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GRADUATE COLLEGE

DIFFUSION PHENOMENA IN THE LIQUID CADMIUM-LEAD BINARY SYSTEM

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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DIFFUSION PHENOMENA IN THE LIQUID CADMIUM-LEAD BINARY SYSTEM



DISSERTATION COMMITTEE

ABSTRACT

The capillary reservoir technique with radioactive lead-210 and cadmium-l15m were used to determine the selfdiffusion coefficients of both cadmium and lead and the chemical diffusion coefficients in the liquid binary cadmiumlead system.

The self-diffusion coefficients of pure cadmium and pure lead were obtained and were compared with the theoretical predictions. Good to excellent agreement between the experimental and predicted values (Walls and Upthegrove) was obtained.

The self-diffusion coefficients of cadmium were measured in alloys containing 2.5, 9.13, 17.4, 31.00, 45.00, 69.00, and 97.00 weight percent cadmium by determining the amount of active cadmium which has diffused out of a small bore capillary into an infinite reservoir for a given time. The effect of temperature on the diffusivity was determined between 290-460°C. The activation energy Q, and frequency factor D_0 , were obtained and the maximum variation of these quantities was also investigated.

The self-diffusion coefficients of lead were measured in alloys containing 2.5, 9.13, 17.4, 31.00, 45.00,

69.00, and 97.00 weight percent cadmium by the same technique that was used for the cadmium self-diffusion measurements. The effect of temperature on the diffusivity of lead was determined between 290-480°C. The values of Q and D_o in the Arrhenius relation were also obtained for lead from selfdiffusivity data.

The chemical diffusion coefficients were measured in the cadmium-lead system. These measurements were made for 2.268, 11.09, 17.4, 31.00, 45.00, 67.02 and 96.00 weight percent cadmium in the alloys. These data were obtained in the temperature interval from 355.0 to 485.0°C. The diffusivities were assumed to be constant in small concentration intervals, and a solution to Fick's second law for constant diffusivity was used.

The self-diffusion coefficients obtained were used with Darken's equation to calculate chemical diffusion coefficients. The results were compared with experimentally determined values of the chemical diffusion coefficients and satisfactory agreement was not obtained. However, the similarity of the shape of these curves and the common minima support Darken's model. When the curve calculated from this model is compared to the values which would be predicted if no thermodynamic correction were included, it is seen that Darken's approach is a significant improvement over the uncorrected model for this system.

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DIFFUSION PHENOMENA IN THE LIQUID CADMIUM-LEAD BINARY SYSTEM

CHAPTER I

INTRODUCTION

The theory of diffusion in liquids, particularly liquid metals, is relatively undeveloped in contrast to that for the gaseous and solid states. Although the practical application of liquid metals as heat transfer media, specially in nuclear reactors, has become increasingly important, few liquid metal systems have been investigated. Experimental data of fundamental significance in this field are not readily obtained; this may explain but not justify the present lack of knowledge. What work has been completed is primarily restricted to liquid diffusion of pure metals; little work has been done in liquid metal diffusion of binary mixtures. Theoretical models correlating chemical and self-diffusion coefficients with thermodynamic behavior have been suggested for binary systems, but have not been extensively tested in liquid metal systems. Therefore, in an effort to add to the engineering knowledge of liquid metal systems and to increase the basic understanding of the diffusion process in liquids,

a study of diffusion in the binary liquid system, cadmiumlead, was undertaken.

The specific objective of this research was to test the applicability of Darken's proposed theoretical relationship between the self-diffusion coefficient and the chemical diffusion coefficient for binary liquid metals¹. It was therefore necessary to determine the self-diffusion coefficient and chemical diffusion coefficient for a binary system over a wide range of composition. The selection of the cadmium-lead binary was based upon the low melting point, simple phase behavior, and comparatively large variations in Darken's thermodynamic factor for this system. No diffusion data have been reported for this system, although two investigations have reported values for the self-diffusion coefficient of pure lead^{2,3}.

Mathematical Models for Diffusion Analysis

Diffusion is a process by which matter is transported from one part of a system to another as a result of random molecular motion. Numerous models, in addition to the Darken Theory, have been proposed to explain the diffusion phenomena in liquid solutions such as the liquid metals.

Fick's Laws

The theoretical work of Adolf Fick⁴, published in 1855, precedes any quantitative experimental work and is still regarded as the phenomenological basis of diffusion

theory. He stated that the flux of diffusing substances is proportional to the concentration gradient of these substances, and is in the direction opposite to the concentration gradient. The expression for the flux, J, takes the form

$$J = -D\left(\frac{\partial x}{\partial c}\right) \tag{1}$$

where D is the diffusion coefficient for the substance under consideration with units of square centimeters per second; c is the concentration of the diffusing substances and has the units of quantity of material per cubic centimeter of the solution; x is the distance measured in centimeters in the direction which diffusion occurs, and J is the flux of diffusing substances having units of quantity of material per unit area per second. Equation (1) is Fick's first law of diffusion. According to this equation the diffusion flux is proportional to the concentration gradient.

Fick's second law is derived from the first law by considering the rate of accumulation of the diffusing substance in a given volume element. Thus Fick's second law can be stated as:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[\left(D \ \frac{\partial c}{\partial x} \right) \right]. \tag{2}$$

Originally, D was considered independent of the concentration of the diffusing substance and the position coordinate

at a given temperature, thus,

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) . \tag{3}$$

Employing vector notation, equation (3) for the three-dimensional case is written as,

$$\frac{\partial c}{\partial t} = D \text{ (div grad } c^*). \tag{4}$$

The assumption that D is independent of concentration is a generalization, not generally valid, therefore,

$$\frac{\partial c}{\partial t} = \operatorname{div} (D \text{ grad } c').$$
 (5)

Fick's second law has been applied to a large number of experimental techniques for diffusivity measurements with suitable boundary and initial conditions. The solution of Fick's second law for the capillary reservoir method with appropriate boundary conditions leads to a series solution and is given in Appendix B. This series has been programed for an IBM 1620 and the tabulated values are available. This solution describes one-dimensional binary diffusion, and assumes the diffusivity is independent of concentration. Also the change in volume due to mixing is neglected. In the case of self-diffusion coefficient measurements where there are no chemical gradients, the diffusivity, D, is independent of the concentration gradient of tagged substances. Equation (3) also can be applied in the measurement of chemical diffusion coefficients in binary solutions, where small concentration intervals are used⁵. More analyses of Fick's first and second laws are given in references^{6,7,8}.

Boltzman-Matano Solution

In 1937 Rhines and Mehl⁹ reported extensive investigations of systems in which the diffusion coefficients depend strongly on concentration, and since then the work of Matano¹⁰ has been recognized. Boltzmann¹¹ has shown that the one-dimensional form of Fick's second law, equation (2) could be solved by substituting a single variable, $\lambda = x/t^{\frac{1}{2}}$ into the equation. Therefore the original partial differential equation is transformed to an ordinary differential equation as follows:

$$d\left(D\frac{\partial c}{\partial \lambda}\right) = -\frac{1}{2}\lambda dc . \qquad (6)$$

Integrating equation (6) from $c = c_0$ to c = c, where $\frac{dc}{d\lambda} = 0$, we arrive at the Matano diffusivity:

$$D = -\frac{\frac{1}{2} \int_{c_0}^{c} \lambda dc}{\frac{dc}{dc} d\lambda} .$$
 (7)

This equation is generally used in evaluation of D from a diffusion penetration curve for metallic solutions¹². By substituting for λ at a specific time, t, equation (7) can be transformed to:

$$D = -\frac{1}{2}t \frac{dx}{dc} \int_{c_0}^{c} xdc . \qquad (8)$$

This equation is discussed by $Matano^{10}$ and $Crank^{13}$ thoroughly, and the correct use of this equation requires that the distance, x, be measured from a plane, x = 0, chosen so that:

$$\int_{c \text{ min.}}^{c \text{ max.}} xdc = 0 .$$
 (9)

The choice of the origin or point from which the distance, x, is measured, was suggested by Matano and is known as $\underline{Matano\ interface}^{10}$. The diffusion coefficient, D, is commonly referred to as the chemical or inter-diffusion coefficient and is considered the same for both components of a binary system.

Darken's Theory of Binary Diffusion

Experimental evidence¹⁴ prior to the theoretical works of Darken¹ and Crank¹⁵ supports the idea that the atoms of different elements in a single phase solution respond in different ways when that phase is acted upon by a field. Thus, in a binary mixture the interaction which arises from concentration gradients cause the atoms of one component to move with a drift velocity different from the velocity of the other component.

Darken's phenomenological treatment of unidimensional

diffusion in a solid binary system is based on the supposition that the two components are diffusing at different rates. He suggested that we must make use of a coordinate system which will reflect not only the diffusion flow but also any mass flow which results from these differential rates. If, in an unidimensional system, 'y' is a distance axis whose origin is fixed relative to a marker, then in the vicinity of the marker all changes in composition as a function of 'y' are due to diffusion. The rate of flow of component one across the plane of the unit area perpendicular to 'y' is described in the following equation:

$$J_{1} = -D_{1} \left(\frac{\partial c_{1}}{\partial y} \right)$$
(10)

where c_1 is the concentration of component one. The above coordinate system is valid only in the vicinity of the marker considered, since at some distance away from the origin other markers move in this system and the rate of passage of component one is not due to diffusion only but in part due to flow with the markers. If we introduce another coordinate 'x' parallel to 'y' but free to move relative to 'y', the above equation becomes:

$$J_{1} = -D_{1}\left(\frac{\partial c_{1}}{\partial x}\right)$$
(11)

which is still the flow across a fixed plane relative to a marker. As the marker in the 'x' coordinate system moves throughout the sample with a velocity of 'v' relative to the

'x' axis, the additional flow of mass, c_1v , must be added to the diffusing flux, then

$$J_{1} = -\left[D_{1}\left(\frac{\partial c_{1}}{\partial x}\right) - c_{1}x\right].$$
(12)

The velocity 'v' is a function of position 'x' and time 't'. The rate of accumulation of component one in any unit of volume is given by

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \left(\frac{\partial c_1}{\partial x} \right) - c_1 v \right] .$$
 (13)

A corresponding equation holds for component two. After substituting these equations into $c = c_1 + c_2$ and integrating Darken found,

$$(D_{1}N_{2} + D_{2}N_{1}) = \frac{-\frac{1}{2} \int_{N_{1}}^{N_{1}} \lambda \, dN_{1}}{dN_{1}/d\lambda}$$
(14)

where $\lambda = x/t^{\frac{1}{2}}$, $N_1 = c_1/c$, and $N_2 = c_2/c$ (c is assumed constant).

The diffusivity, D, from the Matano equation is identical with the right hand side of equation (14). Thus he has shown that:

$$D = (D_1 N_2 + D_2 N_1)$$
(15)

where D_1 and D_2 are the intrinsic diffusivities of components 1 and 2. In equation (14) D_1 and D_2 cannot be evaluated unless the velocity of an inert marker is known.

Later, Darken¹⁶ related the diffusivity of a

particle to its mobility and thermodynamic activity in binary system. The development of this relation is based on his thermodynamical hypothesis which says that the negative of the chemical potential gradient constitutes the effective driving force for the diffusing atoms in binary solutions. This phenomena has been described by other investigators^{6,17} Therefore, the difand is held as a general principle. fusion velocity of an atom is proportional to this force or is equal to the product of $-\frac{1}{N}\left(\frac{\overline{d\mu_1}}{dx}\right)$ and the proportionality factor G_1 , where G_1 is the velocity of the atom per unit force or the mobility and μ_1 is the chemical potential of component 1. Hence the rate of diffusion of component 1 in gram atoms per unit time across a unit plane normal to the direction of the diffusion is the product of the diffusion velocity and concentration, or equal to:

 $-\frac{1}{N_{o}}\left(\frac{\overline{d\mu}_{1}}{dx}\right)G_{1}c_{1}$

where N_0 is Avogadro's number. By definition the rate of diffusion of component 1 is also equal to $-D_1\left(\frac{dc_1}{dx}\right)$. Equating these two expressions we get:

$$-D_{1}\left(\frac{dc_{1}}{dx}\right) = -\frac{1}{N_{0}}\left(\frac{\overline{d\mu}_{1}}{dx}\right) G_{1}c_{1} \qquad (16)$$

or

$$D_{1} = \left(\frac{\overline{d\mu}_{1}}{dc_{1}} \right) \left(\frac{G_{1}c_{1}}{N_{o}} \right) .$$
 (17)

If the gram atomic volume is assumed constant and $\overline{d\mu_1} = RT d \ln a_1$, then we arrive at the following equation:

$$D_{1} = kTG_{1} \left(\frac{d \ln a_{1}}{d \ln N_{1}} \right)$$
(18)

or, from the definition of activity coefficient, $Y_1 = \frac{a_1}{N_1}$;

$$D_{1} = kTG_{1} \left(1 + \frac{d \ln \gamma_{1}}{d \ln N_{1}} \right).$$
 (19)

Similarly, the diffusion mechanism of component 2 is shown by:

$$D_2 = kTG_2 \left(1 + \frac{d \ln \gamma_2}{d \ln N_2} \right)$$
 (20)

where ${}^{'}G_{1}{}^{'}$ and ${}^{'}G_{2}{}^{'}$ are the mobilities of components 1 and 2, 'k' is the Boltzmann constant, 'T' absolute temperature, ' $\gamma_{1}{}^{'}$ and ' $\gamma_{2}{}^{'}$ are the thermodynamic activity coefficients and N_{1} and N_{2} are the mcle fractions of components 1 and 2. Equations (19) and (20) are based on the assumption that the drift velocity of the diffusing atom is proportional to the chemical potential gradient. The mobility ' $G_{1}{}^{'}$ and ' $G_{2}{}^{'}$ are the proportionality constants, and are a function of composition and temperature for each species.

Substituting equations (19) and (20) into equation (15) and making use of the Gibbs-Duhem relationship,

$$N_1 \overline{d\mu}_1 + N_2 \overline{d\mu}_2 = 0$$
 (21)

$$\frac{d \ln \gamma_1}{d \ln N_1} = \frac{d \ln \gamma_2}{d \ln N_2}$$
(22)

we get an expression for the chemical diffusion coefficients D, in terms of G_1 , G_2 and $\frac{\partial \ln \gamma_1}{\partial \ln N_1}$,

$$D = (N_1 D_2 + N_2 D_1) = kT(N_1 G_2 + N_2 G_1)(1 + \frac{d \ln \gamma_1}{d \ln N_1}).$$
(23)

In order to evaluate equation (23), it is desirable to determine some experimentally measureable values for 'G'. In equation (19), when we are dealing with ideal solutions, the thermodynamic factor $(1 + \frac{\partial \ln \gamma_1}{\partial \ln N_1})$ is unity and then the equation will reduce to Einstein's equation

$$D_1 = kTG_1 . (24)$$

For the case of self-diffusion as measured by radioactive isotopes, equation (24) becomes

$$D_1^* = G_1^* kT$$
 (25)

Now, if we assume that the mobility, G_1 , of an atom under given conditions is independent of whether it is a stable or a radioactive isotope (that is $G_1^* = G_1$, and $G_2^* = G_2$) thus the relation becomes

$$D_1^* = G_1 kT$$
 (26)

Eliminating G_1 and G_2 in equation (23), Darken found that

$$D = (N_1 D_2^* + N_2 D_1^*)(1 + \frac{d \ln \gamma_1}{d \ln N_1})$$
 (27)

where the asterisks signify that radioactive isotopes are involved. There are two main assumptions which were considered by Darken in derivation of equation (27):

1. No volume change on mixing of components.

2. Equal partial molar volumes of components. Both of these assumptions are true only in ideal solutions. In the case of silver-gold alloys this assumption was found reasonable¹⁸. In some condensed systems these assumptions are valid within the experimental limits of the accuracy of determining diffusivities.

Other Theories

The possible variation of the chemical diffusion coefficient due to differences in the partial molar volumes of the diffusing substances and variations of these partial molar volumes with composition, were studied by Balluffi¹⁹. The following general relation was proposed

$$D = \frac{1}{2t} \left(\frac{\partial x}{\partial c_1} \right) \left\{ (1 - c_1) \left[\overline{v}_1 - \overline{v}_2 \right] \int_{c_1(-\infty)}^{c_1(x)} x dc_1 + \overline{v}_2 c_1 \int_{c_1(-\infty)}^{c_1(x)} \frac{\overline{v}_1 - \overline{v}_2}{\overline{v}_2} x dc_1 \right\}$$
(28)

where \overline{v}_1 and \overline{v}_2 are the partial molal volumes of components

1 and 2, c is concentration in moles per unit volume, D is the chemical diffusion coefficient, and t time duration of diffusion process. This equation may be solved graphically, and requires the measurement of partial molar volumes for various concentrations. However, equation (28) has not been applied to liquid binary diffusion and the comparison with Darken's equation could not be made.

A similar analysis to Darken's relationship between self-diffusion and chemical diffusion coefficients was made by Crank⁷. A complete analysis of Crank's theory is given in reference (8) and the final expression obtained is:

$$D^{\mathbf{V}} = c_{\mathbf{A}}^{\mathbf{V}} V_{\mathbf{A}} D_{\mathbf{B}} + c_{\mathbf{B}}^{\mathbf{V}} V_{\mathbf{B}} D_{\mathbf{A}} . \qquad (24)$$

The treatment is based on the supposition that the chemical diffusion is "the combined effect of mass flow and true diffusion resulting from the random walk of non-uniformly distributed molecules". D_A^V is the mutual diffusion coefficient defined by Crank in terms of rate of transfer of A atoms across a section fixed so that the net flow of volume through it is zero. Similarly, D_B^V is defined for B atoms. These two coefficients are equal if partial molar volumes of A and B species are constant. Consequently, only one diffusion coefficient is needed and is represented by D^V as shown in equation (24). D_A and D_B are called intrinsic diffusion (14). V_A and V_B are the partial gram volumes of components A and B. D_A and D_B are defined in terms of the rate of transfer

of A and B species across a section fixed so that the net mass flow through it is zero. If the molar volume varies with the composition, the coefficient, D^V , has no physical significance. In equation (24) $c_A^V V_A$ and $\hat{c}_B^V V_B$ are volume fractions of components A and B respectively, which differs from N₁ and N₂ in the equation (15) as derived by Darken. c_A^V and \hat{c}_B^V are in the unit of mass per unit volume of the solutions.

Recently, a new theoretical approach for the calculation of diffusion coefficients in the binary liquid system was proposed by Kamal and Canjar²⁰. The proposed equation is based on the results obtained by applying statistical mechanics to transport phenomena in dense media. By this method the distribution function describing the possibility of one molecular arrangement is determined and its variation with time is predicted. Diffusion, according to this model, is treated as a process controlled by random motion with very small steps. The application of statistical mechanics to the study of the gaseous state has proven to be successful for simple gases. The variables required for the calculations are the heat of vaporization of the solute and the free volume of a molecule obtained from a physical measurement such as the velocity of sound. The recommended equation for the calculation of binary diffusion coefficients at infinite dilution is:

 $D = 1.12021 \left[\left(\frac{RT}{\pi M} \right)^{\frac{1}{2}} \frac{V_{o}^{1/3}}{(V_{o}/V)^{2/3}} \times 10^{-8} \left\{ 1.6 \frac{V_{o}}{V} + \right\} \right]$

$$\frac{2.56v_o^2}{v} Ng^2(\sigma) \} \Big]_{\text{solvent}} \times \Big[\frac{RT}{24L - 15pv - 15RT} \Big]_{\text{solute}}.$$
(30)

The definition of the above symbols is included in Appendix A. The predicted values of diffusion coefficients from the proposed equation for fifty-six different dilute liquid systems gave an average deviation of about 13 percent from the experimental values. This equation was also applied to solid-liquid dilute systems and gave an absolute deviation of 13 percent.

