Diffusion of Silver in Molten Lead-Tin Alloys*

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The diffusion coefficients of silver in the lead-tin system have been studied at various concentrations of tin N_{Sn} , 0.223, 0.405, 0.614 and 0.799, and over the temperature ranges of $410^{\circ}\sim 557^{\circ}\text{C}$, $453^{\circ}\sim 609^{\circ}\text{C}$, $391^{\circ}\sim 609^{\circ}\text{C}$ and $405^{\circ}\sim 690^{\circ}\text{C}$, respectively. The results can be represented by the equations:

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.223) = (2.89 \pm 0.26) \times 10^{-4} \exp \{ -(3090 \pm 130)/RT \} \text{ cm}^2/\text{sec},$$

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.405) = (2.79 \pm 0.26) \times 10^{-4} \exp \{ -(2980 \pm 140)/RT \} \text{ cm}^2/\text{sec},$$

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.614) = (2.46 \pm 0.17) \times 10^{-4} \exp \{ -(2720 \pm 100)/RT \} \text{ cm}^2/\text{sec},$$

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.799) = (5.43 \pm 0.34) \times 10^{-4} \exp \{ -(3780 \pm 90)/RT \} \text{ cm}^2/\text{sec}.$$

With the aid of thermodynamic properties of the Pb-Sn systems and supposing

$$D_i(\text{Ag}) \approx D_i(\text{Sn}),$$

the diffusion coefficients of tin in the Pb-Sn system at 500°C have been calculated by the equation

$$D_{Sn} \text{ in Pb-Sn} = D_i(\text{Sn}) \text{ in Pb-Sn } (1 + d \ln \gamma_{Sn}/d \ln N_{Sn})$$

$$\approx D_i(\text{Ag}) \text{ in Pb-Sn-Ag } (1 + d \ln \gamma_{Sn}/d \ln N_{Sn}).$$

The calculated values of diffusion coefficients at various compositions agree well with those experimentally obtained in a previous study.

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I. Introduction

Niwa et al.⁽¹⁾ studied the diffusion of silver in molten lead, bismuth, tin, cadmium and copper, and made clear that the diffusion coefficient of the solute in dilute solutions depends upon the viscosity coefficient of the solvent and the atomic radius of the diffusions.

In order to find the relation between diffusion coefficients of the third component and thermodynamic properties of the binary system, the diffusion coefficients of silver were measured in alloys of lead-tin, lead-bismuth and bismuth-tin systems with various compositions. These systems were selected as the objects of investigation for the following reasons;

(i) As mentioned above, Niwa et al.⁽¹⁾ have already

measured the diffusion coefficients of silver in molten lead, tin and bismuth.

(ii) The Pb-Sn system shows a positive deviation from Raoult's law, the Pb-Bi system shows a negative deviation from it and the Sn-Bi system has practically a thermodynamic properties nearly equivalent to those of an ideal solution.

(iii) Niwa et al.⁽²⁾ experimentally found the concentration dependence of diffusion coefficients of tin in the Pb-Sn system and bismuth in the Pb-Bi system and in the Sn-Bi system.

(iv) Since these three systems have comparatively low melting points, the experimental techniques and procedures are not so difficult.

According to the thermodynamics of irreversible processes⁽³⁾, the flux of the first component in a ternary system is represented by

$$J_1 = L_{11} \frac{\partial \mu_1}{\partial x} + L_{12} \frac{\partial \mu_2}{\partial x} + L_{13} \frac{\partial \mu_3}{\partial x}. \quad (1)$$

(2) Y. Watanabe, S. Kado, M. Shimoji and K. Niwa: *ibid.* **18** (1954), 274; T. Yokokawa, Y. Watanabe, S. Kado, M. Shimoji and K. Niwa: *ibid.* **19** (1955), 299.

(3) S. R. de Groot: *Thermodynamics of Irreversible Process*, North Holland Publishing Co., Amsterdam (1952).

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(1) K. Tsuchiya, T. Ito, S. Kado and K. Niwa: *J. Japan Inst. Metal.* **26** (1962), 718, 722.; T. Ohno, S. Kado and K. Niwa: *ibid.* **26** (1962), 726.

