

# Interdiffusion of Bi in Liquid Sn

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The diffusion coefficients for the interdiffusion of Bi in liquid Sn were determined using the thin layer, long capillary technique. The effect of 0.5, 0.8, and 1.6 mm diameter capillaries on the apparent diffusion coefficient was investigated. For any temperature up to 600 °C all three diameter capillaries yielded similar interdiffusion coefficients. At 700 °C, the 1.6 mm diameter capillaries yielded concentration-penetration profiles that exhibited considerable scatter and abnormally high diffusion coefficients, indicative of the presence of convective mixing. At 800 °C, both the 0.8 and 0.5 mm capillaries yielded considerable scatter in the concentration-penetration profiles and abnormally high diffusion coefficients. Because of agreement of the results for both the 0.5 and 0.8 mm capillaries up to and including 700 °C (and the 1.6 mm capillaries up to 600 °C), it was concluded that the interdiffusion coefficients obtained are accurate for the temperature range 300 to 700 °C with no significant contribution from buoyancy driven convection, capillary wall effects and/or Marangoni convection. The interdiffusion coefficient for the diffusion of Bi in liquid Sn can be represented by:  $D_{\text{Bi}}^{\text{Sn}} = \{3.4 \pm 0.6 \times 10^{-8}\} \{ \exp [-(13, 600 \pm 1200/RT)] \}$  m<sup>2</sup>/s. The results show that Bi diffuses in Sn at a slower rate than does Sn itself. In addition, it is possible that the interdiffusion coefficient may not be predicated on simple temperature dependence in at least some binary liquid metal systems, and that the diffusion coefficient may be affected by liquid/liquid phase transformations occurring at some temperature within the liquid.

**Keywords** binary diffusion, chemical diffusivity, composition profiles, diffusion constant, experimental study, interdiffusion

## 1. Introduction

Liquid metal diffusion is an important atomic transport phenomenon which influences the solidification and structure of cast materials including metals, polymers, and ceramics. Several theories have been advanced which attempt to predict atomic transport within liquid metals, but a single theory which accurately portrays liquid diffusion remains elusive. The development of an accurate theory has been hindered, at least in part, by discrepancies in experimental data reported in the literature (specifically for experiments performed at elevated temperatures). Of the numerous experimental methods available to determine liquid diffusion coefficients, most utilize a long cylindrical tube (capillary) containing a liquid metal couple. The capillary is orientated in the vertical position, in an effort to stabilize thermal and concentration gradients during experimentation. But, it has been suggested by several authors that experimental technique can significantly alter the value of the diffusion coefficient; for example, the use of the shear cell and capillary reservoir methods may introduce error by

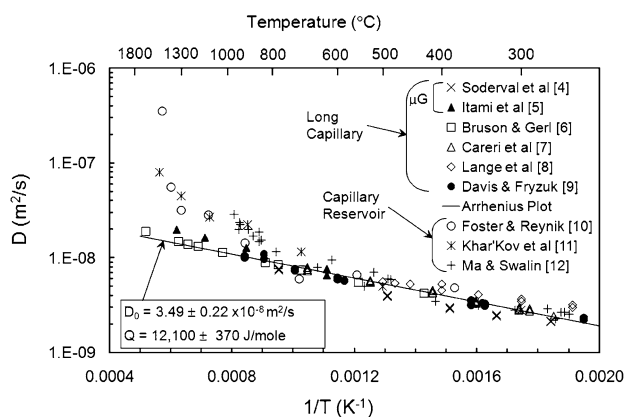
adding additional mass transport mechanisms inflating the value of the diffusion coefficient. One such mechanism is convective mixing, caused by density differences that arise in the melt during annealing within a furnace (difficult to avoid in unit gravity experimentation). But in the absence of gravity, the effect of the density difference is negligible, and experimentation at elevated temperatures generally yields diffusion coefficients that are lower than similar experiments conducted on earth. Unfortunately, microgravity experimentation, although effective, is cost prohibitive and subject to other sources of error such as accelerations caused by vibrations and g-jitter.<sup>[1]</sup>

In a recent investigation, Lee et al.<sup>[2]</sup> determined diffusion coefficients for the interdiffusion of Cu in Al from the measurement of the composition profile ahead of a quenched planar solid-liquid interface. They reported that a systematic reduction of capillary diameter had a stabilizing effect upon convection within the capillary (via minimization of horizontal/radial temperature gradients across the capillary walls during annealing), resulting in consistent diffusion coefficients below a specific capillary diameter. This systematic approach is based upon the hypothesis that the convective atomic transport within the capillary occurs once a specific threshold is overcome, following the Rayleigh's equation as given by

$$Ra = \frac{\beta_T g_0 \Delta T_H H^3}{\nu D} \quad (\text{Eq 1})$$

where  $Ra$  is the Rayleigh's number,  $\beta_T$  is the thermal expansion coefficient,  $g_0$  is the gravity level,  $\nu$  is the kinematic viscosity,  $H$  is the lateral dimension of the capillary,  $\Delta T_H$  is a measure of the horizontal temperature difference, and  $D$  is the diffusion coefficient.

