

Self-Diffusion in Liquid Antimony

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The diffusion of radioactive Sb in liquid Sb has been measured in the temperature range from 672 °C to 1029 °C by use of the long-capillary method. A measuring method is described by which the sectioning of the specimens can be avoided. The self-diffusion coefficient is represented by the equation

$$D = (5.46 \pm 0.78) \cdot 10^{-4} \cdot \exp[-(4230 \pm 310)/RT] \text{ cm}^2 \text{ sec}^{-1}.$$

It is concluded that liquid Sb shows semi-metallic behaviour.

Introduction

In addition to metallic properties liquid Sb also shows marked non-metallic behaviour. In previous work¹ it was shown by neutron diffraction that metallic bonds as well as covalent bonds exist in liquid Sb. The object of the present study was to determine whether the self-diffusivity in molten Sb differs from that in the so-called normal molten metals.

Experimental

The diffusion studies were carried out by use of the long-capillary method. This method has been already described in a preceding paper².

Graphite capillaries (30 mm long, 1 mm inner diameter) were filled with Sb. Half the number of the capillaries were irradiated by neutrons ($10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$) for a short time ($\approx 10 \text{ sec}$) in order to mark the Sb by partial production of the isotopes Sb^{122} and Sb^{124} , both of which are γ - and β -emitters. The counting rate of the capillaries was 40000 c/sec after their storage for two weeks. The activity of the graphite was so small that it could be neglected. Each of the irradiated specimens was joined to an unirradiated specimen. Thus long-capillaries were obtained, which were half-filled with natural Sb(l) and half-filled with Sb containing Sb-tracers (r).

The annealing and quenching of the samples was practiced as described in Reference². Diffusion runs were carried out at annealing temperatures of 672, 728, 912, and 1029 °C with five samples in each case, the annealing times of each of them being different. After diffusion annealing, the specimens were subdivided into the two halves r and l using a 0.2 mm thick cutting-disk. All specimens showed a

cavity in the middle of the original contact face of the two halves. This cavity resulted from shrinking of the metal during cooling after the diffusion anneal. The fraction of Sb which corresponded to the cavity had been pressed out of the sample during the heating procedure.

The counting rate of the radioactive radiation was measured by means of a NaJ-scintillation counter, 5 cm in diameter, which had a hole 2 cm in diameter and 4 cm deep. Before joining the two capillary halves, the counting rate of the irradiated half *r* was measured. After the diffusion run the counting rates of the separated halves *r* and *l* were measured. Before and after each measurement the counting rate of an active Sb-standard was also measured in order to be able to correct for the decay of the isotopes during the time of the experi-

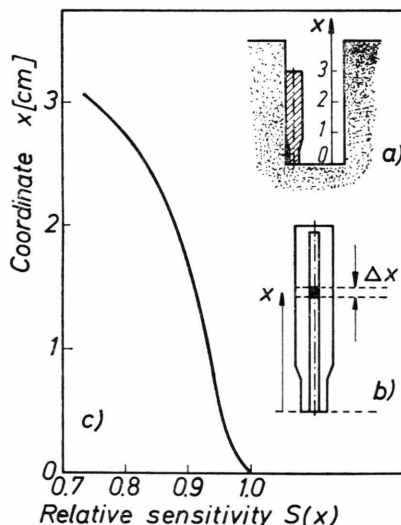


Fig. 1. a) Position of the specimen within the hole of the counter. — b) Specimen for measuring $S(x)$. — c) Relative sensitivity-curve of the scintillation counter.

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ment, as well as for drift in the electronics. During these measurements the respective specimen was placed with its open end at the bottom of the hole within the counting crystal and touching the wall as shown in Figure 1a.

The geometry of this arrangement had to be taken into consideration by a sensitivity-curve $S(x)$, which represents the sensitivity of the counter as a function of the height within the hole of the counting crystal. This is the same as the x -coordinate along the specimen. $S(x)$ was recorded by the use of specimens, which had the same shape as the diffusion specimens, but in which only a part, Δx , of the metal at a defined position x was radioactive. These specimens were fabricated from slices 1 mm thick one of them containing active Sb as shown in Figure 1b. Figure 1c shows the result. $S(x)$ drops from 1 to 0.75 along the specimen.

Evaluation Method and Results

Figure 2 illustrates the method for the evaluation of the measured data. The boundary condition for the left side l is:

$$a(x=L, t) \cong a(x, t=0) = 0$$

and for the right side r :

$$a(x=L, t) \cong a(x, t=0) = a_0,$$

where

$a(x, t)$ = tracer-concentration of Sb at the position x at the time t ,

a_0 = tracer-concentration in the half r at $t=0$, and

$2L$ = total length of the long-capillary.

