capillary sealed around them. After this the tungsten-Pyrex interface was a gold-brown color. It was important to avoid bubble formation in the Pyrex near the sealed end of the capillary. The coated tungsten leads were then bent around a 3.175 mm diameter stainless steel rod so that a U-bend resulted about 2 cm from the sealed end of the capillary. This proved to be the most difficult part of the construction process. The problem was to get the tungsten leads sufficiently hot so that they would bend but not fracture while at the same time keeping them coated with Pyrex and electrically insulated from each other. The typical U-bend radius was about 2 mm after the cell had been removed from the rod and the bend slowly cooled.

The crucible electrode and voltage probe were also coated with Pyrex and were eventually placed as shown in Fig. 1.

After the cell had been constructed the tungsten oxide on the exposed electrodes was removed by electropolishing in a dilute NaOH solution. In the case of the electrodes inside the capillary the NaOH was forced by air at a pressure of 0.5 psi thru a stainless steel tube that had been epoxied to a

hypodermic needle. The tube was 0.014" OD for capillaries with ID smaller than 0.030" and 0.021" for larger capillaries. After the electrodes were electropolished to a metallic luster the capillary was purged of NaOH using water and acetone.

The distance from the capillary potential probe to the open end was measured using a traveling microscope. This distance is called the cell length, L . The microscope could be read to ± 0.0001 cm. However the accuracy in determining L was not this high due to reflection and refraction effects. These effects were partially overcome by filling the capillary with acetone before L was determined. Determination of L was also sometimes hindered by cloudiness of the Pyrex near the electrodes. This apparently resulted from pitting which occurred during electropolishing of the electrodes if the current was excessive.

Once the length had been determined the cell was dried and mounted in the cell holder. The 0.020" OD thermocouple was positioned near the capillary and the relative cell-thermocouple geometry fixed for the entire use of the cell. A crucible of triply distilled Hg was attached to the experimental system. In all cases Hg was removed from its storage flask from under the Hg surface by use of a hypodermic syringe. The syringe contents were then emptied into the crucible. This procedure eliminated transfer of any scum or dust that may have been on the Hg surface in the flask.

The system was pumped to a vacuum of 10^{-5} torr overnight.

2-

and flushed several times with helium gas. The cell was then filled by first placing it under the liquid metal surface while a vacuum was maintained and then introducing an atmosphere of helium gas. This forced the liquid metal into the capillary.

About one half hour after filling when the system should have reached equilibrium a small current, ranging from 1.7 to 7.8 amps/cm² for the cells used in this study, was passed thru the cell. In calibrating the cell the following measurements were made in this order: V_{tc} the thermocouple emf, V_c the cell emf, V_s the standard shunt emf, V_{sr} the standard shunt emf with the current reversed, V_{cr} the cell emf with the current reversed, and finally V_{tc} again. This combination of measurements henceforth will be referred to as a calibration measurement. A calibration measurement took less than one minute. The cell was then emptied, refilled and the calibration measurement repeated. This was done several times to allow determination of cell filling reproducibility. The emptying procedure was especially difficult due to the cell's open end being up. To carry it out the cell was partially withdrawn from the crucible and a stainless steel blow tube was inserted into the capillary to the electrode end. The original blow tube of 0.012" OD proved too stiff and replacing it with a 0.008" OD tube reduced the problem of breaking the capillary off at the electrode end. In either case manipulation of the blow tube from outside the vacuum proved difficult

even with a complex system which allowed both the blow tube and a larger guide tube to be independently translated and rotated. Once the blow tube was in place the pressure over the Hg was reduced and the atmosphere of helium within the blow tube forced the capillary metal out.

The cell constant, K , was determined for each of the several fills. Since the standard shunt and cell were in series

$$R_c = \frac{V_c R_s}{V_s} = \frac{\rho_0}{K} \quad [62]$$

where ρ_0 is the resistivity of pure Hg and V_c and V_s are averaged over both current directions. A temperature correction to ρ_0 was made to the average temperature of the several fills as measured by the chromel-alumel thermocouple. For the low current densities used it was assumed that the thermocouple and capillary were at the same temperature. Since L had been measured the average cross sectional area of the capillary could be determined from K . Table IV lists capillary dimensions.

The next step was determination of the relationship between the thermocouple temperature, T_{tc} , and the actual mean cell temperature, $\bar{T}$, for the fixed cell-thermocouple geometry. This was done by filling the cell with pure Hg and performing measurements similar to the calibration measurements five times at each of a number of different current densities to determine the average resistivity of the liquid

Table IV. Capillary Dimensions

Cell	Run	L, cm	$K \times 10^2$, cm	$\% \sigma_K / K$	L/a , cm^{-1}	a, cm	fills
28	11,12	2.6220	.254189	.020	56.93	.04606	7
32	13	2.6138	.139072	.009	76.85	.03401	6
34	14	2.5911	.119798	.007	82.44	.03143	5
37	15	2.5834	.136485	.016	77.12	.03350	7
38	16	2.8200	.315209	.021	53.02	.05319	5
39	17	3.6743	.490700	.013	48.50	.07576	6
40	18	5.2155	.620590	.004	51.38	.10150	6
41	19	3.2296	.417718	.004	49.28	.06553	5
42	20	2.4801	.187667	.007	64.43	.03849	5
44	21	2.1115	.156934	.010	65.01	.03248	5
45	22	2.2622	.099815	.004	84.38	.02681	5
46	23 ^a	2.0579	.097664	.011	81.34	.02530	5
47	24	3.4385	.407821	.009	51.47	.06681	5
48	25	1.9734	.172867	.006	59.87	.03296	6

^aCell cracked in early stages of run 23, no U or D_e data reported.

Hg in the capillary, $\bar{\rho}_0$. Due to ohmic heating increasing j increased the mean capillary temperature and thus the mean capillary resistivity. The value of $\bar{T}$ was found from $\bar{\rho}_0$ using the relationship⁵⁷

$$\bar{\rho}_0 = 94.0766[1. + .8862 \times 10^{-3} \bar{T} + 1.1056 \times 10^{-6} \bar{T}^2], \quad 0 \leq \bar{T} \leq 30^\circ\text{C}. \quad [63]$$

This relationship was assumed valid to about 32°C . The five values of $\bar{T}$ and T_{tc} determined at each j were averaged and used in the computer program FIT described in Appendix II to find the best fit relation between $\bar{T}$ and T_{tc} . On the basis of the largest computed t-statistic this was found to be

$$\bar{T} = \bar{T}_0 + \gamma T_{tc}^3, \quad [64]$$

where $\bar{T}_0$ and γ are determined from the fit. The results of the fit for each cell are given in Table V. Using Eq. [64] with the assumption that heat generation and thermal conductivity do not differ significantly between pure Hg and a 1 atom % Cd amalgam allows determination of $\bar{T}$ from T_{tc} during the mobility and diffusion coefficient runs in the amalgam.

Next the capillary was emptied and the crucible of pure Hg replaced with a new crucible containing an approximately 1 atom % Cd amalgam. The amalgam was made by weighing an amount of pure Hg in the crucible, subtracting the weight of the crucible to determine M'_{Hg} , making an air displacement correction to give M_{Hg} in vacuum and finally weighing an amount M_{Cd} to give a nominal 1 atom % Cd amalgam. Actual

Table V. Fit of Mean Cell Temperature vs. Thermocouple Temperature According to Eq. [64]

Cell	Run	Number of Fields	$\bar{T}_o, ^\circ\text{C}$	$\gamma \times 10^{-2}, (^\circ\text{C})^{-3}$
28	11&12	10	5.7726	(.16658 $\pm$.00292)
32	13	15	-1.5585	(.24632 $\pm$.00267)
34	14	15	0.2189	(.22564 $\pm$.00151)
37	15	15	-2.8166	(.26032 $\pm$.00081)
38	16	9	7.4174	(.14505 $\pm$.00110)
39	17	8	9.7058	(.12556 $\pm$.00059)
40	18	7	12.454	(.09150 $\pm$.00068)
41	19	7	8.8218	(.13319 $\pm$.00109)
42	20	11	1.4304	(.20985 $\pm$.00278)
44	21	12	-1.4542	(.24335 $\pm$.00190)
45	22	16	-0.5269	(.23514 $\pm$.00133)
47	24	10	6.0531	(.16256 $\pm$.00117)
48	25	7	5.3213	(.17187 $\pm$.01211)

weighed in starting compositions are given in Table VII. Before weighing small holes had been drilled thru the Cd chunks. The Cd was strung on a fine tantalum wire and suspended in the vacuum system over the Hg crucible. A vacuum was pumped overnight, the system flushed several times with purified helium gas and the Cd plunged under the Hg surface. The Cd held under the Hg surface dissolved in less than fifteen minutes. Using a plunger device the crucible contents were vigorously stirred several times over a one hour period. The surface of the alloy did not exhibit scum formation.

The calibration measurement procedure was repeated five times in order to measure the resistivity of the amalgam before any electrotransport took place. Equation [62] was used to calculate this resistivity, $\bar{\rho}_{10}$. The current density was the same as that for the cell calibration. The average of these five measurements served as a measure of $\bar{\rho}_{10}$ in the calculation of U and D_e . During each of the measurements the current was on for less than one minute each time and was reversed in the procedure so that no significant electrotransport should have taken place.

The output current was now increased, usually to a value that would give $j=200$ amps/cm². After the power supply had stabilized for one half hour the current was switched thru the cell in such a manner that Cd was transported out of the cell and a timer was turned on. In order to determine the average cell composition at any time the following measurements were

made in order: V_{tc} , V_c and the experimental time τ simultaneously, V_s , and V_{tc} again. This series of measurements henceforth will be referred to as a measurement. The measurement was repeated 20 to 40 times over 5 to 10 hours and then repeated periodically over several days until no additional significant change in V_c was observed. It was assumed that steady state had then been reached and the following steady state procedure was carried out. Steady state measurements were repeated 10 times at about 5 minute intervals. Next 2 additional measurements were made but for the second the current was reversed during the V_c and V_s determinations. This current reversal lasted about 25 seconds. It allowed determination of V_o , one half the difference of V_c for forward and reverse current. The actual cell voltage was then taken as $V_c - V_o$ to take into account such things as thermal emfs. Finally one or two measurements were made to assure that the mean cell composition had not been altered significantly by the current reversal. This completed the measurements necessary for the calculation of U and D_e at the initial current density.

The value of R_{cc} , and if necessary that of R_{st} , was changed to increment j usually to a larger value. Measurements were made occasionally and when an apparent steady state had been reached the steady state measurement procedure was repeated. Several values of j were used for each cell. The

current density was no longer increased when excessive heating of the cell current leads occurred or when V_c and V_{tc} became appreciably more unstable. Sometimes after the maximum j value measurements had been completed j was reduced to one or more lower j values to check the reversibility of the separation processes. In two cases j was decreased from 200 to 50 amps/cm² in steps of 50 amps/cm².

EXPERIMENTAL RESULTS AND DISCUSSION

Since Cd goes to the cathode during electrotransport of a Cd amalgam, making the capillary electrode the anode causes Cd to be transported from the capillary. The region around the anode is then depleted in Cd and a front marking the division between depleted amalgam and amalgam of the initial composition moves down the capillary from the anode to the open mouth. The front broadens as it moves down the capillary.

Mobility

Prior to the time when the front reaches the capillary mouth Eq. [42] holds. Since $\bar{\rho}$ is proportional to the mean capillary composition Eq. [42] can be written in terms of $\dot{\bar{X}}$, that is the time rate of change of the average Cd composition of the capillary amalgam. Then a plot of $\bar{X}$ vs t during the initial stages of an electrotransport experiment should be linear up to the time when the front reaches the mouth. Figure 5 is such a plot of a typical run. It shows the magnitude of the experimental scatter.

Assuming that the alloy composition at the capillary mouth is fixed throughout the experiment at the initial composition, and that L , K , and β are known leaves only I and $\dot{\bar{\rho}}$ to be determined so that Eq. [42] can be used to find U_{Cd} . In practice I is found by measuring the voltage drop across R_s and $\dot{\bar{\rho}}$ is found by calculating $\bar{\rho}$ for a number of measurements made over a period of time and doing a least squares fit of the

Figure 5. Initial part of $\bar{X}$ vs t of run 21

data to the equation

$$\bar{\rho}(t) = \dot{\rho}t + \bar{\rho}_{int} \quad [65]$$

where $\bar{\rho}_{int}$ can then be taken as the resistivity of the capillary amalgam at zero time.

There are three ways to consistently evaluate the parameters X_{1m} and ρ_m of Eq. [42]. In all cases $X_{2m} = 1 - X_{1m}$. In the first case $\rho_m = \bar{\rho}_{int}$ and Eq. [39] is used so that Eq. [42] becomes

$$U_{1A} = \frac{KL^2 \dot{\rho}}{(\bar{\rho}_{int} - \rho_o) \bar{\rho}_{int} IC1} \quad [66]$$

where

$$C1 = 1 - \frac{.01(\bar{\rho}_{int} - \rho_o)}{\beta} \quad [67]$$

The second method of evaluating U_1 uses the resistivity of the capillary amalgam measured at a low current just prior to the start of the electrotransport run. This value is $\bar{\rho}_{10}$. However a temperature correction to $\bar{\rho}_{10}$ is made to take into account the heat generated at the higher current. Thus

$$\bar{\rho}_j = \frac{d\rho}{dT} (\bar{T} - \bar{T}_{low j}) + \bar{\rho}_{10} \quad [68]$$

Then

$$U_{1B} = \frac{KL^2 \dot{\rho}}{(\bar{\rho}_j - \rho_o) \bar{\rho}_j IC2} \quad [69]$$

where

$$C2 = 1 - \frac{.01(\bar{\rho}_j - \rho_o)}{\beta} \quad [70]$$

The third method uses the weighed in concentration of Cd,

$X_{1m} = XI$, so

$$U_{1C} = \frac{KL^2 \bar{\rho}}{XI(\beta XI + \rho_0) I \beta C3} \quad [71]$$

where

$$C3 = (1 - .01XI) \quad [72]$$

In Eqs. [66] and [69] the assumptions are made that $(\bar{\rho}_{int} - \rho_0)$ and $(\bar{\rho}_j - \rho_0)$ are constant for a given run, that is they are independent of temperature. This is just the earlier assumption that heat generation and conductivity are independent of composition between pure Hg and the 1 atom % amalgam.

Table VI gives the results of the mobility determinations made during the course of this work. It can be seen that the scatter for the three values of U determined for a given run is less than that between runs. Also the scatter tends to increase as capillary size increases possibly due to the presence of convection during early stages of the run. Table VII gives the conditions under which $\bar{\rho}_0$ was measured and the initial cell concentration as calculated from $\bar{\rho}_{int}$, calculated from $\bar{\rho}_{10}$ and weighed in.

In order to calculate D_e from Eq. [50] a value of U_1 must be picked. In this study U_1 was chosen to be the average measured for cells less than 0.035 cm radius and with j about 200 amps/cm². Table VI gives these average values of U_{1A} , U_{1B} , and U_{1C} . Using U_{1A} for comparison with values in the literature gives favorable results. Thus in this study $U \times 10^4 = -9.92 \pm 0.25$ cm²/v-sec compared with literature

Table VI. Mobilities Calculated from Electrotransport Experiments

Run ^a	Points in Fit	Capillary Radius, cm	Mobility, cm ² /v-sec		
			U _{1A}	U _{1B}	U _{1C}
22	35	.02681	-9.5408x10 ⁻⁴	-9.5887x10 ⁻⁴	-9.5204x10 ⁻⁴
14	25	.03143	-10.0995	-10.0747	-10.2887
21	33	.03248	-10.0093	-9.9716	-10.0519
25	29	.03295	-9.7957	-9.7507	-9.7288
15	24	.03348	-10.1463	-10.1769	-10.2585
13	29	.03401	-10.1299	-10.1120	-10.1561
20	38	.03849	-9.4951	-9.4169	-9.5404
11	23	.04597	-9.8569	-9.8014	-10.0895
12 ^b	20	.04597	-10.3398	-10.3540	-10.5981
16 ^c	15	.05319	-10.8429	-10.7658	-10.8682
19	24	.06553	-9.5551	-9.5437	-9.5968
24	27	.06680	-9.2879	-8.9303	-9.0665
17	28	.07573	-9.6646	-9.7526	-9.8070
18	25	.10150	-8.2255	-8.1887	-8.2161
Ave. < .035 cm radius			-9.9150 ₊ .2467	-9.8995 ₊ .2235	-9.9492 ₊ .3166

^aAll runs made with a j of about 200 amps/cm² except for run 15 at about 600 amps/cm²; run 16 at 186 but switched to 200 amps/cm² before steady state reached; and run 17 at about 150 amps/cm².

^bRun 12 made after run 11 using the same cell and the same reservoir amalgam. The cell was not cleaned between runs.