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**Fig. 1** Experimental results for solvent self-diffusion in liquid Sn

In this research, a similar systematic reduction of diameter using the long capillary thin film technique was used to determine interdiffusion coefficients for the diffusion of Bi in Sn under unit gravity conditions. The Bi-Sn system was chosen for experimentation because of low melting temperatures, ease of handling, and the availability of accurate liquid diffusion data for Sn solvent self diffusion<sup>[3]</sup> which serves as a reference for experimental findings. A summary of the solvent self diffusion coefficients for liquid Sn is presented in Fig. 1 where the diffusion coefficient given by  $D_{\text{Sn}} = \{3.49 \pm 0.22 \times 10^{-8}\} \{\exp [-(12,100 \pm 370)/RT]\}$  m<sup>2</sup>/s was determined from the least squares best fit line for the six long capillary studies that avoided use of the capillary reservoir technique.<sup>[3]</sup>

## 2. Experimental

Diffusion couples were prepared using Sn as the solvent material and Bi as the solute. Sn was obtained in the form of wire in the as drawn condition with diameters of 1.6, 1.0, and 0.5 mm at 99.999% purity, while the Bi came in powder form at 99.999% purity.

The 0.8 mm diameter wire was prepared by manually cold rolling 1.0 mm diameter segments back and forth between two steel plates. The graphite rod used for all experiments was 13 mm in diameter, and of 99.997% purity. Three sets of capillaries were created by drilling 1.6, 0.8, and 0.5 mm diameter holes into the center of the graphite rods. The capillary length was set at 80 mm for the 1.6 mm diameter capillaries, and 50 mm for the 0.8 and 0.5 mm diameter capillaries. The thin cylindrical Bi disks were created by sectioning graphite capillaries containing cast solute, and each disk was individually weighed. In the diffusion couple, the Bi film was placed at the bottom of the capillary, and the remaining volume was filled with Sn wire.

Specimens were diffusion annealed within a vacuum furnace under an inert Argon environment. Diffusion temperatures ranged from 573 to 1073 K and diffusion times from 2.5 to 6 h. Upon solidification, the diffusion specimens were

mounted in plastic and polished to 0.25  $\mu\text{m}$  in preparation for analysis. Quantitative compositional analysis was performed using a JEOL 9000 scanning electron microscope equipped with an Oxford Instruments energy dispersive spectrometer. The concentration versus distance distribution was determined in 1 mm increments across the length of the specimen.

The interdiffusion coefficient,  $D$ , was calculated from the concentration-penetration curves using the thin disc solution of Fick's second law given by<sup>[13]</sup>:

$$C(x, t) = \frac{bC_0}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \quad (\text{Eq 2})$$

where  $C$  is the concentration at distance  $x$ ,  $C_0$  is the initial concentration of the solute film,  $b$  is the thickness of the solute disk, and  $t$  is the time of the diffusion anneal. In Eq 2 the effective film thickness,  $b$ , was accurately determined using the equation  $b = 4w/\rho\pi d^2$ , where  $w$  is the weight of the solute disk,  $\rho$  is its liquid density, and  $d$  is the capillary diameter. It has been standard practice to calculate the diffusion coefficient from the slope,  $M$ , of the plot of  $\ln C(x, t)$  versus  $x^2$  which gives the diffusion coefficient,  $D_M$ , from:

$$D_M = [-1/(4Mt)] \text{ m}^2/\text{s}. \quad (\text{Eq 3})$$

However, much more information can be gleaned from Eq 2. The intercept,  $I$ , of the  $\ln C(x, t)$  versus  $x^2$  plot is given by:

$$I = \ln\left(\frac{bC_0}{\sqrt{\pi Dt}}\right), \quad (\text{Eq 4})$$

from which a second value of  $D$  can be extracted since the values of all the components of Eq 4 are known. (A value for  $b$  can even be obtained for a very thin plating of radioactive tracer since the total amount of tracer is given by the area under the concentration-penetration curve.) The diffusion coefficient calculated from the intercept,  $D_I$ , is therefore given by:

$$D_I = \left[\frac{1}{\pi t}\right] \left[\frac{bC_0}{\exp(I)}\right]^2 \text{ m}^2/\text{s}. \quad (\text{Eq 5})$$

A third value for the diffusion coefficient can be determined directly from Eq 2 by calculating the value of diffusivity,  $D_C$ , that gives the least squares best fit concentration-penetration curve.