The coordinate x is measured using the middle of the specimen as the origin and is positive in both directions. The proper solution of Fick's second law

$$\partial a / \partial t = D (\partial^2 a / \partial x^2) \quad (1)$$

is given by³

$$a(x, t) = (a_0/2) [1 \pm \operatorname{erf}(x/2 \cdot \sqrt{Dt})], \quad (2)$$

where the sign (+) applies to the part r and the sign (−) to the part l .

D = self-diffusion coefficient.

In the following a method is described, by use of which D is determined by measuring the integral

$$\int_{x=0}^{x=L} a(x, t) dx$$

for the both halves r and l .

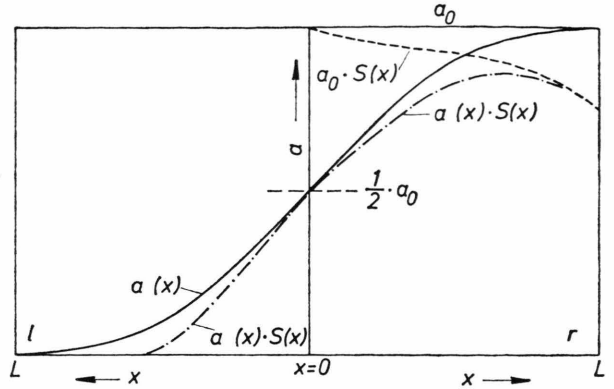


Fig. 2. Schematic diagram for the determination of D .

This method has the advantage, that the run of $a(x, t)$ must not be measured thus avoiding the sectioning of the radioactive specimens. The contribution to the measured counting rate of the entire half r or l given by a section δx at x is

$$\delta I = F a(x, t) S(x) \delta x, \quad (3)$$

where the relative counter-sensitivity is taken into consideration. The factor F contains a counter-sensitivity, which does not depend on x .

The following quantities were measured with each specimen:

I_0 = counting rate of the irradiated part r before diffusion. This value had to be corrected for the fraction of Sb, which escaped from the specimen during the process of heating up and which contained active isotopes.

$I_{r,l}$ = counting rate of the part r and the part l , respectively, after diffusion. This value is not affected by the shrinking of the metal during the cooling process.

These quantities are given in terms of the tracer-concentration by

$$I_0 = F a_0 \int_0^L S(x) dx, \quad (4)$$

$$I_{r,l} = F \int_0^L a(x, t) S(x) dx. \quad (5)$$

With Eqs. (2), (4), and (5) it follows that

$$\begin{aligned} & (2 I_{r,l} / I_0) - 1 \\ &= \pm \left(\int_0^L S(x) \cdot \operatorname{erf}(x/2 \cdot \sqrt{Dt}) \cdot dx \right) / \left(\int_0^L S(x) \cdot dx \right) \\ &= \pm G(Dt), \end{aligned} \quad (6)$$

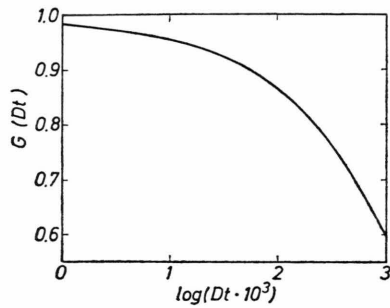
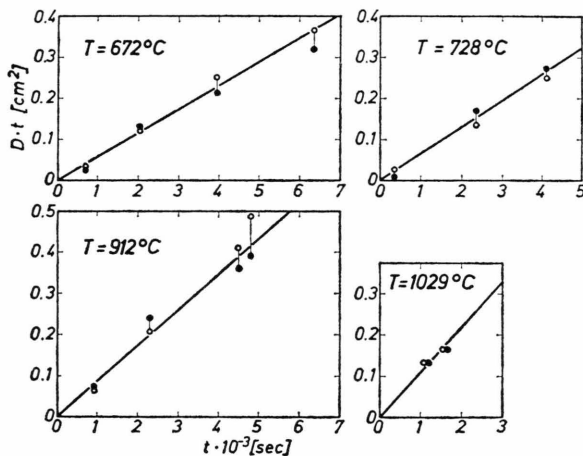
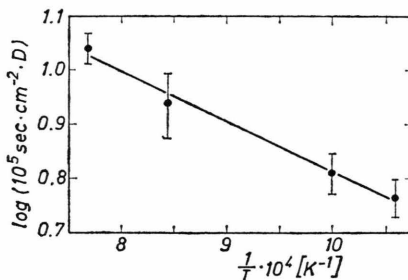
Fig. 3. Function for the determination of D .Fig. 4. Dt versus the diffusion time. ○ from part r ; ● from part l .