Several theoretical models have been proposed by investigators to describe diffusion phenomena in liquid metals. The latest model, recently suggested by Walls and Upthegrove²¹, accurately predicts the self-diffusion behavior of pure metals. Walls and Upthegrove found that self-diffusion in pure liquid metals could be theoretically correlated to a constant geometrical parameter which is equal to the ratio of the effective radius of the diffusing particle to the interparticle spacing. The new theoretical model is represented by the equation:

$$D = \frac{kT\gamma}{2\pi hb(2b+1)} \left[\frac{V}{N_0}\right]^{2/3} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}}$$
(31)
where $\gamma = \frac{N_0 d^3}{V}$
 $k = Boltzmann's constant, 1.38 \times 10^{-16} erg/^{\circ} K$

V = molar volume

 ΔS^* = activation entropy for kinematic viscosity ΔH^* = activation energy for kinematic viscosity

- N_{O} = Avogadro's Number
 - h = Planck's Constant
 - $b = \frac{r}{d}$, atomic radius/interparticle spacing
 - d = interparticle spacing
 - T = absolute temperature.

The term 'b' is postulated to be a constant for a given class of liquids. Walls and Upthegrove also observed that this geometrical parameter for the solute in the amalgam systems relative to that of pure liquid metals is consistent with the deviations from ideal behavior shown by this amalgam. The proposed theoretical relation was applied to compare the experimental values obtained in this research with the values predicted by the equation. See Chapter III for a discussion of these results.

Review of Previous Work

The study of diffusion in molten metal is important, but because of experimental difficulties few reliable measurements have been made. Several studies which indicate the validity of Darken's relationship have been reported for solid binary solutions. Initially the experimental data obtained by Johnson²² were used by Darken¹⁸ to check his theoretical relationship between self and chemical diffusion coefficients. Using thermodynamic data of the silver-gold binary system, Darken found fairly good agreement between the calculated value of the diffusion coefficient from his theory and the observed value. A discrepancy of approximately 10 percent was observed, which was attributed to experimental error.

More complete results on the applicability of Darken's equation for the entire range of composition within a binary system were reported in 1957 by Reynolds, Averbach and Cohen²³. Self-diffusion rates of nickel and chemical diffusion coefficients as a function of compositions and temperatures were measured in solid gold-nickel alloys. The experimental data were combined with self-diffusion coefficients of gold determined by Kurtz²⁴, and the thermodynamic activity data of Seigle, Cohen, and Averbach²⁵ to test the validity of Darken's relationship. These experimental results clearly supported the validity of Darken's equation. From 80 to 100 atomic percent nickel the experimental values of the chemical diffusion coefficients were higher than those predicted by the equation. This was attributed to the uncertainty of the thermodynamic factor in the range where the peak of miscibility gap occurs.

In 1959, Hilliard, Averbach, and Cohen²⁶ presented the results of an experimental study of diffusion rates in aluminum-zinc alloys. Values of the self-diffusion coefficient of zinc and the chemical diffusion coefficient of the aluminum-zinc system were measured. Darken's equation was

assumed valid and an attempt was made to predict values for the self-diffusion coefficient of aluminum because of the lack of a suitable isotope for aluminum. The predicted values for self-diffusion coefficients of aluminum were considerably smaller than the experimental values for zinc.

Babb and co-workers^{27,28,29} have done extensive work in the field of diffusion phenomena of liquid solutions, and reached many conclusions which improved the understanding of the diffusion mechanism. Many binary systems were studied and numerous liquid data were obtained. Liquid mixtures of different thermodynamical behavior, ideal and non-ideal systems, were studied by this group and will be discussed below.

Simple organic liquid mixtures which behaved nearly ideally were studied by Caldwell and Babb²⁷, and chemical diffusion coefficients were obtained for these systems. As was expected, the diffusion data of nearly ideal systems such as benzene-carbon tetrachloride, chlorobenzene-bromobenzene, and chlorobenzene-toluene were approximately a linear function of mole fraction with an average deviation of less than one percent. This deviation increased with non-ideality and also with a decrease in temperature. They concluded that the average forces encountered by a given molecule depends only on the molar average of the forces characteristic of the two species. In addition, it was also found that the quantity $\frac{D\eta}{T}$ (where D is diffusivity, η is viscosity, and T is absolute temperature) was a linear function of mole fraction, which

makes possible the prediction of diffusion coefficients for different concentrations of any non-associated solution from those of infinite dilution. Furthermore it was found that the ratio of activation energy for diffusion to activation energy for viscosity, $\left(\begin{array}{c}Q\\Q\\\eta\end{array}\right)$, remains approximately constant at a value of 1.36 for nearly ideal systems.

Later, Johnson and Babb presented the experimental values of the self-diffusion coefficients to compare with chemical diffusion coefficients previously obtained 27. In the systems which behave nearly ideal, such as benzene-carbon tetrachloride and ethanol-methanol the self-diffusion rates were linear functions of mole fraction within a variation of ±10 percent. Chemical diffusion rates in these systems have shown a better linear relationship to molar concentrations than those of self-diffusion coefficients²⁷. Self diffusion and chemical diffusion coefficients measured in the benzenecarbon tetrachloride system agreed within 10 percent over the entire composition range. In the case of non-ideal systems, significant differences between chemical and selfdiffusion coefficients were observed. For systems such as benzene-methanol and benzene-ethanol the differences were as great as twofold or more over much of the concentration range. A larger deviation was also observed in selfdiffusion rates of methanol than the self-diffusion rates of benzene. From this it was concluded that the behavior of the methanol molecules were primarily responsible for the
large deviation of the chemical diffusion rates from linearity. It was noted that at low concentrations of the diffusing substance the self-diffusion and chemical diffusion rates were in agreement within 10 percent. This discrepancy was attributed to experimental error.

Finally, Hardt and co-workers²⁹, have studied the observed differences in self-diffusion and chemical diffusion rates of these simple organic liquid systems. The experimental values of self-diffusion coefficients of four binary liquid systems were applied to Darken's proposed theoretical equation to test the validity of this equation at 25°C. In the benzene-carbon tetrachloride system which behaves almost ideally, it was expected to obtain a non-linear diffusion curve as was predicted theoretically. But surprisingly, a linear curve, diffusion plotted as a function of molar concentration, was obtained experimentally while the values calculated from Darken's equation were non-linear. They concluded, based on their experimental observations, that Darken's theoretical relationship was not valid for simple liquid systems, especially for the non-ideal systems such as acetone-carbon tetrachloride and acetone-chloroform. The two above systems deviate positively and negatively respectively from Raoult's law. In general their calculated values of chemical diffusion rates agrees fairly well with experimental values in dilute solution. Babb and co-workers conclude that the relation between chemical and self-diffusion

coefficients is not as simple as visualized by previous investigators.

A correlation of diffusion processes in the liquid metal and non-metal liquids can be rationalized on the basis of the deviation of the solution from ideality. This was observed from the experimental work of Niwa and co-workers³⁰. Since the tin-bismuth system is nearly ideal, the chemical diffusion coefficient shows an almost linear change with molar concentration in agreement with the theoretical model which indicates that the diffusion flow is proportional to the gradient of chemical potential. The relation between diffusion coefficients and concentration in the lead-bismuth and lead-tin systems showed a maximum and minimum at the same concentrations where negative and positive deviations from Raoult's law were observed.

The validity of Darken's theoretical relationship was also studied in liquid metal diffusion by Schadler and Grace³² using mercury-zinc amalgam. Their final conclusion was that the Darken model is valid. However, a further analysis of the data shows that the chemical diffusion coefficients calculated by the equation:

$$D = (D_1^* N_2 + D_2^* N_1)$$
(32)

are in better agreement with experimental results than those predicted by Darken's equation. In other words the introduction of the thermodynamic factor did not improve the agreement. This discrepancy could be attributed to experimental

error rather than thermodynamic behavior of the system. However, one might expect this insensitivity to the thermodynamic correction because the dilute solutions of zinc amalgam would approach ideal behavior.

Schadler's³³ observed different values for chemical diffusion rates using different techniques viz., from the measurement of the amount of zinc isotope present and from the concentration of zinc in grams per cubic centimeter as determined from e.m.f. measurements. A comparison of the diffusion coefficients obtained from these two measurements show that the tracer technique resulted in an average of 8 percent larger values than did the e.m.f. concentration measurements. It was found, based on experimental data, that the volume changes due to change of composition associated with chemical diffusion in dilute zinc amalgam were negligible. This was proved by Wells, Batz and Mehl^{12,34} to be a valid assumption for concentration differences of one or two atomic percent only in the solid state.

Several investigators have presented experimental values for liquid metal self-diffusion coefficients of pure components³⁵. Of the two metals studied in these researches, self-diffusion in pure molten lead was first studied by Groh and Hevesy at Budapest². They used a 3mm. inside diameter Y-shaped glass tube, with the trunk of the Y-pointing upwards. The top was kept open and the two arms were sealed at the bottom. A 1.5 cm. long piece of active lead was

placed in one arm and a 4.5 cm. piece of inactive lead in the other. The glass was evacuated and both pieces of lead were melted, and then by proper tilting of the tube the inactive lead was poured on top of the active lead. After the diffusion progressed for the desired time, the specimen was allowed to solidify and was sliced into four pieces. The diffusion coefficients were measured on every piece and a value of 2.55 x 10^{-5} cm²/second was obtained at 343° C.

More recently Rothman and Hall³ also have investigated the self-diffusivity of lead in molten lead, using Radium-D as a tracer. An activation energy of diffusion of (4450 ± 546) cal/mole was obtained.

CHAPTER II

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The capillary reservoir technique³⁶ was selected for the measurement of chemical and self-diffusion coefficients. The experimental apparatus consisted essentially of the following items: constant temperature bath, capillaries, diffusion cell, capillary filling device, and radioactive counting system. The experimental equipment and procedure are described in the following sections.

Constant Temperature Bath

Two constant temperature baths were used for the measurement of diffusion data. A cylindrical steel vessel, eight inches in diameter and fifteen inches deep, surrounded by an insulated heating coil (furnace) was used for the bath. A sodium-potassium nitrate salt mixture was used as the heating medium. The bath was brought up to the approximate temperature by the furnace and a 250 watt control heater, connected to a Bayley proportional temperature controller, was utilized for the final control of the temperature. The temperature variation during any diffusion run was not over 0.1° C. A constant speed mixer was used to stir the salt to

insure a uniform temperature in the bath. Four calibrated chromel-alumel thermocouples of different lengths were placed at various positions in the salt bath to check for the possibility of temperature gradients. The temperature gradients in the salt bath were found to be negligible and, due to the high thermal conductivity of the liquid metals, the temperature gradients were smaller in the metal reservoir than in the salt bath.

The propeller blades of the stirrer were adjusted so that they would not mix the salt strongly and avoid possible vibration of the diffusion apparatus. The entire furnace was also mounted on four shock absorbers to eliminate the vibrations in the building. The vibrations in the reservoir were minimized by these precautions. One of the salt baths and its associated equipment is shown in Figure 1. A detailed schematic diagram of the salt bath is shown in Figure 2.

The temperature of the bath and reservoir were measured with a Leeds and Northrup Precision Potentiometer. Switches were provided so the temperature of the different positions in the salt bath and reservoir could be manually read on the potentiometer or could be recorded on a Micromax temperature recorder.

Diffusion Cell

The diffusion cells and associated parts were the same, except for slight modification, as the ones used by



Figure 1. Constant Temperature Baths and Associated Equipment



Figure 2. Schematic Diagram of Furnace and Diffusion Apparatus A - Salt B - Melt C - Capillary D - Insulation E - Gas Outlet F - Steel Vessel G - Rubber O-Rings H - Brass Flanges I - Graphite Crucible J - Capillary Holder K - Brass Container L - Glass Container M - Dresser Coupling N - Control Heater O - Wilson Seals P - Heating Wire Q - Gas Inlet and Vacuum Line R - (1-5) Chromel Alumel Thermocouple S - Temperature Sensor for Controller T - Mixer Rod Connected to Constant Speed Mixer U - Capillary Holder Drive Shaft Connected to Synchronous Motor

previous investigators³⁷ and are shown in Figures 3 and 4. A graphite crucible, 4 inches long and 40 mm $(1\frac{1}{2} \text{ inches})$ inside diameter, enclosed in a 60 mm $(2\frac{1}{4} \text{ inches})$ Pyrex tube cell about 18 inches long was used as a container for the melt. Graphite was used because of its satisfactory nature as a refractory material and the low solubility of carbon in molten cadmium-lead alloy^{38,39}. In this research the melted alloy in the graphite crucible is known as a reservoir. This reservoir was usually about 40 mm $(1\frac{1}{2} \text{ inches})$ in diameter and 2 to $2\frac{1}{2}$ inches deep. The Pyrex cell was closed at the bottom and fitted at the top (open end) with a 2 inch Dresser coupling. A brass flange was welded to the top of the **Dresser** coupling. The upper part of the diffusion assembly was bolted to this flange and closed with an o-ring seal.

The top assembly, as shown in Figure 3, consisted of two synchronous motors, a drive shaft, a temperature well, and an inlet and outlet for the inert gas. One of the synchronous motors was used for rotation of the capillaries in the reservoir during the diffusion run at a rate of one-half rpm. The other motor was used for the vertical positioning of the capillaries and the capillary holder. The capillary holder was lowered down into the reservoir for the run and raised after the desired diffusion time at a rate of approximately 0.4 inches per minute. During vertical positioning, the entire capillary drive assembly was moved up and down by a fixed screw connected to the vertical drive. A chromel-



Figure 3. Diffusion Cells





alumel thermocouple, enclosed in a Pyrex temperature well, was placed in the reservoir to determine the temperature of the diffusion medium. Two copper tubes were used as an inlet and outlet for hydrogen gas during the melting and diffusion processes. All tubes and the shaft entered the cell through seals that were air tight and vacuum proof. The lower part of the diffusion cell was placed in a 3 inch brass container. The container, as is shown in Figure 3, was cut out in some parts to allow for circulation of salt around the cell. A flange was welded to the upper part of the brass container to support the diffusion assembly through the top of the constant temperature bath and furnace.

Several capillary holders were made out of graphite crucibles and some of them are shown in Figure 4. The initial capillary holders were made out of Armco iron rod, which would not react with the molten alloy. This was found to be unsatisfactory because the liquid alloy adhered to the iron and made it difficult to remove the capillaries from the capillary holder and also to separate the pieces of the holder.

The capillary holders were constructed so they could hold three capillaries for each run. The holes in the holder were of different sizes so that different sized capillaries could be used. The capillaries were spaced at 120° in the holder. A 1/8 inch Armco rod was fitted to the center of the capillary holder and was coupled to the rotating shaft

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as shown in Figure 3. The diffusion cell was immersed in the salt bath so that the salt level was about 6 inches above the surface of the reservoir alloy in the graphite pot.

Capillaries

The capillaries used in this investigation were of varying diameters and lengths. They were made from precision bore Pyrex capillary tubing obtained from the Corning Glass Works Co., Corning, New York. Capillaries of approximately 2.5 cm in length were sealed at one end with an approximately flat bottom. The open throats of the capillaries were ground flat with 600 grit silicon carbide paper and were polished using 3/0 metallographic paper. The throats were polished until the surface appeared smooth under a 20 power microscope. The capillaries also were inspected to insure that the ground surface was normal to the axis. A11 the capillaries were cleaned and washed in a ultrasonic generator cleaning tank and oven dried. The inside length of the capillaries were measured by means of a depth gauge with a precision of about ± 0.0025 cm. Before and after the length measurement the surface was again checked for chips that occured during cleaning and handling. After the capillaries were filled with the materials, they were examined again. The nominal capillary diameters are given in the following table.

TABLE 1

Inside Diameter Millimeters	Outside Diameter Millimeters			
1.000 ± 0.025	2.97			
1.500 ± 0.025	3.20			
2.000 ± 0.025	4.11			

Capillary Filling Device

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The capillary filling device is shown in Figure 5, and consisted of a 30 mm $(1\frac{1}{4} \text{ inches})$ inside diameter graphite crucible 4 inches long, enclosed in a 47 mm (1 7/8 inches)Pyrex tube about 12 inches long. The glass tube was fitted at the top with a Dresser coupling and the upper part of the coupling was brazed to a flange. The top assembly was made of a $\frac{1}{4}$ inch thick brass plate which was cut round to fit the flange. The plate was bolted to the flange and was sealed with an 0-ring. Two copper tubes were mounted through the plate for the purpose of providing a vacuum and the flow of hydrogen to the system. The capillary holder shaft passed through a seal mounted on the top assembly. Two mechanical vacuum pumps were used to evacuate the capillary filling device and the diffusion cells.

The Radioisotope Counting System

The isotope counting system, as shown in Figure 6,



Figure 6. Radioisotope Counting Equipment



Figure 5. Capillary Filling Device

consisted of the following items: I - A Tracerlab Inc. Model RLI-4 Basic Pulse Height Analyzer. II - A Tracerlab Inc. Model P-20cw Scintillation Detector. III - A Nuclear Chicago Corporation Model 183-B Count-O-Matic Scaler.

The scintillation crystal assembly was enclosed in a large lead cylinder, as shown in Figure 6. This cylinder had a 6 inch outside diameter and 3 inch inside diameter and was 8 inches long. The outside surface of the lead cylinder was-covered with a coiled, $\frac{1}{\mu}$ inch copper tube. Cooling water was circulated through the tube to keep the scintillation detector at approximately a constant temperature. This constant temperature was within the limits prescribed by the manufacturer. The pulse height analyzer, and scaler were enclosed in a wooden box and a forced convection cooling system, with some control of air temperature was used to eliminate instrument operating variation due to temperature The power supply was connected to the instruments changes. through a constant voltage transformer.

Diffusion Procedure

Material and Preparation of Alloys

The purity of the cadmium and lead used in the experiments is given in Table 2. These high purity metals were obtained from the Consolidated Mining and Smelting Company of Canada, Limited. Radioactive lead was purchased as the nitrate in nitric acid solution from Atomic Energy of

Canada, Commercial Products Division. Radioactive cadmium was obtained as the nitrate in nitric acid solution from the Oak Ridge National Laboratory. The specifications for these radioactive tracers and their radiation energy spectrum are given in Appendix E.