^cRun 16 exhibited a change in slope of the $\bar{\rho}$ vs t curve between the time periods 0 to 1.25 hours and 2.35 to 6.5 hours. The first period led to even larger mobility values than are given in the table for the second period.

Table VII. Parameters Associated with the Analyses of Mobility Data.

Run	$\bar{\rho}$, $\mu\Omega$ cm/hr	$\bar{\rho}_{int}$, $\mu\Omega$ cm	$\bar{\rho}_j$, $\mu\Omega$ cm	Initial Concentration, Atom %			σ , $\bar{\rho}$ vs t fit
				Based on $\bar{\rho}_{int}$	Based on $\bar{\rho}_j$	Weighed in	
22	.1101 $\pm$.0004	91.8820 $\pm$.0023	91.9030	.99236	.99762	.99988	$\pm$.0078
14	.1039 $\pm$.0002	91.7842 $\pm$.0015	91.7736	1.02243	1.01977	.99996	$\pm$.0035
21	.1246 $\pm$.0005	91.8485 $\pm$.0017	91.8325	1.00834	1.00432	.99982	$\pm$.0057
25	.1290 $\pm$.0004	91.9390 $\pm$.0024	91.9197	.99690	.99206	.99926	$\pm$.0036
15	.3114 $\pm$.0007	91.9987 $\pm$.0016	92.0115	1.00703	1.01024	.99857	$\pm$.0046
13	.1016 $\pm$.0002	91.8631 $\pm$.0013	91.8557	1.00375	1.00188	.99915	$\pm$.0040
20	.1006 $\pm$.0003	91.8270 $\pm$.0015	91.7918	1.01326	1.00445	.99940	$\pm$.0054
11	.1004 $\pm$.0002	91.7871 $\pm$.0011	91.7626	1.03111	1.02497	1.00001	$\pm$.0026
12	.1055 $\pm$.0003	91.7912 $\pm$.0013	91.7971	1.02496	1.02644	--- ^a	$\pm$.0026
16	.0937 $\pm$.0008	91.8595 $\pm$.0036	91.8292	1.01029	1.00270	1.00023	$\pm$.0039
19	.0777 $\pm$.0003	91.9024 $\pm$.0012	91.8974	1.00568	1.00442	.99980	$\pm$.0028
24	.0687 $\pm$.0004	92.0236 $\pm$.0014	91.8591	1.01397	.97278	.99788	$\pm$.0039
17	.0524 $\pm$.0002	91.8636 $\pm$.0010	91.9023	1.00560	1.01528	.99971	$\pm$.0031
18	.0412 $\pm$.0003	91.9913 $\pm$.0017	91.9724	1.00152	.99679	.99799	$\pm$.0044

^aRun 12 made after run 11 using the same cell and the same crucible amalgam.

values of -9.7 at 25°C in a dilute Cd amalgam,¹ -10.3 at 27°C in a 1 atom % Cd amalgam,³² and -10.0 at 43°C in a 1 atom % Cd amalgam.⁵⁹

Diffusion

Equations [48], [49], and [50] were used to calculate D_e by an iterative computer process. The process was carried out by plugging in the correct value of Q and then incrementing S until the right and left sides of Eq. [50] were equal to within .00001. In practice Eq. [39] was used to relate composition to resistivity so

$$Q = \frac{\bar{\rho}_{int} - \rho_{oj}}{\rho_{oj}} \quad [73]$$

where ρ_{oj} was determined from Eqs. [63] and [64], and is the resistivity of pure Hg at the mean cell temperature. Also the left side of Eq. [50] became

$$\frac{\bar{X}_{1ss}}{\bar{X}_{1o}} = \frac{\bar{\rho}_{ss} - \rho_{oj}}{\Delta\rho} \quad [74]$$

where $\Delta\rho = \bar{\rho}_{int} - \rho_{oj}$ and $\bar{\rho}_{ss}$ was the mean capillary resistivity at steady state for a given current density. Finally Eq. [49] was rewritten as

$$S = \frac{U_{1A} \rho_{oj} jL}{D_e} \quad [75]$$

Appendix III lists D_e calculated for each j of each run. These values were determined by substituting the average U_{1A} , U_{1B} , and U_{1C} for U in Eq. [50]. Each listed value of D_e

resulted from the average of about ten measurements at steady state conditions. In some cases, such as run 25, two or more successive values of j are nearly identical. This indicates the experimental scatter at steady state since in these cases at least one day passed between taking of data from which the two D_e values were calculated. Run 13 shows an example of going back to a lower j after the maximum j had been measured. The good agreement between the two D_e values at 300 amps/cm^2 shows the independence of D_e from the experimental procedure. Appendix III also shows that D_e at 200 amps/cm^2 for the cells used in the determinations of the values of U_{1A} , U_{1B} , and U_{1C} ranged from 1.50 to $1.56 \text{ cm}^2/\text{sec}$. Appendix IV presents values of D measured by various investigators with discussion of the methods used. The best value is found to be $1.53 \pm 0.05 \text{ cm}^2/\text{sec}$. Thus it may be safely assumed that convection was minimal in runs 13, 14, 21, 22, and 25 at a current density of 200 amps/cm^2 .

Figure 6 is a plot of $\bar{X}$ vs t for all of run 18. It is of interest to note that the mean cell composition increases with increasing j above 200 amps/cm^2 . This behavior is due to the presence of convection and should be present in all capillaries at a sufficiently high current density. It is particularly emphasized in this large radius cell.

Figure 7 is a plot of D_e vs j for all work done in this project. The points represent the average D_e of what was usually 10 measurements at each j except for the cases with

Figure 6. $\bar{X}$ vs t for all of run 18

Figure 7. D_e vs j for all runs

cell radii of .033, .046, or .066 cm. In the .046 cm case runs 11 and 12 were made in the same cell and the results are averaged for clarity in the figure. Similarly the .033 cm data represent the average from five cells and the .066 cm data the average from two cells. Table VIII gives these averaged values of j and D_e . Also given are δD_e , a measure of the experimental scatter in D_e between observations, and the number of observations made.

The lines drawn on Fig. 7 represent the results of applying the stepwise multiple regression technique FIT described in Appendix II. The broken lines are for the data of Appendix III and the solid lines for the data of Table VIII. In all cases the line represents the equation

$$D_e = D + b_2 j^2 + b_4 j^4. \quad [76]$$

Figure 8 indicates the spread of the D_e values obtained at a given j in several different cells. It is quite evident that the spread increases with increasing j and increasing capillary radius.

Statistical Analyses of D_e Results

The primary motivation for carrying out these measurements was to obtain sufficient data to allow empirical determination of the dependence of D_e on j and a . This determination was made in several ways, using one of the computer programs, FIT or HELARCTOS II. Both of these multiple regression programs are described briefly in Appendix II. In all cases

Table VIII. Average D_e for Nominally .033, .046, and .066 cm Capillaries

j , amps/cm ²	$D_e \times 10^5$ cm ² /sec	δD_e	Number of Observations
Averaged from runs 13,14,15,21, and 25. Nominal .033 cm radius			
50.01	1.500		1
100.00	1.503		1
149.99	1.529		1
200.04	1.545	+.027	5
300.01	1.636	-.050	3
399.82	1.709	.021	3
599.74	1.926	.033	6
799.66	2.208	.044	4
999.28	2.613	.050	4
1099.07	2.840	.043	2
1199.17	3.054	.078	2
1298.70	3.373	.098	2
1398.57	3.563	.296	3
Averaged from runs 11 and 12. .046 cm radius			
199.33	1.679	+.010	2
299.13	1.872		1
398.43	2.232	.003	2
498.38	2.658		1
597.97	3.147	.010	2
697.30	3.634		1
797.16	4.336	.148	2
896.68	4.783		1
996.58	6.139	.293	2
1096.23	7.065		1
Averaged from runs 19 and 24. Nominal .066 cm radius			
50.00	1.508		1
100.00	1.556		1
150.00	1.674		1
199.91	2.050	+.110	3
300.04	3.215	-.080	2
399.90	4.868	.259	2
449.89	5.409		1
499.93	6.557	.285	2
600.00	8.570	.311	2
700.10	11.290		1

Figure 8. Experimental scatter of D_e data from several runs

D_e was the dependent variable and the y-axis intercept of the fit should have represented D .

In all regression analyses the following criteria were used in evaluating the value of a particular model. First a large value of some calculated statistic (a calculated t-statistic for each coefficient calculated with FIT and a multiple correlation coefficient R^2 for HELARCTOS II) indicated a possibly good model. Second the intercept of each fit was expected to have a value close to the mutual diffusion coefficient measured by other investigators. This restriction was relaxed as the extent of the extrapolation from the region of the data points to the y-axis intercept was increased. Finally a negative coefficient for a particular term in a model was assumed to be physically meaningless.

The first regression technique used attempted to determine the j dependence of D_e as shown by each run considered separately. This was also done for the combined runs of nominal radius .033 cm, the .046 cm runs and the .066 cm runs. Input data were from Table VIII or Appendix III. In some cases a sufficient number of data points were not available to allow fitting. Models included the theoretically predicted j^2 and j^4 dependences, a combined j^2 plus j^4 dependence, and a model allowing for j , j^2 , j^3 , and j^4 dependence. Results are shown in Table IX. They indicated that in all cases a j^2 dependence was more closely followed than a j^4 dependence. In several cases the addition of a fourth power term to the predominant

Table IX. Results of Regression Analyses of D_e vs j^a

Run	r, cm	$D_e = D + b_2 j^2$			$D_e = D + b_4 j^4$		
		$D \times 10^5$	$b_2 \times 10^{10}$	t-value	$D \times 10^5$	$b_4 \times 10^{16}$	t-value
11	.04606	1.4765	.44+.01	37.8	2.3163	.35+.03	12.3
12	.04606	1.4300	.50+.01	41.6	2.1992	.46+.06	7.9
13	.03401	1.5083	.116+.003	34.9	1.7748	.060+.004	15.5
14	.03143	1.4886	.109+.005	21.2	1.6758	.10+.02	6.3
15	.03350	1.5871	.102+.003	36.7	1.9673	.047+.005	10.2
16	.05319	.6430	1.48+.05	30.3	2.4875	2.1+.1	21.2
17	.07546	.9732	3.0+.1	22.0	2.3816	10.9+.6	17.5
18	.1015	---b	---b	---b	---b	---b	---b
19	.06553	1.4123	2.06+.09	24.0	3.3619	3.6+.6	6.1
20	.03849	1.5349	1.793+.004	49.9	1.8780	.12+.01	12.4
21	.03248	---b	---b	---b	---b	---b	---b
22	.02581	1.4510	.050+.002	30.3	1.6127	.016+.002	14.9
24	.06581	1.3764	1.948+.003	74.6	1.9596	5.6+.5	10.8
25	.03296	1.4923	.16+.03	6.0	1.5019	3.9+.7	5.8
A11	.033	1.5189	.107+.002	47.6	1.7164	.057+.003	18.1
A11	.046	1.4735	.46+.01	36.4	2.3012	.38+.03	13.8
A11	.066	1.3524	2.04+.03	61.4	2.3289	4.5+.4	12.3

^a D_e is the average of results from the 10 steady state measurements.

^bInsufficient data points for a fit to be made.

Table IX. (continued)

$D_e = D + b_2 j^2 + b_4 j^4$					
Run	$D \times 10^5$	$b_2 \times 10^{10}$	$b_4 \times 10^{16}$	t_2 -value	t_4 -value
11	1.6058	.37 + .04	.06 + .03	9.7	2.1
12	---b	---b	---b	---b	---b
13	1.5734	.083 + .007	.018 + .004	11.7	4.7
14	1.4886	.14 + .01	-.03 + .02	8.8	-1.8
15	1.5596	.11 + .01	-.00 + .01	8.5	-0.6
16	1.3409	.89 + .01	.9 + .1	13.4	9.2
17	1.5500	1.7 + .2	4.9 + .9	7.3	5.7
18	---b	---b	---b	---b	---b
19	.8919	2.6 + .2	-1.1 + .4	13.7	-3.3
20	1.5686	.16 + .02	.01 + .01	10.8	1.4
21	---b	---b	---b	---b	---b
22	1.4882	.037 + .005	.004 + .002	7.9	2.9
24	1.3387	2.1 + .1	-.5 + .2	25.8	-2.0
25	1.4959	.1 + .1	1.6 + 2.5	.9	.6
A11 .033	1.5050	.12 + .01	-.005 + .004	15.0	-1.2
A11 .046	1.5520	.41 + .05	.04 + .04	8.7	1.0
A11 .066	1.3147	2.1 + .1	-.24 + .24	20.1	-1.0

Table IX. (continued)

$D_e = D + b_1 j^1 + b_2 j^2 + b_3 j^3 + b_4 j^4$						
Run	$D_x 10^5$	$b_1 \times 10^7$	$b_2 \times 10^{10}$	$b_3 \times 10^{13}$	$b_4 \times 10^{16}$	Order Terms Entered
11	2.1540	.7 + .4	3. + 1.	-3. + 1.	1.5 + .4	2-4-3-1
12	---b	---b	---b	---b	---b	---b
13	1.3649	.1 + .2	-.2 + .3	.2 + .3	.0 + .1	3-1-2-4
14	1.2273	.2 + .5	.4 + 1.3	1. + 2.	-.3 + .7	2-3-1-4
15	2.7642	-.7 + .6	2. + 1.	-1.3 + .9	.4 + .3	2-1-4-3
16	1.3420	.5 + .3	-2. + 1.	6. + 1.	-3.0 + .7	3-4-2-1
17	3.4097	-2. + 2.	6. + 11.	0. + 24.	0. + 20.	3-4-1-2
18	---b	---b	---b	---b	---b	---b
19	---b	---b	---b	---b	---b	---b
20	1.5270	.0 + .4	.1 + .9	.0 + .9	0. + 3.	2-4-1-3
21	---b	---b	---b	---b	---b	---b
22	1.3690	.1 + .1	-.1 + .2	.1 + .1	.00 + .03	2-4-1-3
24	1.8639	-1.1 + .2	8. + 1.	-13. + 3.	8. + 2.	2-4-1-3
25	---b	---b	---b	---b	---b	---b
A11 .033	1.4667	.04 + .07	.0 + .2	.1 + .2	-.04 + .07	2-1-4-3
A11 .046	1.4650	.0 + 1.	1. + 3.	-1. + 3.	0. + 1.	2-4-3-1
A11 .066	1.9075	-1.1 + .5	8. + 3.	-12. + 6.	7. + 4.	2-4-1-3

quadratic term gave a more reasonable intercept but in other cases the fourth power coefficient was negative. Finally the model allowing all powers of j up thru four gave meaningful data only as to the order in which the various terms were entered into the fit. The latter was determined by the importance of each term in reducing the sum of squares. For example in run 11 the order in which the terms were entered was j^2 , j^4 , j^3 , and j . In fact generally speaking the j^2 term was most important and the j^4 term next most important. The conclusion was thus tentatively reached that $D_e \propto j^2$ suggesting the dominant convection mechanism to be the electrokinetic effect as experimentally observed by Lodding.^{28,29} But, as they observed, a j^4 dependent mechanism also seemed to be present.

In order to further check on the mechanism of convection it was deemed desirable to study the radial dependence of D_e . The experimental observations of D_e could not be used because slightly different j values were used in each run. For example the nominally $j=600$ amps/cm² values were 597.9939 and 600.0088 amps/cm² in runs 11 and 19 respectively. What was done was to use the coefficients of the $D+b_2j^2+b_4j^4$ model for each run to calculate D_e^{calc} at several multiples of $j=100$ amps/cm² covering the range of j at which measurements were made in a particular run. Then these D_e^{calc} values were fit with various powers of the capillary radii being used as independent variables. Of course the weakness of this technique was that the dependent variables D_e^{calc} were not the experi-

mental observables D_e and in fact the D_e^{calc} were dependent on what model has been chosen to calculate them. For this reason no data are reported on these fits individually but the regression analysis using FIT did indicate the predominant convection mechanism to be dependent on a^4 and not on a^2 as predicted by the electrokinetic theory. Also no combination of the radial dependences exhibited by the theoretical mechanism led to as good a fit as the simple a^4 dependence.

Because of the obvious shortcomings of the above described technique for determining the radial dependence of D_e it was decided to attempt fits to the combined j and a dependences. This was done using the program HELARCTOS II.

Since the independent variables for HELARCTOS II were of the form $j^s a^t$ all data points could serve as observations for each model. The measurements made at steady state (usually 10 in number) at a given nominal j in a run were counted as being independent so that a total of 1315 observations were available. However in practice 60 of these were not used. These 60 observations were from run 14 at $j > 1025 \text{ amps/cm}^2$. The justification for not including them was that the mean capillary concentration was observed to decrease as a function of j above 1025 amps/cm^2 whereas it had increased from 800 to 1000 amps/cm^2 . This resulted in a decrease in the calculated D_e . In all of the measurements made in this work this was the only time such behavior was observed. Furthermore it is difficult to imagine a convection process that would slowly decrease D_e .

as j increased. Throwing out these 60 observations left a total of 1255 observations input to HELARCTOS II.

