Determination of diffusivity of sodium in liquid tin using Na– ß″ alumina

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Diffusivity of sodium in molten tin was determined using an electrochemical cell of the type Na/Na–β''-Al$_2$O$_3$/(Na)Sn where Na–β''-Al$_2$O$_3$, which is a sodium-ion conductor, was the solid electrolyte. Using the above cell in which a small amount of sodium dissolved in tin was transported through β''-Al$_2$O$_3$ upon application of an external voltage, and using a known solution to Fick's second law for appropriate boundary conditions, the diffusivity was determined to be

$$ D = 4.4 \begin{pmatrix} + 1.0 \\ - 0.5 \end{pmatrix} \times 10^{-4} \exp \left(- \frac{Q}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} $$

with $Q = 16\,320$ J mol^{-1} over a range of temperatures from 240 to 440° C. From the solution to Fick's second law, it was shown that first term approximations, which have often been used in the past, lead to an estimate of diffusivity which is about a factor of 2 too high indicating that more terms should be considered. The diffusivity was also determined using a transient technique in which the decay in voltage upon removal of externally applied voltage was recorded as a function of time. The diffusivity so determined, in which it was assumed that the only polarization was the concentration polarization, was higher than the previous method. The difference between the two diffusivities became smaller with increasing temperature. These experiments thus suggested that interfacial or activation polarization must also be present.

1. Introduction

Various physical processes are dependent upon the kinetics of mass transport. These include corrosion, phase separation, solidification, crystal growth to name a few. The single most important parameter is the diffusion coefficient or diffusivity. Evidence for this is given by the exhaustive literature on the measurement of diffusion coefficients in a variety of multicomponent systems. Transport of various species in liquid metals has been investigated by a number of researchers over the past three or four decades. Several techniques have been used; these include the capillary reservoir method [1], shear cell method [2], and electrochemical methods [3]. With the advent of solid oxygen ion conductors, namely stabilized zirconia, electrochemical cells have been used by several researchers [4–6]

for the determination of diffusivity of oxygen in liquid metals. Raleigh and co-workers [7,8] have used silver-ion conductors for the study of diffusion in alloys containing silver. Electrochemical methods, however, have not been widely used for the study of diffusion in molten binary metallic systems primarily due to the unavailability of stable high conductivity solid electrolytes. During the past fifteen years or so, the Na–β''-alumina which is a sodium-ion conductor has received much attention as a solid electrolyte for application in the Na–S battery [9] as well as the sodium heat engine [10]. The Na–β''-alumina not only is an excellent ionic conductor ($\sigma \approx 0.5$ Ω^{-1} cm^{-1} at 300° C) with essentially no electronic conductivity but is also quite stable to relatively high temperatures (well in excess of 1200° C). Furthermore, by
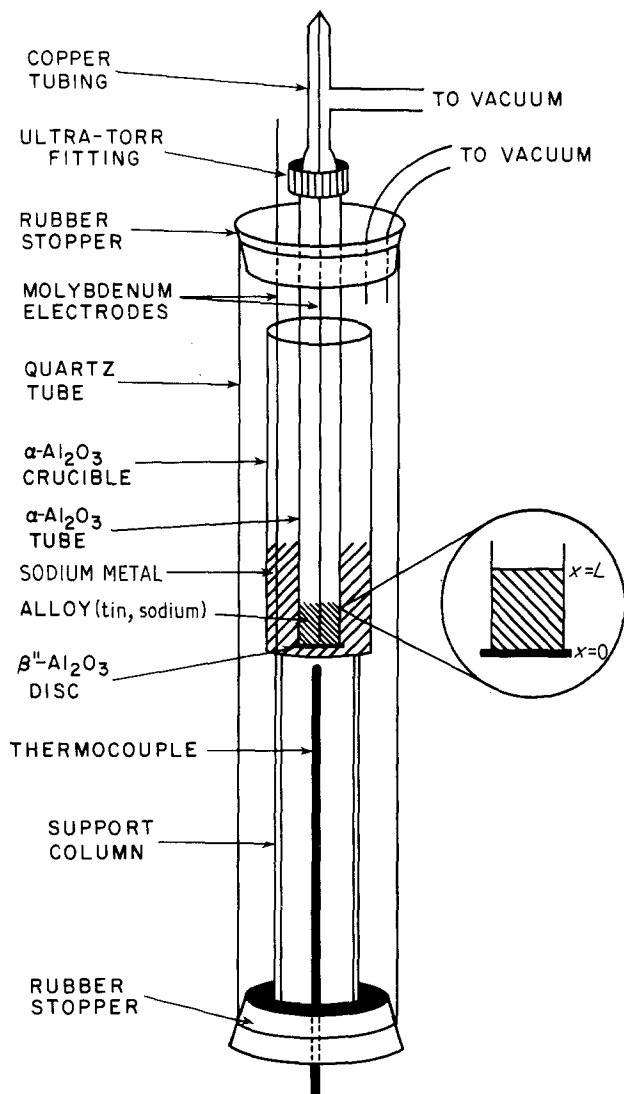
Labels on figure:

