

Oxygen Solubility in Liquid Indium and Oxygen Diffusivity in Liquid Indium and Tin

SHINYA OTSUKA, ZENSAKU KOZUKA, and Y. AUSTIN CHANG

The solubility of oxygen in liquid indium, C_O , at 973 and 1073 K in equilibrium with its oxide was determined by an isopiestic equilibration technique in order to resolve discrepancies reported in the literature. The present results, $C_O = 0.0092$ at. pct at 973 K and 0.0377 at. pct at 1073 K, agree with those obtained by Otsuka, Sano, and Kozuka using a modified coulometric titration method. Oxygen diffusivity in liquid indium from 873 to 1073 K and in liquid tin from 973 to 1273 K was measured utilizing a combined potentiostatic and emf method using the following double electrochemical cells: $\text{Fe, FeO/ZrO}_2(+\text{CaO})/\text{Q}$ in $\text{Me(I)/ZrO}_2(+\text{CaO})/\text{Q}$ in Me(II) . The present results are $D_{O(\text{In})} = 6.6^{(+2.0)}_{(-1.6)} \times 10^{-3} \exp[(-32600 \pm 5600)/RT]$ $873 \text{ K} \leq T \leq 1073 \text{ K}$ and $D_{O(\text{Sn})} = 8.7^{(+13.5)}_{(-3.7)} \times 10^{-4} \exp[(-18800 \pm 6700)/RT]$ $973 \text{ K} \leq T \leq 1273 \text{ K}$. The present results are of the same order of magnitude with the self-diffusivity of the liquid metals, and are about two orders of magnitude greater than the oxygen diffusivity reported by Stevenson and co-workers. The ratio of oxygen diffusivity to self-diffusivity of the solvent was found to be correlated to the enthalpy of formation per mole of oxygen of the respective oxide at 298 K.

I. INTRODUCTION

THE solubility of oxygen in liquid indium has been determined by several investigators using different techniques.^{1-5,8} However, the results reported are not consistent. Fitzner and Jacob¹ determined the saturation solubility of oxygen to be 0.2726 at. pct at 1092 K. The method employed involved equilibration of indium and its oxide at 920 to 1092 K. The sample was quenched in liquid nitrogen and analyzed for oxygen. By utilizing a coulometric titration method employing a linear type of electrochemical cell, Anderson and Donaghey² reported a value of 0.12 at. pct at 908 K. Hahn and Stevenson³ and Heshmatpour and Stevenson,^{4,5} who also used a coulometric titration method, found the solubility to be 0.01095 at. pct at 1123 K. This value is an order of magnitude lower than those found by the other investigators.^{1,2} Using a modified coulometric titration method proposed by Otsuka and Kozuka,^{6,7} Otsuka, Sano, and Kozuka⁸ measured the solubilities of oxygen in liquid indium from 973 to 1173 K at low oxygen potentials. By combining their results with the Gibbs energy of formation for In_2O_3 ,⁹ the saturation solubility of oxygen was found to be 0.065 at. pct at 1123 K.¹⁰ Using a combined method of Knudsen cell mass spectrometry with coulometric titration, Alcock, Ichise, and Butler¹¹ determined the saturation solubilities of oxygen in liquid indium from 1023 to 1223 K. Their value of 0.059 at. pct at 1123 K agrees with the results of Otsuka *et al.*^{8,10} In view of the large discrepancies reported in the literature as noted above, it was decided to determine the solubility of oxygen in liquid indium using an isopiestic method. The general principle employed was similar to the method used by Jacob and co-workers.^{1,12}

The second objective of the present investigation was to determine oxygen diffusivity in liquid indium and in liquid tin utilizing a combined potentiostatic and emf method.

Oxygen diffusivity in liquid indium was previously measured by Stevenson and co-workers^{3-5,13} employing a cylindrical electrochemical cell. The experiments were carried out by pumping out the oxygen coulometrically from the melt to the reference electrode. Values of oxygen diffusivity are about two orders of magnitude lower than the self-diffusivity of liquid indium.^{14,15,16} Moreover, it was found that oxygen diffusivity in liquid indium increases abruptly with small additions of Ga,³ Sn, Pb, Cu, Ag, or Ti.^{3,4,5} Since their results are suspected to be in error, it was decided to repeat the experiment using a combined potentiostatic and emf method. This method was used successfully in determining oxygen diffusivity in liquid copper¹⁷ and copper-lead alloys.¹⁸

II. EXPERIMENTAL METHODS

A. Solubility Study

An indium ingot of 99.999 wt pct purity was purchased from United Minerals Chemical Co., New York. Pieces of the indium were first sealed under vacuum in a quartz tube (5 mm i.d.), and then melted at about 973 K. The indium melt was then slowly cooled in air and quenched into water. The oxygen concentration of the pure indium rod was determined to be less than 0.003 at. pct after removal of the surface oxide. Indium oxide powder, In_2O_3 , of 99.999 wt pct purity was purchased from Cerac Co., Milwaukee.