## 3. Results and Discussion

The three diffusion coefficients for the interdiffusion of Bi in liquid Sn calculated from Eq 2, 3, and 5 for capillary diameters of 0.5, 0.8, and 1.6 mm are presented in Table 1, 2, and 3, respectively. The error limits in Table 1 to 3 for the coefficients determined from the concentration profiles ( $D_C$ ) were calculated using non-linear regression analysis. The error limits for the diffusion coefficients determined from the slopes and intercepts of the  $\ln C(x, t)$  versus  $x^2$ , Eq 3 and 5, were calculated from the standard deviations of the slopes

**Table 1 Diffusion coefficients for Bi in liquid Sn using 0.5 mm capillaries**

Temperature, K	Time, s	Diffusion coefficient, $10^{-9} \text{ m}^2/\text{s}^1$				
		$D_C$	$D_M$	$D_I$	$D_{AV} \text{ (CMI)}$	$D_{AV} \text{ (T)}$
573	10800	$2.47 \pm 0.06$	$2.37 \pm 0.09$	$2.26 \pm 0.23$	2.37	
573	10800	$2.62 \pm 0.05$	$2.58 \pm 0.03$	$2.52 \pm 0.10$	2.57	2.47
673	10800	$2.29 \pm 0.07$	$2.73 \pm 0.13$	$2.77 \pm 0.30$	2.60	
673	10800	$1.98 \pm 0.06$	$2.25 \pm 0.07$	$2.34 \pm 0.22$	2.19	2.40
773	10800	$3.28 \pm 0.20$	$3.46 \pm 0.28$	$3.20 \pm 0.38$	3.31	
773	10800	$3.79 \pm 0.08$	$3.95 \pm 0.08$	$3.86 \pm 0.21$	3.87	3.59
873	10800	$4.78 \pm 0.06$	$5.09 \pm 0.08$	$5.05 \pm 0.21$	4.97	
873	10800	$4.17 \pm 0.09$	$4.39 \pm 0.07$	$4.32 \pm 0.19$	4.29	4.63
973	10800	$6.17 \pm 0.15$	$7.40 \pm 0.22$	$7.77 \pm 0.67$	7.11	
973	10800	$7.14 \pm 0.20$	$6.80 \pm 0.24$	$7.14 \pm 0.51$	7.03	7.07
1073	5400	$26.5 \pm 0.93$	$30.10 \pm 0.96$	$28.4 \pm 1.90$	28.3	28.3

**Table 2 Diffusion coefficients for Bi in liquid Sn using 0.8 mm capillaries**

Temperature, K	Time, s	Diffusion coefficient, $10^{-9} \text{ m}^2/\text{s}$				
		$D_C$	$D_M$	$D_I$	$D_{AV} \text{ (CMI)}$	$D_{AV} \text{ (T)}$
673	10800	$3.05 \pm 0.12$	$3.33 \pm 0.12$	$3.06 \pm 0.21$	3.15	
673	10800	$3.03 \pm 0.16$	$3.00 \pm 0.11$	$2.79 \pm 0.20$	2.94	3.05
773	10800	$3.56 \pm 0.08$	$3.66 \pm 0.07$	$3.62 \pm 0.18$	3.61	
773	10800	$3.18 \pm 0.08$	$3.85 \pm 0.14$	$3.96 \pm 0.40$	3.67	3.64
873	10800	$4.19 \pm 0.16$	$4.73 \pm 0.10$	$4.90 \pm 0.20$	4.61	
873	10800	$6.18 \pm 0.22$	$6.98 \pm 0.21$	$7.25 \pm 0.31$	6.80	5.71
973	10800	$6.41 \pm 0.29$	$6.73 \pm 0.30$	$6.13 \pm 0.46$	6.42	
973	10800	$6.69 \pm 0.36$	$8.10 \pm 0.36$	$6.82 \pm 0.04$	7.20	6.81
1073	10800	$8.99 \pm 1.16$	$15.67 \pm 3.30$	$9.48 \pm 0.84$	11.4	
1073	10800	$11.51 \pm 0.90$	$15.57 \pm 1.60$	$12.29 \pm 1.30$	13.1	12.3

