Steady-state measurements of diffusion coefficients in the liquid bismuth-tin system

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by

Charles Henry Buell, Jr.

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INTRODUCTION

The diffusion of molecules and ions in aqueous and organic solvents has been studied quite extensively for many years. However, there is a limited amount of data on liquid metals. The bulk of the information which does exist involves measurements of self-diffusion or diffusion in dilute solutions. The lack of data in liquid metals is primarily due to experimental difficulties encountered when working at temperatures above 200°C.

Current interest in the purification processes for liquid metal mixtures, as well as the need to clarify the nature of diffusion in liquid metals, indicates an increased need for diffusion information. Some of the processes which require diffusion data are distillation, fused-salt-molten-metal extraction and zone refining. Of the binary liquid metal systems possible for study, a bismuth-tin system was chosen. This system has electric resistivity and electric mobility data available for various temperatures and concentrations (18, 28). The above data are necessary in the design and operation of the equipment used in the constant flux and capillary cell methods.
PREVIOUS WORK

Liquid Diffusion Theories

Many theories have been developed to predict self- and mutual-diffusion coefficients by relating them to other physical properties of the liquid. However, none of these theories have been satisfactory in predicting the variation of diffusion coefficient with composition for all liquids (29).

Diffusion is caused by the random motion of the molecules which, in the absence of external forces such as bulk flow, results in the transport of matter from one part of a system to another. Fick (11) first defined the diffusion coefficient in 1855 as a proportionality constant between the rate of mass transfer and the concentration gradient. He stated his first law for unidirectional mass transfer as:

$$ J = -D \frac{dC}{dx} $$

where $J$ is the mass transfer rate per unit area, $dC/dx$ is the concentration gradient and $D$ is the diffusion coefficient which may be dependent on composition.

Applying Fick's first law to a binary system with components A and B, the resulting equations are:

$$ J_A = -D_A \frac{dC_A}{dx} $$

$$ J_B = -D_B \frac{dC_B}{dx} $$

A single diffusion coefficient, $D_{AB} = D_A = D_B$, may be used to represent both species at a specific concentration if a suitable frame of reference can be defined. A volume frame of reference is usually chosen if the partial molal volumes of A and B are constant over the composition range of the diffusion process.
Darken (8) defined the diffusion coefficient for an ideal solution as:

\[ D_{AB} = N_A D_B + N_B D_A \]  \hspace{1cm} (4)

where \( D_A \) and \( D_B \) are the diffusion coefficients of labeled isotopes of the individual components in a solution of the same composition and \( N_A \) and \( N_B \) are the mole fractions.

The variation of diffusion coefficient with composition for non-ideal solutions has been studied by Darken (8), De Groot (9), Denbigh (10), Hartley and Crank (12), and Lamm (14). If the chemical potential gradient is used instead of the concentration gradient as the mass driving force, then Equation (2) becomes:

\[ J_A = -D_A \frac{d\mu_A}{dx} \]  \hspace{1cm} (5)

where \( \mu_A \) is the chemical potential and \( D_A \) may be considered the chemical potential diffusion coefficient. Inserting the classical expression of chemical potential:

\[ \mu_A = \mu_{A0} + RT \ln \gamma_A N_A \]  \hspace{1cm} (6)

into Equation (5):

\[ J_A = -D_A \frac{RT}{C_A} \left( 1 + \frac{d \ln \gamma_A}{d \ln N_A} \right) \frac{dc_A}{dx} \]  \hspace{1cm} (7)

If the term \( \frac{RT}{C_A} \) is set equal to \( D_A^* \) "where the asterisk denotes a diffusivity determined by the tracer technique in an alloy of the same composition" as \( N_A \) (8), then Equation (4) becomes:

\[ D_{AB} = (N_A D_B + N_B D_A^*) \left( 1 + \frac{d \ln \gamma_A}{d \ln N_A} \right) \]  \hspace{1cm} (8)

for non-ideal solutions.

Sutherland and Einstein using hydrodynamics independently derived the equation:
\[ D^* = \frac{kT}{4\pi r\mu} \]  \hspace{1cm} (9)

where \( D^* \) is the self-diffusion coefficient, \( k \) is Boltzmann's constant, \( \mu \) is the viscosity and \( r \) is the radius of the diffusing particle. There is considerable controversy over the constant \( 4\pi \) as well as whether \( r \) is the ionic or atomic radius (17, 24).

Experimental data are usually compared with Equations (8) and (9). Vignes (29) has found empirically that experimental results which can't be satisfactorily represented by Equation (8) can be represented by the equation:

\[ D_{AB} = (D_A^*)^N_B (D_B^*)^N_A \left(1 + \frac{d \ln V_A}{d \ln N_A} \right). \]  \hspace{1cm} (10)

Although there isn't any relationship which will accurately describe all binary liquid diffusion data, these relations are useful in comparing experimental results.
Experimental Techniques

Diffusion coefficients of liquids have been measured by the capillary cell method, the diaphragm cell method, the constant flux method, and the electrolysis method. The capillary cell method has been used most extensively. Although a form of this method was used as early as 1850, Anderson and Saddington (1) brought the method into its present prominence by measuring the self-diffusion of tungstate ions in an aqueous solution with radioactive tungsten 187. The technique is well suited to studies using radioactive materials, since only a small quantity of diffusing material is required. Therefore, most of the diffusion data available on liquid metals concerns self-diffusion. However, several binary systems have been investigated including: Ag-Sn (16), Bi-Pb (22), Bi-Sn (22), Cd-U (13), Hg-Cd (20), Hg-I (2), Pb-Cd (22), Pb-Sb (22), and Pb-Sn (22).

In the capillary cell method a small capillary 0.5 to 3 mm in diameter and 3 to 5 cm long is filled with an alloy of known concentration and placed in a bath containing molten metal of a different composition. The metal is allowed to diffuse for a sufficient length of time, then the capillary is removed from the molten bath and cooled. Knowing the appropriate solutions to Fick's second law, the diffusion coefficient can be calculated either from the concentration as a function of distance in the solidified sample or from the bulk composition. The major error inherent in this approach seems to be in analyzing small quantities of materials. Another source of error is due to end effects resulting from inserting the capillary into the molten metal bath or removing it from the bath. End effects may also result from accumulation of diffusing material.
at the end of the capillary thus changing the effective length. Also, if the experiment is set up improperly with a metal of a high density above a metal of a low density, an unstable density gradient will be produced. This gradient can cause bulk flow in the capillary tube. Results obtained by Stover (26) on the capillary tube method showed that density mixing can cause the value measured for the diffusion coefficient to be as much as a factor of fifteen too high.

