Experimental measuremnet of the diffusion coefficient of ag[110m], cd[109], in[114m], sn[113] and sb[125] in liquid tin

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Experimental Measurement of the Diffusion Coefficient of Ag^{110m}, Cd^{109}, In^{114m}, Sn^{113} and Sb^{125} in Liquid Tin

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We describe a precise method for measuring the diffusion coefficient of solutes in liquid metals. A thin layer of a radioactive isotope of the solute is allowed to diffuse in capillaries which can be sectioned using a shear cell device. This method allows a precise measurement of the temperature and of the time duration of the experiment, and avoids any solute segregation when cooling the samples. The experimental results show that there is a negligible direct influence of the valence of a solute on its diffusion coefficient in tin.

Nous décrivons une méthode précise de mesure du coefficient de diffusion de solutés dans une matrice métallique, dans laquelle une couche mince de radiotraceur diffuse en milieu infini, dans une cellule à cisaillement. Cette méthode permet de déterminer avec précision la température et la durée de l'expérience et d'éviter toute redistribution du soluté au cours du refroidissement. Les résultats obtenus montrent que l'effet de valence pour la diffusion d'un soluté est faible.

1   INTRODUCTION

The diffusion phenomenon of atoms in a liquid metal is due to their micro-scopic displacements in the host metal. The diffusion coefficient D_i, usually defined by:

$$D_i = \lim_{t \to \infty} \frac{\langle R_i^2(t) \rangle}{6t} \qquad (1)$$

is proportional to the rate of variation in time of the mean square displacement $\langle R_i^2(t) \rangle$ of atoms labelled by the index i. Early models[1,2] describing self

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diffusion in liquid metals attempt to reproduce the linear variation of ln D versus $1/T$ which is usually observed: the diffusion of an atom is assumed to be a discontinuous process in which a given atom oscillates around an "equilibrium" position until (i) a sufficiently large amount of energy is concentrated on it, (ii) the configuration of the surrounding atoms is favorable, that is, a hole has opened in front of the diffusing atom. In these models, which are reminiscent of the vacancy mechanism in solids (i) self diffusion is a thermally activated process with an activation energy Q of the order 0.1 eV/atom; the fact that Q correlates fairly well with the melting temperature T_M or the latent heat of melting supports such theories; (ii) the influence on D_i of the relative valence $z_i = Z_i - Z$ of a solute with respect to the solvent should be important because of the large interaction energy of the solute ion with the hole region. In solid tin for instance,[3] such electrostatic effects are able to produce a variation of D_i by a factor of about 160 when z_i is varied from -3 (Ag) to $+1$ (Sb). It is the aim of the present paper to investigate the valence effect on the diffusion coefficient of some solutes in liquid Sn.

With the development of machine simulations of atom movements in liquids, it appears that a theory appealing to the kinetic theory of gases is closer to reality than any theory built in analogy with solids. It is possible for instance to write $D = kT/\varsigma$ where ς is a friction coefficient due to atom – atom collisions; ς can be calculated using the kinetic theory of gases after correction by the factor $g(\sigma)$ measuring the collision probability of atoms of diameter σ.[4] These models provide values of D[5] about 40% larger than the experimental values in liquid metals, but do not take proper account of the dynamical correlations arising in the liquid with the effect of reducing D.

In the itinerant oscillator models[6,7,8] the diffusing atom oscillates in a cluster of neighbors which moves randomly under the influence of collisions with surrounding atoms. This description, together with the "surrounded atom" model,[9] allows calculating the diffusion coefficient of a solute, given the thermodynamic properties of the corresponding alloy.

On the other hand, by simulation of atom movements in the liquid using proper interatomic potentials, it is possible to determine D:[10] for instance $G_s(r, t)$ the position self correlation function obeys the diffusion equation as soon as t is larger than a few 10^{-12} s, and can be directly calculated in a computer simulation. The diffusion coefficient D is also related to the integral of the velocity correlation function $\langle v(o) \cdot v(t) \rangle$:

$$D = \tfrac{1}{3} \int_0^\infty dt \, \langle v(o) \cdot v(t) \rangle \tag{2}$$

or to its Fourier transform $Z(\omega = 0)$. Any model describing atom movements in a liquid must be adjusted to give a value of D consistent with experimental values.

