Tracer Impurity Diffusion in Liquid Metals: Period 5 Elements in Gallium

S. J. Larsson, P.-E. Eriksson, and A. Lodding

Physics Department, Chalmers University of Technology, Gothenburg, Sweden

(Z. Naturforsch. **29 a**, 961–963 [1974]; received May 2, 1974)

The diffusivities of ^{110}Ag and of ^{121}Sn in liquid Ga have been measured and compared with recent data for ^{115}Cd and ^{114}In in Ga. The results can be reasonably well expressed by Arrhenius-type relations $D=D_0 \exp\{-Q/RT\}$, with $D_0=2.2\times10^{-4}$ cm²/s, $Q=1.68$ kcal/mole for Ag, and $D_0=1.6\times10^{-4}$, $Q=1.49$ for Sn. At temperatures above some 380 °K the diffusion coefficients of Ag, Cd and In in gallium are practically equal, while that of Sn lies about 10% lower. Even at the lowest temperatures the D-values of the different tracers vary by less than 10% from a mean. The low temperature points appear to fall somewhat below the best straight lines in the D vs T diagram. No obvious dependence on valency is discerned; the only reasonable systematics implied by the behaviour of the four elements of period 5 is the inverse root dependence on tracer mass.

In a systematic investigation of tracer diffusion in liquid Ga, we have previously reported the results for ^{72}Ga [1], ^{198}Au [2], ^{65}Zn and ^{115}Cd [3], and ^{114}In [4]. The same "infinite capillary" technique has now been used to measure the diffusion coefficients of ^{110}Ag and ^{121}Sn. The new data are listed in Table 1. In Fig. 1 the experimental points for Ag and Sn are shown together with lines representing self-diffusion and the diffusion of the other two period 5 elements (i. e. Cd and In) in Ga. In the diagram, earlier results for Ag in Ga [5, 6] are also shown (crosses), in obviously good agreement with the present series.

Table 1. Experimental results.

Tracer	Temp. (K)	10^5 D (cm²/sec)
^{110}Ag	319.5	1.27
	322.5	1.35
	323.5	1.59
	369	1.94
	401	2.92
	417	3.26
	431	3.28
	473	3.55
	646	5.61
	677	6.79
	703	6.43
^{121}Sn	344.2	1.83
	375.2	2.19
	378.2	2.17
	510	3.52
	525	4.02

It can be seen in Fig. 1 that above ca. 380 °K the results for the monovalent, the divalent and the trivalent impurity are equal within their limits of

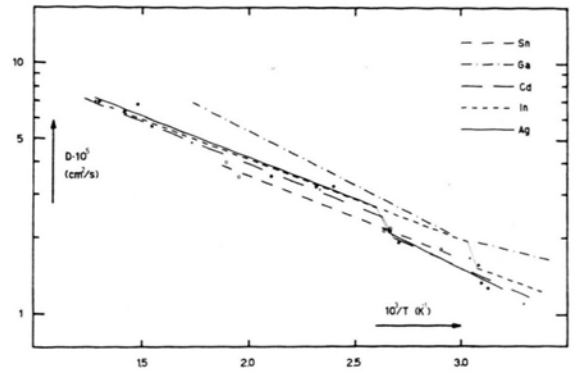

Fig. 1. Arrhenius plot of the diffusion coefficient of Ag, Cd, In and Sn in liquid gallium, and of Ga self-diffusion. Dots: present results, ^{110}Ag. Open circles: present results, ^{121}Sn. Crosses: Ag, References [5, 6].

error. The line for the mass 110 tracer appears to lie just above the best Arrhenius lines for masses 114 and 115, which in turn lie about 10% above that for mass 121. As seen in Table 3, all four ratios D_i/D_s of impurity diffusion coefficients to the self-diffusion coefficient at these temperatures are nearly those expected from the inverse-root relation for single atom tracer masses.

At the lowest temperatures, this relation is also seen to hold approximately. The temperature characteristics of D for the mono-, di- and trivalent impurity however imply a slight discontinuity separating the low temperature region from the rest. Such tendencies were earlier observed also for Zn and Au in Ga; a possible explanation was suggested [2] in terms of di- or polyatomic diffusing clusters, breaking up at higher temperatures. In Fig. 1, a rapid rise by some 20% appears to separate the two regions, the step occuring around 380 °K for Ag and Cd, 325 °K for In. If an inverse root law is indeed obeyed, the 20% increase might reasonably correspond to the breaking up of tracer-solvent atom pairs.

The effect of tracer mass is thus borne out by these experiments at least qualitatively in the way expected from simple theory [4, 7, 8]. As regards the influence of atom size and of valence, no such effect is readily discernible.

According to the model by Cohen and Turnbull [8] a diffusion displacement takes place only if a sufficiently large void opens up (by statistic rearrangement of "free volume") next to the tracer, to accomodate a volume V^* typical for the tracer atom. This gives an "activation term",

$$D \propto \exp\{-\text{const.}\, V^*/T\},$$

and accordingly the slope in the Arrhenius diagram would be expected to depend on the atom or ion

Table 2. Parameters of Arrhenius representation $[D=D_0 \exp\{-Q/RT\}]$ and of linear representation $[D=A(T-B)]$ of the diffusion of period 5 elements in liquid gallium. Q in kcal/mole, D_0 in cm²/s, A in cm²/K, s and B in K.