The diaphragm cell method has been used to measure diffusion coefficients of aqueous solutions, hydrocarbons, and the molten salt system AgNO$_3$-NaNO$_3$ (21). The diaphragm cell consists of two chambers separated by a horizontal porous plug which eliminates convective flow. In order to solve the diffusion equations it is necessary for each chamber to be homogeneous in composition. This is accomplished by stirring the chamber. Stover (26) found that with liquid metals large pores were necessary to insure complete filling of the diaphragm, but they were too large to prevent flow of metal from one chamber to another when the chambers were stirred. Butler (2) was able to successfully measure the diffusion coefficients for indium-mercury amalgams at room temperature with a diaphragm cell. The cell was much smaller than Stover's and the stirring was limited to that induced by convection currents.

Clack (3, 4, 5, 6, 7) has been the only investigator to make extensive use of the constant flux method. He determined the diffusion coefficients for a number of aqueous salt solutions at various concentrations. The concentration changes in the aqueous solutions were detected gravimetrically or optically. The optical approach had several advantages. Besides having
greater accuracy, the optical method required only one experiment to determine the diffusion coefficients over the concentration range at a specified temperature.

The apparatus consisted of a square column 1 cm wide and 5 cm long. The lower end of the column maintained contact with a bath of saturated salt solution and the upper end maintained contact with a slowly moving stream of pure water. The column was initially filled with the saturated salt solution. About 12 days were required to reach steady state after the experiment was initiated. The concentration along the column was then determined from the refractive index of the solution. The amount of material diffusion out of the column per second was determined from a chemical and stoichiometric analysis of the emerging water stream. By using this data, it was possible to determine the diffusion coefficients at various concentrations.

Mangelsdorf (20) used an electrolysis cell to measure the resistivity, electric mobility, and integral diffusion coefficient of cadmium amalgams. The cell was about 0.001 inches thick, 2 mm wide and 8 cm long with a reservoir connected to one end. Seven probe electrodes were placed at equal intervals along the length of the cell. To determine the resistivity, the cell was filled with alloys of known composition and the voltage drop was measured across the probes. By comparing this data with the data obtained for pure mercury, which has an accurately known resistivity, a calibration curve of resistivity versus concentration was obtained.

The electrolysis cell method for measuring diffusion coefficients is similar to the capillary tube method. The cell and reservoir were filled
with an alloy and a large electric current was induced through the metal in such a direction that it forced the metal solute ions into the reservoir leaving the pure solvent metal behind. When the cell contained only pure solvent the current was turned off and the solute was allowed to diffuse back into the cell. Periodically, the resistivity along the chamber was determined by using a small current. From the data obtained on the change in concentration along the cell as a function of time, it was possible to determine the integral diffusion coefficients.
THEORY

Mathematical Treatment

The mathematical model for the constant flux method applied to liquid metal diffusion was derived by considering the diffusion of bismuth into tin in a capillary tube with a reservoir of bismuth attached to the bottom and a reservoir of tin attached to the top. The reservoirs were large enough so that their concentrations were constant during the entire experiment. The equation for the diffusion of bismuth from the lower reservoir to the upper reservoir may be described by Fick's first law for unidirectional mass transfer as:

\[ J_{Bi} = -D(C) \frac{dC}{dx} \frac{\text{moles}}{\text{cm}^2 \text{sec}} \]  (11)

where \( J_{Bi} \) is the mass flux of bismuth, \( D(C) \) is the diffusion coefficient as a function of concentration, and \( C \) is the concentration of bismuth in moles/cm\(^3\) at any position \( x \) centimeters along the tube. By taking a differential material balance around an elemental volume within the tube bounded by \( x \) and \( x + \Delta x \) Fick's second law,

\[ \frac{\partial}{\partial x} (D(C) \frac{dC}{dx}) = \frac{dC}{dt} \]  (12)

is obtained. In this model, diffusion was allowed to continue for a long enough period of time so that the diffusion process could be considered to be at steady state and \( \frac{dC}{dt} = 0 \). Using this condition it may be shown that the diffusion flux is constant by substituting Equation 11 into Equation 12 to obtain

\[ \frac{\partial}{\partial x} (-J_{Bi}) = 0 . \]  (13)

The functional relationship for \( D(C) \) was determined from \( dC/dx \) which was obtained from the concentration profile of the diffusion tube. The
experimental concentration profile was represented as a polynomial function of \( x \) such as
\[
C(x) = b_0 + b_1 x + b_2 x^2 + b_3 x^3. 
\] (14)

This equation was substituted into Equation (11) to obtain the diffusion coefficient
\[
D(C) = -\frac{\partial C}{\partial x} = \frac{-J_{Bi}}{b_1 + 2b_2 x + 3b_3 x^2}. 
\] (15)

The best statistical relationship for \( C(x) \) was found from multiple regression analysis. This method assumes that \( n \) observed data points can be represented by a polynomial of degree \( N \). The sum of squares of deviations:
\[
S = \sum_{i=1}^{n} (C_i - \hat{C}_i)^2 
\] (16)
is minimized by setting the partial derivatives of \( S \) with respect to the \( j \)th regression coefficients \( b_j \) equal to zero and solving the set of simultaneous equations for \( b_j \). The term \( C_i \) refers to the \( i \)th observed data point and the term \( \hat{C}_i \) refers to the concentration calculated from the equation. The best representation of \( C(x) \), which was used in the final result, is the one obtained when the mean square deviation:
\[
S_E^2 = \sum_{i=1}^{n} (C_i - \hat{C}_i)^2/(n - 1 - N) 
\] (17)
starts to become constant as \( N \) is increased.

The absolute value of the diffusion coefficient could not be calculated from Equation (15) since the mass flux \( J_{Bi} \) was not known. If the diffusion coefficient at one concentration could be determined, the absolute diffusion coefficient for the entire concentration range would be known. This can be
seen by rewriting Equation (15) as:
\[ D(C) = \frac{D_0}{1 + b_2' x + b_3' x^2} \]  
where \( D_0 \) is the diffusion coefficient at the concentration where \( b_2' x + b_3' x^2 = 0 \).

The capillary cell method was used to measure \( D_0 \). Since it is necessary to solve Equation (12), it must be assumed that \( D(C) \) is constant over the range of concentrations investigated. It is also necessary to impose the following initial condition and boundary conditions on the system: 1) initially the capillary was filled with a homogeneous alloy of composition \( C_0 \) at \( t = 0 \), 2) the composition at the open end of the tube was maintained at the reservoir concentration \( C_R \) and 3) that no diffusion occurred through the closed end of the tube.