As the last term in the Eq. (1) is zero for a binary system, J_1 can be expressed by a single diffusion coefficient by using the Gibbs-Duhem equation, whereas for the ternary system J_1 cannot be represented by a single diffusion coefficient. For the ternary, system, from Eq. (1) and the Gibbs-Duhem equation

$$N_1 d\mu_1 + N_2 d\mu_2 + N_3 d\mu_3 = 0, \quad (2)$$

the diffusion coefficient⁽⁴⁾ for the first component, D_1 , is given by

$$D_1 = \left(\frac{L_{11}}{N_1} - \frac{L_{12}}{N_2} \right) RT (1 + d \ln \gamma_1 / d \ln N_1). \quad (3)$$

However, under a carefully selected experimental condition, where chemical potential gradients for the components excepting the diffusant do not exist, the system can be treated as the quasi-binary system. The experimental condition may be established by adding a very small quantity of a third component containing a small amount of the radioactive tracer as a diffusion component. Accordingly, measurements of the diffusion coefficient of silver in the molten alloys have been done by using the capillary-reservoir method and Ag^{110} as the radioactive tracer. Under this experimental condition the diffusion coefficients of silver, D_{Ag} , are given by

$$D_{\text{Ag}} = D_{i(\text{Ag})} (1 + d \ln \gamma_{\text{Ag}} / d \ln N_{\text{Ag}}), \quad (4)$$

where $D_{i(\text{Ag})}$ is the mobility of Ag in the alloy.

As the concentration of silver is sufficiently low, and the mole fraction of silver, N_{Ag} , is exceedingly small, Henry's law is to be applicable to silver. Thus,

$$D_{\text{Ag}} = D_{i(\text{Ag})}.$$

By measuring the diffusion coefficients of silver in various compositions of the alloys, the change in the mobility of silver in the alloys can be determined. When the radii of diffusing atoms differ a little from each other, it can be assumed that the mobility of the components of the alloys, $D_{i(\text{M})}$, is nearly equal to that of silver in the alloy, $D_{i(\text{Ag})}$.

By using the thermodynamic properties of the alloys the diffusion coefficients of the components of the alloys, $D_{(\text{M})}$, are to be estimated from the following expressions.

$$D_{(\text{M})} = D_{i(\text{M})} (1 + d \ln \gamma_{\text{M}} / d \ln N_{\text{M}}) \\ \approx D_{i(\text{Ag})} (1 + d \ln \gamma_{\text{M}} / d \ln N_{\text{M}}), \quad (5)$$

where $D_{(\text{M})}$ is the diffusion coefficient of the component M of the alloy, $D_{i(\text{M})}$ is the mobility, of M, $D_{i(\text{Ag})}$ is the mobility of silver ($D_{i(\text{Ag})} = D_{\text{Ag}}$ as shown above), and γ_{M} and N_{M} are the activity coefficient and the mole fraction of the component M in the alloy, respectively. It is shown in the present work that the diffusion coefficients of tin in the Pb-Sn system calculated from the Eq. (5) using the experimental values of D_{Ag} agree within the experimental error with their experimental values.

II. Experiments and Results

The experimental apparatus and procedures are the same as stated in the previous reports⁽¹⁾. In order to prepare

the Pb-Sn alloys, the metals were covered with graphite powder and melted in an alumina crucible. After rapid cooling, the molten alloy was divided into two parts. A small amount of silver containing Ag^{110} was added to the one part and used as the molten metal-bath for a capillary-filling. The other part which was remelted was used as the bath for diffusion. The samples were taken out from the molten metal-bath several times before, during and after the experiments. The composition of each of the samples which was determined by the Shimadzu electrolytic analyzer (Type, AEA-1) was constant within the analytical uncertainty.

Analysis of the Pb-Sn alloys was carried out by Foster's technique⁽⁵⁾ modified by the authors. About 70 mg of the Pb-Sn alloy sample and about 30 mg of copper powder were weighed in the 250 mL-beaker for electrolysis, and dissolved in 15 mL of HCl (2 : 1) and 5 mL of 30% H_2O_2 solution. After the excess of H_2O_2 was removed by boiling, the solution was diluted to an amount of 50 mL with water. After the addition of 2 g of hydrazine dihydrochloride, the solution was heated just before boiling, to which 2 g of urea was added and cooled. This solution was diluted with water until the electrode was completely immersed and then electrolyzed at a voltage of -0.4 V for the deposition of copper.