PURITY AND MELTING POINT OF MATERIALS

يستحد مالغناهم بكم			المتجهين المترجي المشموري الشبيان الأرجيس المتقومين المتوجر والمحمد والمعادر والمحمد	
	Material	Purity Percent	Melting Point	
	Pb	99.999+	327.40	
	Cđ	99.999+	321.00	
				-

Before use, both inert lead and cadmium samples were cleaned to remove any oxide and dirt. To accomplish this they were washed first with a solution of approximately one volume of 20 percent hydrogen peroxide and two volumes of acetic acid, then rinsed with distilled water, and dried in a purified air atmosphere. All chemicals used were of ACS reagent grade. The alloys used as reservoir were prepared by weighing the lead and cadmium separately and melting the desired amount of each in the diffusion cell. The weights were accurate to \pm 0.01 weight percent. Before melting, the cell was evacuated, checked for leaks and repressurized with hydrogen. Hydrogen provided satisfactory protection of the metal melts, especially at temperatures of 350°C and higher. Practically, all metallic oxides decompose above this temperature in a hydrogen atmosphere to produce an oxide free melt. The hydrogen was passed over a Deoxo platinumized catalyst and was dried prior to use. The molten alloys, being continuously stirred, were allowed to remain under the hydrogen atmosphere for 18 to 24 hours to insure complete mixing.

The radioactive alloy was made in the same fashion as those prepared for inert alloys except that the radioactive metals were initially electrodeposited on inert metals to make a mixture of active and inert metal that was used to make the active alloys.

In the case of radioactive lead - 210 the plating was done from a lead fluoroborate electrolyte. The lead nitrate, in a nitric acid solution, was treated with sodium carbonate and the lead isotope was precipitated as lead carbonate as described by Gray⁴⁰. Fluoroboric acid was prepared by reacting boric acid with hydrofluoric acid; this was then added to lead carbonate and lead fluoroborate was formed and carbon dioxide evolved as gas. The lead - 210 nitrate was received with an activity of 2.5 millicuries per milligram. It was diluted to approximately one millicurie per gram with inert lead. This dilution permitted reasonable handling safety and exposure periods.

The radioactive lead solution was poured into a cylindrical inert lead crucible. This cylinder was about 20 mm (3/4 inches) inside diameter and 40 mm (1 1/2 inches)

long. It was used as the cathode of the cell and a lead anode was placed in the solution. A 6 volt D.C. potential was applied to the cell in order to plate the lead in the solution to the lead container. In the meantime, lead was dissolving from the lead anode into the solution to maintain a constant total lead concentration. Using this technique about 99 percent of the radioactive lead was removed from the solution. After the plating was finished, the cathode was washed with distilled water and dried; it was then melted under hydrogen in the capillary filling device. It was held at approximately 400°C for at least 12 hours to insure a uniform concentration of the active lead.

Special precautions were taken when radioactive materials were handled. The solutions left from the plating were concentrated by evaporation to facilitate disposal. Special boxes were made for plating and handling the radioactive materials. A pair of polyethylene gloves were worn during any kind of work in which active materials were involved.

The radioactive cadmium was prepared in the same fashion as the lead isotope except that sulfuric acid was used to make cadmium sulfate solution. This solution was used in the plating. Cadmium-115m was purchased in one millicurie batches (because of its short half-life) from the Oak Ridge National Laboratory. This solution was received with an activity of one millicurie per cubic

centimeter. Additional inert cadmium nitrate was introduced to the active solution to provide enough working volume. Therefore, the final gamma activity of cadmium-115m was very small. The cadmium isotope solution contained a high gamma activity of silver-110m which had to be removed from the solution. This removal is discussed in the Appendix E. The necessary amount of radioactive lead or cadmium was weighed and added to inert lead or cadmium; then this was melted to make an alloy with the desired composition.

Capillary Filling

After the capillaries were prepared, three of them were placed in a capillary holder and secured so they could not float to the surface of the alloy. The holder was then sealed in the capillary filling device. The system was evacuated, checked for leaks, and repressurized with hydrogen. Heat was supplied to the system and after the alloy had melted the hydrogen flow was stopped. The system was evacuated again and the capillaries were immersed into the liquid alloy until the open end of the capillaries was covered. The alloy was forced into the capillaries by repressurizing the system with hydrogen. After the capillaries were filled, the capillary holder was slowly raised out of the melt to the upper part of the system and cooled in hydrogen. The capillaries were inspected visually to make sure they were completely filled; if not, the procedure was repeated. The capillary filling device was pulled out of the small furnace

and allowed to cool. The system was evacuated to remove hydrogen and then was opened to the atmosphere. The capillary holder was then brought out of the system and separated from the capillaries. The capillaries were checked for voids and shrinkage to insure a good contact between the material in the capillaries and melt in the reservoir. The capillary filling process was continued until enough perfectly filled capillaries were obtained. An attempt was made to check the possibility of re-using the capillaries. Lead and its alloy with cadmium adhered to the Pyrex making it difficult to remove all of the alloy. Therefore, the inside of each of the capillaries was coated with a film of silicone oil before being filled with the lead alloy. Under those conditions the alloy was easily removed from the capillary. The method was not ultimately successful however, because after a few diffusion runs it was found that light hydrocarbons in the silicone oil evaporated at high temperatures and caused bubbles, thus pushing most of the materials out of the capillaries. Therefore, it was decided to use new capillaries The radioactive alloys were placed in the for every run. capillaries and inert alloys in the reservoir throughout this experimental program.

Chemical Diffusion Measurement

The capillary reservoir technique was used in the measurement of chemical diffusion. The concentrations were chosen so that density in the reservoir would be lower than

the density in the capillaries to eliminate natural convection due to density gradients. Thus, the concentration of lead was from 2 to 4 weight percent higher in the capillaries than in the reservoir. The average value of these concentrations was considered as the concentration in which diffusion was measured and in analyzing the data it was assumed that D_{chem} should be treated as a constant over this concentration range. In all the chemical diffusion measurements radioactive lead was used as the tracer.

After each capillary was filled with radioactive lead - 210 alloy and inspected carefully, it was counted to determine the initial activity. The initial and final activity level of each capillary, in the case of chemical diffusion, varied from 3100 to 160,000 counts per minute depending on the isotope and concentration of the lead in the alloy. Next, the capillaries were fastened in the capillary holder as shown in Figure 4. The capillary holder, fitted with capillaries, was coupled to the supporting shaft and this, in turn, was connected to the small rotating motor. The reservoir was placed in the glass cylinder and the top assembly was bolted to the diffusion cell. The cell was evacuated and hydrogen was allowed to pass through. These steps were done rapidly before the alloys in the reservoir and capillaries reached their melting point. The capillaries were kept above the reservoir surface for about an hour until the desired temperature was reached. After the temperature

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of the system levelled out, and the capillaries had reached thermal equilibrium with the reservoir, they were lowered into the reservoir at the rate of 0.4 inches per minute. As the top portion of the capillaries were submerged, the time for the diffusion process was started and recorded. The capillaries were lowered until the open ends were about one half inch under the surface of the reservoir. The vertical drive was stopped, and the rotational drive started at the speed of one-half revolution per minute. This was done to fulfill the boundary condition that the concentration of the lead-210 at the mouth of the capillary would be lowered to the reservoir concentration right after diffusion began (see Appendix B for discussion).

After the diffusion run had progressed for the desired length of time, usually from 6 to 12 hours, the capillaries were removed from the reservoir as follows. The rotational drive was stopped and the vertical drive was started to move the capillaries upward. The end of the diffusion run was the time at which the open end of the capillaries were above the surface of the reservoir. Usually, after the diffusion run was over, the capillaries were kept at the same temperature and in the presence of hydrogen for a few hours to eliminate the concentration gradient which developed within the capillaries during diffusion. This was found to be more practical than removing the capillaries rapidly and having to wait at least two weeks to get the

final reading. After the capillaries had reached the desired homogeneous condition the entire diffusion assembly was removed from the bath and allowed to cool down. All of these steps were done under hydrogen atmosphere to avoid oxidation. The cell was evacuated and repressurized with air after the alloys had solidified. The capillaries were removed from the capillary holder and the activity level of each capillary was measured and recorded as the final concentration.

Because of variations in the counting system and changes in the radioactivity due to decay, all count values had to be corrected. The corrections were made by measuring a standard of the same isotope before and after every diffusion run. The ratio of the readings for the initial and final count of the standard was used as a correction factor. A sample of these calculations and also the diffusion coefficient calculations are given in Appendix B. Before and after each counting measurement the background count on the counting system was measured and the average value was recorded. All the counting rates were reduced by the average background value. After a series of diffusion runs for each composition, a few samples of the reservoir were taken to measure the activity of the reservoir for these runs. The reservoir activity level for each capillary was calculated from the initial and final values. An averaging factor depending upon the time of each run and the number and size of capillaries was used.

The temperature of the reservoir was considered as the temperature at which diffusion took place. This temperature was measured by a chromel-alumel thermocouple, inserted into the reservoir, with a 32°F ice-bath as a cold junction. The e.m.f. generated was measured with a potentiometer.

Self Diffusion Measurement

For all the self diffusion measurements, the same procedures were followed as those in chemical diffusion measurement except that there was no difference in the chemical composition of the reservoir alloy and the capillary alloy. The reservoir alloy consisted of a solution of inactive pure lead and pure cadmium; the capillary alloy was a solution of inactive lead and inactive cadmium with appropriate additions of either lead-210 or cadmium-ll5m.

Considerable difficulty was encountered in the self diffusion measurements of cadmium and lead alloys of compositions of 2.5, 9.13 and 17.4 weight per cent cadmium. This unexpected difficulty did not occur during the measurements with a higher percentage of cadmium. The diameter of the first capillaries used for these experiments was 2.00 mm, which did not give reliable results. Therefore, smaller capillaries (1.00 mm diameter) were used but the self-diffusion coefficient was still higher than the expected range. Finally reasonable results were obtained by immersing the capillaries upside down in the reservoir. The operation was not successful for all capillaries because sometimes,

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especially at higher temperatures, the material flowed out of the capillaries into the reservoir. When this happened it was impossible to calculate the diffusion coefficient and the run had to be repeated.

The effects of capillary diameter in the case of self diffusion were studied by using three different capillary diameters. The experiment showed no significant change within the experimental errors.

The possible effect of capillary turning rate on the self diffusion coefficient was studied by Walls³⁷ and no significant effect was found. Therefore, the selection of the $\frac{1}{2}$ rpm drive mentioned earlier satisfied the assumed boundary conditions.

Because of vaporization problems, the measurement of self diffusion rates at a temperature higher than 410°C was very difficult. A few runs were made at higher temperatures but the results showed unreasonable scatter.

All of the data for each diffusion run were recorded on a data sheet as shown in Appendix B. A sample calculation for the evaluation of the diffusion coefficient is presented also.

CHAPTER III

EXPERIMENTAL RESULTS

The experimental results obtained for the liquid cadmium-lead binary system consisted of, a) self-diffusion coefficients of pure molten cadmium and lead, b) the selfdiffusion coefficient of cadmium (115m) in the molten cadmium-lead binary alloy, c) the self-diffusion coefficient of lead - 210 (RaD) in the molten cadmium-lead binary alloy, and d) chemical diffusion coefficients of cadmium-lead - 210 (RaD) in the molten cadmium-lead binary alloy.

Self-Diffusion

The experimental data for self-diffusion measurements of pure cadmium and pure lead are listed in Tables D-1, D-2 and D-6, D-7 respectively, Appendix D.

The self-diffusion coefficients of cadmium and lead were also determined as a function of the temperature and the composition. The selected compositions for these measurements were 2.5, 9.13, 17.4, 31.0, 45.0, 69.0, and 97.0 weight percent cadmium. The temperature range was 290 to 460° C. The rate of self-diffusion was measured by determining the change in activity of the capillaries that

occurred due to diffusion from the capillary of length, L, into an infinite reservoir.

The results of the self-diffusion measurements of cadmium and lead in molten cadmium-lead binary alloys are given in Appendix D, Tables D-3, D-8 and Tables D-4, D-9 respectively.

It was assumed that the diffusion coefficients can be expressed in the form:

$$D = D_{o} \exp\left[-(Q/RT)\right]$$
(33)

where the frequency factor, D_0 , and activation energy, Q, are effectively constant for a given composition. This equation was proved to be valid over the limited temperature range of this research. All correlations (self-diffusion and chemical diffusion coefficients) indicate the linearity of log D versus 1/T for the temperature range of the experiment. The activation energy and frequency factor were obtained from a linear fit, by the method of least squares, of the experimental values of the diffusion coefficients.

In figures 7 and 8, log D is plotted as a function of $1/T^{\circ}$ for the self-diffusion of pure cadmium and pure lead respectively. In both cases the Arrhenius equation D = $D_{O} \exp \left[-(Q/RT)\right]$, provides a reasonable correlation. The number beside each vertical line indicates the number of determinations made at that temperature. The vertical lines indicate the actual variation of experimental data at each



temperature, and the open circles are the average values of the diffusion coefficients.

The standard deviation of the self-diffusion coefficients of pure cadmium and pure lead are presented in Table F-1, Appendix F. The method of calculation is also shown in Appendix F. Average values of self-diffusion coefficients of pure cadmium and pure lead are presented in Table 3.

Log D versus 1/T is plotted for the self-diffusion coefficients of cadmium in Figures 9 through 14, and for the self-diffusion coefficients of lead in Figures 15 through 20 for various compositions. Average values of these coefficients are tabulated in Table 3.

¹ The standard deviation of the average and the standard deviation of the individual determinations for self-diffusivity of cadmium and lead in their molten alloys are given in Tables F-2 and F-3, Appendix F. A joint standard deviation of the self-diffusion coefficients for the various compositions are also given in Table F-5, Appendix F.



Figure 10. Temperature Dependence of Self-Diffusion Coefficient of Cadmium for 9.13 Weight percent Cadmium in the Liquid Cadmium-Lead Alloy



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in the Liquid Cadmium-Lead Alloy










TABLE 3

AVERAGE VALUES OF SELF-DIFFUSION COEFFICIENTS FOR LIQUID CADMIUM-LEAD BINARY SYSTEM, IN VARIOUS COMPOSITIONS, VERSUS TEMPERATURE

· · · · · · · · · · · · · · · · · · ·		••••••••••		· · · ·	•	· · · · · · · · · · · · · · · · · · ·
Temperatur	re	D x 10 ⁵ cm ² /sec	Ten	nperatur C	? e	D x 10 ⁵ cm ² /sec
· ·	CA	DMIUM SEI	F-DIFFU	JSION		
2.50%	Weight	Cadmium		9.13%	Weight	Cadmium
341.0 390.5 440.5		1.979 2.859 3.711		289.85 329.85 361.60 370.15 410.25		1.661 2.328 2.470 3.508 2.837
17.40%	Weight	Cadmium		31.00%	Weight	Cadmium
289.85 329.85 369.85 410.00		2.042 2.679 3.506 4.031		390.00 330.50 371.05 411.00		1.892 2.332 2.883 3.718
45.00%	Weight	Cadmium		69.00%	Weight	Cadmium
289.85 329.85 372.85 407.35		2.311 2.412 3.799 4.233		290.00 330.35 371.00 410.35		1.764 2.356 2.779 3.387
97.00%	Weight	Cadmium				<u>,</u>
432.00		3.423				· · · •
	100.00) percent	weight	Cadmiu	n	
357.35 360.80 361.85 399.05 400.00		2.541 2.687 2.684 3.007 2.966		439.45 440.15 490.15 491.85		3.622 3.335 4.029 4.137
	I	LEAD SELF.	-DIFFUS	ION		
2.5%	Weight (Cadmium		9.13%	Weight	.Cadmium

· · · · · · · · · · · · · · · · · · ·					
Temperatur °C	e	$D \ge 10^5$ cm ² /sec	Temperatur C	е	D x 10 ⁵ cm ² /sec
432.00		2.738	289.30 329.85 370.15 411.45		1.467 2.235 2.578 3.018
17.40%	Weight	Cadmium	31.00%	Weight	Cadmium
290.90 330.55 371.25 411.00		1.559 1.829 2.594 2.946	291.95 329.85 370.85 409.85 456.75		1.699 2.238 3.216 3.319 3.294
45.00%	Weight	Cadmium	69.00%	Weight	Cadmium
290.00 330.85 370.20 411.45 456.00		2.190 2.350 3.201 3.542 3.915	290.85 330.85 374.00 410.85 454.85		1.465 1.980 2.869 3.284 4.172
97.00%	Weight	Cadmium			
340.00 393.00 434.00		1.846 2.583 3.516			
	100,	.00 Percent	Weight Lead		
357.40 357.75 360.75 399.90		1.993 1.790 2.213 2.363	399.40 435.75 483.50		2.215 2.802 2.933

TABLE 3--continued

Chemical Diffusion

The rate of diffusion of lead - 210 in the presence of a chemical gradient was measured in the temperature range of 355 - 485°C. The selected compositions were 2.268, 11.09, 17.4, 31.0, 45.0, 67.02 and 96.0 weight percent cadmium. The radioactive lead was diffused from capillaries into an infinite reservoir. The concentrations of capillary and reservoir alloys are given in the following table.

TABLE 4

DIFFUSION COUPLES FOR CHEMICAL DIFFUSION

Weight	Percent Cad	lmium		Atomic	Percent (Cadmium
Reservoir	Capillary	Average		Reservoir	Capillar	y Average
2.500	2.037	2.268	· · · ·	4.513	3.6 91	4.102
13.050	9.130	11.090		21.670	15.626	18 .648
19.400	15.400	17.400		30.733	25.124	27.928
33.000	29.000	31.000		42. 952	47.587	45.269
46.000	44.000	45.000		59.156	61.093	60.124
70.000	64.040	67.020		76.665	81.136	78.900
97.000	95.000	96.000		98.356	97.224	97.790

The experimental data for the measurement of chemical diffusion coefficients of the cadmium-lead system are given in Table D-5 and D-10, Appendix D. The graphical presentation of the chemical diffusion coefficients is shown in Figures 21 through 27. The average values of these data are presented in Table 5. Table 6 gives the activation energy of diffusion and D_0 . The standard deviation of the average for the calculated diffusivity and also the standard deviation of the individual determination of the diffusivity are given in Table F-4, Appendix F. A joint standard deviation of the chemical diffusion coefficient for the various compositions are also given in Table F-5, Appendix F.





 $D = 4.515 \times 10^{-4} \exp(-4017/RT)$

ι.4 Τ^{-ι} (°K) × 10³ **I.6**

-5.0

1.2







Figure 27. Temperature Dependence of Chemical Diffusion for 67.02 Weight percent Cadmium in Liquid Cadmium-Lead Alloy

TABLE 5

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AVERAGE VALUES OF CHEMICAL DIFFUSION COEFFICIENTS FOR LIQUID CADMIUM-LEAD BINARY SYSTEM, IN VARIOUS COMPOSITIONS, VERSUS TEMPERATURE

•••••			· · · · · · · · · · · · · · · · · · ·
Temperature C	e Dx10 ⁵ cm ² /sec	Temperatur C	e Dx10 ⁵ cm ² /sec
2.268% 1	Weight Cadmium	11.09%	Weight Cadmium
340.00 390.10 436.00	2.119 2.700 3.243	359.90 360.40 360.70 398.60 440.70 482.60	1.846 2.077 1.994 2.173 2.964 2.855
17.40%	Weight Cadmium	31.00%	Weight Cadmium
357.75 400.75 439.40 480.30	1.889 2.147 2.691 3.149	359.60 401.50 438.25 480.40 483.85	1.891 2.108 2.247 2.889 3.200
45.00%	Weight Cadmium	67.02%	Weight Cadmium
359.00 400.00 439.00 483.85	1.669 2.109 2.663 2.734	360.80 359.00 400.05 441.85 481.50	1.769 1.772 2.516 2.602 2.816
96.00%	Weight Cadmium	<u>, , , , , , , , , , , , , , , , , , , </u>	
338.00 390.00 440.00	1.779 2.473 3.226		

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Activation Energy

The calculated values of the Arrhenius activation energy, Q, and frequency factor, D_0 , for pure cadmium and pure lead are given in Table 6 along with Q and D_0 of selfdiffusion and chemical diffusion for the cadmium-lead binary alloys. A statistical analysis of the least-squares variation in the activation energy of diffusion and the frequency factor is given in Appendix F.