The combined j and a dependences of each theoretical mechanism were fit as were various combinations of these dependences. Values of the multiple R^2 statistic, the intercept, and a notation indicating those terms with a negative coefficient are given in Table X. The intercepts and the coefficients with their standard errors are found in Appendix V. The input data were unweighted, that is the experimental errors were assumed independent of j and a .

On the basis of R^2 the $j^4 a^6$ dependent charge density mechanism best explained the data but the y -axis intercept was much too large. In fact of all the theoretical dependences the $j^2 a^2 + j^4 a^{10}$ term had the smallest intercept and even it was about 6% higher than the expected value of D . Taking a clue from the semi-independent fits to j and a models separately, a $j^2 a^4$ model gave the highest R^2 of any fit and also a very reasonable value of D .

It was worthwhile considering whether any other single term fit the data better than the $j^2 a^4$ term. Table XI gives information from several models. The top number in each box is the R^2 value and the bottom is the intercept. The $j^3 a^5$ model came close to explaining the data as well as the $j^2 a^4$ model. In fact $j^3 a^5$ had a slightly larger R^2 but the intercept was about 13% high. The $j^2 a^5$ model corresponding to Kuzmenko's experimental observation⁴⁵ could not satisfactorily

Table X. Fits to Various Predicted Models. 1255 Observations, Unweighted

Model	R^2	Intercept $\times 10^5$	Comments ^a
$j^2 a^2$	.4368	1.7038	
$j^4 a^6$	.8112	1.9400	
$j^4 a^8$	.7314	2.3100	
$j^4 a^{10}$	.4155	2.7171	
$j^2 a^2 + j^4 a^6$	.8168	2.0773	$j^2 a^2 < 0$
$j^2 a^2 + j^4 a^8$	.8271	1.7038	
$j^2 a^2 + j^4 a^{10}$	.6982	1.6027	
$j^4 a^6 + j^4 a^8$	.8432	1.9894	
$j^4 a^6 + j^4 a^{10}$	.8347	1.9587	
$j^4 a^8 + j^4 a^{10}$	.8225	2.1581	$j^4 a^{10} < 0$
$j^2 a^2 + j^4 a^6 + j^4 a^8$	.8458	1.8814	
$j^2 a^2 + j^4 a^6 + j^4 a^{10}$	.8347	1.9689	$j^2 a^2 < 0$
$j^2 a^2 + j^4 a^8 + j^4 a^{10}$	.8570	1.7934	$j^4 a^{10} < 0$
$j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.8462	2.0143	$j^4 a^{10} < 0$
$j^2 a^2 + j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.8573	1.7658	$j^4 a^6, j^4 a^{10} < 0$
$j^2 a^4$	.8922	1.4875	

^aIndicates those terms whose coefficient was negative.

Table XI. Fits to Single Term Models of Form $j^s a^t$. 1255 Observations, Unweighted

t→	1	2	3	4	5	6	7	8	9	10
s ↓										
1										
2		.4368 ^a 1.7038	.8188 1.2130	.8922 1.4875	.7163 2.0126					
3		.1392 2.5866	.3791 2.1094	.7155 1.7024	.8952 1.7052	.8294 2.0043				
4						.8112 1.9400		.7314 2.3100		.4155 2.7171

^aThe top figure is R^2 and the lower figure the intercept of each fit.

explain these data. Thus the conclusion was reached that the best single term fit was one dependent on j^2a^4 .

Assuming a j^2a^4 dependent mechanism as the dominant convection mechanism it is still of interest to see if the addition of one or more of the theoretically predicted dependences might lead to a better fit. Table XII shows data for several such models. These data indicate that if in fact there is some as yet unknown mechanism dependent on j^2a^4 then the data of this work can not be significantly better fit by a model which also includes any of the theoretically predicted dependences.

The following was done to see if one of the predicted mechanisms was most important for one range of j or a and another for a different range. HELARCTOS II was used to first fit all data with $j < 410$ amps/cm² and then all data with $j > 410$ amps/cm². Next data from all cells with radii $< .047$ cm and then all with radii $> .047$ cm were fit. Table XIII shows the results. R^2 for the j^2a^2 and j^4a^6 models was larger than R^2 of the j^2a^4 model when data from cells having radii $> .047$ cm was considered. But the intercept of these two cases was far from the accepted value of D . In all other cases the best model was j^2a^4 . The conclusion was that a j^2a^4 term must predominate in an explanation of the data.

The most obvious fault with the fitting procedures described to this point was that there had been no weighting of the data to take into account variations in experimental error. A determination of experimental error can be made in two ways.

Table XII. Fits to Models Including a $j^2 a^4$ Term. 1255
Observations, Unweighted

Model	R^2	Intercept $\times 10^5$	Comments ^a
$j^2 a^4 + j^2 a^2$	.8963	1.3990	
$j^2 a^4 + j^4 a^6$	.9064	1.5515	
$j^2 a^4 + j^4 a^8$	.8960	1.3788	$j^4 a^8 < 0$
$j^2 a^4 + j^4 a^{10}$	.9122	1.3320	$j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6$	.9065	1.5733	$j^2 a^2 < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^8$	.8973	1.3605	$j^4 a^8 < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^{10}$	.9128	1.3534	$j^2 a^2, j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^8$	.9109	1.4343	$j^4 a^8 < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^{10}$	.9162	1.4040	$j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^8 + j^4 a^{10}$	.9186	1.4490	$j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6 + j^4 a^8$	.9180	1.5425	$j^2 a^2, j^4 a^8 < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6 + j^4 a^{10}$	.9160	1.5271	$j^2 a^2, j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^8 + j^4 a^{10}$	.9187	1.4564	$j^2 a^2, j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.9187	1.4506	$j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.9201	1.5060	$j^2 a^2, j^4 a^{10} < 0$
$j^2 a^4$	.8922	1.4875	

^aIndicates those terms whose coefficient was negative.

Table XIII. Fits to Single Term Models of the Form $j^s a^t$ over Specified Ranges of j and a . Unweighted

Model	$j < 410$ amps/cm ² 617 points	$j > 410$ amps/cm ² 638 points	$a < .047$ cm 796 points	$a > .047$ cm 459 points
$j^2 a^2$	.4435 ^a 1.7217	.2659 1.6862	.7306 1.4707	.9425 1.2748
$j^4 a^6$	.7204 2.1056	.7692 2.1007	.9099 1.7829	.8562 2.4986
$j^4 a^8$	.8206 1.8829	.7478 2.7691	.8893 1.9079	.6848 2.8416
$j^4 a^{10}$	.3890 2.8543	.5816 3.2000	.8171 2.0104	.3830 3.5131
$j^2 a^4$	.8220 1.3974	.8844 1.4299	.9789 1.4714	.8342 1.6003

^aThe top figure is R^2 and the lower figure the intercept of each fit.

First one can look at the standard deviation of the 10 measurements made at steady state at each j . This standard deviation was due to fluctuations during the hour or so during which the 10 steady state measurements were made - primarily uncertainties in the measured emfs due to fluctuations in power supply output and temperature variations in the room or bath.

A second type of fluctuation observed in measurements of D_e made in different cells at nominally the same j and a was usually larger and more important. These fluctuations, δD_e , were mainly due to the uncertainty in filling, the uncertainty in the calibration of the thermocouple against the mean cell temperature and the uncertainty as to whether this calibration was also good during the mobility-diffusion run. This second type of fluctuation could be examined in three cases, given in Table VIII - the .033 cm cells, the .046 cm cells and the .066 cm cells.

By looking at the two types of fluctuations at once, one was able to get an overall measure of experimental uncertainties. The results of this process are shown in Table XIV which gives the combined experimental scatter in D_e and a weighting factor W defined by

$$W = \frac{.05}{\delta D_e(j,a)} , \quad [77]$$

The 1255 values of the dependent variable and of each independent variable in a given model could now be multiplied

Table XIV. Estimated Experimental Scatter in Measurements of D_e over Specified Ranges of j and a

Capillary Radius, cm	Current Density, amps/cm ²	δD_e^a	Weighting Factor
$a < .035$	$0 < j < 825$	$\pm .05$	1.0000
"	$825 < j < 1025$	.15	.3333
"	$1025 < j < 1325$	.20	.2500
"	$1325 < j < 1800$	.30	.1667
$.035 < a < .047$	$0 < j < 725$	.05	1.0000
"	$725 < j < 1025$	.15	.3333
"	$1025 < j < 1400$	.30	.1667
$.047 < a < .110$	$0 < j < 325$	.10	.5000
"	$325 < j < 800$	.30	.1667

^a δD_e is the estimated experimental scatter $\times 10^5$ in units of cm²/sec.

by this weighting factor. In this case HELARCTOS II was made to consider as an independent variable the constant $X_0=1$. This meant that the intercept was now counted as an independent variable and a standard error was calculated for the intercept variable just as for all other variables in a given model.

Using this procedure fits to models corresponding to the theoretically predicted mechanisms were made and are shown in Table XV. The coefficients and their standard errors are shown in Appendix VI. Weighting of the data generally increased the goodness of fit as indicated by a larger R^2 and an intercept more in line with the expected value of about 1.53×10^{-5} cm^2/sec . However none of the theoretically predicted dependences was by itself very satisfactory. The best combination model seemed to be that including $j^2 a^2$ with either $j^4 a^8$ or $j^4 a^{10}$. But as with the unweighted fits a simple $j^2 a^4$ models gave a better fit than any involving the predicted dependences.

Table XVI gives results from fits of the weighted data to several single term models of the general form $j^s a^t$. There is little doubt that a $j^2 a^4$ model most satisfactorily explains the data.

Table XVII shows the results of a number of fits of the weighted data to models including the $j^2 a^4$ term and one or more of the predicted dependences. About all that can be said is that the simple $j^2 a^4$ model explains the data so well that the inclusion of any other terms in a model does not appear to significantly better the fit.

Table XV. Fits to Various Predicted Models. 1255 Observations, Weighted According to Table XIV

Model	R^2	Intercept $\times 10^5$	Comments ^a
$j^2 a^2$	.5190	1.4861	
$j^4 a^6$	.8285	1.7644	
$j^4 a^8$	.7255	1.9161	
$j^4 a^{10}$	.5216	1.9969	
$j^2 a^2 + j^4 a^6$	.8285	1.7685	$j^2 a^2 < 0$
$j^2 a^2 + j^4 a^8$	.8849	1.5584	
$j^2 a^2 + j^4 a^{10}$	.8193	1.5029	
$j^4 a^6 + j^4 a^8$	.8713	1.7897	
$j^4 a^6 + j^4 a^{10}$	.8657	1.7834	
$j^4 a^8 + j^4 a^{10}$	.8542	1.8349	$j^4 a^{10} < 0$
$j^2 a^2 + j^4 a^6 + j^4 a^8$	.8928	1.6253	
$j^2 a^2 + j^4 a^6 + j^4 a^{10}$	.8774	1.6674	
$j^2 a^2 + j^4 a^8 + j^4 a^{10}$	.9101	1.6141	$j^4 a^{10} < 0$
$j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.8747	1.7965	$j^4 a^{10} < 0$
$j^2 a^2 + j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.9177	1.5389	$j^4 a^6, j^4 a^{10} < 0$
$j^2 a^4$	.9348	1.5330	

^aIndicates those terms whose coefficient was negative.

Table XVI. Fits to Single Term Models of the Form $j^s a^t$. 1255 Observations, Weighted According to Table XIV

$t \rightarrow$	1	2	3	4	5	6	7	8	9	10
$s \downarrow$										
1	.4995 ^a 0.9391	.8368 0.8750	.7810 1.4037	.6245 1.7432	.5201 1.8896	.4601 1.9185				
2	.2864 1.6904	.5190 1.4861	.8458 1.3614	.9348 1.5330	.7650 1.7745	.6101 1.9042				
3	.1929 1.9176	.2855 1.8394	.4616 1.7314	.7387 1.6294	.9331 1.6548	.8431 1.8009		.5628 1.9671		
4	.1443 2.0080	.1831 1.9769	.2545 1.9305	.3854 1.8656	.6007 1.7925	.8285 1.7644	.8581 1.8300	.7255 1.9161		.5216 1.9969

^aThe top figure is R^2 and the lower figure the intercept of each fit.

Table XVII. Fits to Models Including a $j^2 a^4$ Term. 1255
Observations, Weighted According to Table XIV

Model	R^2	Intercept $\times 10^5$	Comments ^a
$j^2 a^4 + j^2 a^2$	.9414	1.4771	
$j^2 a^4 + j^4 a^6$	.9475	1.5687	
$j^2 a^4 + j^4 a^8$	.9367	1.5024	
$j^2 a^4 + j^4 a^{10}$	.9436	1.4834	$j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6$	.9481	1.5444	
$j^2 a^4 + j^2 a^2 + j^4 a^8$	.9415	1.4805	
$j^2 a^4 + j^2 a^2 + j^4 a^{10}$	.9442	1.4723	$j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^8$	.9493	1.5389	$j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^{10}$	.9511	1.5285	$j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^8 + j^4 a^{10}$	.9552	1.5426	$j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6 + j^4 a^8$	.9494	1.5473	$j^2 a^2, j^4 a^8 < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^6 + j^4 a^{10}$	.9514	1.5419	$j^2 a^2, j^4 a^{10} < 0$
$j^2 a^4 + j^2 a^2 + j^4 a^8 + j^4 a^{10}$	.9561	1.5301	$j^4 a^{10} < 0$
$j^2 a^4 + j^4 a^6 + j^4 a^8 + j^4 a^{10}$	.9552	1.5433	$j^4 a^{10} < 0$
$j^2 a^4$	.9348	1.5330	

^aIndicates those terms whose coefficient was negative.

Comparison of Predicted and Measured D_c

One can determine the size of D_c as predicted by each of the theoretical convection mechanisms. However several of the parameters contained in the various expressions are not well known. Values of parameters taken from the literature are listed in Appendix VII. The value of $D_c \times 10^5 \text{ cm}^2/\text{sec}$ calculated from three of the expressions of Table I are listed in Table XVIII for several experimental conditions. D_c calculated by the charge density mechanism for the experimental conditions of this work ranged from 1×10^{-13} to 4×10^{-9} . Since these values are much too small to explain the data they are not reported in detail in Table XVIII. As for the values used for the parameter ϵ of the electro-osmosis expression: $\epsilon = .05$ corresponds to mostly inelastic scattering of charge carriers and $\epsilon = .95$ corresponds to mostly elastic scattering and is close to the ϵ found by Regal and Patyanin.³¹ As for values of $\Delta a/\Delta z$ used: $\Delta a/\Delta z$ values of .000054 and .00027 in the .02681 and .1015 cm radius cells, respectively, correspond to δ about .002. Lodding^{28,29} has measured conicities of about this size under microscope but feels that δ really is mainly dependent on local departures from an ideal cylinder and on irregularities at the capillary ends. The δ value needed to explain his I^4 dependent observation was about .007. $\Delta a/\Delta z$ of .00027 and .00066 in the .03320 and .1015 cm cells, respectively, correspond to δ of about .007.

Table XVIII. Theoretical Values of $D_C \times 10^5$ Calculated According to the Expressions of Table I

j, amps/cm ²	a, cm	Electro-osmosis			Magnetohydrodynamic $\Delta a/\Delta z \times 10^{-2}$				Joule Heating	Experi- mental
		.05	.50	.70	.005	.027	.066	.132		
$D_C \times 10^5 \text{ cm}^2/\text{sec}$										
200	.02681	.4	.1	- ^a	-	-	-	-	-	-
800	"	7.2	2.0	.7	-	-	-	-	-	.2
1400	"	22.0	6.1	2.2	-	-	.2	.7	-	.9
200	.03320	.7	.2	.1	-	-	-	-	-	-
400	"	2.8	.8	.3	-	-	-	-	-	.2
1400	"	33.8	9.4	3.4	-	.2	1.0	3.8	.3	2.0
200	.06604	2.7	.8	.3	-	-	.1	.4	.1	.5
700	"	33.4	9.3	3.3	.1	2.5	14.7	59.0	16.6	9.8
200	.1015	6.4	1.8	.6	-	.5	3.1	12.2	8.1	2.6
300	"	14.5	4.0	1.4	.1	2.6	15.5	61.9	41.1	7.9

^a- indicates a value less than .1. Considered too small for comparison.

In comparison with the experimentally measured D_c values, the electro-osmotic mechanism predicts an effect of the right order of magnitude but to explain the data well ϵ would have to vary from about .8 for the capillaries of small radius to about .4 for those of large radius. The magnetohydrodynamic mechanism is less successful in explaining the data but might account for some of the observed convection if $\Delta a/\Delta z$ was not much larger than .0003. Joule heating mechanism predictions are not in good agreement with the experimental data.