After the deposition of the copper, 10 mL of 12 M NaOH solution and 2 M sodium tartrate were added to the solution in a 400 mL-beaker and the solution was regulated to have a pH value between 4.9 and 5.1 by addition of 1 g of succinic acid. The deposition of lead by electrolysis was done at -0.6 V, using the platinum electrode on which copper was electrically deposited. Electrolysis was continued until the electric current dropped to 10 mA or less, followed by the additional electrolysis for ten minutes at a current less than 10 mA. When the current was ascertained to be the residual one, the electrolysis was stopped. Then, the electrode was taken out, washed, dried and weighed, and the concentration of lead was determined. In order to determine the concentration of tin, 20 mL of concentrated hydrochloric acid and 1 g of hydrazine dihydrochloride were added to the solution after the deposition of lead and electrolyzed at -0.6 V.

The diffusion coefficient of silver in the Pb-Sn system, D_{Ag} , was calculated by the following equation⁽¹⁾.

$$\frac{\bar{C} - C_s}{C_0 - C_s} = \frac{8}{\pi^2} \int_{n=0}^{\infty} \frac{1}{(2n+1)^2} \\ \exp \left\{ -(2n+1)^2 \pi^2 D t / l^2 \right\}. \quad (6)$$

The diffusion coefficients of silver in the Pb-Sn system, D_{Ag} , were obtained at the mole fractions of tin, $N_{\text{Sn}} = 0.223, 0.405, 0.614$ and 0.799 and over the temperature ranges of $410^\circ \sim 557^\circ\text{C}$, $453^\circ \sim 609^\circ\text{C}$, $391^\circ \sim 609^\circ\text{C}$ and $405^\circ \sim 695^\circ\text{C}$, respectively, as shown in Tables 1, 2, 3 and 4. Using the least-square method, the experimental points can be represented by the Arrhenius-type equations,

$$D_{\text{Ag}} \text{ in Pb-Sn } (N_{\text{Sn}} = 0.223) = (2.89 \pm 0.26) \times 10^{-4} \\ \exp \{ -(3090 \pm 130) / RT \} \text{ cm}^2/\text{sec}, \quad (7)$$

(4) Y. Kawai : Science Reports of the Research Institutes, Tohoku University, A 209 (1957), No. 6, 520.

(5) D. G. Foster : Anal. Chem., 25 (1953), 669.

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.405) = (2.79 \pm 0.26) \times 10^{-4} \exp \{-(2980 \pm 140)/RT\} \text{ cm}^2/\text{sec}, \quad (8)$$

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.614) = (2.46 \pm 0.17) \times 10^{-4} \exp \{-(2620 \pm 100)/RT\} \text{ cm}^2/\text{sec} \quad (9)$$

and

Table 1 D_{Ag} in Pb-Sn ($N_{Sn}=0.223$)-alloys.

Temp. (°K)	Time (sec)	Length of capillary (cm)	$\bar{C}$ (cpm/g)	C_0 (cpm/g)	C_S (cpm/g)	$D \times 10^5$ (cm ² /sec)
830	1200	1.99	1020	1185	0	4.72
	1200	2.01	1027	1185	0	4.37
	1200	2.00	1023	1185	0	4.66
	3900	1.72	861	1185	0	4.45
	3900	1.80	848	1143	0	4.32
783	1800	1.79	948	1143	4	4.06
	1800	1.78	953	1143	4	3.87
	1800	1.71	940	1143	4	3.90
	1800	1.73	975	1185	4	3.99
	3600	1.93	900	1143	5	3.72
	3600	1.89	894	1143	5	3.77
725	1800	1.75	1000	1143	7	3.23
	3600	1.96	934	1185	9	3.45
	3600	1.97	950	1185	9	3.34
	3600	2.05	953	1185	9	3.50
	3600	2.03	918	1158	9	3.55
683	1800	1.80	1013	1185	2	2.88
	1800	1.82	974	1143	2	3.12
	1800	1.88	985	1143	2	2.74
	1800	1.63	961	1143	2	2.95
	3600	1.90	947	1185	3	3.16

Table 2 N_{Ag} in Pb-Sn ($N_{Sn}=0.405$)-alloys.