Measurements of diffusion coefficients in liquids are not easy to perform however and different techniques have often provided results which have been at variance. A powerful technique to determine D is to measure the incoherent scattering of neutrons by the liquid; D is the limit of the Van Hove function S_{inc} (k, ω) for vanishing energy and momentum transfers:

$$D = \pi \lim_{\omega \to 0} \omega^2 \lim_{k \to 0} \frac{S_{inc}(k, \omega)}{k^2}. \tag{3}$$

Apart from experimental difficulties to determine accurately the total function S(k, ω) near (ω, k) = (0, 0), it is no easy to separate coherent and incoherent intensities because most metals are essentially coherent scatterers. More sophisticated techniques such those employing polarized neutrons or targets of variable isotopic composition allow in principle a precise measurement of S_{inc}(k, ω) but remain difficult to use. On the other hand resonance techniques, such as NMR or Mössbauer effect, are not well adapted to the frequency range of interest in a measurement of diffusion coefficients in liquids. In view of these difficulties in theory and experiment it is more realistic to measure directly the diffusion coefficients and to consider relations (2) and (3) as necessary conditions to be fulfilled by any model in order to be plausible.

Such a direct measurement of diffusion coefficients in liquids consists in observing the evolution in time of the concentration profile of a given isotope. The order of magnitude of diffusion coefficients in liquid metals ($\sim 10^{-5}$ cm^2 s^{-1}) allows a fairly rapid determination of D.

2 EXPERIMENTAL METHOD

In the experimental methods used to measure directly diffusion coefficients in liquids, care must be taken to avoid any convection current in the liquid. On the other hand, in order to measure D at a given temperature T, the corrections due to the duration of heating and cooling the sample must be kept as small as possible. Moreover any segregation of the solute must be avoided when freezing and cooling the system. The methods which are most frequently used are the capillary reservoir[11] and the long capillary[12] techniques. In these methods, any convection can be avoided by reducing the capillary diameter but the boundary conditions are not very well defined. On the other hand, the cooling of the sample is usually too slow to prevent solute segregation or precipitation.[2] In the method developed by Lodding[13] the solute concentration is measured *in situ* during the diffusion run by recording the radioactive intensity along the capillary. Although this method is free of the preceding drawback, it is not well suited to high temperature measurements and can only be applied to a small number of radioactive isotopes.

2.1   Shear cell experimental arrangement

The most precise method for measuring directly diffusion coefficients makes use of a shear cell made of a number of discs centered around a common vertical axis[14,15] (Figure 1). Any leaking of liquid metal can be prevented by making provision for the dilatation of the different parts of the cell. In the apparatus we constructed, inspired by that of Potard and Teillier,[15] 20 discs of nuclear graphite are piled up around a stainless steel axis. In each of these discs 4 holes of diameter 1.5 mm are bored and can be aligned so as to form 4 capillaries. Discs of even label are held fixed in rotation by two cylindrical rods of stainless steel very accurately adjusted into them, whereas odd discs are able to rotate with respect to even ones by an angle of about 20°. The relative position of the two classes of discs is determined by the contact of the
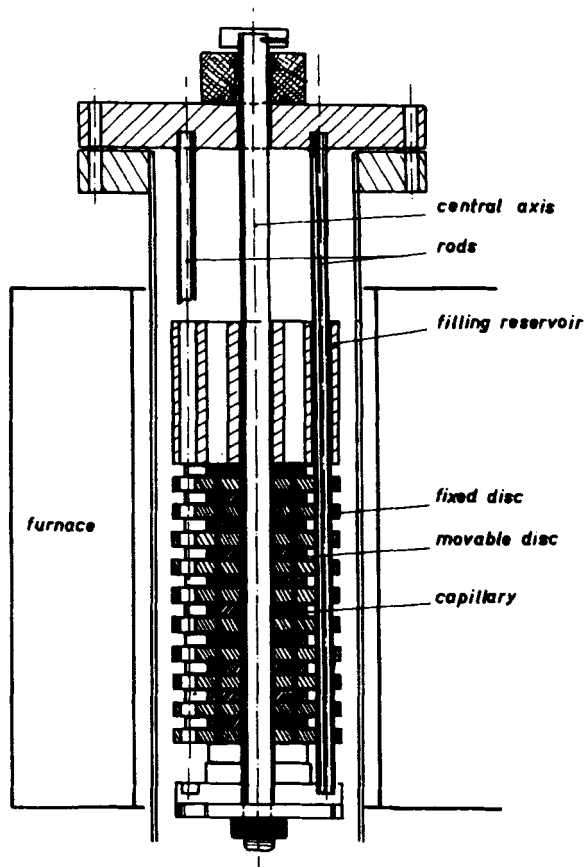
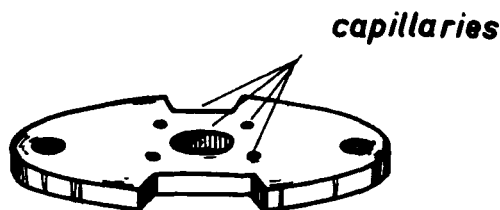FIGURE 1   Schematic drawing of the cell in the furnace.