Discussion of Results

Both the regression analyses and a comparison of the values of D_c calculated from the formulas in Table I with the experimental measurements indicate that no theory or combination of theories in the literature is able to explain the data. The conclusion is inescapable. A $j^2 a^4$ dependent mechanism is needed to explain these data.

Since $I^2 \propto j^2 a^4$ it appears that present results are equivalent to the I^2 dependence reported by Lodding.^{28,29} However Lodding did not study the radial dependence of D_c . Thus he was in error in concluding that the electro-osmotic or electrokinetic mechanism was largely responsible for this observation of convection. The point is that in Eq. [9] the factor I^2/a^2 appears and this is proportional to $j^2 a^2$, not to $j^2 a^4$. Nevertheless, Lodding's observation of a j^2 dependence for the main convection mechanism at low currents offers support to the present findings. The fact that he observed a j^4 depend-

ence at high currents is not necessarily contradictory since he would more likely experience thermal instabilities of a serious nature in his horizontal capillaries with a high current. Lieu³⁴ found a j^2 mechanism with very limited data but made no study of radial dependence. Kuzmenko⁴⁵ found a $j^2 a^5$ dependent mechanism, but again his experimental technique was not good and he had limited data so an a^4 dependence might have been mistakenly taken as a^5 . Kuzmenko also concluded that the convection effect was not reversible and was not dependent on capillary taper. These conclusions rest on very limited data, but they do indicate that neither the electrokinetic nor the magnetohydrodynamic mechanisms explain the observed convection.

Other phenomena should be considered as possible explanations of the data. Rigney and coworkers have studied a reversal in the migration direction sometimes observed with changing alloy composition.^{60,61,62} Following their suggestion⁶³ if a reversal occurred in the migration direction at a composition between that of the initial alloy and pure Hg, then the separation process would be limited so that the final composition at the anode would correspond to the reversal composition. This would result in an increase in the mean capillary composition at steady state over that expected if no reversal occurred. It does not appear that any such behavior is present in Cd amalgams of composition 1 atom % or less. Mangelsdorf³² found the mobility to be well behaved down to

.5 atom % Cd. In fact U_{Cd} even increased slightly with decreasing Cd content. From Appendix III one can see that the mean steady state capillary composition ranged from .75 atom % at 50 amps/cm² in a .03296 cm radius capillary and .51 atom % at 300 amps/cm² in a .1015 cm radius capillary down to .08 atom % at 1600 amps/cm² in a .02681 cm radius capillary. If U_{Cd} changed signs or even changed very much in magnitude over the above range of compositions it is doubtful that a constant value of U_{Cd} used in the determination of D_e would have allowed such consistent results from the regression analyses.

The electronic structure of liquid Hg has been considered anomalous in two respects.⁶⁴ The change in resistivity of Hg on melting is exceptionally large, being about twice that usually observed. Also the addition of most other metals to liquid Hg results in a decrease in the resistivity. The suggestion has been made that in the close packed structure of liquid Hg the number of electrons overlapping the first Brillouin zone is small compared to that for the less symmetrical zone of rhombohedral solid Hg. This may explain the first observation and the second was thought to be explained by considering that the addition of solute distorts the first zone tending to increase the number of electrons available for conduction. Mott⁶⁵ was able to qualitatively explain the Hg experimental data on the basis of a substantial dip in the density of electron states near the Fermi energy. However the presence of this dip has been disputed and it is now felt⁶⁶

that the dip is small with the density of states curve being only slightly shifted from the free electron curve. Thus the n appearing in Eq. [6] is expected to be close to that calculated from a free electron model.

One might suggest that the atomic structure of the Cd amalgam changes with composition. A recent X-ray study⁶⁷ of pure liquid Hg has shown that the first peak of the reduced radial distribution function is sharper than that observed for liquid Al and liquid Pb. This indicated a simple liquid structure in pure Hg. Structure results for dilute Cd amalgams do not appear to be present in the literature. The facts that the partial molar volumes of Cd and Hg are quite constant and that the resistivity varies linearly with composition over the composition range studied seem to indicate no drastic change in atomic structure.

Finally, are the assumptions made in connection with the formalism used to analyze the D_e data in fact obeyed? The ones of importance are: that the composition remains fixed at the capillary mouth throughout the entire electrotransport run; that the only radial mass transport in the capillary is due to diffusion; that the convective velocity is not a function of z ; and that $c(r) \approx \bar{C}$ at any z within the cell. The assumptions can be summarized by saying that end effects are not of importance and that the convective flow is laminar.

The fact that the assumptions are not all obeyed at the closed end of the capillary does not seem to be important

since here the concentration should be uniformly low across the capillary radius in a region extending away from the closed end in the Z direction for a distance of at least several radii.

More serious effects could be present at the capillary mouth where convective eddy currents may be present resulting in a Δl effect. Another possible cause of convection at the capillary mouth is the presence of a negative temperature gradient. These effects might serve to shorten the effective capillary length by moving the position at which the initial composition, X_{10} , was maintained. This position might be expected to move into the capillary rather than be at the mouth. Both the Δl effect and the presence of current related convection might also lead to a non-planar surface of constant composition X_{10} . The analysis assumed such a plane exists at the capillary mouth.

The measurements did not allow a direct determination of whether or not a Δl effect did in fact exist. However from Table IV it can be determined that the average l/a for capillaries with radii less than 0.047 cm is 70.9 while for those with radii greater than .047 cm the average l/a is 50.7. The results of fits to models of the form $j^s a^t$ for data from capillaries having radii less than 0.047 and for capillaries having radii greater than 0.047 cm, shown in Table XIII, indicate that the $j^2 a^4$ model is most satisfactory in each case.

Thus no evidence is seen for the presence of end effects.

There appears to be no theoretical treatment concerning Δl effects at the mouth of an electrotransport capillary. However, Verhoeven¹⁷ has considered the problem of threshold convection in vertical capillaries with the bottom fluid being hotter than the top fluid. We had such a situation near the capillary mouth. Verhoeven's analysis indicated that the critical temperature gradient needed to produce convection in Hg in capillaries of radius .5 and 1 mm was -3150 and -197 °C/cm respectively. It seems highly unlikely that our gradients approached these critical gradients.

Davis¹⁸ observed a Δl region and an enhanced D in normal diffusion experiments carried out in a negative temperature gradient. His alloy was initially 0.022 wt % Ag¹¹⁰ in Sn in a 1 mm diameter capillary with pure Sn in the crucible. However the system Davis studied was less stable than ours for two reasons. First he observed temperature fluctuations of about a degree in the reservoir. These fluctuations were apparently caused by convection in the reservoir. When partially transmitted to the capillary liquid the fluctuations resulted in small volume changes which led to an enhanced D. Our reservoir temperature fluctuations were much smaller ranging from 0.05 to 0.2°C. Secondly, Davis started with a very small stabilizing density gradient due to the presence of the slight amount of Ag¹¹⁰ in the capillary. As his diffusion run progressed the size of this stabilizing gradient decreased.

In our case there was initially present no density gradient due to composition differences but as the Cd was pumped out of the capillary a continuously more favorable gradient was attained until steady state was reached. As j was changed each new steady state solute gradient was favorable to the stabilization of the system. Although a complete solution of the convection problem for the case of combined thermal and solute gradients has not been worked out, it would seem reasonable to expect that a favorable density gradient due to a composition gradient would help stabilize a possibly unstable situation resulting from the presence of a negative temperature gradient.

The assumption has been made throughout this work that fluxes resulting from different forces may be added. However if several convection mechanisms are present and they are not independent then a simple addition of the resulting fluxes is not correct. Fits to models including nonlinear combinations of the dependences of various mechanisms have not been attempted.

Discussion of Experimental Error

Since Eq. [50] can not be solved analytically for S it is not possible to derive an entirely satisfactory expression giving the accuracy of the experimental measurements of D_e . However an estimate of the accuracy in determining D_e can be made if several assumptions are made. This will now be presented.

A general formula for determining the standard deviation of a function $z(y_1, y_2, \dots, y_n)$ where the y_i are independent is⁶⁸

$$\sigma_z = \left[\sum_{i=1}^n \left(\frac{\partial z}{\partial y_i} \right)^2 \sigma_{y_i}^2 \right]^{1/2} . \quad [78]$$

Since R in Eq. [50] is a function of S and Q only, it can be shown that

$$\frac{\partial R}{\partial S} = \frac{1}{Q} \left\{ -\frac{1}{S} \frac{(Q+1)e^{-S}}{(-Q+(Q+1)e^{-S})} - \frac{1}{S^2} \ln(-Q+(Q+1)e^{-S}) \right\} . \quad [79]$$

In the present measurements, $|-0.6| < |S| < |-13.7|$ and $|-0.040| < |Q| < |-0.042|$. For the above range of S values, $1.822 < e^{-S} < 9 \times 10^5$. Thus it will be assumed that $(Q+1)e^{-S} \gg -Q$ so that

$$\frac{(Q+1)e^{-S}}{-Q+(Q+1)e^{-S}} \approx 1 . \quad [80]$$

Then from Eqs. [48], [49], and [50] it is seen that

$$\frac{1}{R^2} \left(\frac{\partial R}{\partial S} \right)^2 = \frac{1}{S^2} . \quad [81]$$

Unfortunately no such simple reduction can be made for the term $\partial R / \partial Q$. However Q changed very little over the entire series of runs and within a run Q changed by less than 1 part in 100. Thus from experimental evidence we assume that $\sigma_Q / Q \approx 0$. Therefore

$$\left(\frac{\sigma_R}{R} \right)^2 = \left(\frac{\sigma_S}{S} \right)^2 . \quad [82]$$

Equation [49] relates D to S. It can be shown that

$$\left(\frac{\sigma_D}{D}\right)^2 = \left(\frac{\sigma_U}{U}\right)^2 + \left(\frac{\sigma_{\rho_{oj}}}{\rho_{oj}}\right)^2 + \left(\frac{\sigma_j}{j}\right)^2 + \left(\frac{\sigma_L}{L}\right)^2 + \left(\frac{\sigma_S}{S}\right)^2 \quad [83]$$

where ρ_{oj} is the resistivity of pure Hg with a capillary temperature distribution identical to that present at steady state for each different j. The fractional uncertainty in S must now be determined. From the left hand equality of Eq. [50]

$$\left(\frac{\sigma_R}{R}\right)^2 = \left(\frac{\sigma_{\bar{X}_{1ss}}}{\bar{X}_{1ss}}\right)^2 + \left(\frac{\sigma_{X_{1o}}}{X_{1o}}\right)^2 \quad [84]$$

Then the final expression for the fractional uncertainty in D is

$$\frac{\sigma_D}{D} = \left[\left(\frac{\sigma_U}{U}\right)^2 + \left(\frac{\sigma_{\rho_{oj}}}{\rho_{oj}}\right)^2 + \left(\frac{\sigma_j}{j}\right)^2 + \left(\frac{\sigma_L}{L}\right)^2 + \left(\frac{\sigma_{\bar{X}_{1ss}}}{\bar{X}_{1ss}}\right)^2 + \left(\frac{\sigma_{X_{1o}}}{X_{1o}}\right)^2 \right]^{1/2} \quad [85]$$

From Table VI $\sigma_U/U \approx 0.025$. Equation [63] is used to calculate ρ_{oj} . Assuming that most of the uncertainty in ρ_{oj} is due to uncertainty in $\bar{T}$, on inspection of the data we take the fractional uncertainty in ρ_{oj} to be about 0.01. The uncertainty in j is expected to be small and will be neglected. There are uncertainties in L due to lack of precision in measuring the position of the voltage probe in the capillary, due to irregularities in the capillary at either end, and due to the fact that there may be a pocket of amalgam behind the current electrode which does not experience an electrotrans-

port force. After looking at a number of cells it was concluded that the fractional uncertainty in L was about 0.015 at the largest. From Table VII the uncertainty in X_{10} was estimated to be about 0.015. Finally the program used to calculate D_e also calculated the mean steady state cell concentration. From these results it was concluded that the fractional uncertainty in $\bar{X}_{1ss}$ within a run ranged from 0.5% at low j to 9% at high j in small radius capillaries where $\bar{X}_{1ss}$ was small.

Table XIX gives the estimated uncertainty in D_e for

Table XIX. Estimated Uncertainty in D_e

$\frac{\sigma_{\bar{X}_{1ss}}}{\bar{X}_{1ss}}$	$\frac{\sigma_{D_e}}{D_e}$
$\pm .01$	$\pm .036$
$\pm .04$	$\pm .053$
$\pm .07$	$\pm .078$

three conditions. Thus for example at low j values in small capillaries where the capillary environment was quite stable and convective effects were minimal so that $D_e \approx D$, Eq. [85] predicted an accuracy in D of about $\pm 0.05 \text{ cm}^2/\text{sec}$. However at high j in small capillaries where a large uncertainty in $\bar{X}_{1ss}$ was observed a much larger uncertainty in D_e is expected.

Because the uncertainty in $\bar{X}_{1ss}$ is determined from the experimental data, when this uncertainty becomes the dominant term in Eq. [85] the predicted accuracy really becomes more a measure of precision rather than of absolute accuracy. Thus in run 15 at a current density of about 1200 amps/cm² we can really only say that $D_e = 2.98 \text{ cm}^2/\text{sec}$ with a calculated precision of $\pm .23 \text{ cm}^2/\text{sec}$.

SUMMARY AND CONCLUSIONS

This project has involved a study of current dependent convection observed during electrotransport of liquid metals in cylindrical capillaries. The motivations for understanding the convection mechanism are three-fold. First, it is hoped that such an understanding will enable convection during electrotransport in liquid metals to be controlled so that the optimum predicted electrotransport separation factors might in fact be achieved. Second, an understanding of convection during electrotransport in liquid metals should allow the determination of mutual diffusion coefficients by the electrotransport method to be made with more confidence. Third, confidence in the interpretation of phenomena occurring in liquid metals should be advanced if convection effects can be taken into account.

A brief review is presented of the theoretical mechanisms postulated as possible causes of convection. The parametric dependences of each are noted, especially the dependences on current density and capillary radius.

The recent applicable experimental work is reviewed and critically analyzed. Particularly noted are the faulty practice of having a positive density gradient due to the presence of either a temperature or solute gradient and the questionable practice of using capillaries in a horizontal position. It is apparent that there has been no general agreement between

various investigators as to the parametric dependences of the observed convection. Further, no investigation has yet studied the dependence of convection on capillary radius although this dependence varies widely in the several theoretical mechanisms.

The formalism necessary to the experimental determination of the electric mobility, U , and the effective diffusion coefficient, D_e , is developed. The latter is shown to be the sum of the mutual diffusion coefficient, D , and a so-called convective diffusion coefficient, D_c .

The experimental procedure is discussed. The suitability of using a 1 atom % Cd amalgam as the initial liquid metal in the four probe capillary reservoir resistivity method of measuring U and D_e is discussed. The equipment is described. A description is given of the experimental methodology needed in the construction of the electrotransport cells and in carrying out the experiments.

The experimentally determined values of U and D_e of Cd in Hg are reported. The average value of U as measured in capillaries with radii less than 0.035 cm with j of about 200 amps/cm² is $(-9.92 \pm 0.25 \times 10^{-4})$ cm²/v-sec. This compares favorably with literature values. Statistical analyses are presented of the D_e results. Goodness of fit in these regression analyses was measured first by a statistical parameter and second by comparing the intercept of a particular fit to the known value of D . The best literature value of the mutual

diffusion coefficient in a dilute Cd amalgam is $(1.53 \pm 0.05) \times 10^{-5} \text{ cm}^2/\text{sec}$. From fits of the data of each run considered separately to a model of the form $D_e = D + b_2 j^2 + b_4 j^4$, it is shown that for five capillaries having radii less than 0.035 cm the average D is $(1.5211 \pm 0.0418) \times 10^{-5} \text{ cm}^2/\text{sec}$. For all data considered at once the best fit results in a D of $1.4875 \times 10^{-5} \text{ cm}^2/\text{sec}$ if the data is not weighted, and $(1.5330 \pm 0.0086) \times 10^{-5} \text{ cm}^2/\text{sec}$ for data weighted according to the estimated experimental scatter. This shows that it is possible to use electro-transport in small capillaries to determine with high precision mutual diffusion coefficients of liquid metals. To do this an extrapolation is made from D_e values measured at high current densities where convection is significant.