Temp. (°K)	Time (sec)	Length of capillary (cm)	$\bar{C}$ (cpm/g)	C_0 (cpm/g)	C_S (cpm/g)	$D \times 10^5$ (cm ² /sec)
882	1800	1.95	2824	3430	63	5.28
	3600	1.95	2518	3334	70	5.01
	3600	2.07	2538	3334	70	5.06
	3600	1.85	2655	3430	70	5.19
823	3600	1.83	2611	3430	83	4.37
	3600	1.95	2638	3430	83	4.64
	3600	1.82	2604	3430	83	4.41
	1800	1.88	2870	3430	79	4.32
	1860	2.03	2903	3430	79	4.35
	1860	1.85	2801	3385	20	4.41
	1860	1.70	2764	3430	20	4.50
	3600	1.95	2610	3385	24	4.40
	3600	1.91	2490	3385	24	4.45
753	1800	2.01	2866	3385	32	4.04
	1800	1.97	2864	3385	32	3.88
	3600	1.90	2664	3430	36	4.01
	3600	1.98	2700	3430	36	3.92
726	3600	2.00	2745	3430	53	3.55
	3600	1.90	2642	3334	53	3.51
	3600	1.59	2635	3334	53	3.77
	3600	2.03	2793	3430	53	3.20
	3600	1.97	2764	3430	53	3.24

$$D_{Ag} \text{ in Pb-Sn } (N_{Sn}=0.799) = (5.43 \pm 0.34) \times 10^{-4} \exp \{-(3780 \pm 90)/RT\} \text{ cm}^2/\text{sec}. \quad (10)$$

Using the equations (7)~(10) and the Arrhenius-type equations for the diffusion coefficients of silver in lead and tin⁽¹⁾,

$$D_{Ag} \text{ in Pb} = (3.19 \pm 0.17) \times 10^{-4} \exp \{-(3470 \pm 80)/RT\} \text{ cm}^2/\text{sec} \quad (11)$$

and

$$D_{Ag} \text{ in Sn} = (7.26 \pm 0.27) \times 10^{-4} \exp \{-(4160 \pm 60)/RT\} \text{ cm}^2/\text{sec}, \quad (12)$$

the most accurate values of D are calculated over the temperature range of experiment and the values of $\log D$ are plotted against $1/T$ in Fig. 1. [As the values of D_{Ag} were not very different over all the compositions of the Pb-Sn system, the above method was used for the pur-

Table 3 D_{Ag} in Pb-Sn ($N_{Sn}=0.614$)-alloys.

Temp. (°K)	Time (sec)	Length of capillary (cm)	$\bar{C}$ (cpm/g)	C_0 (cpm/g)	C_S (cpm/g)	$D \times 10^5$ (cm ² /sec)
882	1800	1.93	6844	8400	70	5.59
	1800	1.94	6955	8400	70	4.91
	1800	1.97	6888	8400	70	5.39
799	1800	2.03	7017	8400	34	4.81
	1800	2.08	7102	8400	34	4.33
	1800	2.04	7086	8400	34	4.39
	1800	2.02	7015	8400	34	4.76
	3600	2.09	6633	8400	46	4.24
	3600	2.06	6613	8400	46	4.24
	3600	2.03	6585	8400	46	4.23
	3600	2.14	6585	8400	46	4.70
	3600	2.05	6597	8400	46	4.31
	3600	2.11	6626	8400	46	4.33
	3600	2.07	6620	8400	46	4.28
725	1800	1.95	7160	8400	190	3.64
	1800	1.76	6974	8400	190	3.80
	1800	1.92	7096	8400	190	3.89
	3600	2.00	6713	8400	266	3.72
	3600	2.05	6749	8400	266	3.73
	3600	2.02	6742	8400	266	3.59
664	1800	2.01	7227	8400	210	3.25
	1800	2.04	7252	8400	210	3.12
	1800	2.05	7308	8400	210	3.03
	3600	1.96	6787	8400	228	3.20

Table 4 D_{Ag} in Pb-Sn ($N_{Sn}=0.799$)-alloys.