This equation was solved by separation of variables and integrated to give the following equation for the average capillary composition:
\[ \frac{C_R - \bar{C}}{C_R - C_0} = 8 \sum_{n=0}^{\infty} \frac{1}{n^2} \exp \left[ \frac{-\left(2n + 1\right)\pi}{2L} \right]^2 \text{Dt.} \]  
The diffusion coefficients were calculated from the average composition.

Resistivity Measurements

The liquid metal concentration was determined from resistivity measurements. The resistivity \( \rho \) of a metal is obtained by passing a known current \( I \) through the metal and measuring potential drop. It is calculated from the equation
\[ \rho = \frac{V}{\rho} \left( \frac{A}{L} \right), \]  
where \( V \) is the potential drop across the metal, \( L \) is the length between
two electrodes measuring the potential drop, and $A$ is the cross sectional area of the metal between the electrodes. The factor $A/L$ can be accurately determined by measuring the voltage across a metal such as mercury with a known resistivity. The value of $I$ can also be accurately determined by measuring the potential drop $V_S$ across a standard resistance $R_S$.

Lieu (18) measured the resistivity of tin-bismuth in the composition range between zero and 100 (at.)% Bi and in the temperature range between 250°C and 500°C. From a least squares fit of the data Lieu found that at constant composition the resistivity was linear with temperature and could be calculated from

$$\rho = A + B T.$$  \hspace{1cm} (21)

These equations were used to calculate the resistivity values for concentrations between zero and 100 (at.)% Bi at 300°C, 340°C and 400°C. The concentration was then determined as a function of resistivity at constant temperature by the method of multiple regression analysis. The functions were found to be linear except at low concentrations of bismuth where a slight curve seemed to exist.

The equation calculated from linear regression analysis is:

$$\hat{x} = (-60.0144 + 1.21764(\rho \times 10^6)) \% Bi$$ \hspace{1cm} (22)

for the concentration interval between 21% and 60% bismuth at 300°C. The standard deviation $S_E$ was 0.272% Bi as compared to 0.137% Bi at 400°C. The 95% confidence interval for any point calculated from Equation (22) is:

$$C.I. = \hat{x} \pm t_{0.975(n-2)} S_E \left[ \frac{1}{n} + \frac{(\rho - \overline{\rho})^2}{\sum (\rho_i - \overline{\rho})^2} \right]^{1/2}$$ \hspace{1cm} (23)

where $t_{0.975(n-2)}$ is the Student's "t" distribution (23), $\rho_i$ is the resistivity at data point $i$, $n = 13$ which is the number of data points used.
to determine the equation, and \( \bar{\rho} = \frac{1}{n} \sum \rho_i \) which is the mean resistivity.

The confidence interval is maximum at \( \rho = 98.4 \times 10^{-6} \) ohm-cm or \( X = 60\% \) Bi and the value is:

\[
\text{C.I.} = X \pm 0.18\% \text{ Bi}.
\]

Therefore, given experimental resistivity data at 300°C, the absolute concentration may be calculated from Equation (22) to within \( \pm 0.18\% \) Bi, 95% of the time.

The resistivity equations were used to calculate the concentration profile for the diffusion tube in the constant flux method and the mean concentration in the capillary method. The concentration in the diffusion tube was obtained by measuring the resistivity between electrodes which were spaced at equal intervals along the tube.

If the resistivity were not a linear function of concentration, a correction would have to be made for the concentration profile when calculating the mean concentration from the mean resistivity. If \( \rho_{mo} \) is the mean observed resistivity which was used to calculate the mean observed concentration \( C_{mo} \), then the mean correct concentration \( C_{mc} \) is:

\[
C_{mc} = C_{mo} \left( \frac{C_{ml}}{C_{mo}} \right) = C_{mo} F
\]

(24)

where \( F \) is the correction factor and

\[
C_{mo} = b_0 + b_1 \rho_{mo} + b_2 \rho_{mo}^2
\]

(25)

\[
\bar{C}_{ml} = \frac{1}{L} \int_0^L \left( b_0 + b_1 \rho_x + b_2 \rho_x^2 \right) dx.
\]

(26)

The resistivity \( \rho_x \) at position \( x \) is calculated from the solution to Equation (25) which would have the approximate form:

\[
\rho_x = a_0 + a_1 C_x + a_2 C_x^2.
\]

(27)
The correction factor could be calculated by substituting the equation for the approximate concentration profile into Equation (27) and then integrating Equation (26) after Equation (27) had been substituted into it. Fortunately, the resistivity is nearly a linear function of composition over the entire concentration range (18).

**Electric Mobility**

The use of the resistivity method produces a side effect which will change the mass flux due to the electromigration of metallic ions. The metallic ions are produced when an electric field is applied to the metal. The electric field $E$ also produces a force on the ions which causes them to migrate. If $v_i$ is the velocity of component $i$ resulting from the electro-transport of the metallic ions, and $C_i$ is the molar concentration of component $i$, then the mass flux due to electrotransport may be described by:

$$J_i = C_i v_i$$  \hspace{1cm} (28)

Since the electric mobility $u_i$ of component $i$ is defined at constant temperature and composition as:

$$u_i = \frac{v_i}{E} C_i T$$  \hspace{1cm} (29)

then Equation (28) may be written as:

$$J_i = C_i E u_i$$  \hspace{1cm} (30)

Verhoeven (28) showed that for a binary system the total mass flux resulting from both the electrotransport flux and the diffusion flux is:

$$J_i = C_i u_i E - D_i \frac{dC_i}{dx}$$  \hspace{1cm} (31)

where $D_i$ is the intrinsic diffusion coefficient at a specific concentration. The mutual diffusion coefficient which was defined for a binary system by
Darken (8) as
\[ D = N_1 D_2 + N_2 D_1 \] (32)
is used along with Equation (31) to obtain
\[ J_1 N_2 - J_2 N_1 = \frac{C_1 C_2}{C_t} E U_{12} - D \frac{dC_1}{dx} \] (33)
where \( N_1 \) is the atomic fraction of component one, \( C_t \) is the total molar concentration, and \( U_{12} \) is the differential mobility which is defined by:
\[ U_{12} = u_1 - u_2 \] (34)
The values of \( U_{12} \) have been obtained experimentally for Sn-Bi from 1 (at.\%) to 95 (at.\%) Bi at several different temperatures by Verhoeven (28).