The j dependence was shown to be quadratic in agreement with the electro-osmotic mechanism. However fits to various models of the general form $j^s a^t$ showed that the most satisfactory model was $j^2 a^4$ whereas the electro-osmotic dependence is $j^2 a^2$. This preferred fit was found if the data were unweighted, if they were weighted according to the estimated experimental scatter, if the low and high j data were considered separately, or if small and large capillaries were considered separately. Neither the $j^2 a^2$ electro-osmotic dependence, the $j^4 a^6$ charge density dependence, the $j^4 a^8$ magneto-hydrodynamic dependence, nor the $j^4 a^{10}$ Joule heating dependence was as successful in describing the present data as was the $j^2 a^4$ model. In fact no model including the latter dependence

plus one or more of the others was significantly more satisfactory than the simple $j^2 a^4$ model alone. Several previous studies had indicated a j^2 dependence for the primary convection mechanism. These results support our findings in part, but the previous investigators erred in not checking the radial dependence.

Values of D_c predicted for a dilute Cd amalgam by each theoretical mechanism are presented. These calculated values also indicate that no mechanism should satisfactorily explain the observed data.

The conclusion is inescapable that a $j^2 a^4$ dependence is needed to explain the results contained herein. Other phenomena are considered as possible explanations of the data. A reversal in migration direction does not seem plausible. Neither the somewhat anomalous electronic behavior of Hg nor the latest data as to the atomic structure of liquid Hg can explain the observed data.

In considering the assumptions made in the development of the formalism used in the analysis of the data it is realized that laminar flow has been assumed and end effects neglected. It seems unlikely that there was present at the capillary mouth a sufficient negative temperature gradient to lead to convection. Although capillaries having radii smaller than 0.047 cm had an average aspect ratio about 40% larger than that of those capillaries with radii larger than 0.047 cm, there is no evidence for significant end effects which would

invalidate application of our formalism to the problem.

A brief discussion of experimental error is presented. The analysis of error is by necessity approximate because the equation used to find D_e cannot be solved analytically. The analysis indicated that D_e can be measured with typical precisions ranging from $\pm 0.05 \text{ cm}^2/\text{sec}$ at low j to $\pm 0.23 \text{ cm}^2/\text{sec}$ at high j . The main factor influencing precision is that temperature instabilities increase as j increases. Experimental data on the reproducibility of D_e agree reasonably well with this analysis.

In conclusion these data indicated the presence of some $j^2 a^4$ dependent convection mechanism. It does not appear that end effects were present. Thus application of the formalism developed herein should be valid for this study. The data indicate that no simple addition of the predicted mechanisms can explain the data. However it is possible that the predicted mechanisms are not independent but rather add in some complicated way to give an overall $j^2 a^4$ dependence. A stronger case for a $j^2 a^4$ dependent mechanism would be made if convection in other liquid metal systems was also observed to be $j^2 a^4$ dependent. As for practical purification schemes based on electrotransport of liquid metals one can only say that to minimize convection while keeping a high separation rate one should use as small diameter capillaries as are experimentally feasible. Determination of mutual diffusion coefficients also

should be done by extrapolating to zero current density the data obtained at finite current densities in a capillary of less than .040 cm radius.

LITERATURE CITED

1. K. E. Schwarz: Electrolytic Migration in Liquid and Solid Metals, Edwards Bros. Inc., Ann Arbor, Mich., 1945.
2. W. Jost: Diffusion in Solids, Liquids, Gases, Academic Press, New York, New York, 1952.
3. W. Seith: Diffusion in Metals, 2nd ed., Springer, Berlin, 1955.
4. J. D. Verhoeven: Met. Rev., 1963, vol. 8, pp. 311-68.
5. D. K. Belashchenko: Russ. Chem. Rev., 1965, vol. 34, pp. 219-37.
6. R. G. R. Sellors and J. N. Pratt: Research Report, Department of Physical Metallurgy and Science of Materials, University of Birmingham, Birmingham, England, 1968.
7. J. D. Verhoeven: J. Metals, 1966, vol. 18, pp. 26-31.
8. R. A. Polovinkina, D. D. Ochirzhapova, and V. A. Mikhailov: Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1970, No. 3, pp. 91-96. (Siberian Chemistry Journal, 1970, pp. 378-82.)
9. L. Nanis, S. R. Richards, and J. O'M. Bockris: Rev. Sci. Instr., 1965, vol. 36, pp. 673-77.
10. E. Berne and J. Berggren: Acta Chem. Scand., 1960, vol. 14, pp. 428-36.
11. K. G. Davis: Can. Met. Quart., 1966, vol. 5, pp. 245-63.
12. N. H. Nachtrieb: The Properties of Liquid Metals, P. D. Adams et al., eds., pp. 309-23, Taylor and Francis, Ltd., London, 1967.
13. J. Rastas and P. Kwalo: Acta Polytech. Scand., Chem. Met. Ser., 1964, vol. 35, pp. 1-19.
14. A. Z. Borucka, J. O'M. Bockris, and J. A. Kitchner: Proc. Roy. Soc., 1957, vol. 241A, pp. 554-67.
15. J. B. Edwards, E. E. Huccke, and J. J. Martin: Met. Rev., 1968, vol. 2 pp. 1-28. Review 120 (parts I and II).

16. J. D. Verhoeven: USAEC Rept. IS-1860, Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research, 1968.
17. J. D. Verhoeven: Trans. TMS-AIME, 1968, vol. 242, pp. 1937-42.
18. K. G. Davis: Can. Met. Quart., 1970, vol. 9, pp. 409-14.
19. J. W. Westhaver: J. Nat. Bur. Stds., 1947, vol. 38, pp. 169-83.
20. G. E. Pikus and V. B. Fiks: Sov. Phys.-Solid State, 1959, vol. 1, pp. 972-80.
21. V. B. Fiks: Sov. Phys.-Tech. Phys., 1957, vol. 27, pp. 1176-82.
22. V. B. Fiks and G. E. Pikus: Sov. Phys.-Solid State, 1959, vol. 1, pp. 1049-59.
23. A. Klemm: Z. Naturforsch., 1958, vol. 13a, pp. 1039-43.
24. A. Lodding and A. Klemm: Z. Naturforsch., 1962, vol. 17a, pp. 1085-88.
25. R. L. Schmidt and J. D. Verhoeven: Trans. TMS-AIME, 1967, vol. 239, pp. 148-55.
26. S. A. Regirer: Zh. Prik. Mekh. i Teor. Fiz., 1962, vol. 15, pp. 15-19. Original not available; translation from Oak Ridge Institute of Nuclear Studies.
27. D. K. Belashchenko: Russ. J. Phys. Chem., 1965, vol. 39, pp. 430.
28. A. Lodding: J. Phys. Chem. Solids, 1967, vol. 28, pp. 557-68.
29. A. Norden and A. Lodding: Z. Naturforsch. 1967, vol. 22a, pp. 215-19.
30. S. I. Patyanin and A. R. Regel : Phys. Metals & Metallurgy, 1965, vol. 19, pp. 42-44.
31. A. R. Regel and S. I. Patyanin: Soviet Atomic Energy, 1963, vol. 14, pp. 114-19.
32. P. C. Mangelsdorf, Jr.: J. Chem. Physics, 1959, vol. 30, pp. 1170-79.

33. P. C. Mangelsdorf, Jr.: Met. Soc. Conf., 1961, vol. 7, pp. 429-45.
34. F. Y. Lieu: Acta Met., 1967, vol. 15, pp. 1405-7.
35. S. I. Drakin: Izvest. Sektora. Fiz. Khim. Anal. AN (USSR) 1950, vol. 20, pp. 341.
36. S. I. Drakin and A. K. Maltsev: Zhur. Fiz. Khim., 1957, vol. 31, pp. 2036-41.
37. S. I. Drakin, A. M. Borisova, and W. M. Pugacewicz: Russ. J. Phys. Chem., 1963, vol. 37, pp. 3-6.
38. S. I. Drakin and Yu. K. Titova: Russ. J. Phys. Chem., 1967, vol. 41, pp. 319-22.
39. J. D. Verhoeven and E. E. Huccke: Trans. TMS-AIME, 1963, vol. 227, pp. 1156-66.
40. V. A. Mikhaylov, R. A. Polovinkina, S. I. Drakin, and G. M. Frolova: Phys. Metals & Metallography, 1966, vol. 22, pp. 63-67.
41. Yu. K. Titova, S. I. Drakin, and I. B. Alikina: Russ. J. Phys. Chem., 1968, vol. 42, pp. 1194-97.
42. V. A. Mikhailov, M. V. Kornievich, and R. A. Polovinkina: DAN SSSR, Phys. Chem., 1966, vol. 171, pp. 718-21.
43. V. A. Mikhailov, R. A. Polovinkina, N. F. Zakharchuk, and S. I. Drakin: DAN SSSR, Chem. Tech., 1969, vol. 184, pp. 718-21.
44. P. P. Kuzmenko, E. I. Kharkov, and V. I. Lozovii: Ukr. Fiz. Zh., 1965, vol. 9, pp. 881-89.
45. P. P. Kuzmenko, E. I. Kharkov, and V. I. Lozovii: Ukr. Fiz. Zh., 1965, vol. 10, pp. 912-13.
46. A. Z. Zhmudskii, E. I. Kharkov, and A. G. Rudenko: Phys. Metals & Metallography, 1967, vol. 23, pp. 559-61.
47. F. P. Golyotyuk, P. P. Kuzmenko, and E. I. Kharkov: Ukr. Fiz. Zh., 1965, vol. 10, pp. 1359-64.
48. F. P. Golyotyuk, P. P. Kuzmenko, and E. I. Kharkov: Phys. Metals & Metallography, 1965, vol. 19, pp. 78-83.

49. P. P. Kuzmenko: Paper submitted at symposium "Elektrotransport und Thermodiffusion in Metallen", Münster, 1965.
50. D. K. Belashchenko and G. A. Grigor'ev: Izvest. Vysshikh Ucheb. Zavedenii SSSR, Chernaya Met., 1961, No. 11, pp. 116-21.
51. D. K. Belashchenko, E. I. Gushchina, and S. A. Armyanov: Izv. Akad. Nauk SSSR, Metally, 1968, No. 6, pp. 212-19.
52. D. K. Belashchenko and E. I. Gushchina: Russ. J. Phys. Chem., 1970, vol. 44, pp. 256-58.
53. D. K. Belashchenko: Russ. J. Phys. Chem., 1961, vol. 35, pp. 923-24.
54. A. Z. Zhmudski, E. I. Kharkov, A. G. Rudenko, and L. V. Kulikova: Ukr. Fiz. Zh., 1967, vol. 12, pp. 482-85.
55. J. D. Verhoeven, J. C. Angus, W. D. Bouwsma, and E. E. Huccke: University of Michigan Research Institute Report 2917-1-T. 1960.
56. D. R. Packard: Masters thesis, IS-T-204; CFSTI, U.S. Dept. Commerce, Springfield, Va., 1967.
57. A. Larsen: Annal. Physik, 1900, vol. 1, pp. 123-31. (Taken from: International Critical Tables of Numerical Data, E. W. Washburn, ed., McGraw-Hill Book Company, Inc., Washington, D.C., 1929.)
58. O. Kubaschewski and J. A. Cottrell: Thermochemical Data of Alloys, Pergamon Press, Ltd., New York, N.Y., 1956.
59. J. D. Verhoeven: Ph.D. thesis, University of Michigan Library, Ann Arbor, Michigan, 1963.
60. D. L. Olson, J. L. Blough, and D. A. Rigney: Scripta Met., 1970, vol. 4, pp. 1023-32.
61. T. S. Lakshmanan, D. L. Olson, and D. A. Rigney: Scripta Met., 1971, vol. 5, pp. 1099-1104.
62. D. L. Olson, J. L. Blough, and D. A. Rigney: Acta Met., 1972, vol. 20, pp. 305-12.
63. J. L. Blough, D. L. Olson, and D. A. Rigney: J. Appl. Phys., 1972, vol. 43, pp. 2476-77.

64. N. F. Mott and H. Jones: The Theory of the Properties of Metals and Alloys, Dover, New York, N.Y., 1958.
65. N. F. Mott: Phil. Mag., 1966, vol. 13, 989-1014.
66. T. Chan and L. E. Ballentine: Can. J. Phys., 1972, vol. 50, pp. 813-20.
67. H. Ruppertsberg and H. Reiter: Acta Cryst., 1972, vol. A28, pp. 233-36.
68. Y. Beers: Introduction to the Theory of Errors, Addison-Wesley, Reading, Mass., 1962.
69. System/360 Scientific Subroutine Package Version III, Programers Manual, 4th ed., IBM, White Plains, N.Y., 1969.
70. W. J. Kennedy: HELARCTOS II: Statistical Numerical Analysis and Data Processing Series, No. 13, Statistical Laboratory, Iowa State University, Ames, Iowa, 1971.
71. E. Cohen and H. R. Bruins: Z. Physikal. Chem., 1924, vol. 108, pp. 397-402.
72. F. Weischedel: Z. Physik, 1933, vol. 85, pp. 29-33.
73. G. Meyer: Ann. Physik u. Chemie, 1897, vol. 61, pp. 255-9.
74. M. von Wogau: Ann. Physik, 1907, vol. 23/24, pp. 234-51.
75. V. H. Strehlow and M. V. Stackelberg: Z. Electrochem., 1950, vol. 54, pp. 51-62.
76. R. C. Turner, and C. A. Winkler: Can. J. Chem., 1951, vol. 29, pp. 469-77.
77. A. G. Stromberg: DAN SSSR, 1952, vol. 85, pp. 831-33.
78. A. G. Stromberg and E. A. Zakharova: Sov. Electrochem., 1965, vol. 1, pp. 922-29.
79. A. Dowgird and A. Galus: Bull. Acad. Pol. Sci., Ser. Sci. Chim., 1970, vol. 18, pp. 255-62.
80. M. V. Stackelberg and V. Toome: Z. Electrochem., 1954, vol. 58, pp. 226-30.
81. N. G. Chovnyk and V. V. Vashchenko: Russ. J. Phys. Chem., 1963, vol. 37, pp. 276-80.

82. M. S. Zakharova and A. G. Stromberg: Russ. J. Phys. Chem., 1964, vol. 38, pp. 68-71.
83. J. Okinaka, I. Kolthoff, and J. Muragyma: J. Amer. Chem. Soc., 1965, vol. 87, pp. 423-30.
84. W. G. Stevens and I. Shain: J. Phys. Chem., 1966, vol. 70, pp. 2276-80.
85. E. A. Zakharova, Z. G. Kilina, and G. A. Rakhmonina: Sov. Electrochem., 1969, vol. 5, pp. 1420-3.
86. International Critical Tables of Numerical Data, E. W. Washburn, ed., McGraw-Hill Book Company, Inc., Washington, D.C., 1929.
87. Liquid-Metals Handbook, R. N. Lyon, ed., Department of the Navy Report No. NAUEXOS P-733 (Rev.), Department of Navy, Washington, D.C., 1952.

NOMENCLATURE

a	capillary radius
a_i	activity of i
A	capillary cross-section
b	external mobility
B_i	absolute mobility of i
c	speed of light
C	capillary concentration
C_i	atoms of i per unit volume
C_0	initial capillary concentration
$\bar{C}_1$	Capillary concentration averaged over cross-section
C_1	constant defined by Eq. [67]
C_2	constant defined by Eq. [70]
C_3	constant defined by Eq. [72]
d_e	density of capillary alloy
D	mutual diffusion coefficient
D_c	convective diffusion coefficient
D_e	effective diffusion coefficient
e	electron charge
E	electric field intensity
F	Faraday's constant
g	acceleration due to gravity
I	current
j	current density
J_i	flux of i in moles or atoms per area and time referred to a fixed observer

k	thermal conductivity
k_b	Boltzmann's constant
K	cell constant
K_ℓ	coefficient of electrodiffusion
L	capillary length
M	weight of cell contents
n	electron density at the Fermi surface
n_t	transport number
N_i	moles of i per unit volume
$\dot{N}_i$	time rate of change of mean capillary N_i
p	impurity concentration in cell
Q	dimensionless ratio defined by Eq. [48]
r	radial coordinate
R	dimensionless ratio defined by Eq. [50]
R'	dimensionless ratio defined by Eq. [46]
R_c	resistance of capillary
R_{cc}	resistance of current control resistor
R_s	resistance of standard shunt
R_{st}	resistance of power supply comparison resistor
S	dimensionless ratio defined by Eq. [49]
S'	dimensionless ratio defined by Eq. [45]
t	time
T	temperature
$\bar{T}$	mean capillary temperature
$\bar{T}_{low j}$	$\bar{T}$ in measurement of $\bar{\rho}_{10}$

T_{tc}	thermocouple temperature
U, U_i	electric mobility of i
U_{i-j}	differential electric mobility
U_{1A}	mobility calculated with Eq. [66]
U_{1B}	mobility calculated with Eq. [69]
U_{1C}	mobility calculated with Eq. [71]
v, v_z	axial convective velocity
v_b	counter current velocity (bulk flow velocity)
v_e	velocity of charge carriers
v_i	terminal velocity of i
V	capillary volume
$\bar{V}$	molar volume
V_c	voltage drop across the capillary
$\bar{V}_i$	partial molar volume of i
V_s	voltage drop across standard shunt
V_{tc}	voltage developed by thermocouple
W	weighting factor defined by Eq. [77]
X_i	mole fraction of i
$\dot{\bar{X}}_i$	time rate of change of mean capillary mole fraction
X_{im}	mole fraction of i at the capillary mouth
X_{1ss}	mole fraction of capillary alloy at steady state
$\bar{X}_{1ss}$	average of X_{1ss}
X_{10}	initial fraction of capillary alloy
XI	weighed in atom concentration of solute
Z	axial coordinate
Z^*, Z_i^*	effective valence

$Z(y_1, \dots, y_n)$	a general function
α	electrokinetic mobility
β	slope of ρ vs X_1 curve
β_e	volume coefficient of expansion
δ	conicity, defined by Eq. [13]
δD_e	estimated experimental scatter in D_e
$\Delta\rho$	$\bar{\rho}_{int} - \rho_{oj}$
ϵ	fraction of electrons undergoing elastic collisions with the capillary wall
γ	constant in Eq. [64]
λ	electron mean free path
η	viscosity
ρ	electrical resistivity
$\dot{\rho}$	time rate of change of mean capillary resistivity
$\bar{\rho}_{int}$	initial amalgam resistivity from least squares fit of ρ vs t
$\bar{\rho}_j$	$\bar{\rho}_{10}$ corrected to mean capillary temperature
ρ_m	alloy resistivity at capillary mouth
ρ_o	resistivity of pure Hg
ρ_{oj}	resistivity of pure Hg corrected to $\bar{T}$ at each j
$\bar{\rho}_{10}$	initial amalgam resistivity measured with small j
σ	electrical conductivity
σ_{yi}	standard deviation of variable y_i
τ	experimental time

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APPENDIX I

Data on Materials and Equipment

Below is listed information on the various commercially supplied materials and equipment used in this work. Information given in order is: type of material or equipment; manufacturer and address; and a brief description including model or catalog number and specifications where applicable.