Fig. 5. Temperature dependence of the self-diffusion coefficient in liquid Sb.

Temperature [°C]	$D \cdot 10^{-5}$ [cm² sec⁻¹]
672	5.81 ± 0.47
728	6.46 ± 0.55
912	8.68 ± 1.17
1029	10.95 ± 0.68

Table 1.
Self-diffusion coefficient
in liquid Sb.

where the sign (+) applies to the part r and the sign (−) to the part l .

With Eq. (6) the ratio of the measured counting rates is given as a function of the product Dt . This function is abbreviated in Eq. (6) as $G(Dt)$. The evaluation of the measured data was carried out graphically. Using the measured function $S(x)$ and the error-function, the function $G(Dt)$ was calculated for values of Dt covering the range from 10^{-3} to 1 cm^2 . The result is shown in Figure 3.

By use of this plot the value of Dt could be determined for each diffusion specimen as the value of $G(Dt)$ was given by the measured ratio I_r/I_0 for the part r and I_l/I_0 for the part l , respectively.

In Fig. 4 the obtained values of Dt are plotted versus the diffusion time. From the slope of the straight lines drawn through the experimental points the diffusion coefficient was calculated for each temperature. The values are listed in Table 1. The errors result from the deviation of the points from the straight lines in Figure 4.

In Fig. 5 the temperature dependence of the diffusion coefficient is shown using the usual Arrhenius-plot. The least-squares line is represented by the equation

$$D = D_0 \cdot \exp(-Q/RT), \quad (7)$$

where T = temperature in K, R = gas constant. The parameters D_0 and Q and the estimated standard errors are listed in Table 2.

Table 2. Diffusivities in liquid Bi and Sb.

Q [cal mole⁻¹]	$D_0 \cdot 10^4$ [cm² sec⁻¹]	Diffusion type Reference
4230 ± 310	5.46 ± 0.78	Self diffusion Sb in Sb. This work.
4230	8.35	Self diffusion Bi in Bi ⁷ .
3800	4.1	Impurity-diffusion Bi in Sb ² .
3300	3.6	Impurity-diffusion Sb in Bi ² .

Discussion

The mean error of the diffusion coefficient measured in this study is 9 pct. This uncertainty is within the range usually found in diffusion studies in liquids. From the fact that the experimental points in Fig. 4 can be represented by straight lines, in other words that the values of D do not depend on the diffusion time it can be concluded that the measurements are not affected by convection. The fact

that the straight lines can be drawn through the origin certainly shows, that no mixing occurred at the original contact layer ($x=0$) during the melting of the metal.

Because of the errors given in Fig. 5 one cannot decide, whether the temperature dependence of the self-diffusion coefficient in liquid Sb follows an Arrhenius-law or one of the temperature-functions proposed by other authors⁴ for diffusion in liquids. Thus the diffusion in liquid Sb is described with the parameters D_0 and Q without assigning to them the same meaning as they have in the solid state, where diffusion is known to be a thermally activated process.

According to Ref.⁵, for normal liquid metals, a fairly linear relationship exists between Q and the melting temperature T_m given by

$$Q/T_m \approx 6.8 \text{ cal mole}^{-1} \text{ grd}^{-1}.$$

Semi-metals and non-metals show a deviation from this relationship. Saxton and Sherby⁶ have proposed $Q/T_m = 5.46$ for semi-metals.

For liquid Sb, from the value of Q determined during this work and the melting temperature, Q/T_m

$= (4.68 \pm 0.34) \text{ cal mole}^{-1} \text{ grd}^{-1}$. This value is considerably smaller than that for normal metals and even smaller than that proposed in Reference⁶.

From the above diffusion measurements it is concluded that molten Sb exhibits non-metallic character as well as metallic properties. This is in agreement with the structure studies in Reference¹.

In Tab. 2 the self-diffusion coefficient of liquid Sb and the self-diffusion coefficient of liquid Bi, as measured by Döge⁷, are compared with the impurity-diffusion coefficient of Bi in liquid Sb, as well as with the impurity-diffusion coefficient of Sb in liquid Bi, which have been measured in Reference². The values of Q show that the impurity-diffusion is less temperature dependent than the self-diffusion in the solvent. This was found previously for other liquid systems^{7,8}.

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