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IS-1325

Chemistry (UC-4)
TID-4500, November 1, 1965

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

DETERMINATION OF LIQUID METAL DIFFUSION COEFFICIENTS BY MOLECULAR DISTILLATION

by

C. H. Buell and F. O. Shuck

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IN NUCLEAR SCIENCE ABSTRACTS

February, 1966

Ames Laboratory
at
Iowa State University of Science and Technology
F. H. Spedding, Director
Contract W-7405 eng-82

IS-1325

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IS-1325

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DETERMINATION OF LIQUID METAL DIFFUSION
COEFFICIENTS BY MOLECULAR DISTILLATION*

C. H. Buell and F. O. Shuck

ABSTRACT

A study of the feasibility of measuring liquid metal diffusion coefficients during molecular distillation was conducted. Although no other data for the zinc-indium system are available, a comparison with similar systems at this temperature (450°C) indicates that the value measured ($1.69 \times 10^{-4} \text{ cm}^2/\text{sec}$) is high by a factor of two to five. The major error in the measurements appears to be caused by the fact that the non-volatile indium is more dense than the volatile zinc.

* This report is based on the M. S. Thesis submitted by C. H. Buell, August, 1965 to Iowa State University, Ames, Iowa.

INTRODUCTION

Over the past several years the diffusion of molecules and ions in aqueous and organic solvents has been studied quite extensively. There is at present, however, very little information available concerning diffusion in liquid metals. This lack is perhaps due in part to a lack of interest in mass transfer processes in liquid metals and in part to the difficulties encountered in determination of diffusion coefficients for such systems. Current interest in purification processes for metal mixtures which involve metals in the liquid phase, such as distillation and fused-salt-molten-metal extraction techniques, indicates an increased need for this diffusion information.

Recently Walsh¹⁶ has established the fact that, under certain conditions, liquid phase diffusion may be a controlling factor in the purification of liquid metal mixtures by molecular distillation. The purpose of this investigation was to determine the feasibility of accurately measuring liquid metal diffusion coefficients by refining the equipment and techniques used by Walsh.¹⁶

Molecular distillation of liquid metals is normally used to separate a volatile metal from an essentially non-volatile component. In this process the volatile metal is vaporized from the mixture under a vacuum. If the rate of vaporization of the volatile component from the surface is more rapid than the rate of replacement of this component at the surface by diffusion through the liquid phase, a concentration gradient will be established within the liquid and the surface concentration of the volatile

component will remain at a lower concentration than that of the bulk of the mixture. Using Fick's law and appropriate boundary conditions, it is possible to determine the diffusion coefficient as a function of the total mass of metal vaporized and the surface concentration at a given time during the distillation.

In this investigation, zinc, as a volatile component, was distilled from mixtures with indium at 450°C. The surface concentration was determined continuously by x-ray fluorescence techniques and the total distillation rate was determined by weight loss of the sample.

Measurement of Liquid Metal Diffusion

Diffusion coefficients of liquids have been measured by the capillary cell method, the diaphragm cell method, the segmented cell method and the constant flux method. However, the capillary cell method has been the only technique applied extensively to the measurement of diffusion in liquid metals. Although a form of this method was used as early as 1850,³ its use was limited because of the duration of experiments and the analytical difficulties involved in measuring small concentration changes for small samples. This technique was revived in 1948 by Anderson and Saddington,¹ who measured the diffusion of tungstate ions in aqueous solution using radioactive tungsten 187. The technique is well suited to studies using radioactive materials, since only a small quantity of the diffusing material is required. Hence, most of the diffusion data available for liquid metals concerns self-diffusion. However, several binary systems have been

investigated. Those which have been investigated are: Ag-Sn,⁷ Bi-Sn,¹² Cd-U,⁵ Pb-Bi,^{2, 12} Pb-Cd,¹² Pb-Sb,¹² Pb-Sn,¹² Sn-Sb,¹².