1. Pyrex capillary tubing; Corning Glass Works, Corning, N.Y.; Special Pyrex Brand 7740 redrawn tubing, .004" to .010" wall thickness, several sizes with nominal ID ranging from .020" to .080".
2. Temperature regulator; Precision Scientific Company, Chicago, Ill.; C-7653 precision micro-set differential range thermoregulator, sensitive to $\pm .005^{\circ}\text{C}$.
3. DC power supply; Kepco, Inc., Flushing, N.Y.; JQE36-15MET, programmable in constant current regulated mode from 0 to 15 amps at 0 to 36 volts with the following output effects; eight hour drift, $< \pm .02\%$; temperature coefficient, $< \pm .02\%/^{\circ}\text{C}$; no load to full load, $< \pm .01\%$; input voltage ranging from 105 to 125 VAC, $< \pm .005\%$.
4. Rotary switch in current circuit; Centralab Electronics Division, Globe-Union Inc., Milwaukee, Wis.; JV-9004, heavy duty rotary power switch, shorting type, designed for 30 amps at 5 VDC.
5. Potentiometer facility; Leeds & Northrup Company, Philadelphia, Pa.; 7555 Type K-5 potentiometer assembly with the following equipment:
 - a) Potentiometer; L & N; specified limits of error:
 $\pm (.003\% \text{ of reading} + 3\mu\text{V})$ on 1.6 volt range;
 $\pm (.005\% \text{ of reading} + .3\mu\text{V})$ on .16 volt range;
 $\pm (.005\% \text{ of reading} + .1\mu\text{V})$ on .016 volt range.
 - b) Null detector; L & N; maximum sensitivity .067 $\mu\text{V}/\text{mm}$ with load resistance up to 2000 Ω .

- c) Constant voltage supply; L & N; 099034, temperature stability of .0005% voltage change/°C between 15 and 35°C.
 - d) Standard cell; Epply Laboratory, Inc., Newport, R.I. Standard Cell No. 805997.
- 6. Rotary switch in Emf circuit; L & N; Type 31-3, shorting type, solid silver contacts, silver alloy brushes, thermal emf at normal switching speeds less than 1.0μV.
 - 7. Chromel-Alumel thermocouple duplex wire; Omega Engineering, Inc., Stamford, Conn.; .004" wires in .020" OD stainless steel sheath.

APPENDIX II

Regression Programs

During the course of this work a number of regression analyses were made. Two computer programs were used. The program STPRG was taken from the IBM Scientific Subroutine Package⁶⁹ where a more detailed description and a listing may be found. STPRG and associated subroutines are herein referred to as the program FIT. The other program HELARCTOS II was written by Dr. W. J. Kennedy of the Iowa State University Statistical Laboratory.⁷⁰ The programs will now be briefly described.

FIT involves use of a stepwise multiple regression, that is a statistical technique for analyzing the relationship between a dependent variable (y) and a set of independent variables ($x_1, x_2, \dots, x_m$). The independent variables are entered into the analysis in the order of their importance in reducing the sum of squares; however a given independent variable may be forced to enter the analysis or deleted from it. The fitting of D_e vs a or j required modifying the input subroutine in order to test each of the theoretical expressions for D_c . Thus the x_i were powers of j or a . The output subroutine was also modified somewhat.

In using HELARCTOS II expressions of the form $j^s a^t$, where s and t are positive integers, were used as models for the fit. One or more such $j^s a^t$ independent variables were

used with the dependent variable being D_e . Output data included the coefficients $\hat{\beta}_i$ of the p independent variables, the intercept $\hat{\beta}_0$, a squared multiple correlation coefficient given by

$$R^2 = \frac{\sum_{i=1}^n (\hat{Y}_i - \bar{Y})^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2}.$$

Here the Y_i are the predicted values given by the equation

$$\hat{Y}_K = \hat{\beta}_0 + \sum_{i=1}^p \hat{\beta}_i X_{ik}.$$

Y_i are the n observed values of the dependent variable and $\bar{Y}$ is their mean. The R^2 statistic was used in evaluating the goodness of fit. In this work the primary reason for using HELARCTOS II instead of FIT was that an option of HELARCTOS II allowed weighting of the data to take into account varying experimental error over the range of measurements.

APPENDIX III

Average D_e Calculated Using U_{1A} , U_{1B} , and U_{1C}
for Each j of Each Run

Following is a computer listing of the average D_e values determined by an iterative computer solution of Eq. [50]. The average D_e was found by considering what was usually ten measurements after steady state had been reached for a given j .

MOB NO. 11 CELL CONSTANT= 0.254189E-02 CM
 LENGTH= 2.62205 CM DIAMETER= 0.092126 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
199.2308	0.166829E-04	-2.97688	-0.43147E-01	0.32553
299.1260	0.187195E-04	-3.98459	-0.43133E-01	0.25167
398.4248	0.222885E-04	-4.46009	-0.43108E-01	0.22648
498.3759	0.265841E-04	-4.68088	-0.43077E-01	0.21631
597.9939	0.313692E-04	-4.76369	-0.43042E-01	0.21271
697.3008	0.363353E-04	-4.79998	-0.43003E-01	0.21116
797.1604	0.418849E-04	-4.76519	-0.42959E-01	0.21263
896.6775	0.478322E-04	-4.69868	-0.42913E-01	0.21551
996.6404	0.586796E-04	-4.26378	-0.42846E-01	0.23627
1096.2227	0.706536E-04	-3.90119	-0.42779E-01	0.25657
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.2308	0.165071E-04	-3.00389	-0.43469E-01	0.32313
299.1260	0.185372E-04	-4.01749	-0.43454E-01	0.24981
398.4248	0.220764E-04	-4.49588	-0.43429E-01	0.22481
498.3799	0.263326E-04	-4.71819	-0.43398E-01	0.21471
597.9939	0.310735E-04	-4.80149	-0.43362E-01	0.21113
697.3008	0.359927E-04	-4.83809	-0.43323E-01	0.20960
797.1604	0.414894E-04	-4.80309	-0.43279E-01	0.21106
896.6775	0.473813E-04	-4.73599	-0.43233E-01	0.21392
996.6404	0.581175E-04	-4.29829	-0.43165E-01	0.23452
1096.2227	0.699639E-04	-3.93349	-0.43097E-01	0.25468
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.2308	0.174742E-04	-2.85188	-0.41669E-01	0.33708
299.1260	0.195265E-04	-3.83308	-0.41655E-01	0.26060
398.4248	0.232267E-04	-4.29468	-0.41631E-01	0.23452
498.3759	0.276927E-04	-4.50899	-0.41601E-01	0.22398
597.9939	0.326735E-04	-4.58929	-0.41567E-01	0.22025
697.3008	0.378442E-04	-4.62449	-0.41529E-01	0.21865
797.1604	0.436271E-04	-4.59068	-0.41487E-01	0.22018
896.6775	0.498253E-04	-4.52629	-0.41443E-01	0.22315
996.6404	0.611716E-04	-4.10419	-0.41378E-01	0.24465
1096.2227	0.737187E-04	-3.75188	-0.41313E-01	0.26568

MOB NO. 12 CELL CONSTANT= 0.254189E-02 CM
 LENGTH= 2.62205 CM DIAMETER= 0.092126 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
199.4331	0.168898E-04	-2.94339	-0.42688E-01	0.32855
398.4385	0.223576E-04	-4.44639	-0.42649E-01	0.22709
597.9556	0.315759E-04	-4.73198	-0.42585E-01	0.21402
797.1548	0.448322E-04	-4.45158	-0.42504E-01	0.22682
996.5247	0.645401E-04	-3.87569	-0.42395E-01	0.25807
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.4331	0.167677E-04	-2.96019	-0.42888E-01	0.32702
398.4385	0.222103E-04	-4.46888	-0.42849E-01	0.22603
597.9556	0.313694E-04	-4.75569	-0.42785E-01	0.21302
797.1548	0.445360E-04	-4.47419	-0.42703E-01	0.22576
996.5247	0.641051E-04	-3.89588	-0.42593E-01	0.25686
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.4331	0.174606E-04	-2.85699	-0.41669E-01	0.33658
398.4385	0.230289E-04	-4.33169	-0.41631E-01	0.23264
597.9556	0.325148E-04	-4.61119	-0.41569E-01	0.21925
797.1548	0.461777E-04	-4.33679	-0.41490E-01	0.23236
996.5247	0.665361E-04	-3.77239	-0.41383E-01	0.26438

MGB NO. 13 CELL CONSTANT= 0.139072E-02 CM
 LENGTH= 2.61379 CM DIAMETER= 0.068021 CM

J	C(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
199.9423	0.155836E-04	-3.18739	-0.41704E-01	0.30697
299.9800	0.167697E-04	-4.44498	-0.41694E-01	0.22705
399.9805	0.173502E-04	-5.73098	-0.41676E-01	0.17765
599.8877	0.188761E-04	-7.90759	-0.41638E-01	0.12912
799.6907	0.214859E-04	-9.27329	-0.41583E-01	0.11013
999.9656	0.266190E-04	-9.37729	-0.41506E-01	0.10891
1099.5447	0.279675E-04	-9.82189	-0.41472E-01	0.10398
1199.6421	0.313210E-04	-9.57929	-0.41427E-01	0.10661
1299.5486	0.347132E-04	-9.37439	-0.41377E-01	0.10894
1399.4417	0.389841E-04	-8.99988	-0.41327E-01	0.11346
300.0058	0.166269E-04	-4.48348	-0.41695E-01	0.22520
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.9423	0.154849E-04	-3.20269	-0.41872E-01	0.30574
299.9800	0.166711E-04	-4.46429	-0.41862E-01	0.22614
399.9805	0.172511E-04	-5.75488	-0.41844E-01	0.17694
599.8877	0.187693E-04	-7.94019	-0.41806E-01	0.12860
799.6907	0.213646E-04	-9.31139	-0.41751E-01	0.10969
999.9656	0.264684E-04	-9.41589	-0.41673E-01	0.10847
1099.5447	0.278091E-04	-9.86239	-0.41639E-01	0.10356
1199.6421	0.311442E-04	-9.61859	-0.41594E-01	0.10618
1299.5486	0.345171E-04	-9.41289	-0.41543E-01	0.10850
1399.4417	0.387642E-04	-9.03679	-0.41494E-01	0.11301
300.0058	0.165291E-04	-4.50299	-0.41863E-01	0.22430
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.9423	0.156640E-04	-3.18198	-0.41644E-01	0.30742
299.9800	0.168541E-04	-4.43799	-0.41634E-01	0.22738
399.9805	0.174371E-04	-5.72209	-0.41615E-01	0.17791
599.8877	0.189694E-04	-7.89588	-0.41578E-01	0.12931
799.6907	0.215924E-04	-9.25939	-0.41523E-01	0.11029
999.9656	0.267505E-04	-9.36339	-0.41446E-01	0.10907
1099.5447	0.281060E-04	-9.80720	-0.41412E-01	0.10413
1199.6421	0.314767E-04	-9.56478	-0.41367E-01	0.10677
1299.5486	0.348850E-04	-9.36038	-0.41317E-01	0.10909
1399.4417	0.391773E-04	-8.98639	-0.41267E-01	0.11363
300.0058	0.167104E-04	-4.47649	-0.41635E-01	0.22553

MOB NO. 14 CELL CONSTANT= 0.119798E-02 CM
 LENGTH= 2.59112 CM DIAMETER= 0.062865 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC .PERCENT
MOBILITY=	-0.991500E-03	BASED ON RHO INTERCEPT		
199.9678	0.149521E-04	-3.29368	-0.42549E-01	0.29851
300.0364	0.156900E-04	-4.71079	-0.42538E-01	0.21493
400.0386	0.168362E-04	-5.85519	-0.42524E-01	0.17402
600.0352	0.189894E-04	-7.79198	-0.42495E-01	0.13109
800.1145	0.227161E-04	-8.69498	-0.42449E-01	0.11751
999.5232	0.253985E-04	-9.72629	-0.42400E-01	0.10505
1099.5651	0.271855E-04	-10.00419	-0.42367E-01	0.10213
1199.4329	0.289441E-04	-10.25759	-0.42335E-01	0.09961
1299.5967	0.296066E-04	-10.87298	-0.42306E-01	0.09397
1399.6199	0.298375E-04	-11.62849	-0.42273E-01	0.08787
1498.0938	0.288654E-04	-12.87478	-0.42243E-01	0.07936
1596.8667	0.289727E-04	-13.68619	-0.42202E-01	0.07465
800.0159	0.215662E-04	-9.15549	-0.42459E-01	0.11160
600.1792	0.189365E-04	-7.81559	-0.42495E-01	0.13070

MCBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.9678	0.148822E-04	-3.30399	-0.42663E-01	0.29772
300.0364	0.156207E-04	-4.72429	-0.42652E-01	0.21436
400.0386	0.167629E-04	-5.87158	-0.42638E-01	0.17355
600.0352	0.189078E-04	-7.81339	-0.42609E-01	0.13074
800.1145	0.226189E-04	-8.71869	-0.42563E-01	0.11719
999.5232	0.252896E-04	-9.75288	-0.42513E-01	0.10477
1099.5691	0.270688E-04	-10.03158	-0.42481E-01	0.10186
1199.4329	0.288199E-04	-10.28568	-0.42448E-01	0.09934
1299.5967	0.294794E-04	-10.90279	-0.42419E-01	0.09372
1399.6199	0.297093E-04	-11.66039	-0.42386E-01	0.08763
1498.0938	0.287421E-04	-12.90979	-0.42356E-01	0.07915
1596.8667	0.288490E-04	-13.72339	-0.42315E-01	0.07445
800.0159	0.214734E-04	-9.18068	-0.42572E-01	0.11130
600.1792	0.188553E-04	-7.83699	-0.42609E-01	0.13035

MCBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.9678	0.153748E-04	-3.21419	-0.41677E-01	0.30476
300.0364	0.160971E-04	-4.60749	-0.41665E-01	0.21943
400.0386	0.172619E-04	-5.73049	-0.41652E-01	0.17766
600.0352	0.194643E-04	-7.62809	-0.41623E-01	0.13383
800.1145	0.232834E-04	-8.51239	-0.41579E-01	0.11997
999.5232	0.260321E-04	-9.52229	-0.41530E-01	0.10725
1099.5691	0.278636E-04	-9.79439	-0.41499E-01	0.10427
1199.4329	0.296657E-04	-10.04258	-0.41467E-01	0.10169
1299.5967	0.303447E-04	-10.64509	-0.41439E-01	0.09594
1399.6199	0.305810E-04	-11.38488	-0.41406E-01	0.08971
1498.0938	0.295849E-04	-12.60499	-0.41377E-01	0.08102
1596.8667	0.296954E-04	-13.39919	-0.41337E-01	0.07622
800.0159	0.221041E-04	-8.96349	-0.41588E-01	0.11394
600.1792	0.194101E-04	-7.65119	-0.41624E-01	0.13343