To reduce Equation (33) to a simpler form the relation between \( J_1 \) and \( J_2 \) must be determined. If the partial molar volumes are independent of concentration,
\[ J_1 \bar{V}_1 + J_2 \bar{V}_2 = 0. \] (35)
Substituting Equation (35) into Equation (32), the total mass flux of component one is
\[ J_1 = \bar{V}_2 C_1 U_{12} E - \bar{V}_2 C_t D \frac{dC_1}{dx} \] (36)
In designing the equipment, this equation was used to compare the magnitude of the electrotransport flux with that of the diffusion flux.
EQUIPMENT DESIGN AND OPERATION

The optimum dimensions and operating conditions for the diffusion tube were based upon the time required to reach steady state, the accuracy desired in the resistivity measurements, the temperature rise and the amount of electrotransport caused by the measuring current. Another factor based on the work of Lange et al. (15) indicates that if the tube is greater than 2 mm in diameter, external vibrations will affect the values of the diffusion coefficients. To eliminate any problems due to vibrations a 1.5 mm I.D. capillary tube was used.

Steady-State Approximation

The time required for the diffusion tube to reach steady state can be found from Fick's second law, Equation (12), in the form:

\[ \frac{\partial^2 N_Bi}{\partial x^2} = \frac{\partial N_Bi}{\partial t} \quad (37) \]

The solution to this equation is similar to that for the capillary tube method since it is also obtained by the method of separation of variables. The details of the solution are shown in the Appendix. The final result

\[ N_{Bi} = (1 - \frac{X}{L}) - \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{2}{n} \sin \left( \frac{mnx}{L} \right) \exp \left[ - \left( \frac{mn}{L} \right)^2 Dt \right] \cos \left( \frac{mn}{2} \right) \quad (38) \]

is shown in Figure 1 for \( D = 2 \times 10^{-5} \text{ cm}^2/\text{sec} \), \( L = 10 \text{ cm} \), and for \( t = 1/2, 2-1/2, 5 \text{ days} \).

As the length of the diffusion time is increased from five days, the percent error in assuming that steady state was reached is approximately
Figure 1. Theoretical concentration profile as a function of time in the diffusion tube.
\[-\frac{1}{n} \exp(-0.642t)\] 100\%. Therefore, after seven days this error is 0.2\% and after 10 days the error is 0.03\%.

The above derivation assumes the reservoirs are infinitely large so that their concentration remains constant. In reality the reservoirs were about 20 cc. When a steady-state concentration profile developed in the tube, the amount of material diffusing into these reservoirs was calculated from Fick's first law:

\[ J_{Bi} = -D \frac{\Delta C}{\Delta x} \]  

By assuming a linear concentration profile, a diffusion coefficient of \(4 \times 10^{-5} \text{ cm}^2/\text{sec.}\), and a two week period of steady-state diffusion it was calculated that the tin concentration in the bismuth reservoir increased by about 0.56 (at.)\% Sn and the bismuth in the tin reservoir increased by about 0.44 (at.)\% Bi. Therefore, the concentration change in a reservoir during a run is insignificant.

**Electrical Equipment**

The precision of the equipment used for resistivity measurements was about the same as Lieu's equipment (18), since his data was used for evaluating concentration from the resistivity. The percent error for any measurement was calculated by Lieu as the ratio of the standard deviation to the average of the measured value times 100\%. Errors in the resistivity measurements ranged from 0.002\% at 300\°C to 0.48\% at 500\°C. These were due to electrical measurements as well as composition changes resulting from oxidation and distillation of the metal and errors in weighing the metal.

A schematic drawing of the electrical equipment used for measuring
the resistivity is shown in Figure 2. The output current through the liquid metal was maintained at a constant amperage by a Kepco Voltage/Current Power Supply. The specifications indicate that the output current changes less than 0.01% due to line variations and by the same amount due to load fluctuations. A Hewlett Packard data acquisition system which contained a Sanborn 8875A wideband differential amplifier connected to a Hewlett Packard 3440A digital voltmeter was used to measure the potential drop across the metal. According to supplier's specifications, the nominal gain accuracy of the amplifier is 0.1% for any range between 1 and 1000 and the gain stability is 0.01%. When the amplifier is operating in a ±8°C ambient temperature the gain accuracy should not deviate more than ±0.05% over a 30 day period. However, the voltage drift referred to the input is ± 3 x 10^{-6} volts at constant ambient temperature for 30 days. The digital voltmeter has an accuracy of about ±0.05% of the reading.

The accuracy of the electrical equipment is limited by the drift voltage of the amplifier at low voltage drops across the metal. If an error of ± 3 x 10^{-6} volts is to produce an error less than 0.2% in the potential measurement between two electrodes 1 cm apart, it is necessary to have a voltage drop greater than 1.5 x 10^{-3} volts. By using the minimum resistivity which is that of tin at 300°C, the maximum current required to produce this voltage drop is:

\[
I = \frac{V}{\rho} \left(\frac{\pi r^2}{L}\right) = \frac{1.5 \times 10^{-3}}{5.0 \times 10^{-5}} \left[\pi(0.075)^2\right] = 0.530 \text{ amperes .}
\]
Figure 2. Schematic drawing of the electrical equipment.
This current will heat the metal to some extent. The heating effect could cause errors in the concentration measurements as well as convection currents in the diffusion tube thus interfering with the diffusion process. In the diffusion tube the maximum temperature rise occurs in pure bismuth at the 400°C temperature. If the main resistance to heat transfer is due to heat conduction through the glass capillary wall then

$$\Delta T = 0.184 \, I^2 \, ^\circ C$$  \hspace{1cm} (41)$$

where $\Delta T$ is the temperature difference between the inner and outer wall of the capillary. Details of the derivation of Equation (41) are shown in the Appendix. Equation (41) indicates that if a current of 0.5 amperes is used the heating effect will be negligible.

The last problem to check in regard to the concentration measurements was to determine the magnitude of the mass flux resulting from electrotransport $J_e$ compared to that of diffusion $J_d$. Equation (36) may be used for this type of comparison. If the mass flux is at steady state and the concentration profile through the tube is linear then

$$\frac{dC}{dx} = \frac{C_t}{L}$$

and

$$\frac{J_e}{J_d} = \frac{\frac{C_1}{L} \frac{C_2}{L} U_{12} E}{\frac{C_t}{L} \frac{C_t}{L}} = \frac{N_1 \frac{N_2}{L} U_{12} E L}{D}$$   \hspace{1cm} (42)$$

This ratio is largest at 300°C when $D = 2.0 \times 10^{-5}$ cm$^2$/sec., $E \, L = V_C = 1.5 \times 10^{-3}$ volts which is the potential drop across the entire length of the tube, $N_1 = N_2 = 0.5$, and $U_{12} = 1.0 \times 10^{-3}$ cm$^2$/volt-sec at $N_1 = 0.58$. Substituting these values into Equation 25, $J_e = 0.188 \, J_d$. Therefore,
at maximum the electrotransport flux is about 18.8% of the diffusion flux. By switching the current in the opposite direction after each 15 second measurement is completed, this error should cancel out. The procedure of measuring the potential drop across the metal for both current polarities has the added advantage of eliminating errors due to the thermocouple voltages which were generated in the electrical connections.