Total range

Tracer	Range K	$D_0 \cdot 10^4$	Q	$A \cdot 10^7$	B
^{110}Ag	310–780	2.2±0.1	1.68±0.04	1.26±0.04	187± 9
^{115}Cd	300–740	2.3±0.2	1.76±0.06	1.31±0.06	204± 9
^{114}In	296–738	2.0±0.1	1.59±0.04	1.24±0.03	176± 4
^{121}Sn	344–525	1.6±0.2	1.49±0.08	1.13±0.08	184±12

Upper range

Tracer	Range K	$D_0 \cdot 10^4$	Q	$A \cdot 10^7$	B
^{110}Ag	380–780	1.9±0.1	1.49±0.07	1.17±0.07	148± 9
^{115}Cd	380–740	1.9±0.2	1.54±0.11	1.21±0.09	171±13
^{114}In	325–738	1.8±0.1	1.46±0.04	1.19±0.03	160± 4

Lower range

Tracer	Range K	$D_0 \cdot 10^4$	Q	$A \cdot 10^7$	B
^{110}Ag	310–380	2.7	1.90	1.25	209
^{115}Cd	300–380	2.1	1.72	1.25	207
^{114}In	296–325	1.2	1.33	0.96	167

Table 3. Computed relations between impurity diffusion and selfdiffusion. m denotes atom mass. Energies in kcal/mole.

Tracer	ΔZ	$(m_s/m_i)^{1/2}$	$(D_i/D_s)_{th}$	$(D_i/D_s)_{exp}$ 300 K	500 K	ΔQ_{exp}	ΔE_{th}
^{110}Ag	−2	0.81	$\gtrsim$ 0.85	0.71	0.79	−0.22	$\gtrsim$ +1.0
^{115}Cd	−1	0.79	$\gtrsim$ 0.95	0.73	0.76	−0.14	$\gtrsim$ +0.4
^{114}In	0	0.79	$\gtrsim$ 1.00	0.80	0.78	−0.31	$\gtrsim$ 0
^{121}Sn	+1	0.77	$\gtrsim$ 1.03	(0.80)	0.68	−0.41	$\gtrsim$ −0.2

radius of the tracer. However, as seen in Fig. 1 and Table 2, all four period 5 tracers exhibit nearly the same slopes in the diagram, in spite of differences in atom and ion sizes.

According to solid-state arguments conserved in the "hole theory" of liquid diffusion [9], valency effects would manifest themselves somewhat as in vacancy diffusion. An impurity of $\Delta Z > 0$ (ΔZ denoting the valency difference between impurity atom and matrix atom) would attract the (negative) voids in the liquid, while more electronegative impurities would repel the voids. One might tentatively assume [10] that this would affect the energy of void formation next to the tracer by a coulomb term

$$\Delta E = -\beta \Delta Z \frac{e^2}{d_0} \exp\{-q\, d_0\}, \qquad (1)$$

where q is a screening factor, d_0 the nearest neighbor distance and β a factor of the order of unity, varying slowly with Z. Using the appropriate Thomas-Fermi value of q (2.0 Å^{-1} for Ga), a calculation gives $\Delta E \cong -0.24\, \beta\, \Delta Z$ (kcal/mole). As $\beta > 1$ for $\Delta Z < 0$[10], the "activation energy" for Ag in Ga (with $\Delta Z = -2$) should be by at least a kcal/mole greater than that of In in Ga; that of Sn should lie by about 0.2 kcal lower than that of In. Such tendencies are, however, not seen in the present experimental results.

Swalin and Leak [10] have attempted to predict the effect of ΔZ in terms of a "continuous fluctuation" model [11]. According to such treatment the slope in the Arrhenius diagram should be the same for all tracers, and only the ratio D_i/D_s should be dependent on ΔZ. The prediction is

$$D_i/D_s \cong 1 - \frac{q^2 \Delta E}{K}\left(1 + \frac{2}{q\, d_0}\right) \qquad (2)$$

where K is the force constant of compressibility [12], for Ga ca $2.5 \cdot 10^4$ ergs/cm². Accordingly for gallium $(D_i/D_s)_{theor} = 1 + 0.036\, \beta\, \Delta Z$. As seen in Table 3 this would place the line for Ag some 15% below that for In, that for Sn some 3% above. Actually, the opposite tendency is observed. Moreover the above valency argument completely neglects the

effect of tracer mass, an effect which in fact appears to dominate over those of valency and size.

This work has been supported by the Swedish Natural Science Research Council.

[1] S. J. Larsson, L. Broman, C. Roxbergh, and A. Lodding, Z. Naturforsch. **25 a**, 1472 [1971].
[2] P.-E. Eriksson and S. J. Larsson, Z. Naturforsch. in press.
[3] S. J. Larsson and P.-E. Eriksson, Z. Naturforsch. in press.
[4] P.-E. Eriksson, S. J. Larsson and A. Lodding. Z. Naturforsch. in press.
[5] G. I. Onoprienko, P. P. Kuz'menko, and E. I. Kharkov. Ukr. Fiz. Zh. **11**, 1264 [1966].
[6] R. V. Ivanova, A. A. Belskii, and M. A. Stepanova, Fiz. Met. Mettalov. **26**, 733 [1968].
[7] A. Lodding, Z. Naturforsch. **27 a**, 873 [1972].
[8] M. H. Cohen and D. J. Turnbull, J. Chem. Phys. **31**, 1164 [1959].
[9] H. Eyring and T. Ree, Proc. Nat. Acad. Sci. **47**, 526 [1961].
[10] R. A. Swalin and V. G. Leak, Acta Met. **13**, 471 [1965].
[11] R. A. Swalin, Acta Met. **7**, 736 [1959].
[12] J. Waser and L. Pauling, J. Chem. Phys. **18**, 747 [1950].