MOB NO. 15 CELL CONSTANT= 0.136485E-02 CM
 LENGTH= 2.58338 CM DIAMETER= 0.067005 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT

MOBILITY=	-0.991500E-03	BASED ON RHO INTERCEPT		
599.1431	0.195056E-04	-7.55598	-0.42054E-01	0.13514
798.8213	0.225535E-04	-8.72379	-0.42002E-01	0.11709
997.9224	0.265794E-04	-9.26298	-0.41931E-01	0.11028
1098.60C1	0.288244E-04	-9.41269	-0.41890E-01	0.10852
1198.70C7	0.297524E-04	-9.95799	-0.41857E-01	0.10258
1297.8467	0.327499E-04	-9.80620	-0.41808E-01	0.10416
1396.1636	0.361256E-04	-9.57388	-0.41762E-01	0.10669
599.1438	0.197145E-04	-7.47488	-0.42060E-01	0.13660
399.4502	0.170716E-04	-5.74929	-0.42102E-01	0.17713

MOBILITY=	-0.989950E-03	BASED ON RHO LOW J		
599.1431	0.187685E-04	-7.84049	-0.43597E-01	0.13036
798.8213	0.217037E-04	-9.05119	-0.43542E-01	0.11295
997.9224	0.255785E-04	-9.61039	-0.43469E-01	0.10638
1098.60C1	0.277388E-04	-9.76579	-0.43426E-01	0.10468
1198.7007	0.286325E-04	-10.33129	-0.43392E-01	0.09895
1297.8467	0.315163E-04	-10.17409	-0.43341E-01	0.10048
1396.1636	0.347655E-04	-9.93289	-0.43294E-01	0.10291
599.1438	0.189698E-04	-7.75619	-0.43603E-01	0.13177
399.4502	0.164186E-04	-5.96859	-0.43646E-01	0.17086

MOBILITY=	-0.994920E-03	BASED ON WEIGHED IN CONC.		
599.1431	0.198203E-04	-7.46168	-0.41543E-01	0.13680
798.8213	0.229163E-04	-8.61529	-0.41491E-01	0.11853
997.9224	0.270073E-04	-9.14769	-0.41422E-01	0.11164
1098.6001	0.292879E-04	-9.29568	-0.41381E-01	0.10986
1198.70C7	0.302314E-04	-9.83399	-0.41348E-01	0.10384
1297.8467	0.332762E-04	-9.68439	-0.41300E-01	0.10545
1396.1636	0.367068E-04	-9.45478	-0.41255E-01	0.10800
599.1438	0.200325E-04	-7.38158	-0.41549E-01	0.13828
399.4502	0.173505E-04	-5.67639	-0.41590E-01	0.17931

MGB NO. 16 CELL CONSTANT= 0.315209E-02 CM
 LENGTH= 2.81996 CM DIAMETER= 0.106375 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
199.9365	0.186695E-04	-2.87039	-0.41708E-01	0.33529
299.7305	0.220629E-04	-3.64279	-0.41691E-01	0.27291
399.9102	0.291166E-04	-3.68498	-0.41667E-01	0.27009
449.6055	0.342121E-04	-3.52699	-0.41654E-01	0.28092
500.0066	0.406866E-04	-3.29939	-0.41639E-01	0.29793
549.6955	0.482065E-04	-3.06278	-0.41621E-01	0.31759
599.4429	0.570672E-04	-2.82249	-0.41605E-01	0.33995
649.5188	0.679702E-04	-2.56898	-0.41584E-01	0.36653
698.9502	0.789933E-04	-2.37959	-0.41569E-01	0.38872
749.0391	0.914476E-04	-2.20409	-0.41545E-01	0.41130
799.3406	0.105072E-03	-2.04809	-0.41525E-01	0.43318
399.9087	0.289860E-04	-3.70129	-0.41670E-01	0.26902
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.9365	0.184266E-04	-2.90369	-0.42098E-01	0.33218
299.7305	0.217975E-04	-3.68139	-0.42081E-01	0.27038
399.9102	0.287666E-04	-3.72399	-0.42057E-01	0.26759
449.6055	0.337965E-04	-3.56478	-0.42044E-01	0.27832
500.0066	0.401834E-04	-3.33549	-0.42028E-01	0.29517
549.6955	0.475949E-04	-3.09729	-0.42010E-01	0.31464
599.4429	0.563215E-04	-2.85539	-0.41994E-01	0.33680
649.5188	0.670495E-04	-2.60019	-0.41973E-01	0.36313
698.9502	0.778844E-04	-2.40969	-0.41958E-01	0.38511
749.0391	0.901190E-04	-2.23309	-0.41934E-01	0.40749
799.3406	0.103483E-03	-2.07629	-0.41914E-01	0.42917
399.9087	0.286382E-04	-3.74039	-0.42060E-01	0.26652
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.9365	0.187450E-04	-2.86869	-0.41688E-01	0.33546
299.7305	0.221512E-04	-3.64078	-0.41670E-01	0.27305
399.9102	0.292329E-04	-3.68298	-0.41646E-01	0.27022
449.6055	0.343497E-04	-3.52499	-0.41633E-01	0.28106
500.0066	0.408518E-04	-3.29739	-0.41618E-01	0.29808
549.6955	0.484013E-04	-3.06098	-0.41600E-01	0.31774
599.4429	0.573007E-04	-2.82069	-0.41584E-01	0.34011
649.5188	0.682497E-04	-2.56729	-0.41563E-01	0.36671
698.9502	0.793192E-04	-2.37798	-0.41548E-01	0.38891
749.0391	0.918257E-04	-2.20259	-0.41524E-01	0.41150
799.3406	0.105512E-03	-2.04659	-0.41505E-01	0.43340
399.9087	0.291018E-04	-3.69929	-0.41650E-01	0.26915

MOB NO. 17 CELL CONSTANT= 0.490700E-02 CM
 LENGTH= 3.67426 CM DIAMETER= 0.151511 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
149.9675	0.210400E-04	-2.49058	-0.42252E-01	0.37558
199.8281	0.224434E-04	-3.11209	-0.42239E-01	0.31340
250.1674	0.270234E-04	-3.23719	-0.42221E-01	0.30298
299.8274	0.339963E-04	-3.08558	-0.42200E-01	0.31569
349.7664	0.441390E-04	-2.77409	-0.42174E-01	0.34486
399.7207	0.554095E-04	-2.52689	-0.42150E-01	0.37138
449.6309	0.711280E-04	-2.21619	-0.42113E-01	0.40978
499.5835	0.875569E-04	-2.00159	-0.42088E-01	0.44018
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
149.9675	0.208896E-04	-2.50459	-0.42432E-01	0.37399
199.8281	0.222937E-04	-3.12809	-0.42419E-01	0.31207
250.1674	0.268469E-04	-3.25339	-0.42400E-01	0.30170
299.8274	0.337701E-04	-3.10139	-0.42379E-01	0.31435
349.7664	0.438362E-04	-2.78888	-0.42353E-01	0.34340
399.7207	0.550181E-04	-2.54088	-0.42329E-01	0.36981
449.6309	0.705932E-04	-2.22949	-0.42292E-01	0.40805
499.5835	0.868687E-04	-2.01429	-0.42267E-01	0.43832
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
149.9675	0.215248E-04	-2.44288	-0.41643E-01	0.38107
199.8281	0.229170E-04	-3.05829	-0.41630E-01	0.31799
250.1674	0.275872E-04	-3.18198	-0.41612E-01	0.30742
299.8274	0.347155E-04	-3.03208	-0.41591E-01	0.32031
349.7664	0.451109E-04	-2.72369	-0.41565E-01	0.34990
399.7207	0.566773E-04	-2.47888	-0.41542E-01	0.37682
449.6309	0.728562E-04	-2.17109	-0.41506E-01	0.41578
499.5835	0.898013E-04	-1.95829	-0.41481E-01	0.44662

MOB NO. 18 CELL CONSTANT= 0.620590E-02 CM
 LENGTH= 5.21552 CM DIAMETER= 0.202997 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
200.0855	0.408528E-04	-2.43049	-0.41408E-01	0.38252
250.0121	0.568792E-04	-2.18298	-0.41375E-01	0.41412
299.9397	0.943068E-04	-1.58088	-0.41341E-01	0.51083
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
200.0855	0.391848E-04	-2.52999	-0.42680E-01	0.37111
250.0121	0.544290E-04	-2.27768	-0.42647E-01	0.40178
299.9397	0.894031E-04	-1.66498	-0.42611E-01	0.49560
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
200.0855	0.408057E-04	-2.44168	-0.41550E-01	0.38120
250.0121	0.567570E-04	-2.19368	-0.41518E-01	0.41270
299.9397	0.940725E-04	-1.59028	-0.41483E-01	0.50908

MOB NO. 19 CELL CONSTANT= 0.417718E-02 CM
 LENGTH= 3.22960 CM DIAMETER= 0.131064 CM

J AMPS/CMSQ	D(EFF) CMSQ/SEC	S	Q	C(SS) ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
199.8786	0.190328E-04	-3.22549	-0.41855E-01	0.30387
300.0767	0.313552E-04	-2.94108	-0.41831E-01	0.32862
399.8860	0.512683E-04	-2.39929	-0.41792E-01	0.38634
499.9639	0.684145E-04	-2.25039	-0.41746E-01	0.40517
600.0088	0.888157E-04	-2.08328	-0.41688E-01	0.42811
700.1006	0.112896E-03	-1.91569	-0.41615E-01	0.45324
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
199.8786	0.186999E-04	-3.27778	-0.42429E-01	0.29975
300.0767	0.307900E-04	-2.99039	-0.42405E-01	0.32417
399.8860	0.502581E-04	-2.44369	-0.42365E-01	0.38111
499.9639	0.670240E-04	-2.29348	-0.42319E-01	0.39969
600.0088	0.869408E-04	-2.12488	-0.42260E-01	0.42232
700.1006	0.110398E-03	-1.95599	-0.42186E-01	0.44711
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
199.8786	0.192116E-04	-3.20649	-0.41646E-01	0.30539
300.0767	0.316559E-04	-2.92319	-0.41622E-01	0.33027
399.8860	0.517927E-04	-2.38319	-0.41583E-01	0.38828
499.9639	0.691297E-04	-2.23479	-0.41538E-01	0.40720
600.0088	0.897769E-04	-2.06809	-0.41480E-01	0.43026
700.1006	0.114156E-03	-1.90109	-0.41408E-01	0.45551

MOB NO. 20 CELL CONSTANT= 0.187667E-02 CM
 LENGTH= 2.48006 CM DIAMETER= 0.076987 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
200.0777	0.161356E-04	-2.92209	-0.42163E-01	0.33045
299.9961	0.172033E-04	-4.11078	-0.42150E-01	0.24438
400.1260	0.185393E-04	-5.08988	-0.42132E-01	0.19947
500.0962	0.197872E-04	-5.96319	-0.42112E-01	0.17088
599.7195	0.213291E-04	-6.63809	-0.42087E-01	0.15371
799.7344	0.245596E-04	-7.11899	-0.42027E-01	0.14339
999.8064	0.336178E-04	-7.04539	-0.41944E-01	0.14487
1100.3269	0.361291E-04	-7.22129	-0.41907E-01	0.14136
1200.1218	0.419066E-04	-6.79949	-0.41851E-01	0.15007
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
200.0777	0.161016E-04	-2.92369	-0.42182E-01	0.33031
299.9961	0.171685E-04	-4.11269	-0.42168E-01	0.24427
400.1260	0.185012E-04	-5.09238	-0.42151E-01	0.19938
500.0962	0.197470E-04	-5.96598	-0.42131E-01	0.17081
599.7195	0.212861E-04	-6.64109	-0.42106E-01	0.15364
799.7344	0.265057E-04	-7.12229	-0.42046E-01	0.14333
999.8064	0.335500E-04	-7.04859	-0.41963E-01	0.14481
1100.3269	0.360556E-04	-7.22469	-0.41925E-01	0.14130
1200.1218	0.418226E-04	-6.80249	-0.41869E-01	0.15000
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
200.0777	0.164308E-04	-2.87949	-0.41665E-01	0.33441
299.9961	0.174903E-04	-4.05729	-0.41651E-01	0.24731
400.1260	0.188382E-04	-5.02639	-0.41634E-01	0.20185
500.0962	0.201022E-04	-5.88998	-0.41614E-01	0.17293
599.7195	0.216674E-04	-6.55698	-0.41590E-01	0.15555
799.7344	0.269794E-04	-7.03239	-0.41530E-01	0.14511
999.8064	0.341491E-04	-6.95969	-0.41448E-01	0.14661
1100.3269	0.366994E-04	-7.13359	-0.41411E-01	0.14305
1200.1218	0.425701E-04	-6.71659	-0.41356E-01	0.15187

MOB NO. 21 CELL CONSTANT= 0.156934E-02 CM
 LENGTH= 2.11152 CM DIAMETER= 0.064948 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
200.0593	0.155002E-04	-2.58988	-0.41719E-01	0.36423
600.0374	0.195594E-04	-6.16578	-0.41651E-01	0.16531
999.7012	0.259413E-04	-7.76519	-0.41546E-01	0.13147
1400.1018	0.317823E-04	-8.90769	-0.41402E-01	0.11464
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
200.0593	0.153786E-04	-2.60629	-0.41922E-01	0.36246
600.0374	0.194305E-04	-6.19698	-0.41854E-01	0.16450
999.7012	0.257713E-04	-7.80419	-0.41748E-01	0.13084
1400.1018	0.315755E-04	-8.95199	-0.41604E-01	0.11408
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
200.0593	0.155735E-04	-2.58659	-0.41678E-01	0.36459
600.0374	0.196466E-04	-6.15959	-0.41611E-01	0.16547
999.7012	0.260570E-04	-7.75739	-0.41505E-01	0.13160
1400.1018	0.319245E-04	-8.89859	-0.41361E-01	0.11475

MOB NO. 22 CELL CONSTANT= 0.998149E-03 CM
 LENGTH= 2.26220 CM DIAMETER= 0.053619 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT

MOBILITY=	-0.991500E-03	BASED ON RHO INTERCEPT		
200.0424	0.148076E-04	-2.90469	-0.41518E-01	0.33199
299.9357	0.149924E-04	-4.30179	-0.41516E-01	0.23415
399.9241	0.153673E-04	-5.59729	-0.41505E-01	0.18178
500.0088	0.156311E-04	-6.88148	-0.41496E-01	0.14827
600.0247	0.163287E-04	-7.90859	-0.41478E-01	0.12909
800.0061	0.174936E-04	-9.85139	-0.41440E-01	0.10367
999.8196	0.188474E-04	-11.44019	-0.41395E-01	0.08927
1199.8538	0.205762E-04	-12.59178	-0.41342E-01	0.08111
1400.2449	0.242051E-04	-12.51369	-0.41269E-01	0.08161
1599.6121	0.268748E-04	-12.89788	-0.41198E-01	0.07917
1800.1182	0.315142E-04	-12.40219	-0.41117E-01	0.08234
600.0281	0.174583E-04	-7.39678	-0.41479E-01	0.13799
199.9180	0.148691E-04	-2.89019	-0.41528E-01	0.33337

MOBILITY=	-0.989950E-03	BASED ON RHO LOW J		
200.0424	0.148443E-04	-2.89298	-0.41381E-01	0.33308
299.9357	0.150228E-04	-4.28639	-0.41379E-01	0.23492
399.9241	0.153960E-04	-5.57809	-0.41369E-01	0.18238
500.0088	0.156597E-04	-6.85818	-0.41359E-01	0.14876
600.0247	0.163584E-04	-7.88188	-0.41342E-01	0.12952
800.0061	0.175255E-04	-9.81809	-0.41304E-01	0.10401
999.8196	0.188815E-04	-11.40169	-0.41258E-01	0.08957
1199.8538	0.206134E-04	-12.54939	-0.41206E-01	0.08137
1400.2449	0.242491E-04	-12.47148	-0.41134E-01	0.08188
1599.6121	0.269232E-04	-12.85459	-0.41062E-01	0.07943
1800.1182	0.315711E-04	-12.36048	-0.40982E-01	0.08261
600.0281	0.174901E-04	-7.37178	-0.41343E-01	0.13845
199.9180	0.149062E-04	-2.87849	-0.41391E-01	0.33447