The results presented in Table 6 are shown graphically in Figures 28, 29 and 30. The average value of the quantity determined is joined by a curve. The variation in Q and D_0 at ninety percent confidence limits is indicated by the vertical bars.



Figure 28. Activation Energy, Q, and Frequency Factor, D_o, for Cadmium Self-Diffusion for Various Compositions in Liquid Cadmium-Lead Alloys







Figure 30. Activation Energy, Q, and Frequency Factor, D_o, for Chemical Diffusion for Various Compositions in Liquid Cadmium-Lead Alloys

ACTIVATION ENERGY AND $\mathbf{D}_{\mathbf{O}}$ for self-diffusion and chemical

DIFFUSION FOR LIQUID CADMIUM-LEAD BINARY ALLOYS

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N _{Cd}	Self ^Q Cd	Self ^Q Pb	Chem. Q	Self D _o Cd	Self D _o Pb	Chem. D _o
Atomic Percent		Kcal/mo	le]	10 ⁴ cm ² /se	9C
0.00	_	3.117	-		2.369	-
4.102	-	-	3.903	-	_	5.184
4.513	5.596	-	-	19.400	-	-
15.626	5.290	3.808	-	18.530	4.923	-
18.650	-	-	3.375	-	-	2.918
27.970	4.549	4.214	4.017	11.910	6.573	4.515
45.300	4.281	3.513	3.958	8.428	4.214	4.228
60.130	4.357	3.090	3.857	10.477	3,353	3.725
78.900	. –	-	3.707	- /		° 3. 538
80.403	4.076	5.018	-	6.800	13.420	-
97.790	-	-	4.971	-	-	10.660
98.35 6	-	5.903	-	-	23.660	-
100.00	3.305	-		3.621	-	-

CHAPTER IV

DISCUSSION OF RESULTS

Sources of error and an analysis of experimental results followed by a comparison of the experimental results with theory are presented in the following paragraphs.

Sources of Error

The estimated errors in the measurement and calculation of the diffusion coefficient are attributed to the errors involved in the measurement of the following quantities: temperature, time, length of capillary, and concentrations. The quantities, T, t, L, and ψ were measured and calculated for each capillary, where ψ is the ratio of concentration in the capillary after and before the diffusion process. The error in the temperature, T, was small enough to be neglected. The error introduced by the measurement of time was also small and it was expected to be less than 0.4 percent. A noticeably higher error was introduced by the measurement of the length of the capillary and produced a maximum error of about 1.0 percent in the diffusivity.

The major error in the measurement and calculation of D is introduced by ψ . A small error in this parameter,

 ψ , produces a much higher error in the parameter, $\theta = \frac{Dt}{r^2}$, and consequently in D. In the solution of Fick's second law for diffusion in the capillary reservoir technique, the parameters ψ and θ are described and given in Appendix B. The numerical values for ψ and correspondingly for θ are tabulated in Table E-1 of Walls³⁷. Walls also has shown that for a \pm 1.0 percent error in ψ higher errors in θ are observed, depending upon the value of ψ . For a one percent error in ψ , the error in Θ is as small as one percent for small values of u and as large as eighteen percent for the large values of ψ . In this research a one percent expected error in the resulted in a maximum error of eight percent in Since θ is directly proportional to the diffusion coefθ. ficient, an error of the same magnitude was expected for the diffusion coefficient.

Thus, the maximum total error in a single determination of diffusivity is less than ten percent for a one percent error in ψ . The maximum error in ψ is expected to be more than one percent in this research, and therefore, the total maximum error in the diffusion coefficient was considered to vary between 15 to 20 percent. The average standard deviation of a single determination of diffusivity as calculated from the experimental data varies between 10 and 20 percent which is in agreement with the above considered error. The estimated error in D could be reduced by using a lower ratio of the concentrations or with longer diffusion times. The errors in c and c_0 , and consequently ψ , were due to imperfect reproduction of counting conditions and randomness of counting conditions. A correction factor was used for material lost from the capillary due to volume expansion. A certain amount of material also is believed to have been lost during lowering and rising the capillary in the reservoir. Before a diffusion run the capillaries were checked for shrinkage cavities, however, undetected small shrinkage cavities in the capillaries probably contributed to the error. Other factors, such as vibration in the building and apparatus, may have contributed to the experimental error to some extent.

Analysis of Experimental Results

A composite of experimental data obtained in this research is given in Figures 28, 29, and 30. Several interesting trends are apparent in the frequency factor and the activation energy behavior with composition.

Q and D_0 for cadmium self-diffusion decrease with increasing cadmium concentration, and Q and D_0 for lead selfdiffusion decrease with increasing concentration of lead in the cadmium lead solution. The dependence of activation energy for chemical diffusion on concentration seems to be very small except at the cadmium concentration of 97.79 atomic percent. The average value of the cadmium and lead activation energies has shown a maximum and minimum, respectively, at 60 atomic percent cadmium. This corresponds

to the maximum deviation of thermodynamic activity from ideal behavior. All conclusions relative to the observed deviations in the average values obtained must be evaluated in terms of the variations calculated at the ninety percent confidence limits.

Figures 9 through 27 show the experimental values of self and chemical diffusivities for the cadmium-lead system for various compositions. No experimental values for these systems have been published to the present time, therefore no comparison could be made.

Comparison of Diffusion Data with the Theory

The theory of diffusion in pure liquids described by Walls and Upthegrove²¹ emphasizes the relation between diffusivity and viscosity. The experimental values of the selfdiffusion coefficients for pure lead and pure cadmium are presented in Figures 31 and 32 respectively. The Walls and Upthegrove equation is presented graphically for comparison of lead self-diffusion, using viscosity and density data given in the <u>Liquid Metals Handbook</u>⁴¹. Figure 31 clearly shows the excellent agreement between values predicted from the theory and the experimental values.

Experimental data for lead self-diffusion obtained by other investigators^{2,3} were compared with those obtained in this work.

Groh and Hevesy³ obtained a value of 2.55 x 10^{-5} cm²/sec at 343°C. This value is higher than what was



Figure 31. Effect of Temperature on Liquid Lead Self-Diffusion Coefficient

Figure 32. Effect of Temperature on Liquid Cadmium Self-Diffusion Coefficient



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obtained in this research at corresponding temperatures. Possibly there was some mixing at the time the inactive lead was poured onto the active lead and higher values of the self-diffusion coefficient resulted.

Rothman and Hall³ also investigated the selfdiffusivity of lead in molten lead. The results obtained were scattered and also showed higher values than those obtained in this research. An activation energy of diffusion of (4450 \pm 546) cal/mole was obtained compared to the value of (3117 \pm 290) obtained in this investigation. These data are also shown in Figure 31.

The theoretical curve for the cadmium self-diffusion coefficients, Figure 32, does not agree with the experimental data as well as the curve for lead. A reason for this disagreement could be the uncertainty in the viscosity data of cadmium. The average of three sets of viscosity data was used to demonstrate the theoretical equation 41,42,43 . It is interesting to see that the slope of the theoretical curve is the same as that for the experimental curve.

In order to examine the validity of the Darken model it was necessary to evaluate the so called thermodynamic factor. Complete information, including a summary of thermodynamic activity, activity coefficients, and thermodynamic factors, for the cadmium-lead binary system is given in Appendix C. The thermodynamic factor was calculated from the activity data of Taylor⁴⁴ at 705°K. The chemical diffusivities calculated from Darken's equation, using experi-

mental values of self-diffusion coefficients, are given in Table 7 along with experimental data. These data are presented graphically in Figure 33 for comparison.

In Figure 33 the experimental values of the various diffusivities are plotted as a function of the atomic fraction of cadmium in the cadmium-lead system at 705°K. Ex~ perimental values of the cadmium self-diffusion coefficients are indicated by the small open triangles pointed upward and connected by a dashed line. The curve indicates the deviation of the self-diffusion coefficient of cadmium from linearity, and as was expected the deviation increases with increase in non-ideality. The experimental values of the self-diffusivities for lead are represented by the small triangle pointed downward and connected with a dotted-dashed The self-diffusion coefficient of lead also shows line. positive deviation from linearity, but the deviation is not as large as that for cadmium self-diffusivities.

The experimental values of the chemical diffusion coefficients show negative deviation from linearity. These values are indicated by closed circles and connected with a solid line. Calculated values of the diffusivity predicted from Darken's equation are indicated by open circles and also connected by a solid line. The values of the self-diffusivities of cadmium and lead were used to calculate the chemical diffusion coefficients. Darken's theoretical expression used in this calculation was

$$D = (D_{1}^{*}N_{2} + D_{2}^{*}N_{1})(1 + \frac{d \ln \gamma_{1}}{d \ln N_{1}}).$$
(27)

The observed values of the chemical diffusivity





Δ self-diffusion coefficient of Cadmium

v self-diffusion coefficient of lead

• chemical-diffusion coefficient (observed) • chemical-diffusion coefficient (calculated) • $D = (N_1 D_2^* + N_2 D_1^*)$ (calculated)

TABLE 7

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SELF-DIFFUSION, CHEMICAL-DIFFUSION COEFFICIENTS, AND THERMODYNAMIC FACTOR IN LIQUID CADMIUM-LEAD SYSTEM AT 705°K

::::::	 				· · · ·	
N _{Cd} Atomic Percent	$\frac{D_{Cd}^* \times 10^5}{\frac{cm^2}{sec}}$	$\frac{D_{Pb}^* \times 10^5}{\frac{cm^2}{sec}}$	D x 10^5 Cal. by Eq.(32) cm^2/sec	$1 + \frac{d \ln \gamma}{d \ln N}$	D x 10 ⁵ (cal.) cm ² /sec	$\begin{array}{c} D \times 10^5 \\ (obs) \\ cm^2/sec \end{array}$
0.000	-	2,556	_	1.000	-	_
4.102	-	-	-	-	-	3.197
4.513	3.554	2.738	3.517	0.900	3.165	-
15.626	4.248	3.259	4.093	0.680	2.804	-
18.650	-	-	-	-	-	2.518
27.970	4.632	3.253	4.246	0.500	2.123	2.566
45.300	4.164	3.432	3.832	0.343	1.314	2,507
60.130	4.674	3.828	4.165	0.297	1.237	2.374
78.900	-	-	-	-	-	2.509
80.403	3.705	3.735	3.729	0.410	1.529	-
97.790	-	-	-	-	-	3.066
98 .356	3.457	3.513	3.512	0.910	3.196	-
100,00	3.422	-	-	1.000	-	-

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agree fairly well with the calculated values obtained by Darken's equation at cadmium concentrations lower than 30 atomic percent. The deviation of calculated values in this range is as high as 18 percent and lies within the experimental error. But as the composition of cadmium is increased this deviation increases to as high as 48 percent, which is too high to be attributed to the experimental error.

The self-diffusion coefficients of lead and cadmium both depart from a simple linear relationship with composition. Both species exhibit an enhanced atomic mobility in the range of 60 atomic percent of cadmium. This behavior is in marked contrast to the observed chemical diffusion coefficients for this system which exhibit minima around 0.60 atomic fraction cadmium.

Although the agreement between the observed and calculated chemical diffusion coefficients is only fair, the similarity of the shape of these curves and the common minima support the validity of Darken's model. Indeed, when the curve calculated from this model is compared to the values which would be predicted if no thermodynamic correction were included, viz.,

$$D = N_{Pb} D_{Cd}^{*} + N_{Cd} D_{Pb}^{*}, \qquad (32)$$

it is seen that Darken's approach is a significant improvement over the uncorrected model for this system. Chemical diffusion coefficient data calculated by equation (32) are

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indicated by rectangles and connected with a dotted line, Figure 33.

The two major assumptions which were made in the derivation of Darken's theoretical relationship are not generally valid in the liquid state. The discrepancies contributed to the chemical diffusion coefficients due to the assumption of equal partial molar volumes of the components are not expected to be as great as those due to changes in volume on mixing. Another important factor which should be considered as a major influence on these discrepancies is the association of diffusing atoms. It is difficult to describe this mechanism since no quantitative results exist that relate the degree of association of diffusing atoms in a binary solution to the diffusion prenomena.

In the measurement of chemical diffusion the radioactive lead was used as the tracer. The exact amount of the radioactive lead was not known, but the ratio of active to inactive was estimated to be less than 10^{-7} . However, the amount of active material in the alloy was not significant enough to study the system in terms of the ternary system.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

The self-diffusion coefficients of pure cadmium and pure lead were obtained experimentally and compared with the theoretical values predicted by equation (31); good to excellent agreement between these values was observed. Both the self-diffusion coefficients of cadmium and lead, and the chemical diffusion coefficient for cadmium-lead alloys were determined for the complete range of composition. These data were measured at four different temperatures. Plots of log D versus 1/T were constructed to illustrate the validity of an Arrhenius type of equation for the temperature range covered.

The magnitude of the consistent error is usually a great problem in the experimental determination of diffusion coefficients in liquids. However, an average of 15 to 20 percent error was considered for the experimental values of diffusion coefficients obtained in this investigation.

Agreement was not obtained between the experimentally determined chemical diffusion coefficients and the values calculated from the Darken relationship. Such an agreement would not be expected because of the

restrictions involved in the Darken's model. However, it was observed that the Darken approach of utilizing a thermodynamic factor is a significant improvement. Darken's model predicts values for the chemical diffusion coefficients that are in better agreement with experimentally determined values than the other models.

It is hoped that the result of this experimental study of diffusion phenomena in binary liquid metals will aid the development of new models for binary systems.

The following recommended researches are believed to be valuable to the understanding of the diffusion phenomena in binary liquid metals system:

First, an experimental study is recommended for the measurement of the viscosity and density data in liquid systems, especially systems for which the diffusion data already exists. Then the theoretical equation suggested by Walls and Upthegrove²¹ could be thoroughly investigated for binary systems.

Second, a theoretical or experimental study which would establish the effect of atomic association on the diffusion phenomena in a binary solution is also recommended.

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APPENDIX A

NOMENCLATURE

NOMENCLATURE

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English Letters

	i	English Letters
a	=	thermodynamic activity
^a 3		proportionality constant in the diffusion equation
b	H	<pre>r/d, ratio of effective radius of diffusing particle to interparticle spacing</pre>
b	=	$\frac{Q}{2.303R}$, proportionality constant
С	E	concentration of diffusing substances at any point at any time
° _A ,c _B	2	concentration in unit of mass per unit volume of the solution
°f	=	final average concentration in capillary after diffusion
°f	=	final concentration, cpm, uncorrected for isotope decay and instrument variation
°o	=	initial concentration in capillary
c ¹	=	initial capillary concentration, cpm, uncorrected for volume expansion
D ₁ *,D ₂ *	-	self-diffusion coefficients for component 1 and 2, respectively, cm^2/sec
D _A ,D _B	=	intrinsic diffusion coefficients for component A and B, respectively as defined by Crank
D ₁ ,D ₂	=	intrinsic diffusivities of components 1 and 2, cm ² /sec
D	1 22	chemical diffusion coefficient, cm ² /sec
Do	=	frequency factor, cm ² /sec

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D ^V	= `	mutual diffusion coefficient defined by Crank, cm ² /sec
F	=	correction factor for isotope decay and instru- ment variation
G	-	correction factor for volume expansion of material between capillary filling temperature and diffu- sion temperature
G ₁ ,G ₂	=	mobilities of components 1 and 2, respectively
g(2)(o)	=	pair correlation function
h	=	Planck's constant, 6.62 x 10 ⁻²⁷ erg-sec/molecule
∆H*	=	activation energy for viscosity, cal/mole
J	=	flux of diffusion substances
k	8	Boltzman's constant, 1.38 x 10 ⁻¹⁶ erg/°K
L	=	inside length of capillary, cm
Li	=	latent heat of vaporization
М	=	molecular weight
m	2	number of determinations for each composition
n	= 1	number of determinations for each temperature
N ₁ ,N ₂	=	atomic fractions of components 1 and 2 respectively
No		Avogadro's number, 6.02 x 10 ²³ atoms/gram molec- ular weight
Р	H	pressure, psia
Q .	=	activation energy of diffusion, Arrhenius' equation
R	=	gas constant, 1.987 cal/mole-°K
r	=	radius of the diffusing atom
∆S*	=	activation entropy for viscosity, cal/mole- $^{\circ}$ K
T	=	absolute temperature, °K
t	=	time duration of diffusion

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V	=	molar volume, cm/mole
v		velocity of markers relative to x-axis
v	=	total volume per molecule
۷ _{.0}	=	occupied volume per molecule
v	=	partial molar volume
х	=	distance, in centimeters
		Greek Letters
β	=	x/L
σ	=	molecular diameter
γ	=	configurational constant dependent on the geometry of the liquid structure, determined by average num- ber of nearest neighbors surrounding the atom
γ	=	activity coefficient, a/N
θ	=	Dt/L ²
η	Ħ	viscosity, centipoise
λ	=	$x/t^{\frac{1}{2}}$, variable
δ	=	standard deviation
δ	÷	standard deviation of the average
δJ	=	joint standard deviation
ξ		c/c _o
ψ	H	$(c_{f} - c_{r})/(c_{o} - c_{r})$
		Abbreviations
Ave	e. Ref	. Cnts. Rate = average reference count rate from initial and final reference count rates
в.	G. Co	unt = background radiation level determination
cpn	n	= count per minute

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Dia	= inside diameter of capillary, mm
emf	= electromotive force
Ref. Cnt.	= number of reference counts taken
Ref. Cnts. time	<pre>= time required to count 128,000 reference counts</pre>
RPM	<pre>= revolutions per minute, capillary turning rate</pre>
Temp.	= temperature

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APPENDIX B

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SOLUTION OF FICK'S LAW DIFFUSION EQUATION FOR CAPILLARY RESERVOIR DIFFUSION TECHNIQUE, SAMPLE DATA SHEET AND SAMPLE

CALCULATIONS

SOLUTION OF FICK'S LAW DIFFUSION EQUATION FOR CAPILLARY RESERVOIR DIFFUSION TECHNIQUE

The method used for measuring the diffusivities in molten alloys is usually the unsteady state method based on Fick's second law. For linear diffusion, this is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}x} \left(D \frac{\mathrm{d}c}{\mathrm{d}x} \right) \tag{B-1}$$

or if D is assumed constant, then

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$
(B-2)

where D is the diffusion coefficient for either selfdiffusion or chemical diffusion. For appropriate conditions the equation (B-1) or (B-2) may be solved in the form of C as a function of D, t, and x, where t is the diffusion time and x is the distance from the reference. Several authors 45,46,47 have described the solution of equation (B-2) for one dimensional binary diffusion. They assumed that the diffusion coefficient is independent of concentration and also neglected the change of volume due to mixing. The mathematical analysis for diffusion in the capillary reservoir technique was carried out by separation of variables³⁷. It was assumed that the diffusion occurs at constant temperature and only in the direction of the longitudinal axis of the capillary. Equation (B-2) may be transformed by letting:

$$\xi = \frac{c}{c_0}$$
 where c is the concentration of the diffusion
particles at any point and c_0 is the initial con-
centration in the capillary.

