Tracer Impurity Diffusion in Liquid Metals: In in Gallium and Ga in Indium

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Diffusion measurements have been made for ^{114}In in Ga between 20° and 455 °C, and for ^{72}Ga in In between the m.p. and 380 °C. Linear plots of D vs T describe the results about equally well as Arrhenius representations. The Arrhenius parameters are $D_0 = 2.1 \cdot 10^{-4}$ cm^2/s, $Q = 1.64$ kcal/mol for In in Ga, $D_0 = 2.4 \cdot 10^{-4}$ cm^2/s, $Q = 1.93$ kcal/mol for Ga in In. Ga diffuses faster than In in both matrices. The effective activation energy of Ga is much higher than that of In in the lighter solvent, but the opposite is the case in In. Simple electrostatic screening arguments cannot be applied to the latter results. A recent model, predicting a nearly linear temperature dependence of D, appears somewhat better applicable.

The self-diffusion of Ga, investigated recently by two independent techniques [1, 2] has revealed that the slope of the $\ln D$ vs T^{-1} plot, as well as that of the D vs T plot, distinctly increases with temperature. Corresponding representations of the self-diffusion of In [3, 4], on the other hand, yield good straight lines. To explain this, and to provide a basis for the development of theory, measurements of impurity diffusion in these systems are of interest. The state of theory regarding impurity diffusion in liquids is yet rather poor [5, 6], and requires more exact data. The "infinite capillary" method [1] first developed for Ga self-diffusion, has since been tested also on In [7] and on alkali metals [8, 9]. Further, a preliminary report has appeared [10] on the diffusion of tracer In in Ga.

The present paper aims at contributing more material to the discussion of homovalent impurity diffusion. The temperature range of the work of Ref. [10] has been considerably extended, and the same experimental procedure has also been applied to ^{72}Ga in In.

Table 1. Experimental results, homovalent impurity diffusion in liquid gallium and indium metals.

System	T (K)	D (cm^2/s)		T	D
^{114}In in Ga	296.4	1.26		503.3	4.30
	296.4	1.32		511.2	4.08
	307.2	1.15		539.2	4.47
	316.4	1.46		595	5.34
	316.4	1.52		644	5.88
	329.7	1.87		650	6.31
	346.2	2.29		677	5.88
	353.2	2.35		703	6.59
	377.2	2.76		727	6.68
	382.2	2.57	^{72}Ga in In	431.6	2.76
	387.2	2.74		438.2	2.55
	401.2	2.91		454.7	2.79
	403.2	2.67		456.4	2.79
	413.2	2.96		477.2	2.96
	426.2	3.07		516.2	3.90
	432.2	3.19		533.6	3.93
	451.2	3.50		549.1	4.08
	473.4	3.77		647	5.15
	475.2	3.65		702	6.26

The results are given in Table 1. They are represented graphically, and compared with self-diffusion characteristics [1–3], in an Arrhenius representation, Fig. 1, and in a linear D vs T plot, Figure 2. The computed parameters in the equations $D = D_0 \exp\{-Q/R\,T\}$ and $D = A(T - B)$ are listed in Table 2. It can be seen in the figures, and also concluded from the fairly narrow error margins in Table 4, that both representations are acceptable to describe the temperature variation of D by smooth

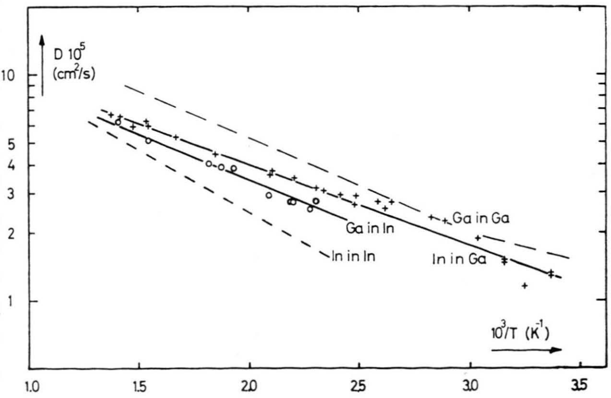

Fig. 1. Arrhenius representation of the diffusion of ^{72}Ga and ^{114}In in liquid In and Ga. Self-diffusion of Ga from Refs. [1, 2], In from Reference [3].