**Diffusion Tube**

A schematic drawing of the diffusion tube inside the stainless steel furnace is shown in Figure 3. The diffusion column itself was 10 cm long and the reservoirs were approximately 20 cm$^3$. The side arm attached to the upper tin reservoir was used to fill this reservoir and the upper part of the column with tin. The center arm was attached to a vacuum system which was used to evacuate the column in order to prevent oxidation of metal. The center arm could also be pressurized with an inert gas. By the combination of pressure and vacuum the movement of tin in the side arm was controlled.

The diffusion tube was constructed from a 1.5 mm I.D. precision bore capillary tube. To start construction, holes about 1.2 mm were drilled with a tungsten carbide drill bit at one centimeter intervals along the tube. Then the reservoirs along with the center outlet arms were attached. Tungsten electrodes which were cut from 20 mil tungsten wire were cleaned in a solution of KOH, oxidized slightly to insure a good glass to metal seal and coated with uranium glass. This was accomplished by shrinking a 30 mil I.D. thin wall capillary of uranium glass onto the tungsten wire.
Figure 3. Cutaway view of the diffusion tube inside the inner furnace.
A carbon rod about 25 cm long and 1.5 mm in diameter was inserted into the capillary tube. This was used to prevent warping the lumen when the electrodes were sealed into the tube. The tube assembly was supported by a graphite block which was placed on a hot plate and heated to 300°C. Then the electrodes were sealed into the tube and the tube was annealed. After annealing electrodes were sealed into the reservoirs and the side arm was attached to the upper reservoir. Then the tube was annealed again and leak tested.

The physical dimensions of the diffusion tube were accurately measured when the tube was ready for operation. The L/A values between the electrodes were measured by using mercury as a standard and then the tube was cleaned. The distances between the electrodes were measured with a sliding scale microscope which could be read to 0.0001 cm. Then the tube was placed in the stainless steel furnace, nickel leads were silver soldered to the tungsten electrodes, and the furnace was packed with boron nitride powder and sealed. The powder was used to protect the tube against vibrations. Boron nitride was chosen since it has a very low electrical conductivity and a high thermal conductivity.

Furnaces and Accessory Equipment

The heating mechanism for maintaining a constant temperature in the diffusion column and reservoirs consisted of an inner and outer furnace. Both furnaces were grounded to prevent stray voltages from interfering with the resistivity readings. The outer furnace was an ordinary resistance furnace 18" long and 18" outside diameter with a 6" center core. The outer furnace was controlled by a Bristol Controller. The
furnace was maintained at a temperature of approximately 10°C higher than the inner furnace.

The inner furnace shown in Figure 3 was made of stainless steel with American Standard AerOrod heating elements silver soldered to the lower part of the furnace. The furnace contained an inner wall of lead-bismuth eutectic. The lead-bismuth alloy was used as a heat transfer medium. Thermocouple wells were placed inside the alloy and thermocouples were seated inside the wells. Chromel-constantan thermocouples, which were calibrated to ± 1/2 °C, were placed at the top, center, and bottom of the inner furnace. Convection currents in the lead-bismuth caused the temperature at the top to be higher than the temperature at the bottom. The temperature gradient from the top to the bottom was reduced to about 1°C by the use of a powerstat regulating the temperature of the heating elements.

Pyrex Crucibles

When the diffusion tube and the furnaces were placed into position, a pyrex crucible containing bismuth was attached to the bottom outlet of the diffusion tube and another containing tin was attached to the upper side arm. The crucible shown in Figure 4 was designed to remove the gas which was entrained in the metal during casting. In operation the crucible was evacuated to about 0.01 microns and heated to the melting point of the metal. When the metal was to be transported to a reservoir, helium gas was bled into the crucible. This forced the metal up the glass tubing into the small chamber where the small gas bubbles in the metal coalesced. The larger bubbles stayed at the top of the
Figure 4. Pyrex Crucible
chamber while the metal was forced out through the bottom.

In order to give the glass diffusion tube system more flexibility so that cracks wouldn't develop during expansion and contraction, a flexible stainless steel tube was inserted between the pyrex crucible and the side arm of the diffusion tube. The flexible tube had the metal kovar of two glass to metal seals silver soldered to each end. Although tin will alloy with silver, the molten tin was in contact with the silver solder for less than one minute. The silver solder junction was inspected after a diffusion run and no observable wetting or corrosion of the surface occurred. Since tin doesn't alloy with iron to any appreciable extent at temperatures below 500°C, this was not a problem.

Capillary Cell

The capillary cell and the constant flux methods utilized the same electrical equipment, since the resistivity technique of concentration analysis was used in both methods. The outer furnace and the pyrex crucibles were also used for both systems. Instead of using the stainless steel furnace, the capillary cell was placed in a large graphite block to maintain a uniform temperature.

The probability of constructing a usable capillary cell is about five times higher than the probability of constructing a usable diffusion tube, since only two electrodes were placed in each capillary tube and nine electrodes were placed in each diffusion tube. Figure 5 is a schematic drawing of the capillary cell placed in the graphite block. A vacuum line, a liquid metal feed line, and a solid metal feed line were attached to the top of the cell. Two capillary tubes were used in the cell to
Figure 5. Capillary diffusion cell.
check the consistency of the results. The lengths of these capillaries were measured with the sliding scale microscope.

Temperature readings were taken from calibrated chromel-constantan thermocouples. A thermocouple was embedded in the graphite at the top of the cell and another at the bottom. A thermocouple was also placed at the top center of the cell.

The capillary tubes were calibrated for the resistivity measurements by using mercury as a resistivity standard. After standardization the cell was cleaned and the liquid metal feed inlet was attached to a pyrex crucible. The system was outgassed at 0.01 microns and 400°C for one day before filling the cell with a 25% bismuth alloy. When the filling process was completed the initial composition was measured. Then one mole of solid bismuth was added through the solid feed line. Helium was forced into the vacuum line and out the solid feed line to reduce oxidation during the filling process.