A schematic drawing of the cell used for solubility measurements in this study is shown in Figure 1. The entire cell was constructed from quartz. The H-shaped cell consisted of two vertical tubes (5 mm i.d.) connected by a 20 mm long (2 mm i.d.) capillary tube. About 1.5 gm of the indium rod was loaded into one side of the cell, while a mixture of indium and indium oxide (In_2O_3) was placed in the other side. The cell was then sealed under vacuum (5×10^{-6} torr). The cell was loaded in a furnace for the equilibration experiment. Normally two cells were placed together in the furnace for the experiment. Two quartz tubes were used to hold the cells vertically inside the furnace.

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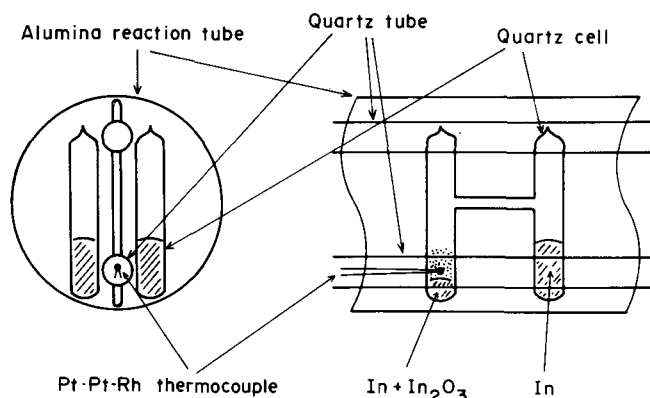


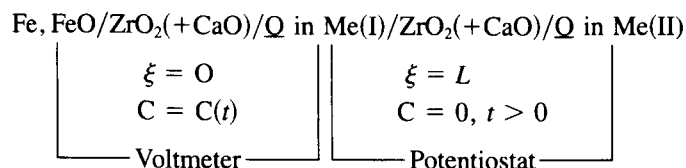
Fig. 1—Schematic drawing of sealed silica cells used in experiments for oxygen solubility.

One of these quartz tubes was also used to position the thermocouple which measured the cell temperature. Special care was taken to position the thermocouple as close as possible to the side of the cell which was being measured. The temperature of both sides of the cells was checked frequently during the experiment. The indium at one end of the cell was heated to 973 or 1073 K. At the other end, In-In₂O₃ mixture was kept to be about 3 K cooler than the indium side. This temperature gradient was necessary to prevent the formation of indium oxide in the liquid indium. After holding the cells at the experimental temperature (within ± 1 K) for a preselected time, the cells were rapidly quenched into liquid nitrogen. The experimental technique is essentially the same as used by Alcock and Jacob.¹² However, in the present study, the quenched indium sample was separated into two portions for oxygen analysis, *i.e.*, the top and the lower one. When the analyzed oxygen concentrations of both portions were within the uncertainty of the analysis, the average value was accepted. Otherwise, the runs were rejected. According to Valderraman and Jacob,¹⁹ vapor *via* In₂O gas species from In + In₂O₃ mixture is an order of magnitude greater than that of In. This implies that oxygen is transported rapidly *via* In₂O gas species from In + In₂O₃ mixture to liquid In. The present results revealed that 24 hours were sufficient for equilibration for experiments at 1073 K, and 100 hours were sufficient at 973 K.

Oxygen analysis was carried out using a Leco RO-116 unit, by reacting the sample in a graphite crucible under an electrical arc. The amount of CO gas formed was measured by infrared absorption method. To minimize possible volatilization of In₂O from the sample, a small amount of carbon powder was added prior to the sample combustion for oxygen analysis.