**Table 3 Diffusion coefficients for Bi in liquid Sn using 1.6 mm capillaries**

Temperature, K	Time, s	Diffusion coefficient, $10^{-9} \text{ m}^2/\text{s}$				
		$D_C$	$D_M$	$D_I$	$D_{AV} \text{ (MIC)}$	$D_{AV} \text{ (T)}$
773	21600	$3.93 \pm 0.06$	$4.05 \pm 0.07$	$4.05 \pm 0.23$	4.01	
773	21600	$4.41 \pm 0.08$	$4.27 \pm 0.08$	$4.20 \pm 0.22$	4.29	
773	21600	$4.18 \pm 0.08$	$4.13 \pm 0.09$	$4.01 \pm 0.23$	4.11	
773	21600	$4.42 \pm 0.07$	$4.57 \pm 0.12$	$4.67 \pm 0.37$	4.55	4.24
873	21600	$5.20 \pm 0.08$	$5.52 \pm 0.13$	$5.46 \pm 0.34$	5.39	
873	21600	$4.82 \pm 0.09$	$5.50 \pm 0.16$	$5.42 \pm 0.25$	5.25	5.32
973	21600	$7.48 \pm 0.14$	$7.54 \pm 0.15$	$7.09 \pm 0.33$	7.37	7.37
973	21600	$15.85 \pm 0.68$	$22.25 \pm 0.87$	$17.75 \pm 1.31$	18.6	
973	21600	$16.29 \pm 0.74$	$20.35 \pm 2.10$	$16.66 \pm 1.38$	17.8	18.2

and intercepts. In Table 1 to 3, the average value of the diffusion coefficient,  $D_{AV}$ , is simply the average of the three determinations,  $D_C$ ,  $D_M$ , and  $D_I$  for each sample.

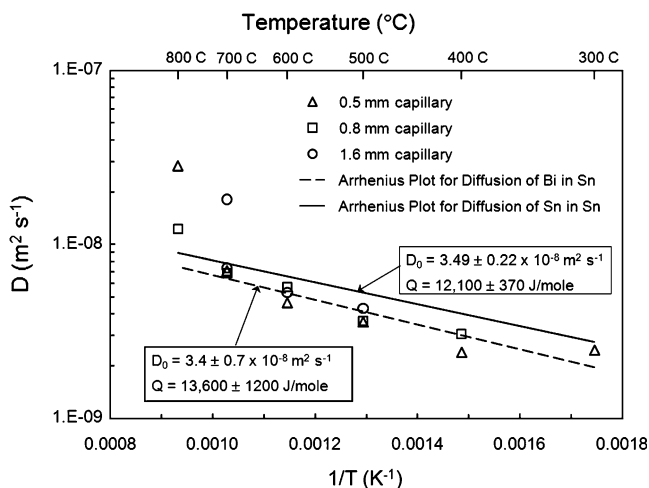
The Arrhenius plot for the interdiffusion of Bi in liquid Sn is presented in Fig. 2 which shows that the results at 800 °C for both 0.5 and 0.8 mm capillaries are inconsistent with the results at lower temperatures. Also, the results at 700 °C for two of the 1.6 mm capillaries are inconsistent with the other results (Table 3). These anomalous results are

almost certainly due to the influence of convective mixing at higher temperatures and/or larger capillary diameters which will be discussed later. Therefore, none of the diffusion coefficients greater than  $D = 1 \times 10^{-8} \text{ m}^2/\text{s}$  were used in the Arrhenius calculations. Further, the use of an Arrhenius plot is not intended to infer that liquid diffusion is necessarily a thermally activated process as is solid diffusion. It is simply a convenient and traditional method for presenting and comparing results.

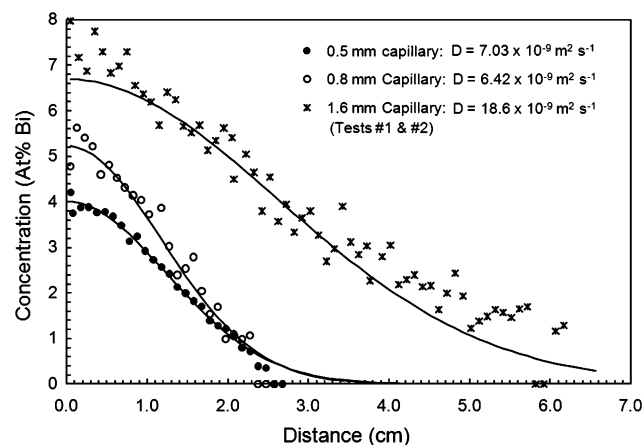
## Section I: Basic and Applied Research