COPPER TUBING

TO VACUUM

ULTRA-TORR FITTING

TO VACUUM

RUBBER STOPPER

MOLYBDENUM ELECTRODES

QUARTZ TUBE

α-Al$_2$O$_3$ CRUCIBLE

α-Al$_2$O$_3$ TUBE

SODIUM METAL

ALLOY (tin, sodium)

β''-Al$_2$O$_3$ DISC

THERMOCOUPLE

SUPPORT COLUMN

RUBBER STOPPER

$x = L$

$x = 0$

ion exchange, β''-alumina capable of transporting various other ions such as K^+, Li^+, Ag^+, Cs^+, Tl^+, Cu^+, etc. can be made [11]. More recent work of Farrington and Dunn [12] has shown that β''-aluminas capable of transporting divalent ions such as Pb^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Sn^{2+}, Hg^{2+} and Cu^{2+} can also be made by ion exchange from fused salts. These β''-aluminas by and large are also quite stable to at least 800 to 1000° C. Thus, diffusion studies can be conducted in a multitude of metallic systems. In the present study, Na–β''-alumina has been employed for determining diffusivity of sodium in molten tin.

Two techniques have been used for determining diffusivity. One of the techniques is similar to that used by Ramanarayan and Rapp [4], Otsuka and Kozuka [5] and several others, except that the first

term approximation is not used in the present study. In fact, it can be shown that the first term approximation leads to a diffusivity which is erroneously too high. The other technique is a transient technique in which the objective is to record the voltage decay upon removal of external voltage and subsequently relate the decay in voltage to the decay of concentration polarization. These results indicated that interfacial polarization is also present.

2. Experimental procedure

A cell of linear geometry of the design shown in Fig. 1 was constructed. Na–β''-alumina discs of ~ 2 cm diameter and ~ 0.25 cm thick were fabricated by the procedure described previously [13]. A disc of β''-alumina was sealed to an α-alumina

insulator tube using a borosilicate sealing glass. A known amount of tin was placed inside the α-alumina tube and the tube (with β''-alumina disc facing downwards) was placed in an α-alumina crucible containing sodium. The entire assembly was placed inside a quartz tube and ends were plugged using rubber stoppers. The open end of the α-alumina tube, which protruded out through a hole in the rubber stopper was connected to a copper tube through a torr-fitting and a "T". Molybdenum was used as electrode material for both the tin and the sodium chambers. The quartz tube and the α-alumina tube were evacuated and sealed by pinching off the copper tubes. A measuring thermocouple was introduced from the bottom rubber stopper. All of the joints on the two ends of the quartz tube were sealed using a silicone sealant prior to evacuation. The cell was placed in a vertical furnace (with ends outside of the furnace). The cell was then heated to 400° C and allowed to equilibrate. Subsequently, a current of density $\sim 0.1\ \mathrm{A\,cm^{-2}}$ was passed using a d.c. power supply causing sodium-ions to transport through β''-alumina into the tin chamber with electrons flowing in the outer circuit. After a certain time, the current was interrupted and the cell was allowed to equilibrate for a day. After equilibration (i.e. when the concentration is presumed to have become uniform), the equilibrium potential was recorded. The corresponding activity of sodium in liquid tin is given by

$$a_{\mathrm{Na}} = \exp\left(-\frac{FE_0}{RT}\right) \qquad (1)$$

where E_0 is the equilibrium potential, F is the Faraday constant, R the gas constant and T is the temperature. Also, as charge transported is known, the mole fraction of sodium in tin i.e. X_{Na}^0, was determined.

Subsequently a large d.c. voltage (1.5 V) was applied with the sodium-chamber being connected to a negative terminal. Since the standard e.m.f. of the reaction

$$2\mathrm{Na^+} + \mathrm{Sn} \rightarrow 2\mathrm{Na} + \mathrm{Sn^{+2}} \qquad (2)$$
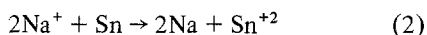
is $E^0 = -5.28\,\mathrm{V}$, under the applied voltage $\mathrm{Na^+}$ cannot oxidize tin. Thus, $\mathrm{Sn^{2+}}$ cannot replace $\mathrm{Na^+}$ from β''-alumina. The applied voltage of 1.5 V, however, is large enough to ensure that a very low activity of sodium is maintained in tin next to the β''-alumina/tin interface. After applying the voltage for a certain time, the voltage was removed and

the system was allowed to equilibrate until it was certain that the open circuit potential became steady, indicating that the concentration of sodium in tin had become uniform. Typically, this time was between several hours to a day. This procedure was repeated several times and after each equilibration step, the open circuit e.m.f. was recorded. Experiments of this type were conducted over a range of temperatures from 240 to 440° C.

In many cases, upon removal of the external voltage, the e.m.f. was recorded on a strip chart recorder. This information was later used for determining diffusivity by a transient method.