B. Diffusion Study

The combined potentiostatic and emf method which was used successfully to determine oxygen diffusivity in liquid copper,¹⁷ lead,^{18,20} and copper-lead alloys¹⁸ was used in the present study. Details of the experimental method have been given elsewhere.^{17,18} The method employs two electrochemical cells as shown below:



The symbol Me indicates the metal used, either In or Sn. Figure 1 of Reference 18 gives a schematic diagram of the double cell arrangement. Oxygen diffusivity, D_O , in metal I was measured. Metal II was used as sink for oxygen, in order to establish the boundary condition that $C = 0$ at $t > 0$ and $\xi = L$. Initially, oxygen concentrations in both metals were equal and uniform. Oxygen was then transported from metal I to metal II, by applying a voltage to the right-hand cell using a potentiostat. With the specified boundary condition, the time-dependent oxygen concentration in metal I at the left-hand electrolyte-metal interface, $\xi = 0$, is related to the oxygen diffusion coefficient in the liquid metal. The oxygen concentration is related to the emf of the left-hand cell. The time-dependent emf, $E(t)$, with respect to Fe-FeO reference electrode, in terms of the diffusion coefficient and cell geometry is²⁰

$$\Delta E(t) = E(t) - E_0 = \frac{RT}{2F} \left\{ \ln \left(\frac{4}{\pi} \right) - \frac{D_O \pi^2 t}{4L^2} \right\} \quad [1]$$

where E_0 is the emf at $t = 0$, R the gas constant, F the Faraday constant, t time, and L column length of liquid metal I. The above Eq. [1] was derived for the conditions of unidirectional diffusion and large t . When all the boundary conditions are fulfilled, plots of $E(t)$ vs t should yield straight lines when t is large. The slopes of the lines depend on D_O and L , as evident from Eq. [1]. Since D_O is an intrinsic quantity, it does not depend on L . So if the cell length, L , is varied and the same value of D_O is obtained, this result should be valid. Furthermore, when the linear portions of the $\Delta E(t)$ vs t lines are extrapolated to $t = 0$, $\Delta E(t = 0)$ should equal $(RT/2F) \times \ln(4/\pi)$. This is another indication of the reliability of the data obtained.

In the present study, two ZrO₂ (+5 wt pct CaO) crucibles with the dimensions of 20 mm o.d., 17 mm i.d., and 8 mm o.d., 5 mm i.d., respectively, were supplied by Nippon Kagaku Tokyo Co. Ltd. The column length, L , was varied from 3 to 5 mm for In and 2 to 5 mm for Sn. The reference electrode was prepared by sintering Fe + Fe₂O₃ mixtures with appropriate proportions to yield a two-phase mixture of Fe + FeO. Rhenium wires connected to Kanthal wires were used as the lead wires for liquid indium while molybdenum wires were used for liquid tin. The emf of the left-hand cell was measured with a Yokogawa model 2502 digital voltmeter. A Hokuto Denko model PS-500 B potentiostat was used to impose a voltage to the right-hand cell.

The emf of the left-hand cell was initially $E_0 \approx -30$ mV for indium and 0 to -30 mV for tin with respect to the Fe + FeO electrode. A large voltage of -0.7 to -0.8 V was then applied between both liquid metals. Within a few minutes, the applied voltage was reduced to -0.5 V, because the IR drop through the lead wires decreased with time and therefore the large voltage applied initially was no longer necessary. During the experiments, the electrical current was stopped for a short period of time, in order to measure the open-circuit emf between the two liquid metal electrodes. This emf was approximately 400 mV, and this implies that the boundary condition, $C = 0$ at $t > 0$ and $\xi = L$, was satisfied as described previously.^{17,18}

III. EXPERIMENTAL RESULTS

A. Solubility Study

The experimental results are given in Table I and Figure 2. Results for sample numbers I-4, I-6, I-7, and II-3 were rejected. As shown in Table I, the analyzed oxygen concentrations in the upper and lower portions of these samples differ significantly. It is believed that In_2O_3 might have formed in these samples during the experiments. Furthermore, when breaking the quartz cells, it was nearly impossible not to contaminate the upper portion of the sample with a minute amount of silica dust. This experimental problem was further complicated by cavity formation as a result of solidification shrinkage. The size and ductility of the sample made it extremely difficult to remove the surface layer of the cavities. If any small amount of oxide was trapped in the shrinkage cavity, the analyzed oxygen concentration would be too high.

As shown in Figure 2, the present results, $C_0 = 0.0092$ at. pct at 973 K and 0.0377 at. pct at 1073 K, are in good agreement with the results of Otsuka *et al.*^{8,10} and in reasonable agreement with those of Alcock *et al.*¹¹ The results of Heshmatpour and Stevenson^{4,5} and Hahn and Stevenson,³ however, are too low, while those of Fitzner and Jacob¹ and Anderson and Donaghey² are too high. In view of the exten-