The metal was allowed to diffuse into the capillaries for about one week while the concentration was monitored at 8 to 12 hour intervals. At the end of the run, a combination of vacuum and pressure was used to replace the metal in the capillaries with the metal from the reservoir. The next run was started by changing the temperature, checking the reservoir concentration, and then adding more bismuth. The diffusion coefficients were calculated from values of the initial concentration, the reservoir concentration, and the monitored concentration along with the time since the beginning of the run.
RESULTS

The relative diffusion coefficients as a function of concentration were obtained from constant flux diffusion runs conducted at 300°C, 340°C, and 400°C. The diffusion experiment was started at 340°C with the concentration interface at the center of the tube. The tube was filled in this manner because, for a constant diffusion coefficient, steady state is reached in the minimum length of time. The experimental concentration profiles shown in Figure 6 appear similar to the theoretical concentration profiles for a constant diffusion coefficient shown in Figure 1.

Steady state was reached about ten days after the tube was filled and concentration readings were taken once a day for about one more week. Then the diffusion tube was cooled to 300°C and another diffusion experiment was started. At each new temperature an attempt was made to place the concentration interface in the center of the tube. This was accomplished by overheating or overcooling the metal since it expands or contracts in the reservoirs with temperature changes. After the steady-state readings at 300°C were obtained the tube was heated to 340°C to check the previous results and then it was heated to 400°C. The steady-state concentration readings at the various positions in the diffusion tube are presented in the Appendix. The concentration was assumed to be at the position exactly halfway between the two measuring electrodes. In calculating the concentration profile the concentration was corrected for the degree polynomial used. These results were used to calculate the diffusion data.

Diffusion coefficient isotherms were obtained from the least squares
Figure 6  Experimental concentration profile as a function of time in the diffusion tube.
analysis of the steady-state diffusion data. The relative diffusion coefficients were referred to the diffusion coefficient at 50% Bi. The diffusion coefficient results from five steady-state readings spaced at one day intervals were used at each temperature, except for 340°C where two sets of data were used. The steady-state data seemed to be adequately described by fourth degree polynomials both for concentration as a function of distance and the diffusion coefficient as a function of concentration. The standard deviations for the relative diffusion coefficients were 0.035, 0.029, and 0.011 for 300°C, 340°C and 400°C respectively.

Since activity coefficient data at 335°C are available for tin-bismuth alloys (30), these data were used to compare Equation (8) obtained by Darken to the 340°C experimental data. Thermodynamic consistency tests were performed on the activity coefficient data. The local thermodynamic consistency test (25) in which the Gibbs-Duhem equation was integrated at 10% concentration intervals over the entire concentration range showed that considerable error exists in the activity coefficient data in the range between 0% and 40% bismuth. The overall area defect of nearly 8% could be attributed almost entirely to data in this concentration range.

The term \( \ln \gamma_{Bi} \) was found to be adequately described as a function of \( N_{Bi} \) in terms of a third degree polynomial. This equation was used to calculate the term:

\[
\phi = (1 + N_{Bi}) \left( \frac{d \ln \gamma_{Bi}}{d N_{Bi}} \right)
\]

Equation (8) also includes the tracer diffusion coefficients for tin and
bismuth which are usually calculated from Equation (9). The viscosity at 340°C is 1.54 cp for tin and 1.53 cp for bismuth (27). The atomic radii were calculated from the atomic volumes to obtain the final result:

\[
\frac{D^*_\text{Sn}}{D^*_\text{Bi}} = \frac{r_{\text{Bi}} \mu_{\text{Bi}}}{r_{\text{Sn}} \mu_{\text{Sn}}} = \frac{(2.025 \times 10^{-8})(1.53)}{(1.890 \times 10^{-8})(1.54)} = 1.06
\]

The values obtained from Equations (8), (43) and (44) are shown in Figure 7 along with the relative experimental diffusion coefficients for 340°C. The curves indicate that if the ratio of the tracer diffusion coefficients in Equation (44) was increased by about 20%, the curves would almost coincide for concentrations up to 90% bismuth.

The combined results of the constant flux method and the capillary cell method are shown in Figure 8 for the temperatures of 300°C, 340°C and 400°C. The diffusion data obtained by Niwa, et al. (22) at 500°C are also shown for comparison purposes. All of the curves are concave and appear to become more linear at lower temperatures.

The absolute values of the diffusion coefficients were obtained from capillary cell data. The initial concentration and the starting time had considerable error because of the method of changing the reservoir concentration. As mentioned previously, the reservoir concentration was changed by adding solid bismuth. This caused turbulence in the reservoir near the capillary inlet and it caused temperature fluctuations. The initial composition was eliminated, and the starting-time error was reduced by dividing Equation (19) by \((C_R - \bar{C}_1)/C_R - \bar{C}_2\), where the time \(t_2\) is greater than 50 hours:

\[
\frac{C_R - \bar{C}_1}{C_R - \bar{C}_2} = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left(-\frac{(2n+1)^2}{4L^2} t_2\right)^2 \frac{D}{L^2} \quad (45)
\]
Figure 7. Comparison of 340°C experimental data with Darken's equation. (Activity coefficient data of Wagner (30) for 335°C).
Figure 8. Experimental results of the diffusion coefficient as a function of concentration.
The average values of the diffusion coefficients calculated from Equation (45) are shown in Table 1, along with the number of data points used in the calculations, the lengths of the capillaries, and the initial and reservoir concentrations. The average of the initial and reservoir concentrations was assumed to be the concentration for which the diffusion coefficient was determined. The ± value of the diffusion coefficient is the maximum difference between the mean and the high or low value of the diffusion coefficient.

Table 1. Capillary run data and diffusivities for tin and bismuth

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Capillary Length, cm</th>
<th>Number of Data Points</th>
<th>Bismuth Concentration atomic percent</th>
<th>$D \times 10^5$ cm²/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.8953</td>
<td>5</td>
<td>26.359 42.926 34.643</td>
<td>3.55 ± 0.01</td>
</tr>
<tr>
<td>average:</td>
<td>4.7477</td>
<td>5</td>
<td>25.673 42.514 34.095</td>
<td>3.96 ± 0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>34.369</td>
<td>3.75 ± 0.21</td>
</tr>
<tr>
<td>340</td>
<td>4.8953</td>
<td>7</td>
<td>42.926 55.574 49.250</td>
<td>2.97 ± 0.03</td>
</tr>
<tr>
<td>average:</td>
<td>4.7477</td>
<td>7</td>
<td>42.514 55.067 48.791</td>
<td>2.80 ± 0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>49.020</td>
<td>2.88 ± 0.09</td>
</tr>
<tr>
<td>300</td>
<td>4.8953</td>
<td>9</td>
<td>40.530 52.405 46.469</td>
<td>1.98 ± 0.06</td>
</tr>
<tr>
<td>average:</td>
<td>4.7477</td>
<td>9</td>
<td>41.440 52.613 47.028</td>
<td>1.87 ± 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>46.745</td>
<td>1.92 ± 0.06</td>
</tr>
</tbody>
</table>

* Defined as follows:

$X_o$ = initial bismuth concentration in the capillary

$X_R$ = bismuth concentration in the reservoir

The differences in capillary tube concentration readings were probably due to errors in calibration, voltage reading, and filling the capillaries (oxidation and air entrainment). The fact that the concentration errors
seemed to remain constant during a run, caused them to cancel in the calculations.