In the capillary cell method a small capillary 0.5 to 3.0 mm in diameter and 3 to 5 cm long is filled with an alloy and placed in a bath of pure metal solvent. After the solute in the alloy diffuses into the bath for a sufficient time, the capillary is removed and the contents cooled. The diffusion coefficients may be determined either from an analysis of the concentration gradients in the solidified sample or from the bulk composition using appropriate solutions of Fick's law. The diffusion coefficients obtained in this way are thought to be within $\pm 10\%$ of the actual values; however, conflicting results have been obtained by different investigators, particularly in the case of high initial solute concentrations. For example, Niwa, et. al.¹² have reported diffusion coefficients for a 50% lead-bismuth alloy which differ from those reported by Grace and Derge² by a factor of 100. Difficulties with this technique include: "end effects" caused by localized concentration gradients at the end of the tube, variation of results with tube diameter, effects of volume changes on melting and solidification and the inherent problem of analysis of small quantities of material. These difficulties indicate that new experimental techniques should be investigated.

Mathematical Relations

The technique used in the present investigation involves distillation of a volatile metal from a stagnant alloy. Under these conditions Walsh¹⁶

has shown that the surface concentration is given by

$$\frac{C_s}{C_o} = \exp\left(-\frac{\alpha^2 t}{D}\right) \operatorname{erfc} \sqrt{\frac{\alpha^2 t}{D}} \quad (1)$$

where, C_s = surface concentration of the volatile component

C_o = initial uniform concentration of the volatile component

t = total time of distillation

D = diffusion coefficient

and α , the proportionality constant between surface concentration and instantaneous distillation rate, is given by

$$\alpha = \frac{G}{A_s \int_0^t C_s d\theta} \quad \frac{\text{cm}}{\text{sec}} \quad (2)$$

where, G = The total grams of volatile component distilled over time t

A_s = The surface area of the distilling melt.

Using these relations and the experimental data for C_s as a function of time during the distillation, the value of the diffusion coefficient, D , may be calculated.

EQUIPMENT

The equipment used for this investigation is shown schematically in Fig. 1. It consists of an electrical resistance furnace, stainless steel vaporization chamber, vacuum system, temperature and vacuum measuring instruments, tungsten x-ray tube, and x-ray spectrometer equipment. Except for minor modifications, it is basically the same equipment as that used by Walsh.¹⁶

Fig. 1. Schematic drawing of equipment

Surface Concentration Measurements

The x-ray equipment was used to measure the surface concentration of the indium-zinc alloy during the molecular distillation. X-rays were produced by a Machlett OEG-50 x-ray tube. The 50,000 volt Phillip's x-ray power supply was operated at 40,000 volts and 20 mA. The voltage input to the power supply was maintained at a constant level by a voltage stabilizer.

The x-ray tube generates polychromatic primary x-rays which are collimated into a narrow beam and directed toward the metal surface. At the surface these x-rays interact with the indium and zinc to produce secondary K-x-rays. (Secondary L-x-rays are also produced, but are of such low energy that they are scarcely detectable) since indium and zinc emit K-x-rays at different energies the concentration of a given sample may be measured by comparing the relative intensities of the indium and zinc K-x-rays. The zinc x-ray intensity alone may be used to determine the zinc concentration if the intensity and orientation of the primary beam is the same for each determination. The secondary x-rays produced are analyzed by passing through the acceptor tube to a thallium-activated sodium iodide crystal scintillation detector which converts them to light impulses which are then converted to electrical impulses by a photomultiplier tube operated at a potential of 1150 volts. The signal is then transmitted through a preamplifier and amplifier to a differential single-channel pulse-height analyzer, operated with a window width of 3.0 volts, which separates the signal according to its energy level. The output of the single-channel analyzer is monitored by

Fig. 2. Typical indium-zinc x-ray spectrum

Fig. 3. Indium-zinc calibration curves

a high-speed scalar from which the x-ray count rate is determined at any desired position along the x-ray spectrum.