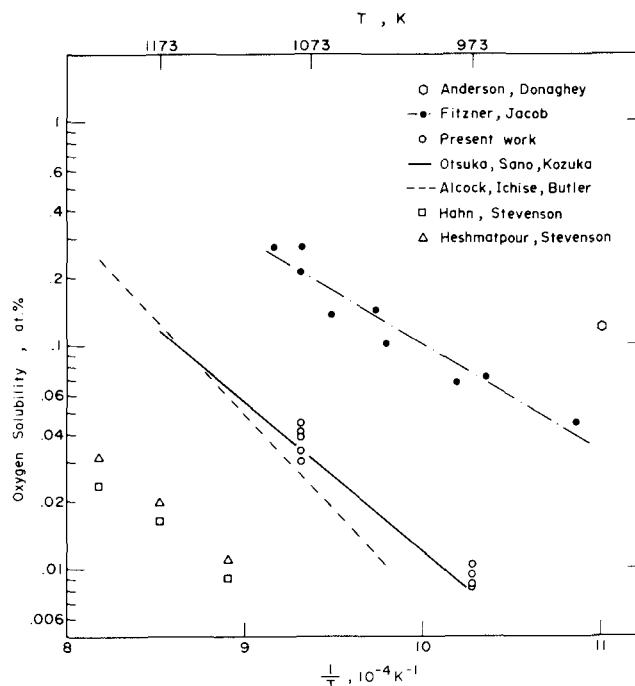


Fig. 2—Saturation solubility of oxygen in liquid indium as a function of temperature.

Table I. Experimental Values for Oxygen Solubility in Liquid Indium

Sample No.	Temp., K	Annealing Time, Hours	Analyzed Value, At. Pct (Upper) (Lower)	Average At. Pct
I-1	973	100	0.0105 0.0103	0.0104*
I-2	973	100	0.0081 0.0088	0.0085*
I-3	973	100	0.0077 0.0088	0.0083*
I-4	973	100	0.0220 0.0115	not adopted
I-5	973	100	0.0091 0.0096	0.0094*
I-6	973	216	0.0202 0.0083	not adopted
I-7	973	100	0.0176 0.0294	not adopted
Ave. of (*) . . . 0.0092 at. pct				
II-1	1073	24	0.0483 0.0425	0.0454**
II-2	1073	24	0.0367 0.0408	0.0388**
II-3	1073	100	0.0733 0.0455	not adopted
II-4	1073	100	0.0393 0.0419	0.0406**
II-5	1073	100	0.0343 0.0327	0.0335**
II-6	1073	100	0.0303 0.0300	0.0302**
Ave. of (**) . . . 0.0377 at. pct				

sive measurements by Otsuka *et al.*^{8,10} the equation for the saturation solubility of oxygen in liquid indium is adopted from their work,

$$\ln C_0(\text{at. pct}) = 10.98 - 15400/T(\text{K})$$

$$973 \text{ K} \leq T \leq 1173 \text{ K} \quad [2]$$

B. Diffusion Study

Figure 3 shows the $\Delta E(t)$ vs time plots for oxygen diffusivity in liquid indium at 973 K. Values of ΔE vary linearly with t , after a few minutes, for both runs with $L = 2.9$ and 4.9 mm. Extrapolation of the linear curves to $t = 0$ yields values in reasonable agreement with the predicted values of $(RT/2F) \ln(4/\pi)$ by Eq. [1]. However, during the initial experiments for one run, extrapolation of the linear portions of the curves yields values larger than that predicted by Eq. [1]. By repeatedly pumping oxygen in and out of the cell, reproducible results as shown in Figure 3 were obtained. This may be due to increased wetting ability of indium by the electrolyte with time. The fact that both runs with different values of L yield the same value of D_0 and the value of $(RT/2F) \ln(4/\pi)$ indicates a negligible amount of convection occurred in the electrochemical cell. Values of D_0 obtained from the present study are plotted in Figure 4 as a function of $1/T$. Assuming linear dependence on $1/T$, the following equation was obtained for oxygen diffusivity in liquid indium using a least squares treatment of the results with a 95 pct confidence interval:

$$D_{O(\text{In})} = 6.6 \left(\begin{smallmatrix} +2.0 \\ -1.6 \end{smallmatrix} \right) \times 10^{-3} \exp[(-32600 \pm 5600)/RT]$$

$$873 \text{ K} \leq T \leq 1073 \text{ K} \quad [3]$$

The results obtained by Heshmatpour and Stevenson,^{4,5} Klindinst and Stevenson,¹³ Hahn and Stevenson,³ and Anderson and Donaghey² shown in the same figure are two orders of magnitude lower than the present results.