FIGURE 2   Graphite disc of the cell.

longitudinal rods with the sides of quasi rectangular holes that have been cut away from the even discs (Figure 2). The four holes of the intermediate disc A are initially filled with an alloy of tin with the solute under study, which can be brought into contact with the two halves of the capillary.

In a standard measurement of a diffusion coefficient, the sequence of operations is as follows:

(a) 4 small rods (1.5 mm diameter, 4 mm long) of pure tin are electroplated with a radioactive isotope of the solute; after the electroplating, these rods are introduced in the holes of the intermediate disc A;

(b) the two halves of each capillary are filled with pure tin initially contained in a reservoir placed at the top of the shear cell; in order to avoid bubble formation, the cell is properly outgased under a vacuum of about 2×10^{-6} torr before the filling operation;

(c) when the furnace is stabilized within $\pm 1\,°C$ around the desired diffusion temperature, the radioactive rods of the intermediate disc are brought into contact with the two halves of each capillary; this operation determines accurately the beginning of the diffusion run;

(d) when the diffusion treatment is completed, odd discs are rotated by an angle of 20° to cut the capillaries into rods 4 mm long;

(e) after this sectioning operation that determines the end of the diffusion experiment, the temperature of the system is allowed to decrease. This procedure allows a precise determination of the temperature and the time duration of the run and avoids any solute segregation when cooling the alloy. All these operations are conducted from outside the furnace, the temperature of which being held fixed at $\pm 1\,°C$, under a vacuum of 2×10^{-6} torr. In order to avoid any convection in the capillaries, a temperature gradient of the order $1°\,C\,cm^{-1}$ is applied to the shear cell, the top of the sample being slightly warmer than its lower part. The temperature profile along the capillaries is obtained by means of seven independent kanthal coils powered through a standard temperature regulation. Coaxial thermocouples are initially inserted into some of the fixed discs of the cell, providing temperature measurements at a distance of about 5 mm from the capillaries.

2.2   Analysis of the experimental data

In all our experiments the thickness of the intermediate disc A is so small with respect to the mean square displacement of solute atoms (of the order $2\sqrt{Dt} \sim 2$ cm) that the solution of Fick's equation corresponding to the thin layer boundary condition can be used. In a typical diffusion run (D = 4×10^{-5} cm^{2}s^{-1}, t = 1.8×10^4 s), the exact solution to Fick's equation differs only by a maximum of 2% from the thin layer solution (Figure 3) what is within the experimental error in the concentration measurements. The atomic solute concentration $c(x, t)$ at point x and time t can therefore be approximated by:

$$c(x, t) = \frac{Q}{2\sqrt{\pi Dt}} \exp\left[-\frac{(x - x_m)^2}{4Dt}\right] \qquad (4)$$