3. Theoretical considerations
3.1. The equilibration method
In the present experiments, the concentration of sodium in tin was generally low ($x_{\mathrm{Na}} \leqslant 0.05$). Thus, diffusivity, D, can be assumed to be a constant. The appropriate diffusion equation for the linear geometry of the cell is given by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad 0 \leqslant x \leqslant L. \qquad (3)$$

The initial and the boundary conditions are given by

$$C(x,0) = C_0 \qquad 0 \leqslant x \leqslant L$$
$$C(0,t) = C^0 \qquad 0 < t$$
$$\frac{\partial C}{\partial x}(L,t) = 0 \qquad 0 < t.$$

The solution to the above differential equation subject to the given initial and boundary conditions is given by [14]

$$C(x,t) = C^0 + \frac{4(C_0 - C^0)}{\pi}\sum_{m=0}^{\infty}\frac{1}{(2m+1)}$$
$$\times \sin\left[\left(m+\frac{1}{2}\right)\frac{\pi x}{L}\right]\exp\left[-\left(m+\frac{1}{2}\right)^2\frac{\pi^2}{L^2}Dt\right].$$
$$(4)$$

After having applied a voltage (tin reservoir positive) for time t_1, the concentration profile will appear schematically as shown in Fig. 2. After time t_1, when the external voltage is removed, the concentration will gradually become uniform. The equilibrated average composition will be given by

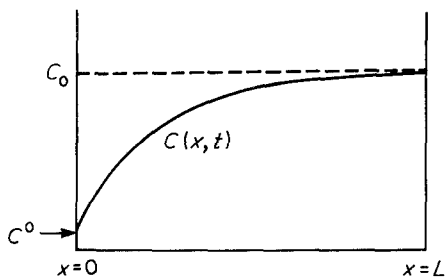$$\bar{C}(t_1) = \frac{1}{L}\int_0^L C(x,t_1)\,\mathrm{d}x \qquad (5)$$

Figure 2 A schematic drawing showing the boundary and the initial conditions of the diffusion problem as well as a schematic illustration of the composition profile for $t > 0$.

which is given by

$$\bar{C}(t_1) = C^0 + \frac{8(C_0 - C^0)}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2}$$

$$\times \exp\left[-\left(\frac{2m+1}{2L}\right)^2 \pi^2 D t_1\right]. \quad (6)$$

Let us assume that a dilute solution of sodium in tin follows Henry's law. Then, with

$$a_{Na} = \gamma_{Na} X_{Na} = \gamma_{Na} \frac{C_{Na}}{C_{Na} + C_{Sn}} \cong$$

$$\gamma_{Na} \frac{C_{Na}}{C_{Sn}} \quad (7)$$

we have

$$C_{Na} = \frac{C_{Sn}}{\gamma_{Na}} \exp\left(-\frac{FE}{RT}\right). \quad (8)$$

Thus

$$C_0 = \frac{C_{Sn}}{\gamma_{Na}} \exp\left(-\frac{FE_0}{RT}\right),$$

$$C^0 = \frac{C_{Sn}}{\gamma_{Na}} \exp\left(-\frac{FE^0}{RT}\right) \text{ with } E^0 = 1.5 \text{ V},$$

and

$$\bar{C}(t_1) = \frac{C_{Sn}}{\gamma_{Na}} \exp\left(-\frac{F\bar{E}(t_1)}{RT}\right).$$

Substituting in Equation 6 we get

$$\frac{\exp\{-[F\bar{E}(t_1)/RT]\} - \exp[-(1.5F/RT)]}{\exp[-(FE_0/RT)] - \exp[-(1.5F/RT)]} =$$

$$\frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\left(\frac{2m+1}{2L}\right)^2 \pi^2 D t_1\right]$$

(9)

where t_1 is the time that a voltage of 1.5 V was

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applied in the reverse direction, E_0 is the equilibrium open circuit potential between the two molybdenum electrodes at $t = 0$ and $\bar{E}(t_1)$ is the equilibrium potential when the cell upon application of 1.5 V for time t_1 was allowed to equilibrate. The diffusivity D was subsequently determined via Equation 9 by taking several terms.

3.2. The transient method

In several experiments, upon removal of the external voltage, the cell e.m.f. was recorded using a strip chart recorder. This problem can be analysed in the following manner.

At the time the voltage was removed, the concentration is given by $C(x, t_1)$, Equation 4. Now, as the voltage is removed, after a long time the concentration will become uniform, which is given by Equation 6. This process can be described by

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial x^2} \qquad 0 \leqslant x \leqslant L \quad (3)$$

Initial condition: $C(x, 0) = f(x) = C(x, t_1)$ from the previous solution e.g. Equation 4.

Boundary conditions: $\frac{\partial C}{\partial x}(0, t) = \frac{\partial C}{\partial x}(L, t) = 0$.

In principle, D and D_1 are the same. However, under experimental situations, there may be other factors arising out of certain assumptions which may lead to D_1 not being identical with D. It is for this reason, that we have chosen to distinguish the diffusivities determined by these two methods.