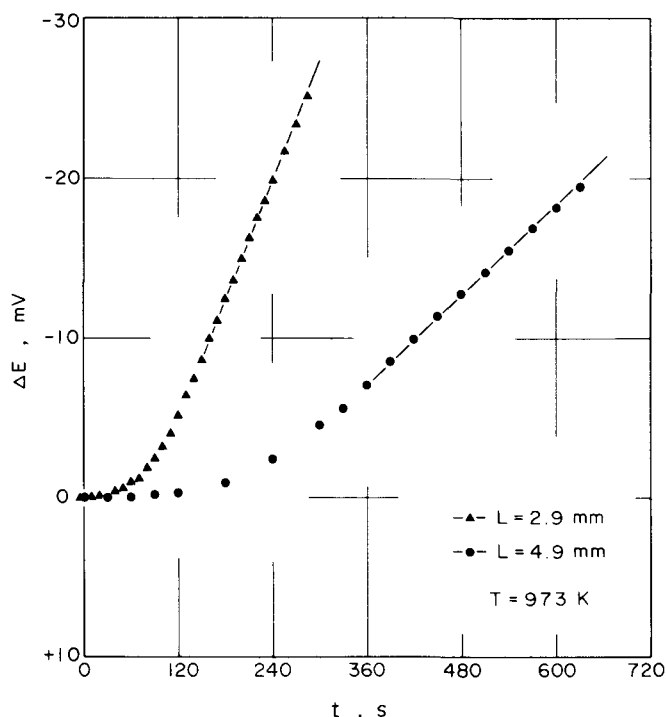


Fig. 3— ΔE plotted vs time in the experiments with liquid indium.

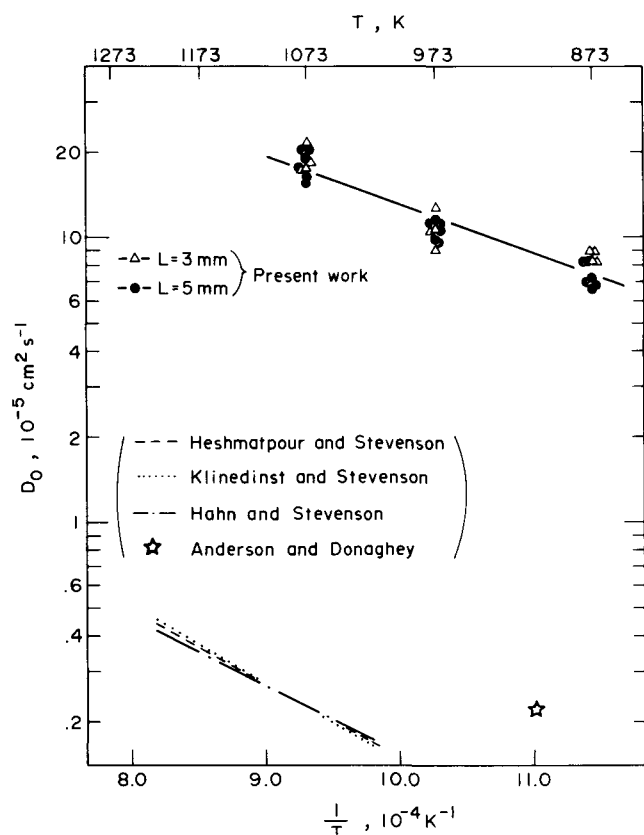


Fig. 4—Diffusion coefficient of oxygen in liquid indium as a function of temperature.

Typical results for $\Delta E(t)$ vs t plots for oxygen diffusivity in liquid tin at 1273 K are shown in Figure 5. The Arrhenius type of plot for $D_{O(Sn)}$ is shown in Figure 6. A least squares treatment of the data with a 95 pct confidence interval

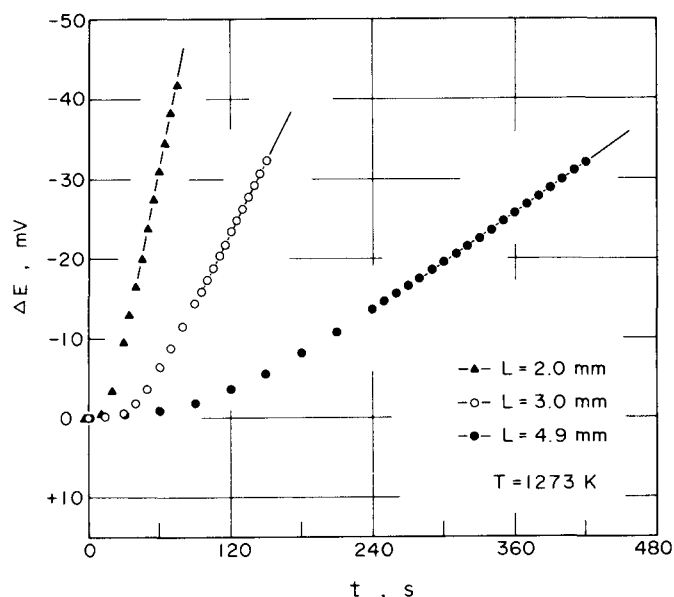


Fig. 5— ΔE plotted vs time in the experiments with liquid tin.