A plot of Equation (19) is shown in Figure 9, along with the 340°C experimental data obtained from each capillary. The curve, which serves as a good illustration of the precision of the results, was calculated by using the average value of the diffusion coefficient and the average of the lengths of the tubes. The largest deviation from the theoretical curve is about 3%. Since the 0.2% error expected in the voltage readings will produce about 0.2% error in the concentration readings, the error in \((C_R - \bar{C})/(C_R - C_o)\) is about 4% for \((X_R - X_o) = 10\%\) bismuth. This error was reduced by taking the average of 10-20 voltage readings at each concentration. The total error involved in the diffusion coefficient measurements can be found for time greater than 50 hours by writing Equation (19) as:

\[
D = - \frac{4L^2}{\pi^2 t} \ln \left( \frac{C_R - \bar{C}}{C_R - C_o} \right). \tag{46}
\]

The main sources of error are the length of the capillary which was accurate to within \(\pm 0.01\) cm, the concentration ratio, and the starting time. A 0.01 cm error in the length will produce an error of about 1% in the length squared term and a 4% error in the concentration ratio will produce about 4% error in the logarithm term. The starting time was adjusted with the use of Equation (45). This reduced the time error to less than 1%. Therefore, the errors involved in determining the diffusion coefficients are about 6%.
Figure 9. Capillary cell concentration ratio as a function of time.
SUMMARY AND CONCLUSIONS

The diffusion coefficients obtained in this project seem to be accurate to within ±10%. The results shown in Figure 7 are in good agreement with one another and with measurements performed by Niwa, et al. (22).

The constant flux method seems to be a reliable method to measure relative diffusion coefficients as a function of concentration. However, the problems involved in constructing a diffusion tube and starting a diffusion run are so great that other methods of measuring diffusion coefficients should be investigated. Other methods of constructing a diffusion tube should also be considered. The time required for the diffusion tube to reach steady state at new temperatures could be reduced by having some type of expansion mechanism in the lower reservoir. This would prevent the column of metal from moving in the diffusion tube when the temperature is changed.

The capillary cell method has the advantages of easily constructed equipment and fairly accurate data. The resistivity techniques eliminates problems of melting and solidifying the metal sample, chemically analyzing the results, and moving the capillary in and out of the reservoir. The major refinement that could be done on the equipment is to feed the bismuth at the reservoir temperature instead of adding it as a solid. The liquid feed should also be designed to reduce turbulence and air entrainment in the reservoir metal.

Future research should be conducted with the capillary cell method on other liquid metal systems. This includes making the resistivity
measurements if they are not available, as well as measuring diffusion coefficients as a function of temperature and composition.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>cross-sectional area through which diffusion occurs, cm$^2$</td>
</tr>
<tr>
<td>$C$</td>
<td>molar concentration, moles/cm$^3$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>initial concentration of the capillary tube, moles/cm$^3$</td>
</tr>
<tr>
<td>$C_R$</td>
<td>reservoir concentration, moles/cm$^3$</td>
</tr>
<tr>
<td>$C_t$</td>
<td>total concentration, moles/cm$^3$</td>
</tr>
<tr>
<td>$C_x$</td>
<td>concentration at any position in the capillary tube, moles/cm$^3$</td>
</tr>
<tr>
<td>$\bar{C}$</td>
<td>mean concentration of the capillary tube, moles/cm$^3$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity, cal./gm °C</td>
</tr>
<tr>
<td>$d$</td>
<td>density, gm/cm$^3$</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient, cm$^2$/sec</td>
</tr>
<tr>
<td>$D(C)$</td>
<td>diffusion coefficient as a function of concentration, cm$^2$/sec</td>
</tr>
<tr>
<td>$D_o$</td>
<td>diffusion coefficient at a specific concentration, cm$^2$/sec</td>
</tr>
<tr>
<td>$D_A$</td>
<td>diffusion coefficient of $A$ determined by the tracer technique in an alloy of $A$, cm$^2$/sec</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field strength, volts/cm</td>
</tr>
<tr>
<td>$F$</td>
<td>mean resistivity correction factor</td>
</tr>
<tr>
<td>$I$</td>
<td>current, amperes</td>
</tr>
<tr>
<td>$J_{Bi}$</td>
<td>mass flux of bismuth, moles/cm$^2$ sec</td>
</tr>
<tr>
<td>$J_d$</td>
<td>diffusion flux, moles/cm$^2$ sec</td>
</tr>
<tr>
<td>$J_e$</td>
<td>electrotransport flux, moles/cm$^2$ sec</td>
</tr>
<tr>
<td>$L$</td>
<td>length, cm</td>
</tr>
<tr>
<td>$m$</td>
<td>mass, grams</td>
</tr>
<tr>
<td>$M$</td>
<td>molecular weight, grams/gram atom</td>
</tr>
<tr>
<td>$n$</td>
<td>number of data points</td>
</tr>
</tbody>
</table>
N \quad \text{degree of a polynomial}

N_{Bi} \quad \text{atomic or mole fraction of bismuth}

r \quad \text{radius, cm}

R_s \quad \text{standard resistance, ohms}

S \quad \text{sum of squares of deviations}

S_E \quad \text{standard deviation}

S_E^2 \quad \text{mean square deviation or variance}

t \quad \text{time}

T \quad \text{temperature, °C}

u_i \quad \text{electric mobility of component i, cm}^2/\text{volt-sec}

U_{12} \quad \text{differential mobility between component 1 and 2, cm}^2/\text{volt-sec}

v_i \quad \text{velocity of component i, cm/sec}

V_C \quad \text{potential measured across the liquid metal, volts}

V_S \quad \text{potential drop across a standard resistance, volts}

\bar{V_i} \quad \text{partial molar volume of component i, cm}^3/\text{mole}

x \quad \text{distance, cm}

X \quad \text{atomic or mole percent}

\gamma \quad \text{activity coefficient}

\mu_A \quad \text{chemical potential of component A}

\mu \quad \text{viscosity}

\bar{\rho} \quad \text{mean resistivity, ohm-cm}

\rho \quad \text{resistivity, ohm-cm}
BIBLIOGRAPHY


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The author wishes to express his appreciation for the encouragement and suggestions given by Dr. F. O. Shuck during this investigation. Thanks are also extended to Dr. J. D. Verhoeven, Dr. F. D. Stevenson, and the other faculty members who have given help and suggestions concerning this project.