The solution to Fick's second law from these initial and boundary conditions is given by [15]:

$$C(x, t) = \frac{1}{L} \int_0^L f(\xi) \, d\xi + \frac{2}{L} \sum_{n=1}^{\infty} \cos \frac{n\pi x}{L}$$

$$\times \exp\left[-\frac{n^2 \pi^2 D_1 t}{L^2}\right] \int_0^L \cos \frac{n\pi \xi}{L} \times f(\xi) \, d\xi$$

(10)

where

$$f(\xi) = C^0 + \frac{4(C_0 - C^0)}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)}$$

$$\times \sin\left[\left(m + \frac{1}{2}\right)\frac{\pi \xi}{L}\right] \exp\left[-\left(m + \frac{1}{2}\right)^2 \frac{\pi^2 D t_1}{L^2}\right]$$

(11)

which is the same as Equation 4.

The instantaneous concentration in tin next to the β''-alumina is then given by

$$C(0, t) = \frac{1}{L} \int_0^L f(\xi)\,d\xi +$$

$$\frac{2}{L} \sum_{n=1}^{\infty} \exp\left[-\frac{n^2\pi^2}{L^2} D_1 t\right] \int_0^L \cos\frac{n\pi\xi}{L} \times f(\xi)\,d\xi.$$

$$(12)$$

Now the instantaneous e.m.f. $E(t)$ is related to $C(0, t)$ via

$$C(0, t) = \frac{C_{Sn}}{\gamma_{Na}} \exp\left[-\frac{FE(t)}{RT}\right]$$

which can be measured. Since D has been determined using the equilibration method, $f(\xi)$ is known. Thus, using Equation 12, D_1 can be determined.

It can be shown that

$$C(0, t) = C^0 + \frac{8(C_0 - C^0)}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m + 1)^2}$$

$$\times \exp\left\{-\left[\left(\frac{2m + 1}{2}\right)\frac{\pi}{L}\right]^2 D t_1\right\}$$

$$+ \frac{8(C_0 - C^0)}{\pi^2} \sum_{n=1}^{\infty} \exp\left[-\frac{n^2\pi^2}{L^2} D_1 t\right]$$

$$\times \sum_{m=0}^{\infty} \frac{2}{[(2m + 1)^2 - 4n^2]}$$

$$\times \exp\left\{-\left[\left(\frac{2m + 1}{2}\right)\frac{\pi}{L}\right]^2 D t_1\right\}.$$

$$(13)$$

The above can be rearranged to show (with concentrations replaced in terms of e.m.f.s) that

$$\frac{\exp\{-[FE(t)/RT]\} - \exp[-(1.5F/RT)]}{\exp[-(FE_0/RT)] - \exp[-(1.5F/RT)]}$$

$$= \frac{8}{\pi^2}\left\{\sum_{m=0}^{\infty} \frac{1}{(2m + 1)^2}\exp\left[-\frac{(2m + 1)^2\pi^2 D t_1}{4L^2}\right] + \right.$$

$$2 \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \exp\left[-\frac{n^2\pi^2 D_1 t}{L^2}\right] \frac{1}{[(2m + 1)^2 - 4n^2]}$$

$$\left.\times \exp\left[-\frac{(2m + 1)^2\pi^2 D t_1}{4L^2}\right]\right\}.$$

$$(14)$$

In the actual calculational procedure, various values of D_1 are substituted in Equation 14 until a good fit with the experimentally measured plot of $E(t)$ against t is obtained.

4. Results and discussion

Diffusivity of sodium in tin was determined using Equation 9. Specifically, a value for D was assumed and inserted into the right-hand side of Equation 9 and the right-hand side was compared with the left-hand side obtained through e.m.f. measurements. The value of D which gave the best fit was then assumed to be the true diffusivity. In evaluating the series, several terms were taken. The number of terms used was determined based on the relative magnitude of the ith term when compared with $(i - 1)$th term. In general, when the individual term was less than 1×10^{-6}, that term as well as all other successive terms were omitted. Typical time (t_1) of application of the voltage was between 30 min and 1 h. Experiments were conducted over a range of temperatures from 240 to 440° C and for two initial mole fractions of sodium in tin, namely 0.01 and 0.05. The diffusivity determined with an initial concentration (mole fraction) of 0.05 increased by about 20% as the concentration decreased suggesting that D is not entirely independent of composition. However, for $0.001 < X_{Na} < 0.01$, D was found to be essentially independent of composition as shown in Table I. Fig. 3 shows a plot of log D against $1000/T$. The diffusivity over this range can be given by

$$D = 4.4\binom{+1.0}{-0.5} \times 10^{-4} \exp\left(-\frac{1960}{T}\right) cm^2\,sec^{-1}.$$

The diffusivity was also determined by the transient method or polarization method in which decay of voltage was analysed using Equation 14. Specifically, various values of D_1 were tried until the calculated decay curve matched with the experimental decay curve. For any given calcu-