 $\beta = \frac{x}{L}$ where x is the distance from the open end of the capillary and L is the inside capillary length. $\theta = \frac{Dt}{L^2}$ where D is diffusion coefficient and t is the time of diffusion.

By substituting these dimensionless variables in the equation we will get:

$$\frac{d\xi}{d\theta} = \frac{d^2\xi}{d\theta^2} \tag{B-3}$$

The initial and final boundary conditions are:

 $\xi = 1 \text{ at } 0 \le \beta \le 1 \text{ for } \theta = 0$ $\xi \text{ is finite for all } \beta \text{ for all } \theta$ $\frac{d\xi}{d\theta} = 0 \text{ at } \beta = 1 \text{ for all } \theta$ $\xi = k \text{ at } \beta \le \theta \text{ for all } \theta$

where k is defined as c_r/c_0 and c_r is the reservoir concentration and is assumed to be constant during every diffusion run. Then the solution of equation (B-3) is:

$$\xi = k + \frac{(1-k)4}{\pi} \sum_{0}^{\infty} \frac{1}{(2n+1)} e^{\frac{-(2n+1)^2 \pi^2 \theta}{4}} \sin\left(\frac{2n+1}{2}\right) \pi^{\beta} (B-4)$$

Since

$$c_{t} = \frac{1}{L} \int_{0}^{L} c dx \qquad (B-5)$$

the above series becomes:

$$\psi = \frac{8}{\pi^2} \sum_{0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-(2n+1)^2 \pi^2 \Theta}{4}}$$
(B-6)

where $\psi = \frac{c_f - c_r}{c_o - c_r}$ and c_r is an average of the concentration of the reservoir at initial and final diffusion times. c_f is the concentration in the capillary after diffusion has occurred for a period of time, t.

The tabulated values of ψ and Θ in the solution of Fick's equation for the capillary reservoir method are given in the literature³⁷. After the ratio ψ was obtained, the value of Θ was read from Table E-1. The diffusion coefficient was calculated as

$$D = \frac{\theta L^2}{t} .$$

A sample of these calculations is given below.

Sample Calculations

Diffusion Run No. 45, Capillary No. 1

The correction factor F, which is a correction for radioisotope decay and instrument variation was determined from reference counting data. The reference counting data were obtained by counting a standard sample before and after counting each sample, as is shown in the sample data sheet. After the background count was obtained, in this case 67 CPM, the average initial value of the reference count rate was obtained as follows:

$$= \frac{1}{2} \left[\frac{128000 \text{ counts}}{4.38 \text{ min.}} - 67 \text{ CPM} + \frac{128000 \text{ counts}}{4.405 \text{ min.}} - 67 \right]$$

= 29040.5 CPM

Similarly, the average final value of the reference count rate was found to be 28793.7. The background count was also subtracted from each capillary count. The ratio of these two reference counts was used as a correction factor, F, for each capillary.

 $\mathbf{F} = \frac{29040.5}{28793.7} = 1.00857$

and

$$= \frac{Fc' - c_{r}}{Gc_{0}' - c_{r}}$$

= $\frac{(1.00857 \times 7015.7) - 182.7}{(1.00 \times 10189.4) - 182.7}$
= 0.68885

From Walls³⁷ table E-1 the value of θ was found to be 0.07605 corresponding to the value of $\varphi = 0.68885$. The diffusion coefficient was calculated by the following equation:

$$D = \frac{\Theta L^2}{t} \frac{(0.07605)(2.58)^2}{25440}$$

= 1.99 x 10⁻⁵ cm²/sec.

G is the correction for the volume expansion of the alloy in the capillary between the capillary filling temperature and the diffusion temperature.

SAMPLE DATA SHEET

Chemical Diffusion

System <u>Cd-Pb</u>	Run No. 49	<u>5</u> I	Date 6/1/63
Temp <u>673.0° K</u> Ref Cnts <u>128,000</u>	Reservoir Alloy Cd(/ CPM-BG_18	Data I 46%)-Pb(54%) 32.7 I H	Diffusion Run Start 6/1/63-1138 End 6/1/63-1842 Elapsed 25440 sec
Capillary Data RPM 1/2 Dia 2.00 mm Counts 64000 Alloy Cd(44%)-Pb(54	BG Count Start <u>5/3</u> Counts <u>32</u> Time <u>477</u> 8) CPM <u>67.0</u>	(1) 1-2400 2000 99 00 0 0 0 0 0 0 0 0 0 0 0 0	BG Count (2) Start 6/17-1200 Counts 6400 Fime 94.2 CPM 67.9
Capillaries Number Length	1 2.580	2.573	32.705
Initial Counting Date-Hour Ref Cnt Time (1) CPM-BG Counting Time c', CPM-BG Ref.Cnt.Time (2) CPM-BG Ave Ref Cnt Rate	6/1-0948 4.39 29090.2 6.24 10189.4 4.405 28990.9 29040.5	$ \begin{array}{r} 6/1-1000 \\ 4.405 \\ \underline{28990.9} \\ \hline 6.28 \\ 10124.1 \\ \hline 4.43 \\ \underline{28826.9} \\ \underline{28908.9} \\ \end{array} $	6/1-1012 4.43 28826.9 5.84 10891.9 4.45 28697.0 28756.9
Final Counting Date-hour Ref.Cnt.Time (1) CPM-BG Counting Time c _f , CPM-BG Ref.Cnt.Time (2) CPM-BG Ave Ref Cnt Rate	$ \begin{array}{r} 6/17 - 1537 \\ 4.42 \\ 28891.2 \\ \overline{9.035} \\ 7015.7 \\ 4.45 \\ 28692.1 \\ 28793.7 \\ \end{array} $	6/17-1551 4.45 28696.1 9.205 6884.8 4.425 28858.6 28777.3	6/17-1605 4.425 28858.6 8.385 7564.8 4.43 28826.0 28842.3
Correction Factor, F	1.00857	1.00457	0,99703

APPENDIX C

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THERMODYNAMICS DATA ON MOLTEN

CADMIUM-LEAD BINARY SYSTEM

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THERMODYNAMIC DATA IN MOLTEN

CADMIUM-LEAD BINARY SYSTEM

Darken¹ has proposed the following equation for binary solutions.

$$D = (D_1 * N_2 + D_2 * N_1) (1 + \frac{d \ln \gamma_1}{d \ln N_1})$$
(C-1)

The second term in the right hand side of this equation is called the "thermodynamic factor". In order to check the validity of this equation it was necessary to determine this The thermodynamic activity is available from the factor. work of Taylor, and hence the thermodynamic factor, $(1 + \frac{d \ln \gamma}{d \ln N})$, can be calculated as shown in Table C-1 and Figure C-1. Because of the positive deviation from ideality in this alloy, the thermodynamic factor is less than unity for all composition and drops to a level of 0.29. This factor has a value of unity at $N_{Cd} = 0$ and $N_{Cd} = 1.0$ where N is the mole fraction of cadmium. The data given in Table C-1 is at a temperature of 705°K. The value of the thermodynamic factor was obtained from a plot of ln γ versus (1 - N)². The slope, $\frac{d \ln \gamma}{d[(1 - N)^2]}$, was measured graphically and from this slope the value of $(1 + \frac{d \ln \gamma}{d \ln N})$ was calculated for

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various compositions for both cadmium and lead. According to Gibbs-Duhem equation the thermodynamic factor should be the same whether determined from cadmium or lead activity data. Due to graphical differentiation and possible errors in activity measurements, the values did not agree exactly. Therefore the average value was used in the study of Darken's equation. The values of $\ln \gamma$ for cadmium and lead are shown graphically in Figure C-3.

TABLE C-1

THERMODYNAMIC DATA FOR MOLTEN

N _{Cđ}	acd	a _{Pb}	$1 + \frac{d \ln Y_{Cd}}{d \ln N_{Cd}}$	$1 + \frac{d \ln Y_{Pb}}{d \ln N_{Pb}}$
0	0	1.000	1.000	1.000
0.1	0.305	0.910	0.775	0.790
0.2	0.500	0.835	0.600	0.624
0.3	0.620	0.780	0.469	0.485
0.4	0.700	0.730	0.376	0.389
0.5	0.755	0.685	0 .3 11	0.324
0 .6	0.800	0.640	0.286	0.306
0.7	0.840	0.585	0.320	0.322
0.8	0.875	0.510	0.424	0.379
0.9	0.925	0.365	0.590	0.601
1.0	1.000	0	1.000	1.000

CADMIUM-LEAD BINARY SYSTEM

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The cadmium-lead phase diagram is shown in Figure $C-4^{48}$. Activities of cadmium and lead are also presented graphically in Figure C-2.



Figure C-1. Thermodynamic Factor for Chemical Diffusion at 705°K



Figure C-2. Activity of Cadmium and Lead in Cadmium-Lead Alloys at 705°K





Figure C-4. Liquidus Curve for Cadmium-Lead System

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APPENDIX D

SELF AND CHEMICAL DIFFUSION COEFFICIENTS AND DATA FOR THE LIQUID CADMIUM-LEAD ALLOYS

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SELF-DIFFUSION DATA VERSUS TEMPERATURE

FOR LIQUID CADMIUM

Run- Capillary	Temp.	Radioact	Radioactivity of Cadmium			
Number	° C	c _o cpm	с _f срт	c _r cpm	F	
11-1 -2 -3	399.05 399.05 399.05	37974 36385 35867	19 675 19100 18150	120.5 120.5 120.5	1.08786 1.08579 1.08188	
12-1 -2 -3	439.45 439.45 439.45	35776 35564 36177	17616 17272 18026	202.0 202.0 202.0	1.107 66 1.10876 1.10723	
13-1 -2 -3	490.15 490.15 490.15	35771 34216 34592	15815 15555 15 6 54	281.0 281.0 281.0	1.09456 1.09551 1.09457	
15-1 -2	400.00 400.00	33617 32488	18447 17017	421.0 421.0	1.13465 1.13228	
16-1 -2 -3	440.85 440.85 440.85	34496 34543 34214	1835 3 18151 19056	486.0 486.0 486.0	1.12858 1.12892 1.13000	
17-3	491.85	3131 9	13664	6 58.5	1.10255	
18-2	361. 85	29939	11472	700.0	1.61463	
20-1	357.35	2308 3	10806	800.0	1.26100	
22-1	360.80	17755	9118	500.0	1.15514	

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SELF-DIFFUSION DATA VERSUS TEMPERATURE FOR

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Run-	Temp.	Radioa	Radioactivity of Lead			
Number	°C	co cpm	cr cpm	cpm	F	
3-1	360.75	33708	21812	128.8	0.99800	
-2	360.75	33708	20915	128.8	0.99160	
-3	360.75	34436	218 6 9	128.8	0.99 33 0	
4-1	357.75	32755	19566	182.0	0.99210	
-2	357.75	32671	20221	182.0	0.99090	
-3	357.75	32504	20748	182.0	0.98832	
5-1	357.40	33708	21777	245.8	1.00450	
-2	357.40	33619	2105 6	245.8	1.00450	
-3	357.40	32095	20241	245.8	1.00540	
6-1	399.90	34812	1999 7	305.0	1.00170	
-3	399.90	33707	188 6 9	305.0	1.00227	
7-1	435.75	34717	22273	356.0	1.00628	
-2	435.75	34022	21520	356.0	1.00510	
-3	435.75	33 3 55	21741	356.0	1.00450	
8-1 -2a -2 -3	483.52 483.52 483.52 483.52 483.52	33311 33663 34343 34576	20252 20513 19299 20 613	397.0 397.0 397.0 397.0	1.00500 1.00340 1.00450 1.00280	
9-1 -2 -3 -4 -5 -6	399.40 399.40 399.40 399.40 399.40 399.40 399.40	33619 33442 33009 34529 35148 34251	21269 21630 21023 22119 22978 21594	470.0 470.0 470.0 470.0 470.0 470.0	0.99542 0.99884 0.99769 0.99598 0.99655 0.99599	

SELF-DIFFUSION DATA FOR CADMIUM VERSUS TEMPERATURE FOR VARIOUS COMPOSITION IN LIQUID CADMIUM-LEAD ALLOYS

Run- Canillary	Temp.	Radioac	tivity of (Cadmium	Corr. Factor
Number	° C	с _о срт	c _f cpm	c _r cpm	F
2.50 ± 0.01	. Weight per	cent Cadmi	um (4.513 /	Atomic pe	rcent)
123-1	341.00	5413.4	3874.7	32.4	1.01456
-2	341.00	5787.1	3826.2	32.4	1.02290
-3	341.00	5792.1	4100.4	32.4	1.03030
124-1	390.50	5325.5	3390.3	44.8	0.99192
-2	390.50	5517.8	3437.7	44.8	0.99280
-3	390.50	5822.0	3617.1	44.8	0.99545
125-1	440.50	5676.7	3298.0	59.5	1.00893
-2	440.50	5778.4	3435.1	59.5	1.00805
-3	440.50	5855.7	3455.0	59.5	1.03119
9.13 ± 0.01	L Weight Per	rcent Cadmi	um (15.626	Atomic P	ercent)
23-1	361.56	6860	3517	8.0	1.14939
-2	361.56	7073	3972	8.0	1.14013
24-1	361.65	6438	3773	16.0	1.09741
-2	361.65	6495	3748	16.0	1.11727
-3	361.65	6354	3779	16.0	1.10666
79-1*	329.85	1617.2	805.6	3.0	1.33400
-2*	329.85	1644.0	842.1	3.0	1.31294
-3*	329.85	1614.8	727.7	3.0	1.38316
90-1*	410.25	1527.6	773.6	13.0	1.12737
_2*	410.25	1657.9	880.7	13.0	1.13731
_3*	410.25	1709.8	888.2	13.0	1.12415
94-1*	370.15	1401.1	851.5	15.0	0.94812
-2*	370.15	1410.9	889.5	15.0	0.95489
-3*	370.15	1520.5	916.6	15.0	0.94891

* -- Capillary Diameter = 1.00 mm

Run-	Temp.	Radioad	etivity of (Cadmium	Corr
Number	°C	co cpm	cr cpm	cpm	Factor F
111-1 *	289.85	1630.8	1193.9	20.0	1.013
-2*	289.85	1538.1	1085.1	20.0	1.028
17.40 ± 0.01	Weight H	Percent Cadn	nium (27.95	Atomic P	ercent)
65-1*	289.85	3170.4	2185.2	17.0	1.000
6 5a - 1*	290.00	3114.0	2287.6	18.5	1.001
72-1*	289.85	3013.7	1546.1	20.0	1.163
-2*	289.85	2989.3	1505.4	20.0	1.163
-3*	289.85	314 6 .8	1563.0	20.0	1.157
74-1*	329.85	3038.8	1540.4	22.0	1.154
-2*	329.85	3149.9	1648.9	22.0	1.158
-3*	329.85	3142.2	1640.2	22.0	1.159
75-1*	369.85	3003.0	1339.8	26.0	1.162
-2*	369.85	3142.7	1381.6	26.0	1.149
-3*	369.85	3087.6	1398.9	26.0	1.146
77-2*	410.00	3088.4	1370.9	28.0	1.149
-3*	410.00	3179.1	1340.9	28.0	1.140
31.00 ± 0.01	Weight H	Percent Cadr	nium (45.3 /	Atomic Pe	rcent)
55-1	290.55	19009.0	11063.1	7.8	1.160
-2**	290.55	12042.0	7036.7	5.3	1.173
-3*	290.55	6471.2	3710.6	3.6	1.152
56-1**	330.50	11 662. 8	7062.3	15.2	1.088
-2	330.50	17855.0	10502.3	22.2	1.086
57-1* -2** -3	371.05 371.05 371.05	5838.9 11857.1 17877 0	3034.0 6219.0 9039 1	17.2 25.5 37 3	1.081 1.093

** -- Capillary Diameter = 1.50 mm

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Run-	Temp.	Radioac	tivity of (Cadmium	Corr.
Number	°C	co cpm	cf cpm	cpm	F
58-1	411.00	1 6663.5	8488.6	52.2	1.09276
_2**	411.00	10801.7	5369.2	35.8	1.11691
_3*	411.00	5449.8	2867.7	23.8	1.08066
45.00 ± 0.0	Ol Weight P	ercent Cadm	ium (60.13	Atomic P	ercent)
59-1	289.85	16801.6	10204.3	10.0	1.13070
_2**	289.85	10883.6	6107.9	6.5	1.11991
_3*	289.85	5419.5	3073.1	4.4	1.11254
60-1*	329.85	4931.4	2590.2	14.0	1.14439
-2**	329.85	10255.8	5237.5	20.6	1.13723
-3	329.85	16222.5	8064.8	31.9	1.12731
61-1*	372.85	5268.0	2890.2	23.1	1.12506
-2**	372.85	10745.6	5218.0	34.2	1.12043
-3	372.85	16984.7	7822.3	53.0	1.11852
62-1*	407.35	5035.0	2447.7	31.2	1.07095
-2**	407.35	10377.9	5130.5	46.1	1.08399
-3	407.35	16272.1	8492.9	71.4	1.07 637
69.00 ± 0.0	01 Weight P	ercent Cadm	nium (80.40	3 Atomic	Percent)
66-1	330.35	16452.9	9782.5	27.5	1.12320
_2**	330.35	9411.1	5369.5	18.3	1.13651
~3	330.35	4816.3	2699.2	12.3	1.13523
67-1	371.00	15158.0	7639.9	48.8	1.10602
-2	371.00	15101.9	7651.5	48.8	1.10794
-3	371.00	15661.6	8116.7	48.8	1.10735
68-1	410.35	15792.0	8102.4	69.5	1.18783
-2	410.35	16339.2	8068.9	69.5	1.18521
-3	410.35	16672.1	8879.6	69.5	1.18517

TABLE D-3--continued

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*--Capillary Diameter = 1.00 mm **--Capillary Diameter = 1.50 mm

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Run-	Temp.	Radioa	ctivity of	Cadmium	Corr.
Number	°C	co cpm	c _f cpm	cpm	F
69-1 -2 -3	290.00 290.00 290.00	15153.2 15209.6 15537.7	8805.8 9048.0 9528.6	87.1 87.1 87.1	1.16298 1.17885 1.19174
97.00 ± 0.0	l Weight P	ercent Cadr	nium (98.35	Atomic F	Percent)
115-1 -2 -3	432.00 432.00 432.00	14566.9 15669.7 16620.4	7658.6 9449.3 10219.0	15.0 15.0 15.0	1.00733 1.01935 1.01503
*Capilla **Capilla	ry Diamete ry Diamete	r = 1.00 mr r = 1.50 mr	n n		<u> </u>