yielded the following equation for oxygen diffusivity in liquid tin:

$$D_{O(Sn)} = 8.7 \left(\begin{smallmatrix} +13.5 \\ -5.7 \end{smallmatrix} \right) \times 10^{-4} \exp[(-18800 \pm 6700)/RT] \\ 973 \text{ K} \leq T \leq 1273 \text{ K} \quad [4]$$

Earlier results of Otsuka and Kozuka^{21*} and Ramanarayanan

*Otsuka and Kozuka measured oxygen diffusivity in tin and silver by monitoring the amount of oxygen absorbed from $H_2 + H_2O$ gas mixtures and air, respectively. The results were evaluated using the proper equation and therefore the diffusivity values calculated are correct. However, unfortunately the quantity π^2 in the exponential term was inadvertently left out of Eq. [3] of Reference 21, Eq. [5] of Reference 23, and Eq. [5] of Reference 24.

and Rapp²² are also shown in Figure 6 for comparison. The present results are slightly higher than those previously reported.^{21,22}

IV. DISCUSSION

A. Solubility Study

As shown in Figure 2, the solubilities determined by Fitzner and Jacob¹ are too high. In their experiment, Fitzner and Jacob equilibrated indium melt with its oxide, In_2O_3 , in an evacuated and sealed quartz capsule. After the sample was equilibrated for 24 hours, the quartz capsule was quenched in liquid nitrogen. In view of the problems encountered in the present study, it seems likely that some oxides may have contaminated their quenched indium sample. The fact that they reported higher oxygen solubilities supports this assumption.

Anderson and Donaghey² carried out a coulometric titration experiment to determine oxygen solubility in liquid indium with the cell: \underline{Q} in $In/ZrO_2(+CaO)/In, In_2O_3$. The cell was designed to allow the passage of oxygen ions unidirectionally. In their experiments, oxygen concentration in liquid indium was reduced electrochemically by passing a specified quantity of electrical charge through the cell. The

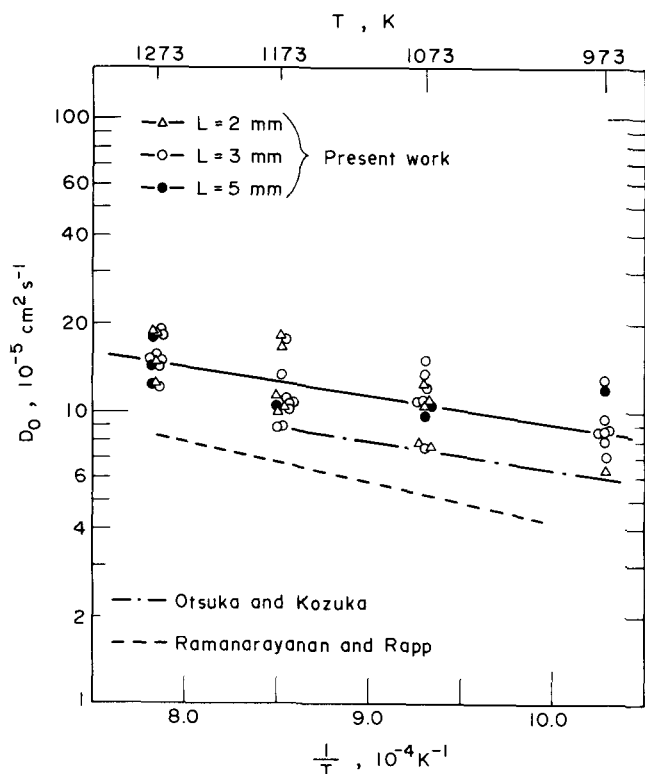


Fig. 6—Diffusion coefficient of oxygen in liquid tin as a function of temperature.

emf was then monitored as a function of time. Since the atmospheres over the two electrodes were not satisfactorily isolated, there must have been some oxygen leakage from one electrode to the other. This would cause an error in their measurements. The fact that they obtained a strong dependence of (K/γ_0) , with emf of the cell, further casts doubt on the reliability of their experiments.