TABLE I

Initial potential, E_0 (V)	Equilibrated potential, $\bar{E}(t)$ (V)	Time of application of external voltage (sec)	Diffusivity (cm² sec⁻¹)
0.573 33	0.587 22	2040	1.9×10^{-5}
0.587 22	0.608 90	4380	1.9×10^{-5}
0.608 90	0.630 50	4200	1.95×10^{-5}
0.630 50	0.651 75	4080	1.96×10^{-5}
0.651 75	0.674 14	3900	1.91×10^{-5}
0.674 14	0.694 47	4500	1.93×10^{-5}
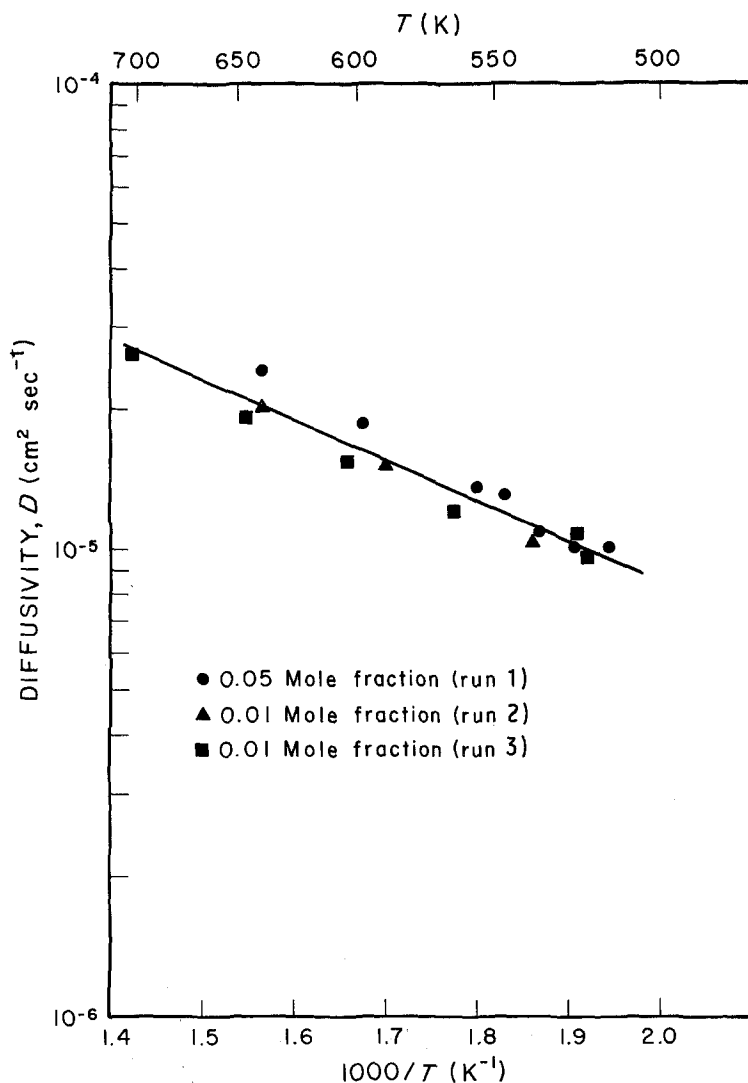
lation, D was used from the equilibration method. If the decay in voltage is strictly due to the decaying of concentration gradients (concentration polarization), then D and D_1 would be the same. Fig. 4 shows the experimental decay curve at 250° C, as well as points calculated with $D_1 = D = 1.08 \times 10^{-5}$ cm^2 sec^{-1} and points corresponding to $D_1 = 1.5 \times 10^{-5}$ cm^2 sec^{-1} which gave the best fit. Clearly, D_1, determined from the transient method is higher than that determined from the equilibration method. At higher temperature (440° C), however, it is found that best fit is obtained with the experimental decay curve with $D_1 \approx D = 2.6 \times 10^{-5}$ cm^2 sec^{-1} as shown in Fig. 5. The log of the diffusivity determined by the transient method, log D_1, is plotted against $1000/T$ in Fig. 6.

The fact that the D_1 is greater than D at lower temperatures implies that the decay in voltage not