Temp. (°K)	Time (sec)	Length of capillary (cm)	$\bar{C}$ (cpm/g)	C_0 (cpm/g)	C_S (cpm/g)	$D \times 10^5$ (cm ² /sec)
968	3600	2.01	1301	1807	64	7.31
	3600	2.21	1324	1807	64	8.14
815	1800	2.24	1399	1674	71	5.25
	3600	1.94	1367	1806	78	5.31
	3600	1.91	1272	1674	78	5.04
	3600	1.96	1276	1674	78	4.80
	3600	1.98	1296	1674	78	5.14
753	1800	2.07	1392	1674	0	4.36
	3600	2.02	1295	1674	2	4.59
	3600	1.90	1280	1674	2	4.36
	3600	1.96	1304	1674	2	4.08
	3600	1.92	1292	1674	2	4.20
723	3600	1.94	1282	1674	2	4.56
	1800	1.97	1831	1807	47	4.04
	1800	2.11	1443	1674	46	3.96
	3600	1.97	1424	1807	52	4.10
	3600	2.03	1444	1807	52	3.82
687	3600	2.00	1326	1674	52	4.03
	3600	2.06	1342	1674	52	3.85
	3600	1.97	1335	1674	52	3.70
	1800	2.17	1469	1674	29	3.27
	3600	2.19	1383	1674	32	3.22
	3600	2.14	1470	1807	32	3.22
	3600	2.23	1501	1807	32	3.17
	3600	2.18	1492	1807	32	3.14
	3600	2.16	1475	1807	32	3.54

pose of clarifying the figure. The experimental results (Tables 1~4) lie within a deviation of $\pm 8\%$ from the values determined by the least-square method.]

As shown by the Eqs. (7)~(12) and in Fig. 1, the diffusion coefficients of silver in the Pb-Sn system are

larger than those in pure lead, smaller than that in pure tin and regularly increase as the concentration of tin increases.

III. Discussion

When a radius of a solute atom is not very different from that of a solvent atom, the diffusion coefficient of the former in a dilute solution is anticipated to be nearly equal to that of the latter. Similarly both of mobilities may be assumed to be nearly the same. From the above assumptions and the Eq. (5), the diffusion coefficient of tin in the Pb-Sn system, D_{Sn} , can be given by

$$D_{Sn} \text{ in Pb-Sn} = D_{i(Sn)} \text{ in Pb-Sn} (1 + d \ln \gamma_{Sn} / d \ln N_{Sn}) \\ \approx D_{Ag} \text{ in Pb-Sn-Ag} \\ (1 + d \ln \gamma_{Sn} / d \ln N_{Sn}). \quad (5)'$$

Using the data⁽⁶⁾⁽⁷⁾ of the thermodynamic properties of the Pb-Sn system, the activity of tin, a_{Sn} , at 500°C is shown in Fig. 2. From Fig. 2, $\log \gamma_{Sn}$ and $d \log \gamma_{Sn} / d$

Fig. 1 Diffusion coefficients of silver in Pb-Sn alloys.

Fig. 2 Activity of tin in the Pb-Sn system at 500°C.

$\log N_{Sn}$ can be estimated for $N_{Sn} = 0.223, 0.405, 0.614$ and 0.799 . Therefore, D_{Sn} is to be calculated by putting in (5)' the above data and D_{Ag} for each concentration. From the Eqs. (7)~(12) the values of D_{Ag} at 500°C are calculated as shown in Fig. 3. The diffusion coefficient of tin in the Pb-Sn system, calculated from D_{Ag} and d

$\log \gamma_{Sn} / d \log N_{Sn}$ for $N_{Sn} = 0.223, 0.405, 0.614$ and 0.799 , shows a minimum value in the proximity of $N_{Sn} = 0.6$, as shown in Fig. 4.

Niwa et al.⁽²⁾ have already measured the concentration dependence of the diffusion coefficients of tin in the

Fig. 3 Diffusion coefficients of silver in Pb-Sn alloys at 500°C.

Fig. 4 Comparison between calculated and observed D_{Sn} in the Pb-Sn system at 500°C.

Pb-Sn system. In Fig. 4 their experimental results are compared with the values calculated in the above-mentioned way. In Fig. 4, both diffusion coefficients show minimum values at about the same composition and these values are approximately equal within the limit of experimental error over the whole range of compositions.

As mentioned above, it appears that the assumption represented by the Eq. (5) or (5)'—when the concentration of a third component in a binary system is sufficiently low, the diffusion coefficients of the first and second components can be estimated from that of the third component—may be established within the experimental error. As the atomic radii⁽⁸⁾ of silver and tin are 1.44 and $1.52 \text{ \AA}$, respectively, the assumption that the size of the solute atoms is not so different from that of the solvent can be used. The effect due to the difference in atomic size will be discussed in a succeeding paper.