The best fit straight line for the Arrhenius plot of the present results for the diffusion of Bi in Sn is shown by the broken line in Fig. 2 and compared with the results for the solvent self-diffusion of Sn given by the solid line taken from Fig. 1. The Arrhenius parameters for the diffusion of Bi in Sn are  $D_0^{\text{Bi}} = 3.4 \pm 0.7 \times 10^{-8} \text{ m}^2/\text{s}$  and  $Q_{\text{Bi}}^{\text{Sn}} = 13,600 \pm 1200 \text{ J/mol}$ . The equivalent parameters for the diffusion of Sn in Sn are  $D_0^{\text{Sn}} = 3.49 \pm 0.22 \times 10^{-8} \text{ m}^2/\text{s}$  and  $Q_{\text{Sn}}^{\text{Sn}} = 12,100 \pm 370 \text{ J/mol}$ . The error limits are standard deviations. For the diffusion of Bi in Sn, the Arrhenius plot was determined using all the average values,  $D_{\text{AV}}$  (MIC) in Table 1 to 3. For clarity, only the averaged values for each temperature,  $D_{\text{AV}}(T)$  in Table 1 to 3, are plotted in Fig. 2.

The effect of capillary diameter on the concentration-penetration curves for diffusion of Bi in Sn at 700 °C is shown in Fig. 3. For a capillary diameter of 0.5 mm, the concentration profile exhibits little scatter and the calculated



**Fig. 2** Results of the present investigation for the interdiffusion of Bi in liquid Sn (*broken line*) in comparison with Sn in Sn (*solid line*)



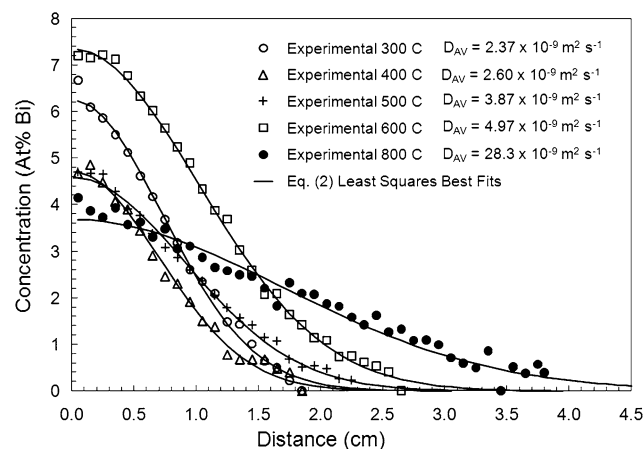
**Fig. 3** Effect of capillary diameter on concentration-penetration profiles for the interdiffusion of Bi in liquid Sn at 700 °C

diffusion coefficient is consistent with those calculated at lower temperatures (Fig. 2).

For a capillary diameter of 0.8 mm, some scatter in the experimental points is evident as shown in Fig. 3 and this scatter is likely due to convective mixing. However, the diffusion coefficient for the 0.8 mm capillary,  $6.42 \times 10^{-9} \text{ m}^2/\text{s}$ , is slightly less than that for the 0.5 mm capillary,  $7.03 \times 10^{-9} \text{ m}^2/\text{s}$ . It is suggested that for the 0.8 mm capillary, convective currents are localized resulting in some scatter of the concentrations but transport of liquid metal along the length of the capillary is small and does not contribute significantly to the diffusion coefficient. Froberg et al.,<sup>[14]</sup> using 2 mm diameter capillaries, noted similar concentration variations for In-In 25% Sn diffusion couples that they attributed to convection. However, in their case significant mass transport due to convection did occur increasing the apparent diffusion coefficient by 15 to 30% over zero-gravity results.

For the 1.6 mm capillary diffused at 700 °C, a large degree of scatter is evident in the concentration profile shown in Fig. 3. The apparent diffusion coefficient,  $18.6 \times 10^{-9} \text{ m}^2/\text{s}$ , is almost three times that for the 0.5 and 0.8 mm diameter capillaries where convective mixing is assumed to be minimal.

The effect of temperature on the concentration-penetration profiles for 0.5 mm diameter capillaries is illustrated in Fig. 4 along with the 0.5 mm profile for 700 °C given in Fig. 3. At temperatures up to 700 °C, the profiles exhibit very little scatter, indicating the absence of any significant convective mixing. However, the concentration profile at 800 °C shows considerable scatter and a very high-diffusion coefficient of  $D = 28.3 \times 10^{-9} \text{ m}^2/\text{s}$  which is over three times the value that would be expected from an extrapolation of the results at lower temperatures as shown in Fig. 2. Also, it should be noted that the diffusion anneal time for the 800 °C profile was only 5,400 s compared to 10,800 s for the other profiles. It is interesting that this apparent diffusion coefficient for the 0.5 mm capillary is twice that for the 0.8 mm capillaries where the effects of convective mixing are even more apparent from the concentration profile shown in Fig. 5.