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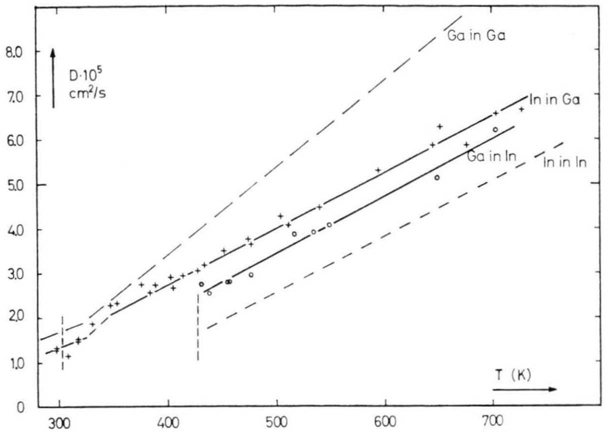

Fig. 2. Linear plot of D vs T for the diffusion of ^{72}Ga and ^{114}In in liquid In and Ga. Self-diffusion of Ga from Refs. [1, 2], In from Reference [3].

straight lines. For In in Ga, a slight discontinuity seems to occur around 325 K, near the apparent knee in the Ga self-diffusion characteristic. The experimental error margin of the individual points being between 2 and 10%, only the low temperature points for In in Ga deviate significantly from the best straight lines.

The recent results [9] of homovalent impurity diffusion studies in liquid alkalis could be at least qualitatively reconciled with electrostatic screening arguments as proposed for vacancy diffusion in solid metals [11, 6]. In such a model the impurity is treated as a point of positive or negative excess charge, which exercises, respectively, attraction or repulsion on the "free volume" in the liquid (as on vacancies in the solid). If the impurity has a higher valency than the solvent, the effective activation energy of impurity diffusion should be lower than that of self-diffusion, and vice versa. For homovalent impurities, the effective excess valency can be assessed [11] from the solute-solvent differences in Fermi energies, heats of sublimation, and ionization energies, using a suitable function of interatomic potential. In liquids, the uncertainty concerning the defect configurations and the diffusing species naturally introduces complications to such a picture. Further, particularly for polyvalent matrices, the potential shape as well as the effective number of free electrons per atom, on which such calculations critically depend, are insufficiently known quantities. One may conclude from such calculations for the present system, however, that the In ion is more positive than the Ga ion, and that the corresponding differences in effective activation energy should be about the same in both matrices, the diffusion of Ga showing a greater slope in the Arrhenius diagram than that of In. Looking at Fig. 1 or Table 4, one sees that although the results for the Ga matrix are in qualitative agreement with such predictions, those for In are not, showing quite the opposite tendency. The analogy with the solid-state theory of impurity diffusion thus cannot be said to be supported by the present results.

According to a recent model [12] based on the concept of a liquid counterpart of the Debye frequency

Table 2. Parameters of Arrhenius representation ($D=D_0 \exp(-Q/R\,T)$) and of linear representation ($D=A(T-B)$) for homovalent tracer diffusion in liquid Ga and In.

System	Range (K)	$D_0\cdot 10^4$ (cm²/s)	Q (kcal/mol)	$A\cdot 10^7$ (cm²/s·deg.)	B (K)
In in Ga	296–727	2.1	1.64 ± 0.04	1.27 ± 0.03	184 ± 4
	340–727	1.8	1.45 ± 0.04	1.18 ± 0.03	157 ± 4
Ga in Ga	280–680	3.45	1.85 ± 0.05	2.00 ± 0.04	228 ± 4
	340–680	4.13	2.01 ± 0.03	2.09 ± 0.02	240 ± 2
Ga in In	431–702	2.4	1.93 ± 0.14	1.32 ± 0.09	239 ± 16
In in In	440–1020	2.9	2.43 ± 0.05	1.22 ± 0.02	295 ± 5

Table 3. Relation between homovalent impurity diffusion and self-diffusion in liquid Ga and In. See Eqs. (5) – (7) for definitions of symbols.

System	$r=m_i/m_s$	T (K)	$(D_i/D_s)_{exp}$	$(M_i/M_s)_{calc}$ $\gamma=0$	$\gamma=0.5$	p_{calc} $\gamma=0$	$\gamma=0.5$
^{114}In in Ga	1.64	650	0.72	1.93	3.57	0.69	0.43
		450	0.78	1.65	3.18	0.99	0.52
		300	0.82	1.49	2.96	1.3	0.71
^{72}Ga in In	0.62	650	1.25	0.64	0.49	1.06	0.75
		550	1.28	0.61	0.45	0.97	0.70
		450	1.42	0.50	0.31	0.75	0.55

and the assumption that all non-vibrational thermal energy goes to diffusion, a linear relation of the form