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TABLE D-3--continued

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TABLE D-4

SELF-DIFFUSION DATA FOR LEAD VERSUS TEMPERATURE FOR VARIOUS COMPOSITION IN LIQUID CADMIUM-LEAD ALLOYS

Run-	Temp.	Radioa	ctivity of	Lead	Corr.
Number	°C		cf cpm	cpm	F
2.50 ± 0.01	l Weight Pe	rcent Cadmi	um (4.512	Atomic P	ercent)
18a-1*	339.00	13223.2	8966.2	3.0	1.00508
118-1*	432.00	12805.3	7512.5	10.0	1.00058
-2*	432.00	13223.2	7732.9	10.0	1.00622
-3*	432.00	13335.5	8385.9	10.0	1.01129
9.13 ± 0.01	l Weight Pe	rcent Cadmi	um (15.626	Atomic	Percent)
104-1*	289.30	4790.1	3167.2	5.0	0.99738
-2*	289.30	4775.4	2983.0	5.0	0.99633
-3*	289.30	4957.3	3287.0	5.0	0.99947
103-1*	329.85	4732.2	3113.1	4.0	1.01935
_2*	329.85	4849.8	3030.5	4.0	1.01499
_3*	329.85	5021.2	3254.3	4.0	1.01610
101-1*	370.15	48 32.6	3138.7	3.0	0.99297
-2*	370.15	4870.3	3001.4	3.0	0.99884
-3*	370.15	5051.4	3823.8	3.0	0.99353
106-1*	411.45	4864.5	2882.8	6.0	1.01114
-3*	411.45	4897.0	2733.9	6.0	
17.40 ± 0.0	Ol Weight F	ercent Cadn	11um (27.97	Atomic	Percent)
100-1*	290.90	4036.9	2351.0	3.0	1.01549
-2*	290.90	4117 .3	2541.2	3.0	1.01879
-3*	290.90	4167.1	2516.1	3.0	1.02101

* -- Capillary Diameter = 1.00 mm

Run- Canillary	Temp.	Radioa	ctivity of	Lead	Corr. Factor
Number	°C	co cpm	cr cpm	cpm	F
102-1*	330.55	3882.7	2707.5	4.0	1.0150
-2*	330.55	3931.8	2798.8	4.0	1.0156
105-1*	371.25	4152.1	2599.2	7.0	1.0063
-2*	371,25	4208.3	2603.8	7.0	1.0074
107 -1*	411.00	3896.9	2220.8	9.0	1.0005
-2*	411.00	4028.2	2509.8	9.0	1.0015
-3*	411.00	42 36.7	2679.0	9.0	0.9968
31.00 ± 0.0	91 Weight P	ercent Cadm	nium (45.30	Atomic	Percent)
71-1	370.85	1055 3.4	5518.0	50.0	1.0797
-2	370.85	10579.9	5586.9	50.0	1.0797
-3	370.85	10579.9	5493.7	50.0	1.0800
78-1**	329.85	7381.1	4401.2	26.6	1.0542
-2**	329.85	7398.5	4522.7	26.6	1.0602
-3	329.85	10741.4	6790.4	38.2	1.0602
80-1**	409.85	7170.3	3537.7	38.8	1.0539
-2**	409.85	7253.1	3603.9	38.8	1.0638
-3	409.85	10474.1	5329.9	51.2	1.0674
92-1	291 .3 5	8650.8	5120.4	68.0	1.0 63 5
-2	291.35	8832.7	5192.7	68.0	1.0748
-3	291.35	9180.0	5611.9	68.0	1.0720
951	456.75	8838.5	4817.2	83.8	1.0691
-2	456.75	8656.6	4808.8	83.8	1.0652
-3	456.75	8493.4	4977.6	83.8	1.0620
45.00 ± 0.0)l Weight P	ercent Cadn	nium (60.13	Atomic	Percent)
821	290.00	7603.2	4834.9	31.0	1.0607
2	290.00	7485.4	4483.6	31.0	1.0609
3	290.00	7603.2	4779.3	31.0	1.0638

TABLE D-4--continued

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Run-	Temp.	Ra	adioactiv	Corr.		
Number	°C	co cpn) n c	c _f pm	cpm	F
⁸ 5-1	330.85	7585	5.2 47	86.7	44.8	1.07014
-2	330.85	7821	1.2 51	41.4	44.8	1.06021
-3	330.85	7687	7.2 50	28.8	44.8	1.05220
86-1	370.20	7736	5.1 43	72.5	58 .6	1.05816
-2	370.20	7434	4.1 40	47.0	58 .6	1.05571
-3	370.20	7891	1.4 46	23.4	58 .6	1.05 39 1
88-1	411.45	6679	9.8 33	60.2	100.0	1.00314
-2	411.45	6679	9.8 35	65.4	100.0	1.00580
89-1	456.00	7613	3.0 42	253.8	86.4	1.07200
-2	456.00	7753	3.9 3 ⁸	888.8	86.4	1.07816
-3	456.00	8198	3.6 42	90.1	86.4	1.07764
69.00 <u>+</u> 0.01	Weight	Percent	Cadmium	(80.40)3 Atomic	Percent)
91-1	374.00	6268	8.1 39	945.7	29.9	1.06644
-2	374.00	6119	5.1 37	705.1	29.9	1.05325
-3	374.00	627 ¹	4.4 39	973.5	29.9	1.03877
93-1	290.85	6333	1.5 43	345.9	35.8	1.06233
-2	290.85	6383	3.1 42	186.9	35.8	1.06533
-3	290.85	6318	8.7 42	19 3. 4	35.8	1.06747
97-1	410.85	6180	6.5 3 ¹	420.2	49.4	1.05432
-2	410.85	6579	5.5 36	63.5	49.4	1.05109
-3	410.85	639 ¹	4.6 37	705.1	49.4	1.04408
98-1	330.85	601	3.6 38	331.1	57.2	1.04819
-2	330.85	607	7.7 38	383.9	57.2	1.04979
-3	330.85	629	7.5 40	017.2	57.2	1.04737
99-1	454.85	6 580	6.2 36	590.7	64.4	1.00650
-2	454.85	7173	3.2 41	14 3. 7	64.4	1.01367
97.00 ± 0.01	Weight	Percent	Cadmium	(98.35	5 Atomic	Percent)

TABLE D-4-continued

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<u>....</u>

Run-	Temp.	Radioa	ctivity of	Lead	Corr.
Number	°C	cpm	cr cpm	cpm	F
112 -1*	340.00	92300.0	63 404.4	12.5	0.99300
-2**	340.00	148718,3	100272.9	12.5	0.99258
113-1*	393.00	89078.7	58191.1	35.0	0.99056
-2*	393.00	89825.8	59550.4	35.0	0.99786
-3*	393.00	89078.7	558 33. 1	35.0	1.00351
114~1*	434.00	84929.7	45675.9	59.0	1.00000
-2*	434.00	89234.2	50273.5	59.0	1.00114
-3*	434.00	90179.7	52554.7	59.0	1.00 6 80

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CHEMICAL DIFFUSION DATA IN LIQUID CADMIUM-LEAD ALLOY VERSUS TEMPERATURE FOR VARIOUS COMPOSITION

Run- Capillarv	Temp.	Radic	activity o	f Lead	Corr. Factor
Number	°C	com cpm	cf cpm	cr cpm	F
Capillary Reservoir	Alloy 2.0 Alloy 2.9	037 ± 0.01 50 ± 0.01	. Weight Pe . Weight Pe	rcent Cadm rcent Cadm	ium ium
120-1 -2 -3	340.00 340.00 340.00	10776.4 11151.0 25679.9	75 43.6 7636.5 16632.8	7.5 7.5 7.5	0.98414 0.98806 0.99475
121-1 -2 -3	390.10 390.10 390.10	1102 6. 1 10854.0 24974 .3	7007.7 7071.8 15663.9	18.2 18.2 18.2	0.99760 0.99203 1.00049
122-1 -2	436.00 436.00 426.00	10563.0 11430.8 11863 5	6665.0 7268.5 7779.4	27.6 27.6 27.6	1.00050 0.99717 1.00113
-3	450.00		11120	•	
-3 Capillary Reservoir	Alloy 9 Alloy 13	.13 ± 0.01 .05 ± 0.01	Weight Pe Weight Pe	rcent Cadm rcent Cadm	nium nium
-3 Capillary Reservoir 28-1 -2 -3	Alloy 9 Alloy 13 360.70 360.70 360.70	13 ± 0.01 .05 ± 0.01 20987 20646 21091	14645 14921 15391	rcent Cadm rcent Cadm 10.0 10.0 10.0	1.00976 1.00974 0.99774
-3 Capillary Reservoir 28-1 -2 -3 29-2** -3**	Alloy 9 Alloy 13 360.70 360.70 360.70 360.40 360.40	13 ± 0.01 .05 ± 0.01 20987 20646 21091 15062 14696	14645 14921 15391 9979 10238	10.0 10.0 10.0 10.0 20.0 20.0	1.00976 1.00976 1.00974 0.99774 1.00797 1.00683
-3 Capillary Reservoir 28-1 -2 -3 29-2** -3** 30-1* -2**	Alloy 9 Alloy 13 360.70 360.70 360.70 360.40 360.40 359.90 359.90	13 ± 0.01 $.05 \pm 0.01$ 20987 20646 21091 15062 14696 9101 15600	Weight Pe Weight Pe 14645 14921 15391 9979 10238 6247 11482	rcent Cadm rcent Cadm 10.0 10.0 20.0 20.0 20.0 25.0 30.0	1.00976 1.00974 0.99774 1.00797 1.00683 1.00856 1.00968
-3 Capillary Reservoir 28-1 -2 -3 29-2** -3** 30-1* -2** 32-1 -3 -2	Alloy 9 Alloy 13 360.70 360.70 360.70 360.40 360.40 359.90 359.90 359.90 398.60 398.60 398.60	13 ± 0.01 $.05 \pm 0.01$ 20987 20646 21091 15062 14696 9101 15600 20479 20297 20746	Weight Pe Weight Pe 14645 14921 15391 9979 10238 6247 11482 14578 14234 14545	rcent Cadm rcent Cadm 10.0 10.0 20.0 20.0 25.0 30.0 41.0 41.0 41.0	1.00976 1.00974 0.99774 1.00797 1.00683 1.00856 1.00968 0.99500 0.99320

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Run- Capillary	Temp.	Radioa	ctivity	of Lead	Corr. Factor
Number C	C	co cpm	c _f cpm	cr cpm	म्
35-1	482.60	21443	14628	97.0	0.99710
-3	482.60	21 33 5	14338	97.0	0.98 36 8
Capillary	Alloy 15.	40 ± 0.01	Weight :	Percent Cadmi	um
Reservoir	Alloy 19.	40 ± 0.01	Weight :	Percent Cadmi	um
36-1	400.75	18600	12770	118.3	0.97081
-2	400.75	20396	14798	118.3	0.98540
-3	400.75	19640	14282	118.3	0.97665
37-2	357.75	19261	13210	137.6	0.98626
-1	357.75	18565	13074	137.6	0.99074
-3	357.75	18442	12835	137.6	0.991 3 4
38-1	439.40	20041	13845	155.9	0.98978
-2	439.40	20199	14107	155.9	0.99143
-3	439.40	20163	13695	155.9	0.99313
39-1	480.30	199 47	12605	175.6	0.99 7 11
-2	480.30	1985 3	11740	175.6	0.99769
-3	480.30	20089	12299	175.6	0.99543
Capillary	Alloy 33.	0 ± 0.01	Weight Po	ercent Cadmiu	m
Reservoir	Alloy 29.	0 ± 0.01	Weight Po	ercent Cadmiu	m
40-1	359.60	14747	9923	163.5	0.99 436
-2	359.60	14747	10220	163.5	0.99777
-3	359.60	14577	10162	163.5	0.99833
41-1	401.50	14428	9 66 4	180.6	1.00261
-2	401.50	14560	9954	180.6	0.99918
-3	401.50	14713	9884	180.6	0.99265
42-1	438.25	15026	10918	197.3	0.99376
-2	438.25	15353	10388	197.3	0.99320
-3	438.25	14729	9792	197.3	0.99321
43-1	480.40	14457	8996	213.3	0. 994 3 8

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TABLE D-5--continued

Run-	Temp.	Radioa	Radioactivity of Lead			
Capillary Number	°C	co cpm	c _f cpm	cpm	Factor F	
108-1	483.85	7770	46 10	155.0	1.00779	
-2	483.85	7751	4945	155.0	1.00571	
-3	483.85	7892	4827	155.0	1.00830	
Capillary	Alloy 44	.0 ± 0.01	Weight Per	cent Cadmi	um	
Reservoir	Alloy 46	.0 ± 0.01	Weight Per	cent Cadmi	um	
44-1	359.00	10599	7643	168.0	1.00456	
-2	359.00	10529	7578	168.0	1.00000	
-3	359.00	9704	6799	168.0	1.00284	
45-1	400.00	10189	701 6	182.7	1.00857	
-2	400.00	10124	6885	182.7	1.00457	
-3	400.00	10892	7565	182.7	0.99783	
46-1	439.00	10339	6599	198.4	1.00116	
-2	439.00	10272	6316	198.4	1.00000	
-3	439.00	10726	6690	198.4	0.99830	
47-1	480.40	10928	7383	210.9	1.00055	
-2	480.40	11033	7213	210.9	1.00399	
-3	480.40	11043	7446	210.9	1.01143	
Capillary	Alloy 64	.04 ± 0.01	. Weight Pe	rcent Cadm	lium	
Reservoir	Alloy 70	.00 ± 0.01	. Weight Pe	rcent Cadm	lium	
49-1	400.05	4665	3128	120.0	1.01942	
50-1	400.05	5636	3740	122.5	1.00060	
-2	400.05	5595	3607	122.5	1.00289	
-3	400.05	5660	3744	122.5	1.00403	
51-1	360.80	5496	3908	125.0	1.00456	
-2	360.80	5434	3749	125.0	1.00000	
-3	360.80	5438	3724	125.0	0.99885	
52-1	441.85	5764	3686	128.0	1.00629	
-2	441.85	5664	3518	128.0	1.00284	
-3	441.85	5675	3567	128.0	1.00340	

TABLE D-5--continued

Run-	Temp.	Radioac	tivity of	Lead	Corr.
Number	°C	co cpm	cf cpm	cpm	Factor F
53-1	359.00	5808	3850	131.0	1.00689
-2	359.00	581 3	4007	131.0	1.00402
-3	359.00	5791	408 6	131.0	1.00572
54-1	481.50	5796	3461	134.0	1.00916
-2	481.50	6030	3669	134.0	1.00859
-3	481.50	6125	3891	134.0	1.00400
Capillary	Alloy 95.	00 ± 0.01 W	eight Perc	ent Cadi	nium
Reservoir	Alloy 97.	00 ± 0.01 W	eight Perc	ent Cadi	nium
116-1	338.10	143694.3	98909.4	86.0	1.01580
-2	338.10	148279.9	103941.5	86.0	1.01294
-3	338.10	149681.7	101868.5	86.0	1.01809
117-1	390.00	150022.6	91796.3	115.0	1.01296
-2	390.00	152256.9	93992.9	115.0	1.01466
-3	390.00	146161.7	91631.6	115.0	1.01238
119-1	440.00	148278.6	95217.3	140.0	0.98261
-2	440.00	152253.7	103516.5	140.0	0.97819
-3	440.00	154555.6	104362.6	140.0	0.97765

TABLE D-5--continued

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TABLE D-6

SELF-DIFFUSION	COEFFICIEN	T VERSUS	TEMPERATURE
1	FOR LIQUID	CADMIUM	

Run- Capillary Number	Temp. °C	$\frac{c_{f} - c_{r}}{c_{o} - c_{r}}$	Length cm	Time sec	D x 105 cm ² /sec
11-1	399.05	0.56224	2.753	38280	2.981
-2	399.05	0.56854	2.779	38280	2.949
-3	399.05	0.54594	2.703	38280	3.091
12-1	439.45	0.54337	2.692	33540	3.541
-2	439.45	0.53584	2.733	33540	3.770
-3	439.45	0.54918	2.733	33540	3.556
13-1	490.15	0.47987	2.687	36420	4.224
-2	490.15	0.49387	2.672	36420	3.953
-3	490.15	0.49119	2.644	36420	3.912
15-1	400.00	0.61784	2.644	29340	2.733
-2	400.00	0.58773	2.652	29340	3.200
16-1	440.15	0.59473	2.720	27780	3.435
-2	440.15	0.58739	2.700	27780	3.508
-3	440.15	0.62402	2.769	27780	3.063
17-3	491.85	0.59520	2.624	36780	4.137
18-2	361.85	0.60957	2.713	32820	2.684
20-1	357.35	0.57561	2.593	37440	2.541
22-1	360.80	0.58142	2.418	29955	2.687

::::: D x 10⁵ Time Temp. °r Length Run c_{f} Capillary °r °C °0 cm²/sec Number cm sec ÷ . . 0.64444 34860 2.092 3-1 360.75 2.710 34860 2,287 -2 360.75 0.61379 2.609 360.75 2.730 34860 2.260 -3 0.63315 357.75 357.75 357.75 1.937 4-1 0.59034 46740 2.621 2.649 46740 -2 -3 0.62878 46740 1.647 2.667 37800 37800 357.40 0.64638 5-1 2.715 1.915 357.40 0.62631 2.675 2.076 -2 2.654 -3 357.40 37800 0.63124 1.990 6-1 399.90 399.90 0.57164 2.776 46560 2.386 2.341 46560 -3 0.55705 2,659 7-1 435.75 0.64192 2.763 25860 2.973 435.75 435.75 -2 0.63190 2.680 25860 2.954 2.479 25860 -3 0.65100 2.593 483.50 8-1 0.60631 2.674 32580 2.671 483.50 32580 3.517 2.652 -2 0.60679 2.669 483.50 32580 0.55938 2.740 -2a -3 0.59316 2.697 32580 2.892 399.40 2.687 9-1 0.62450 35400 2,258 399.40 399.40 0.64101 35400 35400 -2 2.664 2.029 -3 -4 0.63014 2.654 2.138 399.40 0.63302 2.781 35400 2.311 35400 35400 -5 -6 2.789 2.758 399.40 2.153 399.40 2.402 0.62275 . .