**Fig. 4** Effect of temperature on concentration-penetration profiles for the interdiffusion of Bi in liquid Sn in 0.5 mm diameter capillaries

The results of the present investigation are compared with previous investigations in Fig. 6. For clarity, only the averages of all the results for each temperature for the present investigation are shown. Different techniques and various capillary diameters were used in the different investigations and these are summarized in Table 4. For the present investigation, the three diffusion coefficients calculated from the concentration-penetration curve, and the slope and intercept of the  $\ln C$  versus  $x^2$  plot generally agreed to within  $\pm 6\%$  of the average value. The error limits in Fig. 6 are therefore  $\pm 6\%$ . In Fig. 6, all the results except those of Buell and Shuck<sup>[16]</sup> show that Bi diffuses more slowly in liquid Sn than does Sn itself. However, Buell and Shuck used the capillary reservoir technique with a reservoir at each end of the capillary, as well as a fairly large, 1.5 mm diameter capillary. It is now known that convective flow in the reservoirs induces convection in the capillary thus increasing the value of the “apparent” diffusion coefficient.<sup>[21]</sup> Verhoeven et al.<sup>[15]</sup> also used the capillary reservoir technique

but with only one reservoir and a smaller, 1 mm diameter, capillary. Therefore, it is to be expected that the results of Verhoeven et al. would give lower “apparent” diffusivities than those of Buell and Shuck but higher than those of the present investigation where convective effects should be minimal. Figure 6 shows these expected results. It is interesting to note that the present diffusion coefficient for the diffusion of Bi in liquid Sn at 300 °C,  $D = 2.47 \times 10^{-9} \text{ m}^2/\text{s}$  (Table 1), agrees well with the zero gravity result of Garandet et al.,  $D = 2.3 \times 10^{-9} \text{ m}^2/\text{s}$ ,<sup>[18]</sup> and the magnetic field results of Botten et al.<sup>[17]</sup> extrapolated to 300 °C, also  $D = 2.3 \times 10^{-9} \text{ m}^2/\text{s}$ . Therefore, we consider that the present results obtained in unit gravity are not significantly affected by convection providing that the concentration-penetration curves exhibit little scatter and if different diameter capillaries give similar results. Also, for the same reasons, wall effects, and Marangoni convection are expected to be minimal.

The difficulties in obtaining accurate values for liquid diffusion coefficients are illustrated by the results obtained at

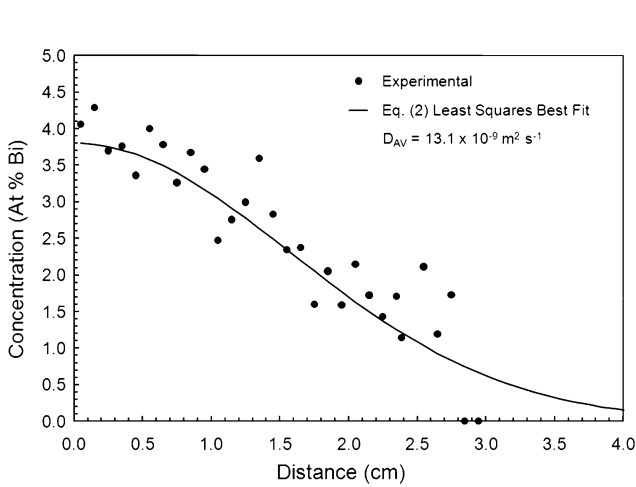


Fig. 5 Concentration-penetration profile for the interdiffusion of Bi in liquid Sn in a 0.8 mm diameter capillary at 800 °C, test #2

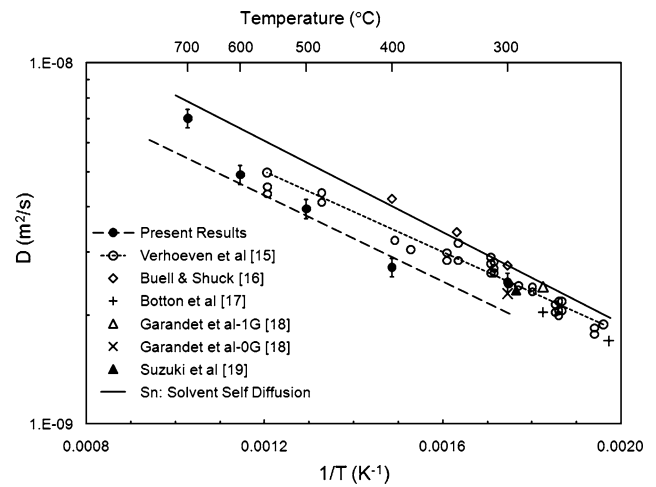
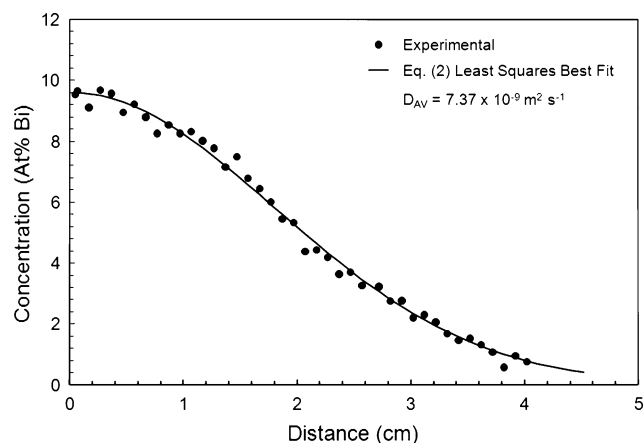