$$D = A(T - B) \tag{1}$$

is predicted, where A contains the mass and the vibration frequency, and B is related to the heat and temperature of melting. The model has been successful in describing the experimentally observed behaviour of self-diffusion in the alkalis and other liquid metals [8, 13], and can in principle also be extended to impurity diffusion. It follows from Ref. [12] [Eq. (9)] that for self-diffusion (suffix s)

$$A_\mathrm{s} = \tfrac{1}{2} f_\mathrm{s}\, k/\nu_\mathrm{s} M_\mathrm{s}$$

and

$$B_\mathrm{s} = (1 - \alpha) T_\mathrm{m} \tag{2 a, b}$$

where f is the correlation factor (neglected in Ref. [12]), k Boltzmann's constant, ν the vibration frequency, M the mass of the diffusing species, T_m the melting temperature, and α a factor containing the heat and temperature of melting. For impurity diffusion (suffix i) one may write

$$A_\mathrm{i} = \tfrac{1}{2} f_\mathrm{i}\, k/\nu_\mathrm{i} M_\mathrm{i}$$

$$B_\mathrm{i} = B_\mathrm{s} - \Delta T \tag{3 a, b}$$

but the term ΔT may be expected to be small for a dilute tracer, its presence not appreciably affecting the total energy content. Thus when comparing impurity diffusion with self-diffusion

$$A_\mathrm{i}/A_\mathrm{s} = D_\mathrm{i}/D_\mathrm{s} = f_\mathrm{i}\, \nu_\mathrm{s} M_\mathrm{s} / f_\mathrm{s}\, \nu_\mathrm{i} M_\mathrm{i}\,. \tag{4}$$

If the impurity represents an excess charge, it may to a more or less significant degree attract or repell "free volume", in which case ν_i may depend not only on mass but also on temperature. In the present discussion of homovalent diffusion, this will be neglected, as a first approximation. Nor are differences in atom size taken into account here. It is practical to simplify the picture further by considering M_i as consisting of the tracer atom plus $(p-1)$ solvent atoms, oscillating together in antiphase to a surrounding of effectively infinite mass. Then the inverse root mass law can be applied. Introducing the ratio of the solute atom mass to the solvent atom mass, $r = m_\mathrm{i}/m_\mathrm{s}$, one may write

$$\nu_\mathrm{s} M_\mathrm{s}/\nu_\mathrm{i} M_\mathrm{i} = (M_\mathrm{s}/M_\mathrm{i})^{1/2} = \sqrt{p/(r+p-1)}\,. \tag{5}$$

The correlation factor one may express as

$$f_\mathrm{i} = (1 + \gamma\, \nu_\mathrm{i}/\nu_\mathrm{s})^{-1} \tag{6}$$

where γ is zero for perfect random walk and at most of the order of unity. For solid-like vacancy diffusion γ is between 0.2 and 0.4.

Equation 4 now becomes

$$D_\mathrm{i}/D_\mathrm{s} = (1+\gamma)/\sqrt{1+\gamma(M_\mathrm{s}/M_\mathrm{i})} \cdot \sqrt{M_\mathrm{s}/M_\mathrm{i}} = (1+\gamma)/[\sqrt{r+p-1/p+\gamma}] \tag{7}$$

In Table 3 the experimental $D_\mathrm{i}/D_\mathrm{s}$ values are used to compute, via Eq. (7), the corresponding p-values (i. e. the effective number of atoms in the diffusing species). One computation is made under neglect of correlation $(\gamma = 0)$, another with an arbitrarily chosen value $\gamma = \tfrac{1}{2}$, to show in which direction the result is influenced by departures from random-walk.

The table shows that the present experimental data, combined with the model of Ref. [12], lead to the inference that p is approximately unity, i. e. that the diffusing tracer atoms behave as nearly independent. The introduction of appreciable correlation would, however, lead to values of p significantly less than unity, implying $\nu_\mathrm{Ga}/\nu_\mathrm{In} > \sqrt{m_\mathrm{In}/m_\mathrm{Ga}}$, which does not seem easily acceptable. Thus, if the model, in spite of several simplifications, is reasonably correct, the implication is that diffusion takes place by small and nearly uncorrelated position adjustments of single atoms. This is qualitatively understandable if the small "free volume", into which the atom drifts, is dispersed during the elementary step.

For the points at the low temperature end in the results for the Ga solvent system, the p-value appears to exceed unity. Although this is only just within the margins of experimental uncertainty, it may possibly be an indication of the presence of two-atom clusters under and near the melting point of gallium, breaking up at higher temperatures. This would also be in line with the great difference observed (see Figs. 1 and 2) between the low and high temperature slopes of the temperature characteristcs of Ga self-diffusion.

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