where Q is the number of solute atoms put initially into the thin layer, and x_m denotes the position of the maximum of the gaussian distribution. There
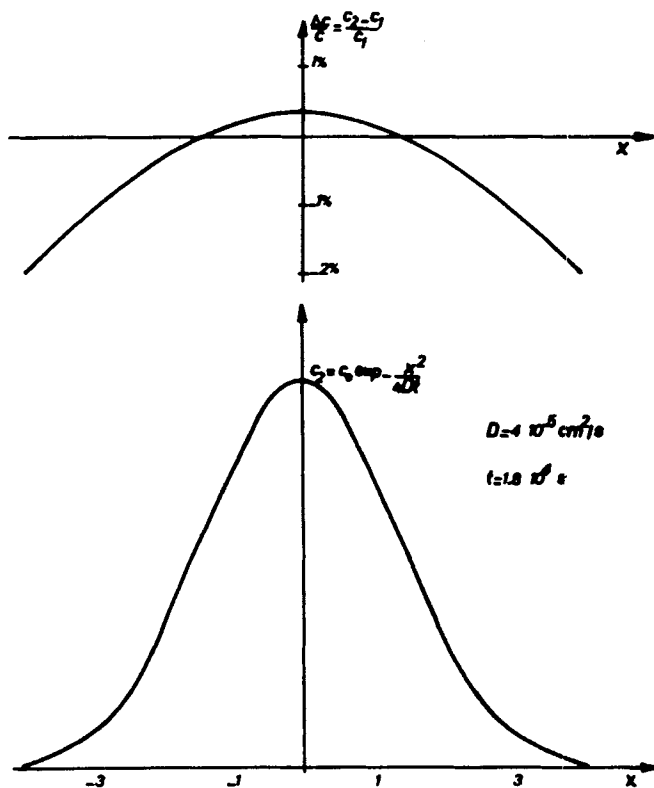

FIGURE 3   Comparison between the real thick layer solution of the Fick's equation c_1 and the thin layer approximation c_2 in a typical case of diffusion.
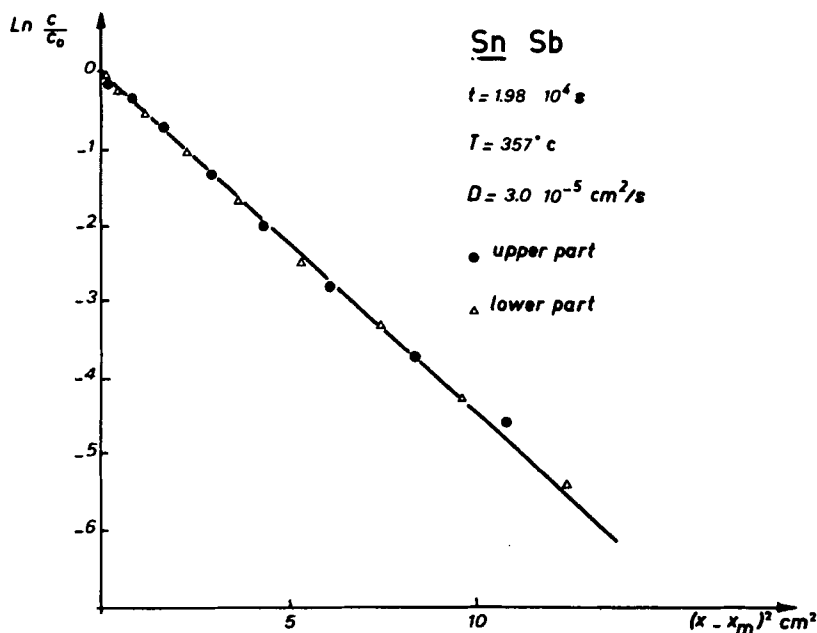
FIGURE 4   Plot of lnc as function of $(x - x_m)^2$ for diffusion of Sb^{125} in Sn.

are many advantages to use this geometry: (i) it allows an accurate deter-mination of D through the measurement of the slope $- 1/4Dt$ of the straight line $\ln c = f(x - x_m)^2$ (Figure 4); (ii) any accidental imperfection occurring during the diffusion run (convection, spurious temperature gradient, lack of solubility of the solute, ...) is clearly exhibited in the observed con-centration profile.

The precise location x_m of the maximum of the gaussian curve is deter-mined by a mean square deviation method: as a first guess we locate x_m at the very center of the intermediate disc and, by successive iterations, we adjust x_m so that the mean square deviation of the experimental points with respect to an ideal gaussian curve is minimum (Figure 5). In all our experiments, the shift of x_m with respect to the middle of the central disc is never larger than 2 mm.