Fig. 6 Comparison of the present results for the diffusion of Bi in liquid Sn with those of previous investigations

Table 4 Summary of experimental conditions for the interdiffusion of Bi in liquid Sn

Reference	Technique	Maximum conc., at.% Bi	Capillary diameter, mm	Conditions
This work	Thin disk, long capillary	10(a)	0.5-1.6	1G
[15]	Capillary reservoir	$5.7 \times 10^{-4}$	1.0	1G
[16]	Capillary reservoir(b)	10	1.5	1G
[17]	Long capillary, shear cell(c)	0.47-0.54	2.0	1G, 1.5-2.0 T
[18]	Long capillary, shear cell(d)	1.44	1.5	0G and 1G
[19, 20]	Long capillary, shear cell, thick layer(e)	1.44	1.5	1G

- (a) The thin disk of pure Bi diffuses sufficiently quickly that about 80% of the time of diffusion anneal occurs over the concentration range from 0 to 10 at.% Bi
- (b) Buell and Shuck<sup>[16]</sup> used a 100 mm long capillary joining two reservoirs, one with pure Bi and the other with pure Sn. They calculated the concentration dependence from the steady state solution to Fick’s first law
- (c) 200 mm long capillary, 100 mm of pure Sn, and 100 mm of alloy. Experiments were conducted in 1.5-2.0 T magnetic field to reduce convection
- (d) 60 mm long capillary, 30 mm of pure Sn, and 30 mm of alloy
- (e) 60 mm long capillary, 57 mm pure Sn, and 3 mm disk of alloy. Diffusivity calculated from thick disk solution to Fick’s 2nd law

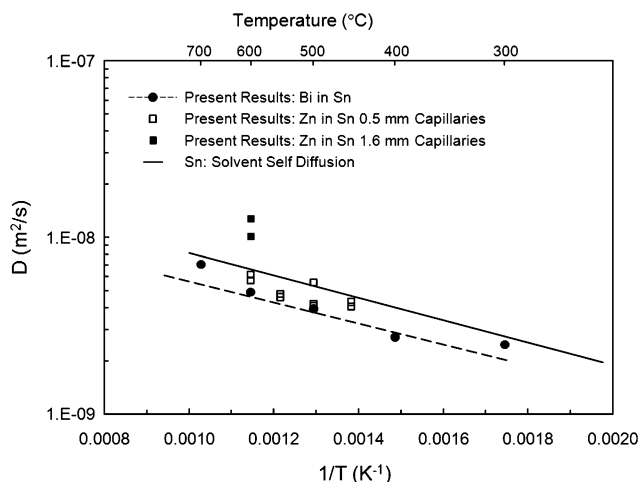


**Fig. 7** Concentration-penetration profile for the interdiffusion of Bi in liquid Sn in a 1.6 mm diameter capillary at 700 °C, test #3

700 °C for 1.6 mm diameter capillaries. Two of the results exhibited considerable scatter in the concentration-penetration curves (Fig. 3) and resultant high “apparent” diffusivities,  $D \approx 18 \times 10^{-9} \text{ m}^2/\text{s}$ , Table 3, whereas a third result yielded a concentration-penetration curve with little scatter shown in Fig. 7 and a diffusivity of  $D = 7.37 \times 10^{-9} \text{ m}^2/\text{s}$ , similar to the diffusivities of  $D = 7.07 \times 10^{-9} \text{ m}^2/\text{s}$  and  $D = 6.81 \times 10^{-9} \text{ m}^2/\text{s}$  obtained for the 0.5 and 0.8 mm capillaries, respectively. Such variations in the measurement of diffusivities can result from differences in horizontal temperature gradients, particularly in capillaries greater than 1.5 mm diameter, or by misalignments of only a few degrees of the axis of the capillary with the gravity vector.<sup>[22]</sup>