MOBILITY=	-0.994920E-03	BASED ON WEIGHED IN CONC.		
200.0424	0.147905E-04	-2.91810	-0.41674E-01	0.33075
299.9357	0.149832E-04	-4.31929	-0.41671E-01	0.23327
399.9241	0.153599E-04	-5.61929	-0.41661E-01	0.18110
500.0088	0.156249E-04	-6.90799	-0.41652E-01	0.14771
600.0247	0.163220E-04	-7.93910	-0.41634E-01	0.12861
800.0061	0.174870E-04	-9.88909	-0.41596E-01	0.10328
999.8196	0.188402E-04	-11.48408	-0.41550E-01	0.08894
1199.8538	0.205686E-04	-12.63989	-0.41497E-01	0.08080
1400.2449	0.241960E-04	-12.56158	-0.41424E-01	0.08130
1599.6121	0.268646E-04	-12.94729	-0.41352E-01	0.07888
1800.1182	0.315027E-04	-12.44949	-0.41271E-01	0.08203
600.0281	0.174512E-04	-7.42529	-0.41635E-01	0.13748
199.9180	0.148516E-04	-2.90359	-0.41683E-01	0.33212

MOB NO. 24 CELL CONSTANT= 0.407821E-02 CM
 LENGTH= 3.43848 CM DIAMETER= 0.133629 CM

J AMPS/CMSQ	D(EFF) CMSQ/SEC	S	Q	C(SS) ATOMIC PERCENT
MOBILITY=	-0.991500E-03	BASED ON	RHO INTERCEPT	
199.9286	0.211390E-04	-3.09258	-0.40549E-01	0.31482
299.9993	0.329526E-04	-2.97889	-0.40522E-01	0.32493
399.9114	0.460903E-04	-2.84159	-0.40487E-01	0.33788
449.8938	0.540927E-04	-2.72539	-0.40463E-01	0.34953
499.8914	0.627193E-04	-2.61329	-0.40440E-01	0.36144
600.0000	0.825928E-04	-2.38519	-0.40380E-01	0.38782
199.9105	0.213266E-04	-3.06509	-0.40549E-01	0.31721
149.9959	0.166464E-04	-2.94559	-0.40560E-01	0.32799
150.0000	0.168173E-04	-2.91599	-0.40557E-01	0.33076
149.9868	0.167419E-04	-2.92889	-0.40556E-01	0.32955
100.0039	0.155528E-04	-2.10159	-0.40567E-01	0.42528
99.9994	0.155627E-04	-2.09998	-0.40570E-01	0.42551
49.9967	0.151536E-04	-1.07839	-0.40566E-01	0.62025
49.9963	0.149329E-04	-1.09409	-0.40575E-01	0.61635
49.9966	0.151491E-04	-1.07859	-0.40570E-01	0.62020

MOBILITY=	-0.989950E-03	BASED ON	RHO LOW J	
199.9286	0.207879E-04	-3.13989	-0.41068E-01	0.31085
299.9993	0.323575E-04	-3.02519	-0.41040E-01	0.32083
399.9114	0.453009E-04	-2.88659	-0.41004E-01	0.33362
449.8938	0.531482E-04	-2.76949	-0.40981E-01	0.34512
499.8914	0.616076E-04	-2.65629	-0.40957E-01	0.35688
600.0000	0.810666E-04	-2.42629	-0.40896E-01	0.38292
199.9105	0.209704E-04	-3.11229	-0.41068E-01	0.31321
149.9959	0.163643E-04	-2.99168	-0.41078E-01	0.32385
150.0000	0.165314E-04	-2.96178	-0.41075E-01	0.32659
149.9868	0.164578E-04	-2.97478	-0.41075E-01	0.32539
100.0039	0.152463E-04	-2.14048	-0.41086E-01	0.41991
99.9994	0.152557E-04	-2.13889	-0.41089E-01	0.42014
49.9967	0.146952E-04	-1.11029	-0.41084E-01	0.61243
49.9963	0.144858E-04	-1.12609	-0.41093E-01	0.60857
49.9966	0.146909E-04	-1.11049	-0.41089E-01	0.61238

MOBILITY=	-0.994920E-03	BASED ON	WEIGHED IN CONC.	
199.9286	0.205926E-04	-3.18558	-0.41568E-01	0.30711
299.9993	0.320871E-04	-3.06978	-0.41540E-01	0.31696
399.9114	0.448554E-04	-2.92989	-0.41504E-01	0.32960
449.8938	0.526096E-04	-2.81189	-0.41480E-01	0.34097
499.8914	0.609645E-04	-2.69778	-0.41456E-01	0.35258
600.0000	0.801655E-04	-2.46588	-0.41394E-01	0.37831
199.9105	0.207733E-04	-3.15759	-0.41568E-01	0.30944
149.9959	0.162065E-04	-3.03598	-0.41579E-01	0.31995
150.0000	0.163711E-04	-3.00579	-0.41576E-01	0.32266
149.9868	0.162983E-04	-3.01899	-0.41575E-01	0.32147
100.0039	0.150597E-04	-2.17788	-0.41587E-01	0.41485
99.9994	0.150688E-04	-2.17629	-0.41590E-01	0.41508
49.9967	0.143730E-04	-1.14088	-0.41585E-01	0.60505
49.9963	0.141722E-04	-1.15678	-0.41594E-01	0.60124
49.9966	0.143675E-04	-1.14119	-0.41590E-01	0.60500

MOB NO. 25 CELL CONSTANT= 0.172867E-02 CM
 LENGTH= 1.97339 CM DIAMETER= 0.065913 CM

J	D(EFF)	S	Q	C(SS)
AMPS/CMSQ	CMSQ/SEC			ATOMIC PERCENT
MOBILITY= -0.991500E-03 BASED ON RHO INTERCEPT				
200.0982	0.153828E-04	-2.44059	-0.41231E-01	0.38128
149.9912	0.152141E-04	-1.84919	-0.41243E-01	0.46380
149.9962	0.153717E-04	-1.83059	-0.41236E-01	0.46684
149.9907	0.152867E-04	-1.84059	-0.41239E-01	0.46520
99.9940	0.149871E-04	-1.25148	-0.41242E-01	0.57904
99.9993	0.150200E-04	-1.24879	-0.41243E-01	0.57964
99.9989	0.150801E-04	-1.24388	-0.41241E-01	0.58078
50.0124	0.149952E-04	-0.62560	-0.41242E-01	0.75065
50.0137	0.149007E-04	-0.62950	-0.41248E-01	0.74935
50.0115	0.151406E-04	-0.61960	-0.41241E-01	0.75259
50.0143	0.145684E-04	-0.62670	-0.41245E-01	0.75029
200.1160	0.158261E-04	-2.37239	-0.41232E-01	0.38955
MOBILITY= -0.989950E-03 BASED ON RHO LOW J				
200.0982	0.153386E-04	-2.44378	-0.41272E-01	0.38090
149.9912	0.151666E-04	-1.85208	-0.41284E-01	0.46335
149.9962	0.153234E-04	-1.83349	-0.41277E-01	0.46638
149.9907	0.152396E-04	-1.84339	-0.41280E-01	0.46474
99.9940	0.149326E-04	-1.25409	-0.41283E-01	0.57847
99.9993	0.149654E-04	-1.25139	-0.41284E-01	0.57907
99.9989	0.150263E-04	-1.24639	-0.41281E-01	0.58021
50.0124	0.149193E-04	-0.62780	-0.41283E-01	0.74991
50.0137	0.148232E-04	-0.63180	-0.41288E-01	0.74862
50.0115	0.150610E-04	-0.62190	-0.41282E-01	0.75185
50.0143	0.148927E-04	-0.62890	-0.41286E-01	0.74955
200.1160	0.157807E-04	-2.37549	-0.41273E-01	0.38916
MOBILITY= -0.994920E-03 BASED ON WEIGHED IN CONC.				
200.0982	0.152373E-04	-2.47239	-0.41634E-01	0.37759
149.9912	0.150365E-04	-1.87749	-0.41646E-01	0.45931
149.9962	0.151907E-04	-1.85879	-0.41640E-01	0.46232
149.9907	0.151079E-04	-1.86879	-0.41642E-01	0.46070
99.9940	0.147409E-04	-1.27678	-0.41645E-01	0.57343
99.9993	0.147725E-04	-1.27409	-0.41646E-01	0.57403
99.9989	0.148316E-04	-1.26909	-0.41644E-01	0.57516
50.0124	0.145245E-04	-0.64810	-0.41645E-01	0.74338
50.0137	0.144361E-04	-0.65200	-0.41651E-01	0.74210
50.0115	0.146604E-04	-0.64210	-0.41644E-01	0.74531
50.0143	0.144995E-04	-0.64920	-0.41648E-01	0.74303
200.1160	0.156732E-04	-2.40379	-0.41635E-01	0.38578

APPENDIX IV

Mutual Diffusion Coefficient of Cd in Hg

A number of investigators have measured the mutual diffusion coefficient of Cd in Hg. Values of D and the method used in determining them are given below. Unfortunately most investigators have given no indication of the accuracy or reproducibility of their work. Cooper and Furman have given an excellent review of the early experimental results.

Most of the later methods have involved polarography. D seems to be dependent on the electrode radius or drop size used in this technique. The amalgams used with the polarographic technique must be dilute in order for the drop to properly form. Table XX does not list the compositions of the amalgams used in this technique but it is safe to assume that they were much more dilute than those used in connection with this work.

Mangelsdorf³² found no significant change in D from 0.3 to 2.8 atom % Cd. This range includes most of the mean capillary compositions observed in this work. His results agree with those of Cohen and Bruins⁷¹ and those of Weischedel.⁷² Given the facts that the polarographic technique uses more dilute amalgams, that the values of D so obtained seem to be dependent on the drop or orifice radius, and that most of the values obtained by polarography cluster about Mangelsdorf's value, one can conclude that the mutual diffusion coefficient

of Cd in Hg is 1.53×10^{-5} cm²/sec with an uncertainty of about .05 cm²/sec.

Table XX. Values of the Mutual Diffusion Coefficient of Dilute Cd Amalgams

$D \times 10^5$, cm ² /sec	Method ^a	T, °C	Concentration	Diffusion ^b Path Size	Comments	Ref.
1.81	Emf	15	.1 wt %	17 mm diam	pool	73
1.76+.11	Emf	8.7	.116-.150 wt %	20 mm diam	shear cell	74
1.523+.005	Emf	20	independent	40 mm diam	pool	71
1.53+-.08	C	20	.9-1.5 wt %	4 mm diam	two semi-infinite rods; vertical cap.	72
1.52	P	25	dilute	n.d. ^c	given by ref. 76	75
2.07	P	25	dilute	n.d.	given by ref. 78	77
1.45	P	25	dilute	n.d.	given by ref. 79	77
1.66+-.03	P	22	dilute	$r_d = .38, .56,$ or 1.0 mm	n.d.	80
1.53	C	25	.3-2.8 atom %	.025x2 mm	thin horizontal slot	32
2.45	P	20	dilute	$r_o = .562$ mm	$Q = 1695$ cal/mole	81
1.52	P	--	dilute	$r_d = .45-.55$ mm	n.d.	82
1.45+.07	P	25	dilute	$r_d = .39$ mm	n.d.	78
0.98-	P	25	dilute	$r_o = .05$ mm	n.d.	83
1.61+-.05	P	25	dilute	$r_d = .52-.75$ mm	independent of drop size	84
1.51+-.10	P	25	dilute	$r_o = .48$ mm	$D_o = 6.5 \pm 1.1,$ $Q = 850$ cal/mole	85
1.45	P	25	dilute	$r_d = .34$ mm	n.d.	79
1.53	P	25	dilute	$r_d = .43$ mm	n.d.	79
1.54	P	25	dilute	$r_d = .54$ mm	n.d.	79

^aC means conductance and P means polarographic.

^bPolarographic diffusion paths given by r_d for drop radius and r_o for orifice radius.

^cn.d. = no appropriate information given.

APPENDIX V

Coefficients and Standard Errors of Fits of Unweighted Data
to Several Models

The coefficients and their standard errors are shown below for fits to models corresponding to the dependences shown by the predicted convection mechanisms. The data were unweighted. All models listed in Table X are included here.

Table XXI. Intercepts and Coefficients with Standard Errors for Various Predicted Models. Unweighted Data

Inter- cept	$j^2 a^2$ coefficient x10 ⁸	$j^4 a^6$ coefficient x10 ⁸	$j^4 a^8$ coefficient x10 ⁶	$j^4 a^{10}$ coefficient x10 ⁴
1.7038	2.076 $\pm$.067			
1.9400		.585 $\pm$.008		
2.3100			1.208 $\pm$.021	
2.7171				.127 $\pm$.004
2.0773	-0.380 $\pm$.061	.647 $\pm$.013		
1.7038	1.088 $\pm$.041		.988 $\pm$.019	
1.6027	1.712 $\pm$.050			1.030 $\pm$.031
1.9894		.403 $\pm$.013	.469 $\pm$.029	
1.9597		.515 $\pm$.009		.369 $\pm$.028
2.1581			2.111 $\pm$.039	-1.390 $\pm$.055
1.8814	.330 $\pm$.073	.307 $\pm$.025	.578 $\pm$.038	
1.9689	-0.029 $\pm$.066	.521 $\pm$.016		.362 $\pm$.031
1.7934	.748 $\pm$.043		1.649 $\pm$.044	-0.912 $\pm$.056
2.0143		.313 $\pm$.023	.910 $\pm$.094	-0.425 $\pm$.086
1.7658	.872 $\pm$.088	-0.072 $\pm$.045	1.848 $\pm$.131	-1.054 $\pm$.105
$D_e = 1.4875 + (9.910 \pm .097) \times 10^{-6} j^2 a^4$				

APPENDIX VI

Coefficients and Standard Errors of Fits of Weighted Data
to Several Models

The coefficients and their standard errors are shown below for fits to models corresponding to the dependences shown by the predicted convection mechanisms. The data were weighted according to Table XIV. All models listed in Table XV are included here.

Table XXII. Intercepts and Coefficients with Standard Errors for Various Predicted Models. Data Weighted According to Table XIV

Intercept	$j^2_a^2$ Coefficient $\times 10^8$	$j^4_a^6$ Coefficient $\times 10^8$	$j^4_a^8$ Coefficient $\times 10^6$	$j^4_a^{10}$ Coefficient $\times 10^4$
1.4861 $\pm$.0269	1.743 $\pm$.052			
1.7644 $\pm$.0128		.648 $\pm$.009		
1.9161 $\pm$.0155			1.058 $\pm$.020	
1.9959 $\pm$.0202				.933 $\pm$.028
1.7685 $\pm$.0171	-0.017 $\pm$.048	.652 $\pm$.014		
1.5584 $\pm$.0132	1.131 $\pm$.027		.856 $\pm$.014	
1.5029 $\pm$.0165	1.469 $\pm$.032			.787 $\pm$.017
1.7897 $\pm$.0111		.456 $\pm$.012	.434 $\pm$.021	
1.7834 $\pm$.0114		.544 $\pm$.010		.336 $\pm$.018
1.8349 $\pm$.0116			2.612 $\pm$.049	-1.736 $\pm$.052
1.6253 $\pm$.0145	.750 $\pm$.047	.193 $\pm$.020	.660 $\pm$.024	
1.6674 $\pm$.0152	.517 $\pm$.047	.397 $\pm$.016		.446 $\pm$.020
1.6140 $\pm$.0121	.816 $\pm$.029		1.751 $\pm$.049	-0.937 $\pm$.050
1.7965 $\pm$.0111		.338 $\pm$.024	1.092 $\pm$.116	-0.554 $\pm$.096
1.5389 $\pm$.0135	1.244 $\pm$.049	-0.359 $\pm$.033	2.911 $\pm$.118	-1.771 $\pm$.091

$$D_e = 1.5330 \pm .0086 + (8.594 \pm .067) \times 10^{-6} j^2_a^4$$

APPENDIX VII

Parameters Appearing in Theoretical Expressions for D_c

In the course of this work values of the parameters appearing in the theoretical expressions for D_c were required. Values are listed below along with the source from which the value was taken. In several cases the assumption was made that a value measured in pure Hg was a good measure of that parameter in a dilute Cd amalgam. This applies particularly to the values of n and λ . Also the value of n was based on there being two free electrons per atom. The value of λ was determined from measurements of λ in solid Hg by assuming that at the melting point of pure Hg $\rho\lambda(\text{solid Hg}) = \rho\lambda(\text{liquid Hg})$.

Table XXIII. Values of Some Parameters Appearing in Theoretical Expressions for D_c

Parameter	Symbol	Value	Ref.
electron density	n	$8.4 \times 10^{22} \text{cm}^{-3}$	31
electron mean free path	λ	$3.7 \times 10^{-7} \text{cm}$	31
resistivity	ρ	$95 \times 10^{-6} \text{cm}$	86
viscosity	η	$1.55 \times 10^{-2} \text{ poise}$	87
velocity of charge carriers	v	$4.2 \times 10^8 \text{cm/sec}$	27
volume expansion coefficient	β	$1.8156 \times 10^{-5} \text{cm}^3/\text{°C}$	86
density	d_e	13.50gm/cm^3	87
thermal conductivity	k	$2.05 \times 10^{-2} \text{cal/sec-cm-°C}$	87