2.3   Experimental results

In order to determine the influence of the valence of a solute upon its trans-port properties in Sn, we have measured the diffusion coefficients of solutes whose mass neighbors that of Sn. The capillaries are filled with tin of purity 5N supplied by Metal Research. Radioactive isotopes of the solutes deli-vered by the Département des Radioéléments (C.E.A., Saclay), are electroplated from a properly neutralized chlorhydric solution, onto a small
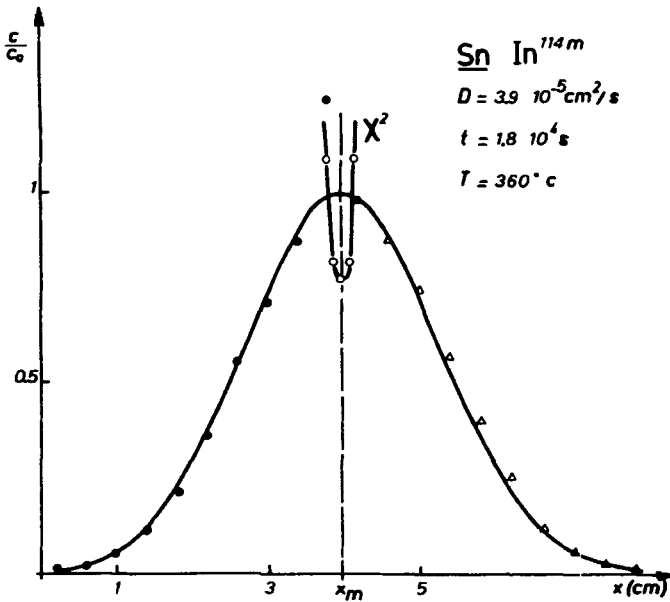
FIGURE 5   Typical curve of diffusion for In^{114m} in Sn.

rod of pure tin, so that the maximum concentration is of the order 10 ppm. The radioactive activity of the samples is measured with a INa (Tl) crystal and a standard counter.

As shown in Figure 4, the dispersion of the measured activity around the straight line $\ln c = f(x - x_m)^2$ is small, leading to a standard deviation of about 3%. In view of all the experimental errors, the reproducibility of the experiments is of about 5%. The results we have obtained for Ag^{110m}, Cd^{109}, In^{114m}, Sn^{113} and Sb^{125} in liquid Sn are recorded in Table I. Each value of D is the average of at least 3 measurements.

TABLE I

Diffusion coefficients of Ag^{110m}, Cd^{109}, In^{114m}, Sn^{113} and Sb^{125} in liquid tin; z_i is the valence of the solute relative to Sn; n is the number of different measurements of D_i and D_s is the diffusion coefficient of Sn^{113}.

Solute	z_i	T (°C)	t (10^3 s)	n	D_i (10^{-5} cm^2 s^{-1})	D_i/D_s
Ag^{110m}	−3	355	18.0	3	3.8 ±0.2	0.97
Cd^{109}	−2	354	28.8	4	2.1 ±0.1	0.52
In^{114m}	−1	360	18.0	5	3.9 ±0.2	0.98
Sn^{113}	0	355	19.8	6	4.0 ±0.2	1
Sb^{125}	+1	357	19.8	3	3.0 ±0.2	0.75
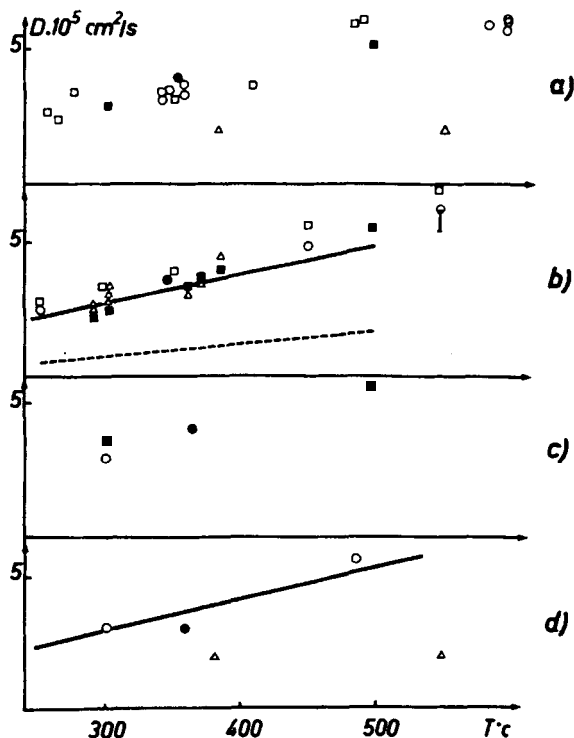
FIGURE 6   Comparison with other authors' results:

(a) Sn	(b) Ag
	/ Davis – Fryzuck
□ Ma – Swalin	/ Ma – Swalin
■ Kharkov	I Golovchenko
○ Davis – Fryzuck	■ Kharkov
△ Foster – Reynik	○ Teillier
● This work	△ Kuzmenko
	□ Tychima
	● This work