Figure 2 shows the x-ray spectrum for an indium-zinc alloy containing 20% zinc.* Figure 3 shows a plot of maximum indium and zinc count rates as a function of zinc concentration. This plot was used as a calibration curve for determination of zinc concentration from measured count rates. The shapes of these calibration curves agree with the theoretical equation presented by Liebhafsky.⁸ The equation for zinc x-ray intensity as a function of concentration is:

$$I_{Zn} = K \frac{x}{x(U_{Zna} + U_{Zne}) + (1-x)(U_{Ina} + U_{Ine})} + b \quad (3)$$

where, I_{Zn} = zinc x-ray intensity

x = weight fraction of zinc

U_{Zna} = zinc x-ray mass absorption coefficient

U_{Zne} = zinc x-ray mass emission coefficient

U_{Ina} = indium x-ray mass absorption coefficient

U_{Ine} = indium x-ray mass emission coefficient

b = back ground intensity

Using x-ray absorption and emission data⁶ for indium and zinc Eq. (3) becomes:

$$I_{Zn} = K \frac{x}{x(33) + 290} + b \quad (4)$$

*All concentrations given are weight percent.

At low zinc concentrations this equation degenerates into a straight line. Consequently, a least squares fit to a straight line was applied to the data between 0% and 20% zinc to determine b and K. The resulting equation is:

$$I_{Zn} = 7.9 \times 10^5 \left[\frac{x}{33x + 290} \right] + 121 \quad (5)$$

Using a similar technique the indium intensity was found to be:

$$I_{In} = 5.13 \times 10^4 \left[\frac{1 - x}{55 - 31x} \right] + 214 \quad (6)$$

Vaporization Chamber

The stainless steel vaporization chamber is shown in Fig. 4. It is 3 in. i. d. and 12 in. high. During operation the chamber was placed in a graphite block which rested inside the resistance furnace. The upper part of the chamber was water cooled to prevent overheating the condenser flange, the connection to the vacuum system, and the neoprene O-ring in the conax fitting which contained the thermocouple leads.

Vacuum System

The vaporization chamber was connected to a copper manifold system which contained a vacuum thermocouple gauge, an ionization gauge, an argon gas inlet and a diffusion pump by-pass line. When the chamber pressure was above 200 μ , the forepump was connected directly to the vaporization chamber, by-passing the diffusion pump. Below 200 μ pressure the forepump, diffusion pump and vaporization chamber were connected in series. Using the forepump and diffusion pump combination pressures as low as 0.02 μ could be obtained.

Fig. 4. Vaporization Chamber

Condenser System

A profile view of the condenser system is shown in Fig. 5. A $1/8$ in. i.d., 5 in. long stainless steel tube was inserted through the condenser flange to collimate the primary x-rays. This tube was fitted with a special attachment so that the x-ray tube could be connected in exactly the same position for all experiments. A $3/8$ in. i.d., 5 in. long stainless steel tube was also inserted through the flange to channel the secondary x-rays to the scintillation detector. The two tubes were vacuum sealed by cementing 0.00025 in. mylar sheeting to the top surfaces with Eastman 910 adhesive.

The condenser system was required to prevent condensation of zinc on the mylar windows. It was designed to condense as much zinc vapor as possible without being so large as to interfere with the x-ray beams. The primary condensation surface was an annular ring $2\ 3/4$ in. o.d. and $1\ 1/2$ in. i.d., extending $7\ 1/2$ in. below the top of the flange. When inserted into the vaporization chamber this surface was about $2\ 1/2$ in. above the surface of the distilling metal. Although the diameter of the crucible containing the distilling sample was only 1.0 in., which was less than the inside diameter of the condenser, the condenser was effective in preventing condensation on the mylar windows.

The condenser could be cooled either by circulating water through the annular ring or by allowing the heat to conduct through the copper water tubing to the top of the flange which was water cooled. The latter method was used to prevent excessive radiation losses from the sample surface.

PROFILE OF THE CONDENSER SYSTEM

Fig. 5. Schematic drawing of the condenser system

For zinc distilling at 450°C calculations showed that the condenser surface would be at 365°C. Although this temperature was not verified experimentally, the condenser was effective in condensing zinc which has a melting point of 419°C.

Argon Purifier

In an effort to eliminate a source of oxygen for oxide formation, the argon used was purified by passing through a bed of zirconium turnings at 650°C. Although this technique reduced the oxygen content of the argon below the one part per million originally present, it did not eliminate formation of oxide on the sample during distillation.