The viscosity and density in the Pb-Sn system have

(6) J. F. Elliott and J. Chipman: J.A.C.S., **73** (1951), 2682.

(7) C. Wagner: Thermodynamics of Alloys, Addison-Wesley Press, Cambridge, Mass. (1952).

(8) C. J. Smitel: Metal Reference Book, Butterworth Scientific Publication (1949).

already been measured by Fisher and Phillips⁽⁹⁾. According to them, the viscosity coefficient has a minimum value at the eutectic composition ($N_{\text{Sn}}=0.75$). On the other hand, the diffusion coefficient of silver in the Pb-Sn system (i. e. the mobility of silver in this alloy) does not show any marked change at the eutectic composition. Further, contrary to the expectation from the data of the viscosity that the diffusion coefficient of tin in the Pb-Sn system has a maximum value at the eutectic composition, the experimental results show the tendency to take a minimum value. Accordingly, the diffusion coefficient may be considered as strongly dependent upon the factor except for the viscosity of the Pb-Sn system. However, the values of D_0 and Q for the diffusion of silver in the Pb-Sn system regularly decrease as N_{Sn} increases and they have a minimum values at $N_{\text{Sn}}=0.799$. The changes in D_0 and Q with N_{Sn} are found to correspond to that of the viscosity with N_{Sn} and the structure of the Pb-Sn system is supposed to change with the concentration of tin. According to Fisher and Phillips⁽⁹⁾, the density of the Pb-Sn system shows a slightly negative deviation from an additivity law at 300°C, while the additivity law is established at 400° and 500°C. So, the diffusion coefficients of silver (i.e. the mobilities of silver) in the Pb-Sn system show the same linear change with the concentration as that of a molar volume. The diffusion coefficients of the components of the Pb-Sn system depend largely upon the thermodynamic properties of the system, independently of the change of the molar volume.

As shown in Fig. 3 Niwa et al. have experimentally confirmed that the diffusion coefficients of silver in the Pb-Sn system show a linear change with N_{Sn} and that the diffusion coefficients of tin calculated by the Eq.(5)', based on the assumption of equality between observed

D_{Ag} and $D_{i(\text{Ag})}$ and also between $D_{i(\text{Sn})}$ and $D_{i(\text{Ag})}$, agree within the limit of experimental error with the observed values.

IV. Conclusion

The diffusion coefficients of silver in the Pb-Sn system were measured by a capillary-reservoir technique using a tracer, Ag^{110} , for various concentrations of tin N_{Sn} , 0.223, 0.405, 0.614 and 0.799, and over the temperature ranges of 410°~557°C, 453°~609°C, 391°~609°C and 405°~690°C, respectively. The experimental results are as follows :

System	$D_0 \times 10^4$	Q
D_{Ag} in Pb-Sn ($N_{\text{Sn}}=0.223$)	2.89 ± 0.26	3090 ± 130
($N_{\text{Sn}}=0.405$)	2.79 ± 0.26	2980 ± 140
($N_{\text{Sn}}=0.614$)	2.46 ± 0.17	2720 ± 100
($N_{\text{Sn}}=0.799$)	5.43 ± 0.34	3780 ± 90

Under the experimental condition, the Pb-Sn-Ag ternary system is treated as a quasi-binary system. The observed values of diffusion coefficients, D_{Ag} , are equal to $D_{i(\text{Ag})}$ at $N_{\text{Ag}} \approx 0$. On the assumption that $D_{i(\text{Ag})}$ for the ternary system is equal to that of tin in the Pb-Sn system, $D_{i(\text{Sn})}$, the diffusion coefficient of tin in the Pb-Sn system, D_{Sn} , is expressed by

$$\begin{aligned}
 D_{\text{Sn}} &\text{ in Pb-Sn} \\
 &= D_{i(\text{Sn})} \text{ in Pb-Sn } (1 + d \ln \gamma_{\text{Sn}} / d \ln N_{\text{Sn}}) \\
 &\approx D_{\text{Ag}} \text{ in Pb-Sn-Ag } (1 + d \ln \gamma_{\text{Sn}} / d \ln N_{\text{Sn}}).
 \end{aligned}$$

It is found that the values of D_{Sn} , calculated from the above equation, agree within the limit of experimental error with the values experimentally obtained in a previous work.

(9) H. J. Fisher and A. Phillips: Trans. AIME, 200 (1954), 1060.