(c) In	(d) Sb
■ Kharkov	/ Niwa
○ Wenger – Shuck	○ Teillier
● This work	△ Foster – Reynik
	● This work

Our experimental data are compared (Figure 6) with some of the results obtained in preceding investigations.[16,25] There is a generally good agreement between our values and that of other experiments, except for Ag for which our data differ from those of Ma and Swalin[16] and for Sn and Sb where a discrepancy with the results of Foster and Reynick[23] is to be observed. In this last case especially it seems that the length correction of the sample,

intended to take account of boundary effects occurring at the end of the capillary, has been largely overestimated. This can explain the discrepancy with other results.[26]

3   DISCUSSION

Contrarily to the investigations carried in solid tin,[3] the diffusion coefficients of solutes in liquid tin seem to be rather insensitive to their relative valence z_i with respect to the solvent. In solid tin the diffusion coefficient decreases by a factor of 160 from Ag to Sb. Although it is actually possible that Ag diffuses in solid tin by an interstitial mechanism it remains true that, from Cd to Sb which diffuse by a vacancy mechanism, the diffusion coefficient decreases by a factor of 10 when it remains of the same order of magnitude in liquid Sn. In solids the dependence of D on the valence of the solute is explained[27,28] by the electrostatic interaction between the solute and the neighboring vacancy. If the diffusion in liquid metals were to occur by a kind of hole mechanism, it seems likely that such an interaction would similarly affect the diffusion coefficient. As our experimental observations do not exhibit such a dependence, we conclude that a hole mechanism does not operate in liquid tin. Our results can be explained however by use of an itinerant oscillator model: the solute atom oscillates in a cage of neighbors and its drift results from a collective motion and not from a jump process through a potential barrier. An especially attractive model is that developed by Hicter et al.[7] and Bernard et al.,[8] where the parameters involved in the theoretical expression of D are adjusted on thermodynamic properties of the liquid alloy. For self diffusion it is assumed that, as far as its energy E is smaller than a critical value ϵ, a given atom oscillates in a shell of nearest neighbors like an Einstein oscillator of characteristic temperature θ. These oscillations give rise to an irreversible drift of the atom and contribute to the diffusion coefficient.[2] As soon as E is larger than ϵ, the atom under consideration is assumed to move freely along a distance δ. Using these assumptions the free energy and the entropy of melting can be calculated and the parameter ϵ is estimated. This procedure leads to values of D in good agreement with experimental values, the vibrational part accounting for 10 to 20% of the net self diffusion coefficient. The model is also used[8] to calculate impurity diffusion coefficients in liquid metals: the temperatures θ, the critical energies ϵ involved in the calculation are adjusted so that partial and integral heats as well as excess entropies of mixing fit correctly to the experimental values. In the systems Sn–Al, Sn–Cd, Sn–Pb, Sn–Zn, the solute diffusion coefficients are smaller than the self diffusion coefficient D_s (Table II), even though these solutes exhibit a very large difference of mass and valence with respect to the solvent. This

TABLE II

Calculated[8] and experimental values of the ratio of the impurity diffusion
coefficients D_i to the self diffusion coefficient D_s of liquid tin

		Al	Cd	Pb	Zn	Ag	In	Sb
$\dfrac{D_i}{D_{s_{calc}}}$	(8) (232°C)	0.42	0.83	0.47	0.51			
$\dfrac{D_i}{D_s}_{exp}$	(350 °C)		0.52			0.97	0.98	0.75

indicates that an adjustment of the theory to experimental thermodynamic
results is a powerful mean of calculating impurity diffusion coefficients.

4   CONCLUSION

The·main result of our experiments is that, contrary to solids, the valence
effect on the impurity diffusion coefficients in liquid tin does not seem to
govern directly the values of D. This suggests that a hole mechanism does
not operate in liquid tin and that an itinerant oscillator model is more real-
istic. The method described in the present paper produces values of D
with a reproducibility of about 5% between different measurements. Using
our thin layer technique, this precision can be considerably enhanced in
order to measure the isotope effect. Two radioactive tracers can be electro-
plated simultaneously on the intermediate rod of pure tin and can diffuse in
the capillaries at the same time. This method should be accurate enough to
allow a comparison between the diffusion coefficients of two isotopes, which
should provide useful informations on the diffusion mechanism in liquid
metals.

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