Operation of Equipment

Prior to a distillation run, the vaporization chamber and crucible were outgassed at 700°C until the pressure dropped to 1 μ . When this pressure was reached, the furnace was switched off and the system was allowed to cool, under vacuum, to room temperature. Both alumina and graphite crucibles were used to contain the alloy during distillation runs. Both were 1.0 in. i.d. and 2 1/2 in. deep. The alumina crucibles were weighed after outgassing. However, the graphite crucibles were not weighed since they sustained additional weight loss by decomposition during a diffusion run. It was also found that during the run the graphite crucibles produced small flakes of graphite which floated to the metal surface, changing the surface area available for vaporization.

The alloy was prepared from metal with a manufacturer's rating of 99.999% purity. Surface oxides were removed from the metal by etching with HCl for several minutes. The metal was then soaked in triple-distilled de-ionized water, washed with methyl alcohol, dried and weighed.

Two alternate procedures were used to melt the pure metal into an alloy. Either the metal was placed in a crucible and melted under an argon atmosphere in the vaporization chamber, or it was melted in a special crucible which could be capped. After placing the metals in this special crucible it was evacuated in a vacuum desiccator and filled with argon. It was then heated to 500°C in a furnace and shaken thoroughly to insure a uniform alloy. The molten metal was then poured out through a 1/16 in. hole in the cap, into an outgassed crucible which was submerged in liquid nitrogen. By pouring the metal through the small hole it was possible to remove most of the oxides formed during melting since they clung to the walls of the crucible. The distillation crucible containing the metal alloy was allowed to warm to room temperature in a vacuum desiccator, then weighed and placed in the vaporization chamber. The vacuum pumps and furnace were switched on. The crucible and metal sample were allowed to outgas any absorbed nitrogen until the temperature reached about 200°C at which time the pressure was normally 1 μ . The valve to the pumping system was then closed and 2/3 of an atmosphere of argon introduced to prevent distillation loss as the chamber heated up to the steady-state temperature of 450°C. While the chamber was heating, the x-ray tube and scintillation detector were positioned and the x-ray

equipment switched on. The spectrometer equipment was turned on 48 hours prior to an experiment in order to eliminate drift.

When the steady temperature was reached, the distillation was started by opening the valve to the forepump. The pressure in the chamber dropped to $200\ \mu$ in about 1 min. At $200\ \mu$ pressure, the diffusion pump was connected. When the pressure reached $100\ \mu$, the timer was started. This pressure was chosen as the start of distillation as a result of the distillation data presented by Spendlove¹⁴ for zinc at low pressures. His data showed that the distillation rate increased as the pressure was reduced to this point and then became constant with further reduction in pressure. Since some zinc does distill at higher pressures, some "start-up" error is present.

During the distillation process, surface concentration was measured from the zinc x-ray count rate. The distillation time, crucible temperature and chamber pressure were also recorded.

A diffusion run normally lasted about 40 min. At the end of this time the valve to the pumping system was closed and one atmosphere of argon introduced to stop the distillation. After the chamber had cooled to room temperature, the alloy was removed from the chamber and weighed to determine the weight loss and distillation rate.

RESULTS AND DISCUSSION

Ten diffusion experiments were conducted during this investigation. Of these the results for five are shown in Fig. 6 to 10. The remaining

DIFFUSION RUN I

0.8499 GRAMS DISTILLED

$C_o = 6.085\% \text{ Zn}$

$C_b = 6.085\% \text{ Zn}$

$\alpha = 1.54 \times 10^{-4} \text{ cm/sec}$

$D = 1.79 \times 10^{-4} \text{ cm}^2/\text{sec}$

Fig. 6. Diffusion run I

Fig. 7. Diffusion run II

DIFFUSION RUN III

0.3140 GRAMS DISTILLED

$C_0 = 9.2\% \text{ Zn}$

$C_b = 7.18\% \text{ Zn}$

$a = 2.935 \times 10^{-5} \text{ cm/sec}$

$D = 1.46 \times 10^{-4} \text{ cm}^2/\text{sec}$

Fig. 8. Diffusion run III

DIFFUSION RUN IV

0.5962 GRAMS DISTILLED

$C_0 = 12.96\%$ Zn

$C_b = 10.94\%$ Zn

$\bar{a} = 3.73 \times 10^{-5}$ cm/sec

$\bar{D} = 1.41 \times 10^{-4}$ cm²/sec

Fig. 9. Diffusion run IV

Fig. 10. Diffusion run V

five were not considered because the total distillation was so low (less than 0.2 grams distilled) that accurate weight loss could not be determined. In the runs discarded, the low distillation rate was attributed to the heavy oxide layers observable on the sample surface. In fact, diffusion run II, Fig. 7, was the only sample which appeared to be completely oxide free at the end of the distillation.