SELF-DIFFUSION COEFFICIENT VERSUS TEMPERATURE FOR LIQUID LEAD

SELF-DIFFUSION COEFFICIENT FOR CADMIUM VERSUS TEMPERATURE FOR VARIOUS COMPOSITION IN LIQUID CADMIUM-LEAD ALLOYS

	<u> </u>	· · · · ·	· ·	- ·	
Run- Capillary	Temp.	c _f - c _r	Length	Time	D x 10 ⁵
Number	°C	$c_0 - c_r$	cm	sec	cm ² /sec
2.5 ± 0.01	Weight Per	cent Cadmiun	n (4.513 /	Atomic Per	rcent)
123-1*	341.00	0.68682	2.451	23280	1.987
-2*	341.00	0.67447	2.542	23280	2.308
-3*	341.00	0.72785	2.563	23280	
124-1*	390.50	0.62834	2.433	25560	2.512
-2*	390.50	0.61541	2.548	25560	2.952
-3*	390.50	0.61549	2.616	25560	3.108
125-1*	440.50	0.58873	2.486	21960	3.738
-2*	440.50	0.60220	2.509	21960	3.563
-3*	440.50	0.61163	2.664	21960	3.830
9.13 ± 0.0	1 Weight Pe	rcent Cadmin	am (15.62)	ó Atomic I	?ercent)
23-1	361.56	0.58887	2.553	29220	2.962
-2	361.56	0 .63 989	2.545	29220	2.257
24-1	361.65	0.64231	2.471	26040	2.356
-2	361.65	0.64381	2.558	26040	2.490
-3	361.65	0.65724	2.540	26040	2.287
79-1*	329.85	0.66448	2.568	25320	2.302
_2*	329.85	0.67192	2.507	25320	2.090
_3*	329.85	0.62261	2.423	25320	2.593
90-1*	410.25	0.56723	2.504	23880	3.862
-2*	410.25	0.60102	2.601	23880	3.555
-3*	410.25	0.58078	2.662	23880	4.095
94-1*	370.15	0.57162	2.581	25920	3.422
-2*	370.15	0.59774	2.545	25920	3.176
-3*	370.15	0.59774	2.634	25920	3.927

* -- Capillary Diameter = 1.00 mm

		· · · · · · · · · · · ·			
Run- Capillary	Temp.	c _f - c _r	Length	Time	D x 10 ⁵
Number	°C	c ₀ - c _r	cm	sec	cm ² /sec
111-1* -2*	289,85	0.73982	2 .6 14 2.550	22860 22860	1.601 1.721
17.40 ± 0.0	Ol Weight P	ercent Cadm	ium (27.97	Atomie 1	Percent)
65-1*	289.85	0.68925	2.474	255 60	1.815
65a-1*	290.00	0.73461	2.530	19800	1.788
72-1*	289.85	0.58327	2.387	32820	2.134
-2*	289.85	0.59436	2.458	32820	2.144
-3*	289.85	0.58725	2.520	32820	2.331
74-1	329.85	0.58535	2.423	28860	2.748
-2	329.85	0.60737	2.502	28860	2.627
-3	329.85	0.60224	2.487	28860	2.664
75-1	369.85	0.52462	2.456	33300	3.2 19
-2	369.85	0.50704	2.583	33300	3.829
-3	369.85	0.5211 6	2.532	33300	3.471
77-2	410.00	0.50308	2.586	33360	3. 895
-3	410.00	0.48454	2.578	33360	4.16 8
31.00 ± 0.0	Ol Weight F	ercent Cadm	ium (45.3	Atomic P	ercent)
55 - 1	290.55	0.67517	2.608	30000	1.879
-2	290.55	0.68367	2.562	30000	1.7197
-3	290.55	0.66039	2.611	30000	2.059
56-1	330.50	0.66296	2.532	25680	2.227
-2	330.50	0.64289	2.499	25680	2.437
57-1	371.05	0 .56734	2.575	32340	3.016
-2	371.05	0.57897	2.517	32340	2.727
-3	371.05	0 .566 25	2.487	32340	2.905
58-1	411.00	0.56464	2.520	25320	3.734
-2	411.00	0.56305	2.540	25320	3.822
-3	411.00	0.57635	2.542	25320	3.598

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* -- Capillary Diameter = 1.00 mm

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TABLE D-8--continued

Run- Capillary Number	Temp. °C	c _f .− c ₀ −	c _r Le	ength cm	Time sec	D x 10 ⁵ cm ² /sec
45.00 ± 0.01	Weight	Percent	Cadmium	(60.13	Atomic	Percent)
59-1	289.85	0.686	53 2.	636	28200	1.902
-2	289.85	0.646	09 2.	603	28200	2.364
-3	289.85	0.631	37 2.	657	28200	2.666
60-1	329.85	0.604	154 2.	,403	33000	2.148
-2	329.85	0.584	135 2.	,446	33000	2.460
-3	329.85	0.563	183 2.	,410	33000	2.629
61-1	372.85	0.623	869 2.	.550	26130	2.767
-2	372.85	0.549	977 2.	.58 3	26130	4.067
-3	372.85	0.520	939 2.	.5 6 8	26130	4.565
62-1	407.35	0.526	81 2	575	25560	4.566
-2	407.35	0.543	325 2	499	25560	4.006
-3	407.35	0.551	.96 2	586	25560	4.126
69.00 ± 0.01	Weight	Percent	Cadmium	(80.40	3 Atomio	e Percent)
66-1	330.35	0.672	232 2	. 63 9	25620	2.291
-2	330.35	0.652	266 2	. 487	25620	2.287
-3	330.35	0.640	009 2	. 504	25620	2.489
67-1	371.00	0.562	2 30 2	.504	34560	2.730
-2	371.00	0.559	925 2	.487	34560	2.731
-3	371.00	0.579	95 3 2	.675	34560	2.875
68-1	410.35	0.618	84 2	.639	24000	3.311
-2	410.35	0.594	21 2	.657	24000	3.803
-3	410.35	0.643	20 2	.690	24000	2.048
69-1	290.00	0.67	395 2	. 499	25740	2.026
-2	290.00	0.69	960 2	. 545	25740	1.784
-3	290.00	0.729	9 3 2 2	. 575	25740	1.482

* -- Capillary Diameter = 1.00 mm

Run-	Temp.	c _f - c _r	Length	Time	D x 10 ⁵
Number	° C	$c_0 - c_r$	cm	sec	cm ² /sec
115-1* -2* -3*	432.00 432.00 432.00	0.52912 0.61432 0.62465	2.522 2.611 2.723	26280 26280 26280	4.218 3.030 3.122

TABLE D-8--continued

-- Capillary Diameter = 1.00 mm

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SELF-DIFFUSION COEFFICIENT FOR LEAD VERSUS TEMPERATURE FOR VARIOUS COMPOSITION IN LIQUID CADMIUM-LEAD ALLOYS

		· · · · · · · · · · · · · · · · · · ·	· ·		· · · · ·
Run-	Temp.	c _f - c _r	Length	Time	D x 10 ⁵
Number	°C	$\overline{c_0 - c_r}$	cm	sec	cm ² /sec
2.5 ± 0.01	Weight Per	cent Cadmiu	m (4.513 A	tomic Per	cent)
118a-1*	339.00	0.68143	2.629	26100	2.110
118-1* -2* -3*	432.00 432.00 432.00	0.59 364 0.59509 0.64 3 19	2.377 2.476 2.484	26040 26040 26040	2.814 3.032 2.369
9.13 ± 0.01	Weight Pe	rcent Cadmi	um (15.626	Atomic P	ercent)
104-1 -2 -3	289.30 289.30 289.30	0.65910 0.62201 0.66205	2.525 2.568 2.657	44430 44430 44430	1.310 1.665 1.425
103-1 -2 -3	329.85 329.85 329.85	0.67443 0.63782 0.66232	2.433 2.499 2.611	26040 26040 26040	1.892 2.470 2.344
101-1 -2 -3	370.15 370.15 370.15	0.65251 0.64129 0.64110	2.520 2.547 2.588	25020 25020 25020	2.406 2.620 2.709
106-1 -3	411.45 411.45	0.60909 0.56858	2.520 2.591	28890 28890	2.640 3.397
17.40 ± 0.0	01 Weight P	ercent Cadm	ium (27.97	Atomic F	ercent)
1001 -2 -3	290.90 290.90 290.90	0.59109 0.62852 0.61621	2.449 2.471 2.497	46380 46380 46380	1.697 1.427 1.555
<u> </u>	• • • • • • • • •		· · · · · · ·		
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Run-	Temp.	c _f - c _r	Length	Time	D x 10 ⁵
Number	° C	c _o - c _r	cm	sec	cm ² /sec
102-1	330.55	0.71561	2.441	19920	1.899
-2	330.55	0.72643	2.441	19920	1.759
105-1	371.25	0 .6366 2	2.520	26550	2.480
-2	371.25	0 .6 2989	2.585	26550	2.708
107-1	411.00	0.57907	2.481	26340	3.253
-2	411.00	0.63399	2.639	26340	2.782
-3	411.00	0.64046	2.697	26340	2.804
31.00 ± 0.0	l Weight	Percent Cadm	ulum (45.30	Atomic 1	Percent)
71-1	370.85	0.56898	2.570	30720	3.137
-2	370.85	0.57474	2.647	30720	3.239
-3	370.85	0.56519	2.613	30720	3.273
78-1	329.85	0.63122	2.448	26700	2.397
-2	329.85	0.65095	2.497	26700	2.235
-3	329.85	0.67330	2.575	26700	2.081
80-1	409.85	0.52658	2.420	31260	3.301
-2	409.85	0.53536	2.467	31260	3.304
-3	409.85	0.55033	2.568	31260	3.352
92-1	291.35	0.61232	2.603	43140	1.855
-2	291.35	0.62905	2.606	43140	1.702
-3	291.35	0.65279	2.649	43140	1.541
95-1	456.75	0.59155	2.588	26700	3.290
-2	456.75	0.60077	2.681	26700	3.371
-3	456.75	0.61229	2.699	26700	3.222
45.00 ± 0.0	l Weight	Percent Cadn	nium (60.13	Atomic	Percent)
82-1	290.00	0.67331	2.553	27600	1.979
-2	290.00	0.63395	2.550	27600	2.478
-3	290.00	0.66735	2.591	27600	2.114
85-1	330.85	0.67763	2.593	22560	2.432

TABLE D-9--continued

				· · · · · · · · · · · · · · · · · · ·			
Run- Capillary Number	Temp. °C	$\frac{c_{f} - c_{r}}{c_{0} - c_{r}}$	Length cm	Time	$D \ge 10^5$ cm ² /sec		
• • • • · · • • · ·					<i></i>		
85-2	330.85	0.69956	2.652	22560	2.210		
-3	330.85	0.69081	2.690	22560	2.409		
86-1	370.20	0.60237	2.639	27660	3.127		
-2	370.20	0.57832	2.639	27660	3.517		
-3	370.20	0.62212	2.702	27660	2.960		
88-1	411.45	0.50567	2.651	36120	3.739		
-2	411.45	0.53912	2.690	36120	3.345		
89-1	456.00	0.60767	2.613	25260	3.268		
-2	456.00	0.54752	2.613	25260	4.349		
-3	456.00	0.57039	2.682	25260	4.129		
69.00 ± 0.01	Weight	Percent Cadmi	Lum (80.40	03 Atomic	Percent)		
91-1	374.00	0.67750	2.614	21600	2.584		
-2	374.00	0.64375	2.601	21600	3.122		
-3	374.00	0.66380	2.657	21600	2.902		
93-1	290.85	0.727 63	2.657	24960	1.649		
-2	290.85	0.74744	2.664	24960	1.424		
-3	290.85	0.75773	2.677	24960	1.323		
97-1	410.85	0.58962	2.550	26460	3.251		
-2	410.85	0.59262	2.629	26460	3.405		
-3	410.85	0.61236	2.677	26460	3.197		
98-1	330.85	0.66878	2.578	29260 ⁻	1.933		
-2	330.85	0.67194	2.614	29620	1.964		
-3	330.85	0.66927	2.654	29620	2.043		
99-1	454.85	0.57220	2.649	22680	4.449		
-2	454.85	0.60936	2.715	22680	3.895		
97.00 ± 0.01	Weight	Percent Cadmi	lum (98.35	5 Atomic P	ercent)		
122-1*	340.00	0.68208	2.588	27660	1.922		
* Capillar	* Capillary Diameter = 1.00 mm						

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TABLE D-9--continued

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Run- Capillary Number	Temp. °C	$\frac{c_{f} - c_{r}}{c_{0} - c_{r}}$	Length cm	Time sec	D x 10 ⁵ cm ² /sec
122-2*	340.00	0.66923	2.388	27660	1.771
113-1*	390.00	0.64773	2.482	22200	2.501
-2*	390.00	0.66140	2.502	22200	2 .34 8
-3*	390.00	0.62883	2.537	22200	2.901
114-1*	434.00	0.53748	2.423	26340	3.524
-2*	434.00	0.56374	2.540	26340	3.662
-3*	434.00	0.58646	2.568	26340	3.363

TABLE D-9--continued

* -- Capillary Diameter = 1.00 mm

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TABLE D-10

CHEMICAL DIFFUSION IN LIQUID CADMIUM-LEAD ALLOY VERSUS TEMPERATURE FOR VARIOUS COMPOSITION

Run- Capillary Number	°C	$\frac{c_{f} - c_{r}}{c_{0} - c_{r}}$	Length cm	Time sec	D x 10 ⁵ cm ² /sec
Capillary Reservoir	Alloy 2.0 Alloy 2.9	037 ± 0.01 500 ± 0.01	Weight Per Weight Per	cent Cadm cent Cadm	ium ium
120-1* -2* -3*	340.00 340.00 340.00	0.68869 0.67643 0.64419	2.587 2.733 2.659	28680 28680 28680	1.776 2.141 2.450
121-1* -2* -3*	390.10 390.10 390.10	0.63342 0.64743 0.62723	2.550 2.565 2.591	25440 25440 25440	2.669 2.524 2.879
122-1* -2* -3*	436.00 436.00 436.00	0.63032 0.63845 0.65568	2.481 2.657 2.773	21600 21600 21600	3.057 3.357 3.314
Contllor			Todaulat Down		
Reservoir	Alloy 9. Alloy 13	13 ± 0.01 % $.05 \pm 0.01$	Weight Per	cent Cadm	ium 1um
28-1 -2 -3	Alloy 9. Alloy 13 	0.70449 0.72960 0.72797	2.555 2.591	20220 20220 20220	2.215 1.839 1.929
28-1 -2 -3 29-2** -3**	Alloy 9. Alloy 13 360.70 360.70 360.40 360.40	0.70449 0.72960 0.72797 0.66692 0.70124	2.555 2.545 2.591 2.413 2.359	20220 20220 20220 20220 20220 21600 21600	2.215 1.839 1.929 2.348 1.806
28-1 -2 -3 29-2** -3** 30-1* -2**	Alloy 9. Alloy 13 360.70 360.70 360.40 360.40 359.90 359.90	$\begin{array}{c} 13 \pm 0.01 \\ .05 \pm 0.01 \\ 0.72960 \\ 0.72797 \\ 0.66692 \\ 0.70124 \\ 0.69126 \\ 0.74264 \end{array}$	2.555 2.545 2.591 2.413 2.359 2.509 2.606	20220 20220 20220 20220 20220 21600 21600 22320 22320	2.215 1.839 1.929 2.348 1.806 2.111 1.582
28-1 -2 -3 29-2** -3** 30-1* -2** 32-1 -2 -3	Alloy 9. Alloy 13 360.70 360.70 360.40 360.40 359.90 359.90 359.90 398.60 398.60 398.60	$\begin{array}{c} 13 \pm 0.01 \\ .05 \pm 0.01 \\ 0.72960 \\ 0.72960 \\ 0.72797 \\ 0.666692 \\ 0.70124 \\ 0.69126 \\ 0.74264 \\ 0.70768 \\ 0.69492 \\ 0.69794 \end{array}$	2.555 2.545 2.591 2.413 2.359 2.509 2.606 2.479 2.474 2.453	20220 20220 20220 20220 20220 21600 21600 22320 22320 19800 19800 19800	2.215 1.839 1.929 2.348 1.806 2.111 1.582 2.083 2.260 2.176

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Run- Capillary Number	Temp. °C	$\frac{c_{f} - c_{r}}{c_{o} - c_{r}}$	Length cm	Time sec	D x 10 ⁵ cm ² /sec
35-1	482.60	0 .6 7873	2.545	19440	2.700
-3	482.60	0 .6 5952	2.535	19440	3.010
Capillary	Alloy 15	.40 ± 0.01	Weight Per	cent Cadm	ulum
Reservoir	Alloy 19	.40 ± 0.01	Weight Per	cent Cadm	ulum
36-1	400.75	0 .66 439	2.378	21720	2.303
-2	400.75	0.71329	2.639	21720	2.071
-3	400.75	0.70844	2.593	21720	2.066
37-1	357.75	0.69541	2.370	23700	1.725
-2	357.75	0.67412	2.479	23700	2.162
-3	357.75	0.68759	2.347	23700	1.780
38-1	439.40	0.68130	2.540	19500	2.638
-2	439.40	0.69000	2.570	19500	2.557
-3	439.40	0.67202	2.563	19500	2.877
39-1	480.30	0.62683	2.522	24540	2.833
-2	480.30	0.58630	2.517	24540	3.469
-3	480.30	0.60599	2.517	24540	3.147
Capillary	Alloy 33	.00 ± 0.01	Weight Per	rcent Cadn	nium
Reservoir	Alloy 29	.00 ± 0.01	Weight Per	rcent Cadn	nium
40-1	359.60	0.66527	2.479	26160	2.067
-2	359.60	0.68805	2.497	26160	1.822
-3	359.60	0.69253	2.507	26160	1.7 3 4
41-1	401.50	0.67219	2.423	23700	2.091
-2	401.50	0.68397	2.463	23700	2.006
-3	401.50	0.66745	2.463	23700	2.226
42-1	438.25	0.71836	2.634	24840	1.740
-2	438.25	0.66214	2.631	24840	2.498
-3	438.25	0.65567	2.585	24840	2.504
43-1	480.40	0.62314	2 .3 85	21960	2.889

TABLE D-10--continued

					<u> </u>
Run- Capillary Number	Temp. °C	$\frac{c_{f} - c_{r}}{c_{0} - c_{r}}$	Length cm	Time sec	D x 10 ⁵ cm ² /sec
108-1	483.85	0.60541	2.588	23400	3.501
-2	483.85	0.65128	2.606	23400	2.772
-3	483.85	0.62526	2.657	23400	3.328
Capillary	Alloy 44	.00 ± 0.01	Weight Per	cent Cadm	nium
Reservoir	Alloy 46	.00 ± 0.01	Weight Per	cent Cadm	nium
44-1	359.00	0.71993	2.674	26400	1.668
-2	359.00	0.71524	2.656	26400	1.702
-3	359.00	0.69741	2.453	26400	1.639
45-1	400.00	0.68885	2.580	25440	1.990
-2	400.00	0.67732	2.573	25440	2.127
-3	400.00	0.68722	2.705	25440	2.209
46-1	439.00	0.63188	2.540	28800	2.383
-2	439.00	0.60728	2.588	28800	2.817
-3	439.00	0.61559	2.626	28800	2.790
47-1	483.85	0 .66 956	2.647	22740	2.642
-2	483.85	0.64965	2.649	22740	2.975
-3	483.85	0.67582	2.669	22740	2.584
Capillary	Alloy 64	.04 ± 0.01	Weight Per	cent Cadn	nium
Reservoir	Alloy 70	.00 ± 0.01	Weight Per	cent Cadn	nium
49-1	400.05	0.67515	2.520	21840	2.410
50-1	400.05	0.65658	2,502	22860	2.543
-2	400.05	0.63852	2,423	22860	2.635
-3	400.05	0.65679	2,474	22860	2.477
51-1	360.80	0.70770	2.535	26040	1.656
-2	360.80	0.70 6 23	2.519	26040	1.651
-3	360.80	0.67659	2.519	26040	2.002
52-1	441.85	0.63540	2.575	28500	2.429
-2	441.85	0.61409	2.583	28500	2.739
-3	441.85	0.62206	2.588	28500	2.637

TABLE D-10--continued

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Run- Capillary Number	'Temp. °C	$\frac{c_{f} - c_{r}}{c_{o} - c_{r}}$	Length cm	Time sec	D x 10 ⁵ cm ² /sec
53-1	359.00	0.65980	2.512	28260	2.030
-2	359.00	0.68500	2.512	28260	1.739
-3	359.00	0.70291	2.512	28260	1.547
54-1	481.50	0.60455	2.481	25920	2.916
-2	481.50	0.61688	2.562	25920	2.920
-3	481.50	0.64517	2.616	25920	2.611
Capillary /	Alloy 95	.00 ± 0.01	Weight Per	cent Cadm	nium
Reservoir /	Alloy 97	.00 ± 0.01	Weight Per	cent Cadm	nium
116 -1**	338.10	0 .6 990 3	2.357	22860	1.729
-2**	338.10	0.70988	2.390	22860	1.651
-3**	338.10	0.69270	2.456	22860	1.957
117-1**	390.00	0.61952	2.588	30480	2.498
-2**	390.00	0.62610	2.626	30480	2.484
-3**	390.00	0.63439	2.659	30480	2.436
119-1**	440.00	0.63812	2.481	18000	3.538
_2**	440.00	0.67262	2.515	18000	2.959
_3**	440.00	0.66809	2.573	18000	3.181
** Cant	llam Diom	atan - 1.50		·····	

TABLE D-10--continued

APPENDIX E

RADIOACTIVE MATERIALS SPECIFICATION

RADIOACTIVE MATERIALS SPECIFICATION

The specifications for the radioactive tracers used in this investigation are given in the following table.