only signifies decay of concentration polarization but also decay of interfacial or activation polarization. Since at the β''-alumina/liquid metal interfaces oxidation and reduction reactions take place, these interfaces can be represented as electrical double layers which in turn can be represented as resistor—capacitor elements. Thus, during the application of external voltage, these interfacial capacitors will be charged and when the external voltage is removed, these capacitors will be discharged. The relaxation time for the discharge of these interfacial capacitors, which is a function of the resistances and capacitances, is generally small; of the order of a few seconds to a few minutes. This relaxation time in general will be smaller than the relaxation time of the decay of concentration gradients. In the actual experiments, the decay of voltage will be due to these two
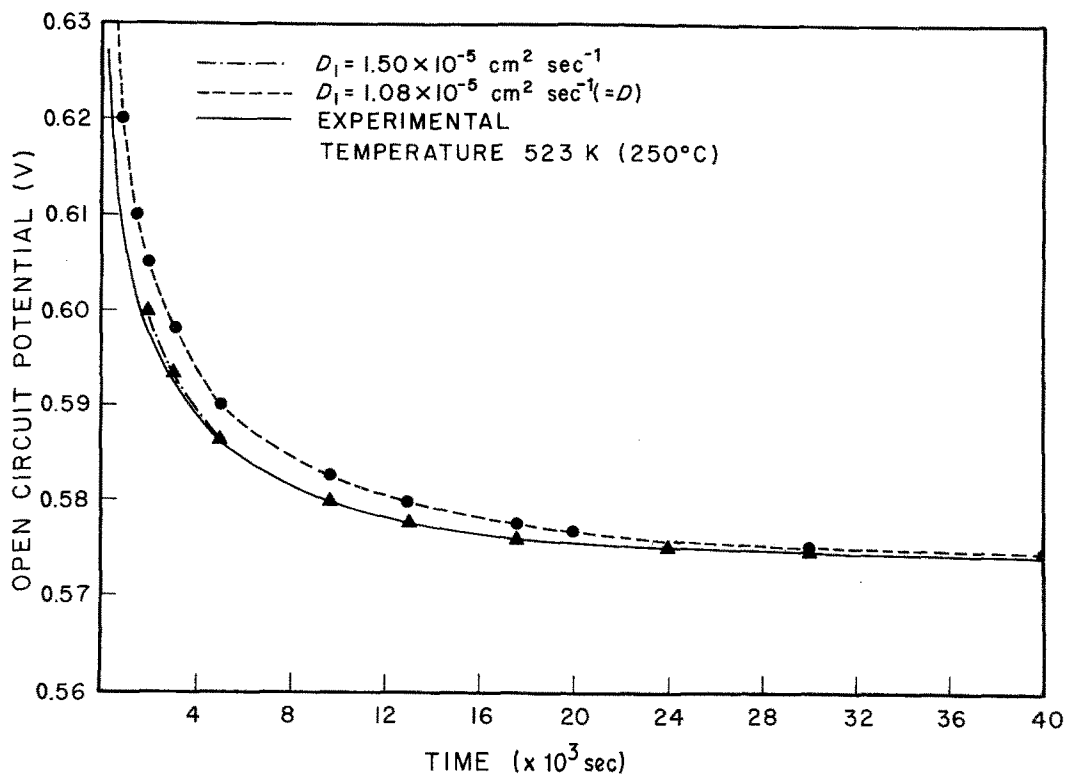
Figure 4 Curve of open circuit potential against time at 250° C obtained after removal of the externally applied voltage. Also shown in the figure are calculated potential against time curves for $D_1 = D = 1.08 \times 10^{-5}$ cm^2 sec^{-1} and for $D_1 = 1.5 \times 10^{-5}$ cm^2 sec^{-1}. Note that best fit with the data is obtained for $D_1 = 1.5 \times 10^{-5}$ cm^2 sec$^{-1} \neq D$.