Using Eq. (1) and (2), the diffusion coefficients for these runs were calculated for several times during the run. These coefficients are shown in Table I. Since the development of the equations used for this analysis assumed a constant value of D , the results of runs III and V were considered to be unreliable because of the large variation in the D calculated at different times during the run. The average value of D for the remaining three runs was $1.79 \times 10^{-4} \text{ cm}^2/\text{sec.}$

No other diffusion data for this system is presently available. However, comparison with data on other low melting-point metals at 450°C indicates that this value is, perhaps, a factor of 2 to 5 too high. The Sutherland-Einstein equation,

$$D = \frac{1}{4 \pi r} \left(\frac{kT}{\mu} \right), \quad (7)$$

for diffusing solute atoms of equal or smaller size than the solvent atoms, may be used to estimate a value of D from data on self-diffusion of indium. In using this equation for dilute zinc solutions, μ is the viscosity of pure indium and r the radius of the solute atom. Therefore,

Table 1. Summary of the data and results obtained from the diffusion experiments

Diffusion Run	C_{s_o}	C_s	t	$D \times 10^4$	$\bar{D} \times 10^4$
I	6.085%	4.83%	379 sec	1.87 $\frac{\text{cm}^2}{\text{sec}}$	1.79 $\frac{\text{cm}^2}{\text{sec}}$
		4.38	783	1.77	
		4.14	1259	2.03	
		3.63	1954	1.59	
II	16.0	12.20	360	2.12	1.87
		10.44	1000	2.15	
		8.68	2000	1.84	
		7.64	2640	1.51	
III	9.2	8.80	540	2.95	1.46 ^a
		8.44	960	1.32	
		8.07	1536	0.901	
		7.68	2040	0.610	
IV	12.96	11.78	760	1.38	1.41
		11.41	1470	1.47	
		11.04	2220	1.39	
V	26.5	22.00	600	7.19	5.26 ^a
		19.95	1200	5.82	
		18.09	1800	4.54	
		16.31	2400	3.51	

^aThis value was not considered because of the large variations in D during the diffusion run.

$$\frac{D_{\text{Zn - In}}}{D_{\text{In-Self}}} = \frac{r_{\text{In}}}{r_{\text{Zn}}} \quad (8)$$

Taking r_{In} as 1.66×10^{-8} cm and r_{Zn} as 1.38×10^{-8} cm, and using the self-diffusion data of Lodding⁹ ($D_{\text{In-Self}} = 5.32 \times 10^{-5}$ cm²/sec at 450°C) the mutual diffusion coefficient is calculated to be 6.40×10^{-5} cm²/sec. This value falls about a factor of three below the average value obtained from the experimental runs.

Oxides

It was found that with the best vacuum which could be produced with the equipment used that oxides could not be eliminated. Although no quantitative measure of oxide effects was made, a visual inspection indicated that for those tests for which the total distillation was very low, a heavy oxide layer was present at the end of the distillation period. A calculation of possible errors in measured concentrations because of the presence of the oxide layer indicated that the surface oxide should not affect the x-ray count rate.

Possible sources of oxygen for oxide formation include slow desorption from the sample crucible and undetected leaks. It was not possible to trace the source of the oxygen. Furthermore, it was not possible with the equipment used to observe, even qualitatively, the formation or rate of formation of oxide on the surface. Since the factor α contains all the factors contributing to the interfacial resistance, including oxides, and it was assumed that α remains constant; it is possible that a significant

error may have been introduced into the calculations if oxide formed gradually during the course of the run.