TABLE E-1

Isotope Item Lead-210 (Radium D) Cadmium-115m · · · · · · · · · · · Half Life 43 days 22 years $Pb(NO_3)_2$ in HNO_3 $Cd(NO_3)_2$ in HNO₃ Chemical Form 0.73N Acidity 2.5N 0.242 ±10% mc/ml Concentration 8.0 mc/ml1.99 mg Cd/ml 3.4 mg Pb/ml Specific Activity 2.35 mc/mg 121 mc/gm90% Purity

SPECIFICATIONS OF RADIOACTIVE TRACERS

The radiation energy spectrums for the radioactive lead and cadmium listed above were obtained from the counting system used in this research. The energy spectrums are plotted in Figure E-1. The cesium-137 spectrum is also given in this figure. The instrument settings for these measurements were:

Fine Gain 1.6

Window Width 020 (0.20 volts)

Coarse Gain 16 The instrument settings for the cadmium isotope and the lead isotope were different during diffusion measurements

and are given in the following table.

TABLE E-2

		····
	Lead	Cadmium
Window Width	150	200
Threshold	85	550
Fine Gain	1.6	1.6
Coarse Gain	16	640
High Voltage	900	800

INSTRUMENT SETTINGS

The good linear characteristics of the amplifier is shown in Figure E-1. This line should not intercept the origin, and, as may be seen from the figure, it does not.

Other isotopes were associated with cadmium-115m and therefore resolution of the gamma spectrum was very difficult. Silver-110m was found in one batch of the radioactive cadmium solution received from the Oak Ridge National Laboratory. Therefore, silver-110m was precipitated as silver chloride from this solution to obtain a better energy spectrum for cadmium-115m as shown in Figure E-1.



APPENDIX F

STATISTICAL ANALYSIS FOR DIFFUSION DATA

:

STATISTICAL ANALYSIS OF THE RESULTS

The scatter of the results raises the question whether the differences in the diffusion coefficient data and also the calculated values of parameters Q and D_0 in Arrhenius' equation are significant. This question could be answered by statistical analysis. The standard deviation is defined ^{49,50} as:

$$\delta = \frac{\sum_{n=1}^{n} (D - \overline{D})^{2}}{n - 1} = \frac{\sum_{n=1}^{\infty} (D^{2}) - (\sum_{n=1}^{\infty})^{2}/n}{n - 1}$$
F-1

where $\overline{D} = \frac{\Sigma D}{n}$, n is the number of measurements in a single group and δ is the standard deviation. The standard deviation of the average was defined as

$$\overline{\delta}^2 = \frac{\delta}{n}$$
 F-2

and was calculated at various temperatures and compositions. The calculated values of the standard deviation of a single determination and standard deviation of the average are tabulated in Tables F-1 through F-4.

A joint standard deviation of the diffusion coefficient was also calculated for each individual data group by the following equation:

$$\delta_{J}^{2} = \frac{(n_{1} - 1)\delta_{1}^{2} + (n_{2} - 1)\delta_{2}^{2} \dots (n_{t} - 1)\delta_{t}^{2}}{n_{1} + n_{2} + \dots n_{t} - t}$$
 F-3

In the above equation δ_J is the joint standard deviation, n is the number of determinations in each group, subscripts indicate the data groups, and t is the total number of groups. These values are presented in Table F-5 for various compositions.

The Arrhenius equation was assumed to be valid for the small temperature range used in this investigation. The best-fitting straight line through the data was obtained by the method of least squares. To calculate the line of best fit⁵¹, the equation:

$$D = D_{o} exp \left[- \frac{Q}{RT} \right]$$
 F-4

was transformed to the following linear equation:

$$Y = A + bX$$

where $Y = \log D$, $A = \log D_0$, $b = \frac{Q}{2.303R}$ and X = 1/T.

For the best straight line the least-square principle was employed and the parameters were estimated as follows:

$$b = \frac{\sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{j=1}^{m} \sum_{j=1}^{m} \frac{\sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{j=1}^$$

$$A = \frac{\Sigma Y_1}{m} - b \frac{\Sigma X_1}{m} \qquad F-7$$

After the parameters A and b were obtained, the values for

the activation energy of diffusion and ${\rm D}_{_{\rm O}}$ were calculated as follows:

$$Q = 2.303 \text{ Rb}$$
 F-8

$$\log D_0 = A \dots F-9$$

For the data given in Table D-1 of Appendix D for the selfdiffusion coefficient of pure lead, the calculation was as follows:

$$\sum_{\Sigma Y_{i}}^{m} = -111.30234$$

$$\sum_{\Sigma X_{i}}^{m} = 35.663 \times 10^{-3}$$

$$\sum_{\Sigma X_{i}}^{m} Y_{i} = -165.53372 \times 10^{-3}$$

$$\sum_{\Sigma X_{i}}^{m} Z_{i}^{2} = 53.2037 \times 10^{-6}$$

$$(\sum_{\Sigma X_{i}}^{m})^{2} = 1271.8495 \times 10^{-6}$$

Substituting these values in the above equation gives:

$$b = -681.14$$
 $A = -3.62545$

Thus:

$$Q = 3116.9 \text{ Cal./mole}$$

 $D_0 = 2.369 \times 10^{-4} \text{ cm}^2/\text{sec.}$

Now, the next step was to determine the variation of Q and D_0 for a single group of experiments. The method for estimation of the variation of A and b is given by Dixon and Massey⁵⁰.

The variation limit is defined as:

for b
$$\frac{\pm t_1}{2} \frac{S_{XY}}{S_X(m-1)^2}$$
 F-10

and for A
$$\pm t_{\frac{1}{2}} \frac{XY}{m^{\frac{1}{2}}}$$
. F-11

where $t_{\frac{1}{2}}$ was given in table 2.1 (reference 49) as a function of the degrees of freedom and confidence limit.

$$S_{XY}^{2} = \frac{m-1}{m-2} (S_{Y}^{2} - b_{X}^{2}S_{X}^{2})$$
 F-12

$$s^{2}y = \frac{\frac{m}{\Sigma}Y_{1}^{2} - \frac{(\frac{m}{\Sigma}Y_{1})^{2}}{m}}{\frac{m}{m} - \frac{1}{m}}$$
 F-13

$$S_{\chi}^{2} = \frac{\sum_{\chi}^{m} 2_{1} - \frac{(2\chi_{1})}{m}}{m - 1}$$
 F-14

The calculation of the variation of Q and D_0 for the self-diffusion data of pure lead are listed below.

$$S_X^2 = 0.00913 \times 10^{-6}$$

 $S_Y^2 = 0.00594$
 $S_{XY} = 4.23 \times 10^{-2}$
 $m = 24$
 $t_x = 0.686 \text{ st. 50 percent}$

 $t_{\frac{1}{2}} = 0.686$ at 50 percent confidence limit

 $t_{\frac{1}{2}} = 1.717$ at 90 percent confidence limit.

Substituting these values in equations F-10 and F-11 we get for the variation in b and A at confidence limit of 50 and 90 percent respectively:

variation in b \pm 63.3 and \pm 158.5

variation in A $\pm 59.22 \times 10^{-4}$, $\pm 148.25 \times 10^{-4}$.

The variation in b times 2.303R gives the variation in Q as \pm 290 and \pm 725.0. The variation in D_o is also

 $\pm 0.032 \times 10^{-4}$ and $\pm 0.0086 \times 10^{-4} \text{ cm}^2/\text{sec.}$ Then: D = (2.369 ± 0.032) 10⁴ Exp. - (3117 ± 290)/RT.

The variation of Q and D_0 for all systems are calculated at a 90 percent confidence limit and are summarized in Table F-6.

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TABLE F-1

STANDARD DEVIATION FOR SELF-DIFFUSION COEFFICIENT OF PURE LIQUID CADMIUM AND LEAD

· · · · · · · · · · · · · · · · · · ·					
Temperature °C	Number of Determinations n	Standard Deviation 10 ⁵ cm ² /sec	Standard Deviation of the Average 10 ⁵ cm ² /sec		
PURE LEAD					
360.75 357.60 399.50 435.75 483.52	4 6 8 3 4	0.135 0.158 0.133 0.297 0.354	0.078 0.065 0.047 0.171 0.177		
PURE CADMIUM					
360.00 399.40 440.15 490.55	3 5 3 4	0.264 0.175 0.238 0.148	0.152 0.078 0.137 0.074		

STANDARD DEVIATION OF SELF-DIFFUSION COEFFICIENT OF CADMIUM FOR VARIOUS COMPOSITIONS IN LIQUID CADMIUM-LEAD ALLOY				
Temperature	Number of Determination	Standard ns Deviation	Standard Deviation of the Average	
°C	n	$10^5 \text{ cm}^2/\text{sec}$	$10^5 \text{ cm}^2/\text{sec}$	
9.13 ± 0.01	Weight percent	Cadmium (15.626 At	tomic percent)	
289.85	2	0.085	0.060	
329.85	3	0.252	0.145	
301.00	5	0.209	0.129	
410.25	3	0.271	0.156	
17.40 ± 0.01	Weight percent	Cadmium (27.97 A	tomic percent)	
289.85	5	0.233	0.104	
329.85	3	0.062	0.036	
369.85	3	0.306	0.177	
410.00	2	0.136	0.000	
31.00 ± 0.01	Weight percent	Cadmium (45.3 At	omic percent)	
290.55	3	0.169	0.098	
330.50	2 .	0.148	0.104	
3/1.05 411 00	3 3	0.145	0.065	
		0.115		
45.00 ± 0.01	. Weight percent	Cadmium (60.13 A	tomic percent)	
289.85	3	0.385	0.222	
329.85	3	0.244	0.140	
3(2.05	3	0.938	0.540	
CC+10T	د 	0.294	0.1(0	

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Temperature °C	Number of Determinations n	Standard Deviation 10 ⁵ cm ² /sec	Standard Deviation of the Average 10 ⁵ cm ² /sec
69.00 ± 0.01	Weight percent	Cadmium (80.403	Atomic percent)
290.00 330.35 371.35 410.35	3 3 3 3	0.272 0.115 0.083 0.383	0.157 0.066 0.048 0.221
2.5 ± 0.01 W	eight percent Ca	dmium (4.513 Ato	omic percent)
341.00 390.50 440.50	3 3 3	0.333 0.309 0.136	0.245 0.178 0.078

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STANDARD DEVIATION OF SELF-DIFFUSION COEFFICIENT OF LEAD FOR VARIOUS COMPOSITION IN LIQUID CADMIUM-LEAD ALLOY

· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·
Temperature	Number of Determination	Standard Deviation	Standard Deviation of the Average
° C	n	10 ⁵ cm ² /sec	$10^5 \text{ cm}^2/\text{sec}$
9.13 ± 0.01	Weight percent (Cadmium (27.87)	Atomic percent)
289.30 329.85 370.15 411.45	3 3 3 2	0.181 0.303 0.171 0.534	0.104 0.175 0.099 0.308
17.40 ± 0.01	Weight percent (Cadmium (27.85	Atomic percent)
290.90 330.55 371.25 411.00	3 2 2 3	0.135 0.070 0.114 0.265	0.078 0.040 0.066 0.153
31.00 ± 0.03	l Weight percent	Cadmium (45.30	Atomic percent)
291.35 329.85 370.85 409.85 456.75	3 3 3 3 3	0.157 0.158 0.071 0.028 0.074	0.091 0.091 0.041 0.016 0.043
45.00 ± 0.0	l Weight percent	Cadmium (60.13	Atomic percent)
290.00 330.85 370.20 411.45 456.00	3 3 3 2 3	0.258 0.122 0.286 0.197 0.566	0.149 0.070 0.165 0.139 0.326

Temperature	Number of Determinations	Standard Deviation	Standard Deviation	
°C	n	$10^5 \text{ cm}^2/\text{sec}$	of the Average 10 ⁵ cm ² /sec	
69.00 ± 0.0 1	Weight percent Ca	dmium (80.403	Atomic percent)	
290.85 330.85 374.00 410.85 454.85	3 3 3 3 3 3 3 2	0.166 0.057 0.270 0.108 0.391	0.096 0.033 0.155 0.062 0.277	
97.00 ± 0.01	Weight per cent (admium (98.35	Atomic percent)	
340.00 393.00 434.00	2 3 3	0.10 6 0.285 0.145	0.075 0.171 0.086	
2,5 ± 0.01 W	eight percent Cadn	nium (4.513 Atc	omic percent)	
432.00	3	0.344	0.276	

TABLE F-3--continued

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COEFFICIENT FOR VARIOUS COMPOSITION OF LIQUID CADMIUM-LEAD ALLOY						
Temperature	Number Determin	of ations	Sta Dev	indard viation	s I of t	Standard Deviation the Average
° C	n		10 ²	cm ² /se	c 10 ⁵	5 cm ² /sec
Capillary Reservoir	Alloy Alloy	9.13 <u>+</u> 13.05 <u>+</u>	0.01 0.01	Weight Weight	percent percent	; Cadmium ; Cadmium
360.40	7 3		C).264		0.100
440.70 482.60	32		C C).132).219		0.076 0.055
Capillary Reservoir	Alloy Alloy	15.4 ± (19.4 ± (0.01 W 0.01 W	leight leight	percent percent	Cadmium Cadmium
357.75 400.75	3		C).238).135		0.1 37 0.078
439.40 480.30	33		().166).318		0.096 0.183
Capillary Reservoir	Alloy Alloy	33.00 ± 28.00 ±	0.01 0.01	Weight Weight	percent percent	t Cadmium t Cadmium
359 .6 0 401.50	3		().154		0.089 0.0 6 4
438.25 483.85	33		(0. 4 39 0. 3 81		0.254 0.220
Capillary Reservoir	Alloy Alloy	44.00 ± 46.00 ±	0.01 0.01	Weight Weight	percent	t Cadmium t Cadmium
359.00 400.00	3		(0.0 3 1 0.110		0.018 0.063
439.00 483.85	33		(0.243		0.140 0.122

STANDARD DEVIATION OF CHEMICAL-DIFFUSION DEFFICIENT FOR VARIOUS COMPOSITION OF LIQU

Temperature °C	Nun Deter	nber mir n	r of nation:	3	Sta Dev 10 ⁵	andard viation cm ² /sec	Sta Dev of the 10 ⁵ d	andard viation Average cm ² /sec
Capillary Reservoir	Alloy Alloy		64. 04 70.00	± ±	0.01 0.01	Weight Weight	percent percent	Cadmium Cadmium
359.00 360.80 400.05 441.85 481.50		33433				0.243 0.205 0.096 0.158 0.177	((((0.140 0.118 0.048 0.091 0.102
Capillary Reservoir	Alloy Alloy		2.037 2.50	+ + +	-0.01 0.01	Weight Weight	percent percent	Cadmium Cadmium
340.00 390.10 436.00		3 3 3 3				0.337 0.177 0.162	((;	0.195 0.102 0.094
Capillary Reservoir	Alloy Alloy		95.00 97.00	+++	0.01 0.01	Weight Weight	percent percent	Cadmium Cadmium
338.10 390.00 440.00		3 3 3			· : (0.158 0.031 0.292		0.091 0.018 0.169

TABLE F-4--continued

JOINT STANDARD DEVIATION FOR THE DIFFUSION COEFFICIENTS VERSUS CONCENTRATION

	· · · · · · · · · · · · · · · · · · ·
Concentration Weight percent	Joint Standard Deviation cm ² /sec x 10 ⁵
Cadmium Self-Diff	usion
2.50 9.13 17.40 31.00 45.00 69.00 100.00	0.273 0.287 0.218 0.145 0.538 0.235 0.200
Lead Self-Diffus	ion
0.00 9.13 17.40 31.00 45.00 69.00 97.00	0.205 0.291 0.180 0.110 0.334 0.206 0.209
Chemical Diffus	ion
2.268 11.09 17.40 31.00 45.00 67.02 96.00	0.239 0.217 0.236 0.306 0.171 0.176 0.193

ACTIVATION ENERGY AND D_o WITH THEIR VARIATION AT 90 PERCENT CONFIDENCE LIMIT

Alloy Composition Weight percent Cadmium	Activation Energy Kcal/mole	$D_{o} \ge 10^{+4}$ cm^2/sec			
	Chemical Diffusion	•••			
2.268 11.090 17.400 31.000 45.000 67.020 96.000	$\begin{array}{r} 3.903 \pm 1.472 \\ 3.375 \pm 1.026 \\ 4.017 \pm 0.994 \\ 3.958 \pm 0.846 \\ 3.857 \pm 0.974 \\ 3.707 \pm 1.009 \\ 4.971 \pm 1.280 \end{array}$	5.184 \pm 0.359 2.918 \pm 0.140 4.515 \pm 0.221 4.228 \pm 0.182 3.725 \pm 0.183 3.538 \pm 0.179 10.660 \pm 0.680			
C	admium Self-Diffusion				
2.500 9.130 17.400 31.000 45.000 69.000 100.000	5.596 \pm 1.482 5.290 \pm 1.139 4.549 \pm 0.841 4.281 \pm 1.180 4.357 \pm 1.614 4.076 \pm 0.820 3.305 \pm 0.384	$\begin{array}{r} 19.400 \pm 1.410 \\ 18.530 \pm 1.020 \\ 11.910 \pm 0.500 \\ 8.428 \pm 0.281 \\ 10.480 \pm 1.010 \\ 6.800 \pm 0.336 \\ 3.621 \pm 0.065 \end{array}$			
Lead Self-Diffusion					
0.000 9.130 17.400 31.000 45.000 69.000 97.000	$\begin{array}{r} 3.117 \pm 0.725 \\ 3.808 \pm 1.815 \\ 4.214 \pm 0.702 \\ 3.513 \pm 0.628 \\ 3.090 \pm 0.690 \\ 5.018 \pm 0.978 \\ 5.903 \pm 1.160 \end{array}$	$\begin{array}{r} 2.369 \pm 0.086 \\ 4.923 \pm 0.540 \\ 6.573 \pm 0.357 \\ 4.214 \pm 0.200 \\ 3.353 \pm 0.173 \\ 13.420 \pm 0.930 \\ 23.660 \pm 1.180 \end{array}$			