In the coulometric titration experiments of Hahn and Stevenson³ and Heshmatpour and Stevenson,^{4,5} oxygen was initially pumped out coulometrically. The oxygen activity was reduced several orders of magnitude lower than the equilibrium pressure of oxygen for indium and its oxide mixtures. A specified amount of oxygen was then added coulometrically to the melts. After interrupting the current, the indium melt was homogenized by annealing for three hours⁵ and oxygen activity measured. However, at such low oxygen potential, the release of oxygen from the electrolyte and leakage of oxygen from the reference electrode, air, to the melts would cause error in the measurements. This problem was further enhanced when the emf of the cell was 900 mV and the annealing time of three hours. Furthermore, no consideration was given to the contribution of electronic conduction of the electrolyte. In the coulometric titration experiment of Otsuka *et al.*,⁸ the annealing time prior to the emf measurement was only a few seconds. The problems mentioned above may have been the cause of the low oxygen solubility values reported by Stevenson and co-workers.

B. Diffusivity Study

Values of $D_{O(\text{In})} = 2.9 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ at 1123 K reported by Stevenson and co-workers^{3-5,13} are two orders of magnitude lower than those reported in the present study

and the self-diffusion coefficient of indium.^{14,15,16} Moreover, Stevenson and co-workers^{4,5,13} found that small additions of Ga, Sn, Pb, Cu, Ag, and Ti to In significantly increased oxygen diffusivity. It is difficult to conceive that oxygen diffusivity in In would be orders of magnitude lower than the self-diffusivity of indium. It is also difficult to believe that all six added elements, with drastically different properties, would have the same effect on the oxygen diffusivity in In. Thus, the reliability of the data reported by Stevenson and co-workers is questionable.

In their experiments, Stevenson and co-workers used either a stabilized zirconia or an yttria electrolyte tube with 7 mm i.d. A controlled amount of oxygen potential at the metal-electrolyte interface was reduced by applying a voltage to the cell so that the unsteady state, radial diffusion of oxygen was affected. The ionic current, I_{ion} , at a given time induced by oxygen diffusion in the melts may be expressed by^{25,26}

$$I_{\text{ion}} = \frac{8FD_0M_\infty}{a^2} \sum_{n=1}^{\infty} \exp\left[-\frac{\alpha_n^2 D_0 t}{a^2}\right] \quad [5]$$

where M_∞ is the amount of oxygen diffused in $t = \infty$, a the radius of the cylindrical sample, $\alpha_1, \alpha_2, \dots, \alpha_n$ the first, second, \dots n th root of the Bessel function of the zeroth order. Their values are 2.40, 5.52, \dots , respectively. When t is large, terms involving $n \geq 2$ may be neglected. Eq. [5] is reduced to,

$$I_{\text{ion}} = \frac{8FD_0M_\infty}{a^2} \exp\left[-\frac{\alpha_1^2 D_0 t}{a^2}\right] \quad [6]$$

Stevenson and co-workers^{3-5,13} used Eq. [6] to evaluate oxygen diffusivity from current decay curves obtained after 100 to 150 seconds. The calculated values determined from the curves which were presented in their reports were $D_0 = 8.6 \times 10^{-5}$, 2.9×10^{-6} and $1.3 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ in Ga,³ In,³ and an In-Ga alloy,⁴ respectively. Using these numerical values, the ratio of the first to second term in Eq. [5] was recalculated. This calculation shows that the contribution of the second term cannot be ignored even after 200 seconds for $D_0 = 8.6 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, 2000 seconds for $D_0 = 1.3 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and 5000 seconds for $D_0 = 2.9 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. Stevenson *et al.* should have evaluated oxygen diffusivity from the decay curves after much longer times. However, proper analysis of their data leads to very small values of oxygen diffusivity, which is unlikely. One may also point out, that the linear portion of the I_{ion} vs t plots starts at almost the same time for the different melts studied. In view of this point and considering the low oxygen potentials measured, Stevenson *et al.* may have monitored oxygen released from the electrolyte instead of oxygen transferred from the liquid metal. This type of oxygen release is related to the properties of the electrolyte and the electrolyte-melt interface.^{6-8,27}

The $D_{O(\text{Sn})}$ values determined in the present study and those reported by Otsuka and Kozuka²¹ and Ramanarayanan and Rapp²² are reasonably close. However, the present results may be better as discussed below. In the experiment by Otsuka and Kozuka, a rather long time, *i.e.*, three hours, was necessary to make a measurement, in contrast to 20 minutes in the present study. In the experiment by Ramanarayanan and Rapp, a correction was not made for possible release of oxygen from the electrolyte. The most

Table II. Values of D_O , D^* , D_O/D^* and $\Delta H_{f,298}^\circ$ (oxide)