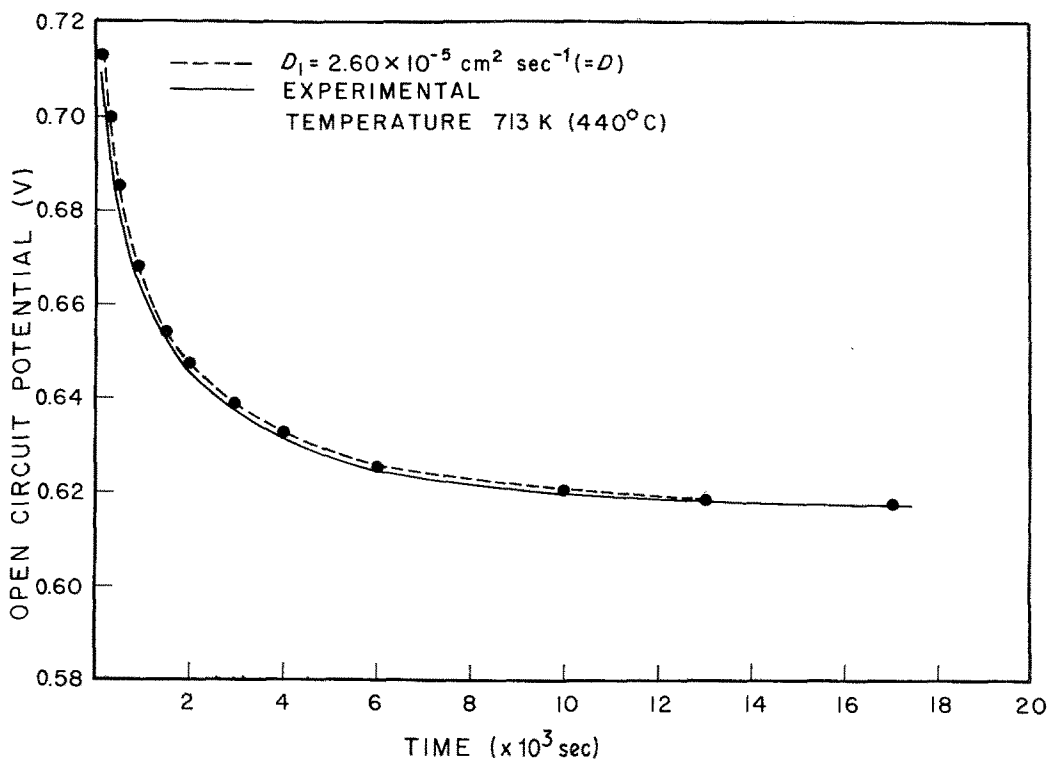*Figure 5* Curve of open circuit potential against time at 440° C. The decay curve calculated with $D_1 = D = 2.6 \times 10^{-5}$ cm^2 sec^{-1} agrees well with the experimental decay curve.
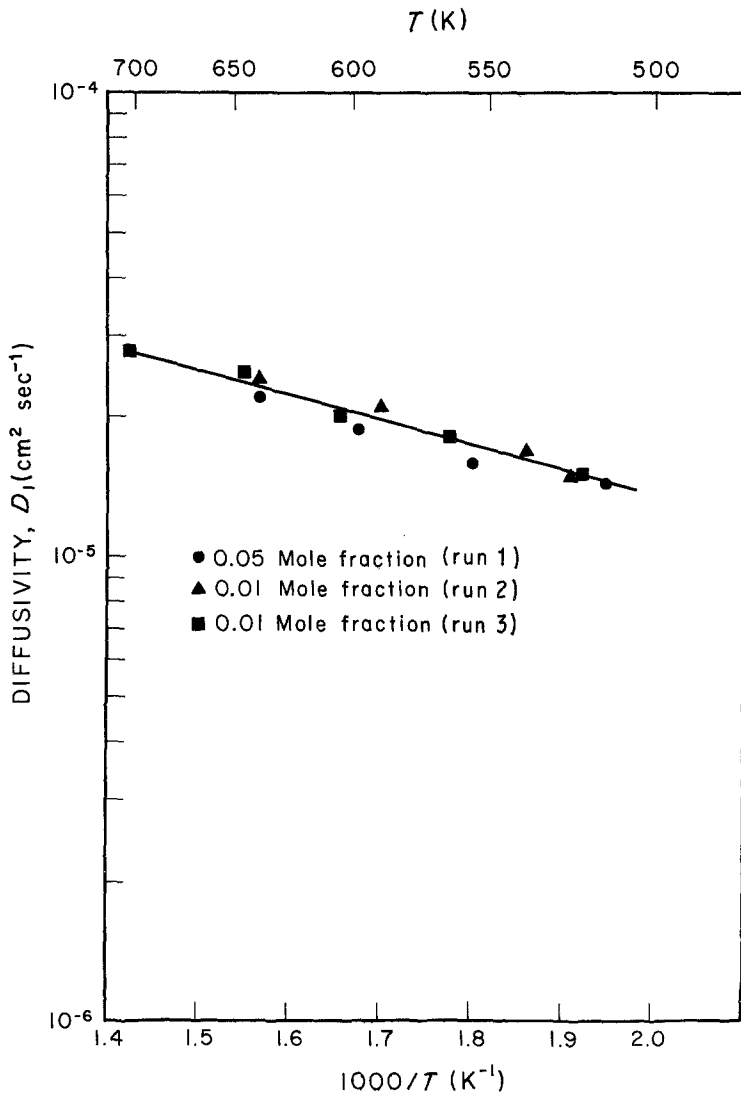
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Figure 6 A plot of log D_1 against $1000/T$ determined using the transient method.

The figure shows a plot with axes:
- Top axis: T (K) with values 700, 650, 600, 550, 500
- Left axis: DIFFUSIVITY, D_1 (cm^2 sec^{-1}) with values 10^{-4}, 10^{-5}, 10^{-6}
- Bottom axis: $1000/T$ (K^{-1}) with values 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0

Legend:
- ● 0.05 Mole fraction (run 1)
- ▲ 0.01 Mole fraction (run 2)
- ■ 0.01 Mole fraction (run 3)

phenomena occurring simultaneously. The decay curve should in principle be fitted using two relaxation times. However, if they are fitted using a single relaxation time, this relaxation time would be smaller than the relaxation time for the decay of concentration gradients which would lead to a higher value for the estimated diffusion coefficient. Furthermore, if one only attempts to fit the decay curve for very short times, the relaxation time will be even closer to the relaxation time for the discharge of interfacial capacitors thereby yielding even higher values of diffusivity. This is precisely what has been found. Furthermore, at higher temperatures, the relaxation time for the discharge of interfacial capacitors must be very small. Consequently, almost the entire decay curve can be fitted with a single relaxation time; that corres-

ponding to concentration polarization. Thus, at high temperatures, both methods yield approximately the same value of diffusivity.

Several researchers [4, 5] have used first term approximations for determining diffusivity. The experimental procedure involves applying a large reverse voltage (about 1.5 V, sodium chamber being made positive) for some time, removing the voltage and recording the equilibrated e.m.f. This procedure is repeated and the e.m.f. is plotted against cumulative time.