Non-Uniform Initial Concentration

Examination of Fig. 6 to 10 indicates that in all cases except run I the measured initial surface concentration was higher than the bulk concentration of the sample. This increase was attributed to the fact that the indium-zinc system forms a hypereutectic at 2.18% zinc.⁴ Since pure zinc is slightly less dense than the eutectic liquid at the eutectic melting point, the zinc tended to float to the surface as the sample was melted prior to distillation. Analysis of solid alloys prepared in the same manner as the distillation samples indicated that the rapidly solidified samples were uniform in concentration. The segregation occurred during the re-melting of the sample just prior to distillation. Since the distillation chamber was not provided with a stirrer to maintain uniform composition during melting, attempts were made to increase the heating rate to melt the sample faster and thereby minimize the segregation. This effort was not successful because the heating rate could be increased only slightly. It was not possible to analyze the exact nature of the gradient thus formed.

To determine the possible effect of this initial gradient, the data were analyzed in several ways. The coefficients shown in Table 1 were those obtained using Eq. (1) with C_b replaced by the measured initial surface concentration, C_{so} . The data were also analyzed by an equation

similar to Eq. (1) but derived on the basis of an initial linear gradient of zinc concentration rather than a uniform composition. Using various possible initial linear gradients, coefficients were calculated for the same runs. In general, these results were quite similar to those obtained by using a C_{so} in Eq. (1), so only those values obtained from Eq. (1) are reported. In particular, the more complicated analyses did not reduce the wide variation of D for runs III and V. It is not too surprising that this simple analysis leads to results very similar to those using more complicated initial conditions, since for the experimental conditions used, the penetration of the gradient formed during distillation should be less than 1 cm in a sample 5 to 6 cm deep.

Convection

In a liquid metal sample of the size used for this investigation one would expect to observe some convective effects. There are a number of possible causes of convection in such a system. The most obvious source is the presence of localized temperature gradients. Such gradients may be caused by uneven heating of the sample, radiation from the liquid surface or, in this case, by evaporative cooling at the surface since all vaporization takes place at the sample surface. It would be expected that these effects would be small since the high thermal conductivity of the metal will tend to dissipate such local gradients quite rapidly. Furthermore, it is unlikely that any significant fluctuations would be caused by unequal heating in the experimental equipment used. Vibrations of the

sample constitute another potential source of convective currents. An attempt was made to eliminate the major cause of vibration by insulating the vacuum pump from the distillation system. Visual observation indicated that the insulation significantly reduced the sample vibration. However, no effort was made to thoroughly insulate the system against vibrations present in the building.

The most likely cause of convection in the present case was the density gradient which formed as a result of the concentration gradient near the surface. It is readily apparent that as the concentration gradient develops during distillation, the system will become unstable if the non-volatile metal is more dense than the volatile component. When the present study was undertaken, it was assumed that zinc and indium had approximately the same density at 450°C, based on the density data given in the Liquid Metals Handbook¹⁰ for zinc ($\rho_{\text{Zn}} = 6.90 \text{ gm/cm}^3$) and that of McGonigal, et. al¹¹ for indium ($\rho_{\text{In}} = 6.82 \text{ gm/cm}^3$). Subsequent investigation indicates that the density of zinc at 450°C may be considerably less than that of indium ($\rho_{\text{Zn}} = 6.54 \text{ gm/cm}^3$, [ref. 15] $\rho_{\text{Zn}} = 6.63 \text{ gm/cm}^3$ [ref. 13]). Thus, it would seem that the major cause of convective mixing in the system was the fact that the volatile zinc was less dense than the non-volatile indium.

CONCLUSIONS

The diffusion coefficients obtained in this study appear to be high because of convection within the liquid sample. The major part of the convective error can be attributed to the fact that the non-volatile indium was more dense than the volatile zinc. Additional errors of unknown nature and extent are certainly present as a result of oxide formation on the distillation surface.

Although this technique has the potential for rapid and accurate measurement of liquid phase diffusion coefficients, it is restricted to a very limited number of systems, namely, those composed of one volatile and one non-volatile component in which the volatile component is the denser of the pair. Furthermore, much more elaborate techniques to eliminate vibration and other possible sources of convection should be used. Oxides which form on the surface must, also, either be eliminated or a method must be developed to analyze their effect on vaporization rate and their rate of formation.

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