A special thanks is extended to the personnel of the Iowa State University Glass Shop for their patience and cooperation in the construction of the glass equipment.
APPENDIX

Steady-State Concentration Profile

The steady state concentration profile was derived from Fick's second law:

\[
D \frac{\partial^2 N}{\partial x^2} = \frac{\partial N}{\partial t} .
\]  (47)

Initially, one half of the diffusion tube was filled with a metal with composition \(N = 1\), the other of the tube was filled with metal of composition \(N = 0\), and the concentrations at the ends of the tube were kept constant during the diffusion process. These conditions are expressed mathematically as:

\[
N = 0 \quad x = L \quad t > 0 \]  (48)
\[
N = 1 \quad x = 0 \quad t > 0 \]  (49)
\[
N = 1 \quad 0 < x < L/2 \quad t = 0 \]  (50)
\[
N = 0 \quad L/2 < x < L \quad t = 0 \]  (51)

Equation (47) may be solved by the method of separation of variables. This method assumes the solution is in the form:

\[
N = X(x) \cdot T(t) = X \cdot T .
\]  (52)

Substituting this relation into Equation (47) and rearranging yields:

\[
\frac{1}{D} \frac{\partial T}{\partial t} = \frac{1}{X} \frac{\partial^2 X}{\partial x^2} .
\]  (53)

Since the left hand side of the equation remains constant as \(x\) varies and the right hand side of the equation remains constant as \(t\) varies, both sides must be equal to the same constant. Therefore, Equation (53) may be written as two total differential equations:
\[ \frac{1}{T} \frac{dT}{dt} = -\lambda^2 D \]  

(54)

\[ \frac{1}{X} \frac{d^2X}{dx^2} = -\lambda^2 \]  

(55)

If \( \lambda \neq 0 \), these equations have the solutions:

\[ T = \exp(-\lambda^2Dt) \]  

(56)

\[ X = E \sin \lambda x + G \cos \lambda x \]  

(57)

If \( \lambda = 0 \), these equations have the solutions:

\[ T = A' \]  

(58)

\[ T = A'' + Bx \]  

(59)

Combining these solutions the equation

\[ N = A + Bx + \exp(-\lambda^2Dt)[E \sin \lambda x + G \cos \lambda x] \]  

(60)

is obtained where \( A, B, E, G \) and \( \lambda \) are unknown constants. These constants are determined from the boundary conditions and are presented in Table 2 in the order in which they are most easily evaluated.

Table 2. Evaluation of unknown constants

<table>
<thead>
<tr>
<th>Boundary Condition</th>
<th>Value of Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N = 1 ) ( x = 0 ) ( t \to \infty )</td>
<td>( A = 1 )</td>
</tr>
<tr>
<td>( N = 0 ) ( x = L ) ( t \to \infty )</td>
<td>( B = -\frac{1}{L} )</td>
</tr>
<tr>
<td>( N = 1 ) ( x = 0 ) ( t &gt; 0 )</td>
<td>( G = 0 )</td>
</tr>
<tr>
<td>( N = 0 ) ( x = -L ) ( t &gt; 0 )</td>
<td>( \sin \lambda L = 0 )</td>
</tr>
</tbody>
</table>

\[ \lambda = \frac{n\pi}{L} \]

The resulting equation is:
\[ N = 1 - \frac{x}{L} + \sum_{n=1}^{\infty} E_n \exp\left[-\left(\frac{mn}{L}\right)^2 Dt\right] \sin \frac{mn}{L} x . \]  
(61)

It remains to determine \( E_n \) such that the initial conditions, Equations (50) and (51), are satisfied. Therefore \( E_n \) is determined from the equation:

\[ E_n = \frac{\int_0^L \left[N - (1 - \frac{x}{L})\sin \left(\frac{mn}{L} x\right)\right] dx \int \sin^2 \left(\frac{mn}{L} x\right) dx \int_0^\infty \frac{2}{mn} \cos \frac{mn}{2} \]  
(62)

The final equation expressing the concentration along the diffusion tube as a function of time is:

\[ N = (1 - \frac{x}{L}) - \frac{2}{n} \sum_{n=1}^{\infty} \frac{1}{n} \exp \left[-\left(\frac{mn}{L}\right)^2 Dt\right] \sin \frac{mn}{L} x \cos \frac{mn}{2} \]  
(63)

Capillary Temperature

The current passing through liquid metal in a capillary caused the temperature of the metal to increase. Assuming the main resistance to heat transfer from the metal is the capillary wall, then the heat generated is equal to the heat conducted to the outside of the tube:

\[ q = -k A \frac{dT}{dr} = I^2 R \]  
(64)

where \( k \) is the thermal conductivity of glass equal to 0.63 BTU/hr. ft.°F, \( A \) is the area perpendicular to heat transfer, \( T \) is the temperature, \( r \) is the radius of the tube, \( I \) is the current and \( R \) is the resistance.

Equation (64) was integrated from the inside of the capillary \( r_1 \) to the
outside $r_o$ to obtain:

$$\int_{r_i}^{r_o} dT = -\frac{R}{k} \int_{r_i}^{r_o} \frac{dr}{2\pi rL}$$

(65)

$$\Delta T = T_i - T_o = \frac{12R}{2\pi Lk} \ln \frac{r_o}{r_i}$$

(66)

Equation (66) was evaluated for the maximum resistance, which was calculated from the resistivity of pure bismuth, for $r_i = 0.075$ cm and $r_o = 0.35$ cm to obtain:

$$\Delta T = 0.184 \degree C$$

(67)

Steady-State Concentration Data

The steady-state concentration data at various positions in the diffusion tube are presented in Table 3. These were used to calculate the relative diffusion coefficients as a function of composition.
Table 3. Steady-state concentration data for tin and bismuth

<table>
<thead>
<tr>
<th>Positions, x</th>
<th>0.4908</th>
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