The first term approximation involves neglecting all terms except the first one from Equation 9. Furthermore, the term exp $[-(1.5F/RT)]$ in general is very small compared to exp $-[FE(t)/RT]$ and is generally neglected. Then, taking natural logarithm of both sides of Equation 9
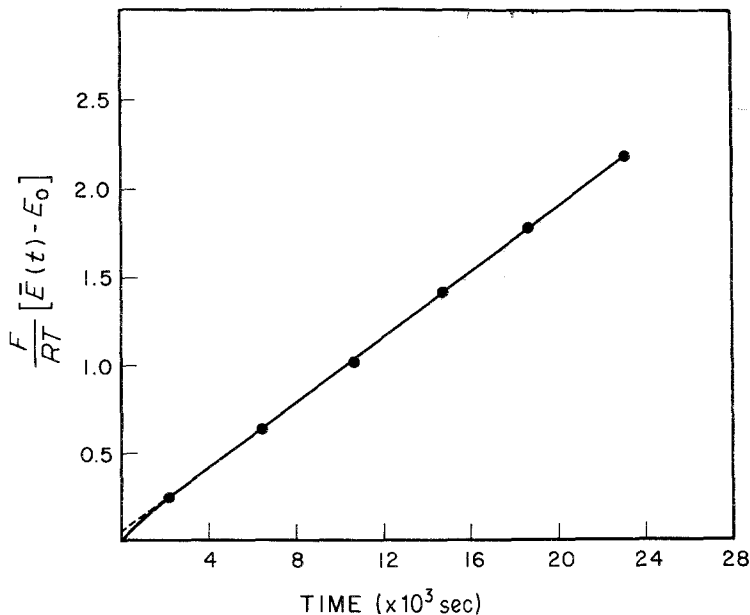
Figure 7 A plot of (F/RT) $[\bar{E}(t) - E_0]$ against t where $\bar{E}(t)$ is the equilibrated open circuit potential and t is the cumulative time of application of the external voltage.

gives

$$\frac{F}{RT} \; [\bar{E}(t) - E_0] \;\; = \; -\ln\left(\frac{8}{\pi^2}\right) + \frac{\pi^2 D}{4L^2} \; t. \;\; (15)$$

The procedure involves plotting $(F/RT)(\bar{E}(t) - E_0)$ against t such that the slope is given by $\pi^2 D / 4L^2$. Fig. 7 shows such a plot at $373°$ C. The corresponding diffusivity, determined from the slope was found to be 3.9×10^{-5} cm^2 sec^{-1} which is nearly a factor of 2 larger than that obtained using several terms as shown in Fig. 3. Edward *et al.* [16] also used an electrochemical method, using molten salts impregnated in a porous alumina matrix as the electrolyte. In their study, D was determined explicitly without making a first term approximation. At $352°$ C and $X_{Na} \approx 0.01$, the diffusivity of sodium in tin was found to be $\sim 2 \times 10^{-5}$ cm^2 sec^{-1} which is in excellent agreement with the present study. The purpose of the following discussion is to demonstrate that first term approximations are incorrect.

To elucidate this, consider that after the application of voltage for say time t_1, the equilibrated e.m.f. is $\bar{E}(t_1)$. Subsequently, consider that the voltage is now applied for an additional time Δt_1. Upon equilibration, the e.m.f. is $\bar{E}(t_1 + \Delta t_1)$. If the first term approximation were valid, a similar equation such as Equation 15 can be written, namely

$$\frac{F}{RT} \; [\bar{E}(t_1 + \Delta t_1) - \bar{E}(t_1)]$$

$$= \; \ln\left(\frac{\pi^2}{8}\right) + \frac{\pi^2 D}{4L^2} \; \Delta t_1. \;\;\;\; (16)$$

Note that the initial e.m.f. of the cell is no longer E_0. In fact it is $\bar{E}(t_1)$. The sum of Equations 15 and 16 gives

$$\frac{F}{RT} \; [\bar{E}(t_1 + \Delta t_1) - E_0]$$

$$= \; 2\ln\left(\frac{\pi^2}{8}\right) + \frac{\pi^2 D}{4L^2} \; (t_1 + \Delta t_1), \;\;\;\; (17)$$

where $t_1 + \Delta t_1$ is the cumulative time. After n such Δt intervals after t_1, we obtain

$$\frac{F}{RT} \left[\bar{E}\left(t_1 + \sum_{i=1}^{n} \Delta t_i\right) - E_0 \right]$$

$$= \; n\ln\left(\frac{\pi^2}{8}\right) + \frac{\pi^2 D}{4L^2} \left(t_1 + \sum_{i=1}^{n} \Delta t_i\right),$$

where the cumulative time t is given by

$$t_1 + \sum_{i=1}^{n} \Delta t_i.$$

The important difference between Equations 15 and 18 is the magnitude of the intercept; namely $\ln(\pi^2/8)$ in Equation 15 as against $n\ln(\pi^2/8)$. Clearly, if the first term approximation were indeed valid, the plot of $(F/RT)[\bar{E}(t) - E_0]$ against t should not be a straight line. The slope of this curve should decrease such that the intercept after successive application of external voltage increases by $\ln(\pi^2/8)$. The fact that $(F/RT)[\bar{E}(t) - E_0]$ against t is often a straight line in fact implies that a first term approximation is invalid. Therefore, it appears that the approach used where only the first term is considered is not correct.

5. Conclusions

The equilibration method was used to determine diffusivity of sodium in tin over a range of temperatures. At lower temperatures, the polarization method gave values of diffusivity that were somewhat higher than those obtained through the equilibration method. This difference was rationalized in terms of interfacial polarization. It was also shown that one term approximations which are often used are not accurate. The present study demonstrates the applicability of cationic conductors for the study of diffusion in liquid metal systems.

Acknowledgements

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