There has been considerable emphasis upon determining the temperature dependence of liquid diffusion coefficients,  $D \propto T^2$  being a common one.<sup>[23]</sup> It is possible, however, that there is no simple relationship between  $D$  and  $T$  (in at least some liquid metals and alloys). Recent investigations suggest that liquid Sn and Sn (rich) Bi alloys undergo phase transitions at about 400 and 800 °C.<sup>[24,25]</sup> Further, an investigation on the density of liquid Sn showed abnormalities at about 400, 800, and 1200 °C<sup>[26]</sup> which could indicate a structural change. However, a more recent investigation<sup>[27]</sup> showed no density anomaly at 400 °C. Liquid/liquid phase transitions have also been suggested for Al (rich)-Cu alloys<sup>[24]</sup> and supercooled liquid Si.<sup>[28]</sup> Any such structural changes would almost certainly give rise to anomalies in the temperature dependence of the diffusion coefficient. Figures 2 and 6 show that the diffusivity at 400 °C appears low compared to those at 300 and 500 °C. Figure 2 shows that the diffusivity for 0.5 mm diameter capillaries obtained at 400 °C is actually lower than that obtained at 300 °C and we consider the results for 0.5 mm capillaries the most accurate. This apparent anomaly for the diffusion coefficients at 400 °C may well be a result of a liquid/liquid phase transition.

It should be noted that, for interdiffusion in liquid alloys in unit gravity, the use of a solute with a substantial difference in density from the solvent can produce “stable density layering” which will tend to minimize convective



**Fig. 8** Comparison of present results for the interdiffusion of Zn in liquid Sn with those for Bi in liquid Sn

flow.<sup>[19]</sup> For the present investigation, considerable “stable density layering” should result since liquid Bi has a density of 10,500 kg/m<sup>3</sup> and liquid Sn has a density of 6,990 kg/m<sup>3</sup>. Some preliminary results were obtained for the interdiffusion of Zn in liquid Sn using 0.5 and 1.6 mm capillaries and these are presented in Fig. 8. The experimental conditions were identical to those for the Sn-Bi alloys except that the Zn was added to the top of the Sn capillary because liquid Zn has a lower density than does liquid Sn. All of the Sn-Zn concentration-penetration curves showed some scatter indicating the presence of convective mixing. For the Sn-Zn alloy diffused at 600 °C, both the 0.5 mm capillaries and the 1.6 mm capillaries gave concentration-penetration profiles exhibiting a great deal of scatter. Also, the 1.6 mm capillaries gave diffusion coefficients considerably higher than did the 0.5 mm capillaries. For the Bi-Sn alloys diffused at 600 °C all three capillary sizes (0.5, 0.8, 1.6 mm) gave similar results with no evidence of convective mixing (Fig. 2). This difference in behavior is likely due to the absence of any significant “stable density layering” for the Sn-Zn alloys since liquid Sn and Zn have similar densities, 6,990 and 6,570 kg/m<sup>3</sup>, respectively.

The results of the present investigation have shown that it is possible to obtain accurate liquid interdiffusion coefficients in unit gravity using the long capillary technique providing that

1. Different diameter capillaries give equivalent results indicating minimal contributions of buoyancy driven convection, capillary wall effects and Marangoni convection.
2. The concentration-penetration curves exhibit little concentration scatter.
3. The liquid densities for solute and solvent are sufficiently different that “stable density layering” exists.

While it may be possible to minimize convection utilizing a strong magnetic field of about 2 T, a strong magnetic field could also affect the diffusion coefficient.

Youdelis et al.<sup>[29]</sup> reported that a magnetic field of 3 T reduced the interdiffusion coefficient of Cu in Al by 25%.

A compilation of the present results and those of other investigations, one performed in zero gravity, shows that Bi diffuses more slowly in liquid Sn than does Sn itself. A previous compilation of results for the interdiffusion of Sb in liquid Sn<sup>[3]</sup> showed that Sb diffuses at essentially the same speed in liquid Sn as does Sn itself.

#### 4. Conclusions

From the present and previous investigations it is possible to conclude the following:

1. Accurate liquid interdiffusion coefficients can be obtained in unit gravity using the long capillary technique providing certain conditions of capillary diameter and relative solute-solvent densities are met.
2. Bismuth diffuses in liquid Sn more slowly than does Sn itself.
3. The liquid interdiffusion coefficient may be affected by liquid/liquid phase transformations in some metals and alloys. Therefore, a simple relationship between diffusivity and temperature may not exist for these metals and alloys.

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