	Temp., K	$D_O \times 10^5$, $\text{cm}^2 \cdot \text{s}^{-1}$	$D^* \times 10^5$, $\text{cm}^2 \cdot \text{s}^{-1}$	D_O/D^*	$\Delta H_{f,298}^\circ$ (oxide), kJ
Ag	1273	14.5 ²⁶	2.67 ⁴⁴	5.43	-30.5
		10.4 ³³		3.90	
		10.1 ³⁴		3.78	
		9.58 ³⁵		3.59	
		9.51 ³⁶		3.56	
		9.33 ^{23,37}		3.49	
Cu	1423	8.79 ³⁸	4.65 ⁴⁵	3.29	-170.3
		9.46 ³⁹		2.03	
		8.47 ¹⁷		1.82	
		7.36 ²⁶		1.58	
Pb	1273	7.09 ³³	15.7 ⁴⁶	1.52	-219.3
		26.3 ⁴⁰		1.68	
		23.5 ²⁰		1.50	
Sn	973	12.3 ⁴¹	7.77 ¹⁶	0.78	-290.4
		8.52 ^{present work}		1.10	
In	873	3.81 ²²	7.66 ^{15,16}	0.49	-308.6
		7.40 ^{present work}		0.97	
Ni	1773	6.3 ⁴²	4.2 ⁴⁷	1.50	-240.6
Fe	1833	2.5 ~ 5.5 ⁴²	4.1 ⁴⁸	0.61 ~ 1.34	-272.0
		2.64 ⁴³		0.64	

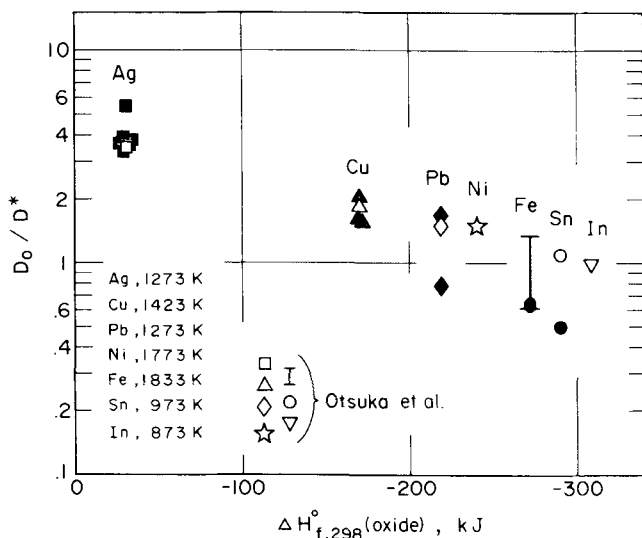


Fig. 7— D_O/D^* as a function of the standard enthalpy of formation per mole of O of the respective oxide at 298 K. $\square \triangle \diamond \star \circ \nabla$; experimental values of Otsuka *et al.*, $\blacksquare \blacktriangle \blacklozenge \blackstar$; experimental values of other investigators.

important point is that neither group of investigation sufficiently varied the column length L or the radius a , in order to check the consistency and reproducibility of the $D_{O(Sn)}$ values.

C. Correlation of Oxygen Diffusivity in Liquid Metals

Since oxygen diffusivity data in liquid metals are difficult to obtain experimentally, attempts have been made to formulate an empirical correlation which may be used to predict data for systems where experimental values are not available. Otsuka and Kozuka²⁰ suggested an empirical cor-

relation between (D_O/D^*) and ΔG_O° , where (D_O/D^*) is the ratio of oxygen diffusivity to the self-diffusivity of the solvent metal and ΔG_O° is the standard Gibbs energy of solution of oxygen in the solvent. In the present study, instead of ΔG_O° , $\Delta H_{f,298}^\circ$ is used where $\Delta H_{f,298}^\circ$ is the standard enthalpy of formation of the oxides at 298 K expressed in terms of one mole of O.^{28,29} This avoids the arbitrary choice of temperature when ΔG_O° is used. Furthermore, it has been found that ΔH_O° is related to $\Delta H_{f,298}^\circ$ where ΔH_O° is the standard enthalpy of solution of oxygen in the solvent.^{1,10} The values of D_O , D^* , (D_O/D^*) and $\Delta H_{f,298}^\circ$ used in the correlation are given in Table II. As shown in Figure 7, a definite trend exists between (D_O/D^*) and $\Delta H_{f,298}^\circ$. The data reported by Fitzner for oxygen in liquid antimony³⁰ and bismuth³¹ are not shown in Figure 7. Since the variation of I with t reported by Fitzner using a coulometric titration is not in accord with Eq. [5], the reliability of his results is suspected.³²

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