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# Self-Diffusion in Tin at High Pressure

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Measurements are reported for *a*-axis and *c*-axis self-diffusion in tin from 0 to 10 kbars and for temperatures in the range 160–228°. At zero pressure,  $D_a = 10.7 \exp(-25,100 \pm 800)/RT$  and  $D_c = 7.7 \exp(-25,600 \pm 1000)/RT$ . The activation volume is  $5.3 \pm 0.3$ cm.<sup>3</sup> g.-atom<sup>-1</sup> (33% of the g.-atomic volume) for both principal directions and appears to be independent of temperature. The data are most simply interpreted in terms of a vacancy mechanism, in which two distinct kinds of jumps occur.

## Introduction

Activation energies  $\Delta H$  determined from the temperature dependence of the diffusion rate in single crystals of the elementary metals are most satisfactorily correlated with theoretically calculated activation energies for a vacancy diffusion mechanism.<sup>1</sup> Recent work on the pressure dependence, which leads to the activation volume  $\Delta V$ , has supported this mechanism.<sup>2</sup> The work of Simmons and Balluffi<sup>3</sup> provides near-conclusive evidence for the existence of high concentrations of vacancies in the noble metals and aluminum near their melting points. Hence, a vacancy diffusion mechanism is reasonable in these and similar metals.

Solid-state diffusion has been considered an activated process, with a Gibbs free energy of activation  $\Delta G$ . For the vacancy mechanism, it is natural to distinguish between contributions to  $\Delta G$  from the formation of sessile vacancies at equilibrium in the lattice,  $\Delta G_{\rm f}$ , and from the additional free energy  $\Delta G_{\rm m}$ necessary to move the vacancy from the equilibrium position to the midpoint of the diffusive jump. The activation enthalpy and volume have analogous components; diffusion studies yield only their sum. For close-packed hard spheres,  $\Delta V_f$  should be 1 molar volume, and  $\Delta V_{\rm m}$  should be of this order.<sup>2</sup> Other crystal structures will have smaller motional contributions. Measured values of  $\Delta V$  range from about 25% of an atomic volume (lithium) to 90% (silver), and are greater than 50% for close-packed structures.<sup>2</sup>

Rice and co-workers<sup>4-6</sup> have developed a dynamical theory of diffusion which, while formally equivalent to activated state theory, avoids the least tenable assumptions of the activated state, and which identifies the important microscopic contributions to the diffusive process. The activation energy is replaced by

$$\Delta II = U_0 + \sum_j U_j + \sum_{k>l} H_{kl} + \Delta H_l \quad (1)$$

where  $U_0$  is the translational energy a diffusing atom must obtain to successfully effect the jump,  $\sum_{j} U_j$  is the excess energy over the thermal average for any atoms hindering the motion of the diffusing atom to move sufficiently aside for that atom to pass, and  $\sum_{k>l} H_{kl}$  accounts for adjustments of the surrounding atoms not specifically included in the jump process.

atoms not specifically included in the jump process.  $\Delta H_{\rm f}$  is the formation enthalpy of a vacancy.

Using this approach, Rice and Nachtrieb<sup>5</sup> conclude that a correspondence between diffusion and melting should exist in the form

$$\left[\frac{\partial \ln \left(D/\gamma a^2 \nu\right)}{\partial T_m/T}\right]_{T_m} = \text{constant} \qquad (2)$$

and that

(4) S. A. Rice, ibid., 112, 804 (1958).

(5) S. A. Rice and N. H. Nachtrieb, J. Chem. Phys., 31, 139 (1959).
(6) A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, *ibid.*, 32, 447 (1960).

<sup>(1)</sup> D. Lazarus, "Advances in Solid State Physics," Vol. 10, F. Seitz and D. Turnbull, Ed., Academic Press, Inc., New York, N. Y., 1960, p. 71.

<sup>(2)</sup> D. Lazarus and N. H. Nachtrieb, "Solids Under Pressure," W. Paul and D. M. Warschauer, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p. 43.

 <sup>(3)</sup> R. O. Simmons and R. W. Balluffi, *Phys. Rev.*, 117, 52 (1960);
 119, 600 (1960); 125, 862 (1962); 129, 1533 (1963).

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$$\Delta H = \frac{\Delta H_{\rm m}}{\Delta V_{\rm m}} \,\Delta V \tag{3}$$

where the subscript m refers to fusion. While (2) and (3) hold remarkably well for a large number of metals to 10 kbars<sup>7</sup> Hudson and Hoffman<sup>8</sup> have found large deviations for lead at higher pressure. The correspondence between diffusion and melting probably exists only in the limit of zero pressure.

From the foregoing it is evident that vacancy diffusion occurs in metals which crystallize in close-packed structures in which the void volume is a minimum. Anisotropic structures typically have larger void volumes; and if interstitial self-diffusion occurs in metals, those with anisotropic structures should be relatively favored. Since no theoretical calculations for activation energies have been made for such systems, it is necessary to determine the activation volumes, as well as activation energies, to form reliable conclusions about the diffusion mechanism. White tin is anisotropic, with a void volume at  $25^{\circ}$  of 46.5%. and is thus a favorable metal. Self-diffusion studies in tin at zero pressure have been reported by Fensham<sup>9</sup> and by Meakin and Klokholm.<sup>10</sup> The results of Fensham are anomalous, giving activation energies which disagree with results for similar metals. Meakin and Klokholm found close agreement with other low melting metals, but could show only that a vacancy mechanism was consistent with their results, not that it was required. This study was undertaken to determine unequivocally the diffusion mechanism in tin.

It is perhaps desirable to ask at this point what is the significance of the quantity  $(\partial \ln D/\partial P)_T$  in an anisotropic system. Girifalco and Grimes<sup>11</sup> have analyzed the effect of strain on the diffusion relations as developed by Vineyard.<sup>12</sup> Their results are generalized to anisotropic systems in the Appendix, and it is clear that the measured quantity is indeed a volume, related to the usual activation volume in isotropic systems. This result adds confidence in the conclusions drawn from this study.

#### Experimental

Large single crystals were grown from 99.999%tin<sup>13</sup> by a modified Bridgman technique. Crystal quality was checked with a modified Laue backreflection technique, in which the only collimation of the X-ray beam was a 0.10-in. diameter pinhole. This gave a beam which struck about 1 cm.<sup>2</sup> of the crystal surface. Any crystal defects in this area appeared as irregularities in the X-ray film spots. Only crystals which gave nearly perfect spots were accepted for diffusion studies.

The large crystals were oriented by the usual Laue back-reflection technique. Cubes approximately 1 cm, on an edge and with their faces oriented close to perpendicular to the (100) or (001) axis, principle axes for diffusion, were cut out with a Servomet spark cutter. These cubes were again checked for quality with large-spot X-rays. No difference in quality of faces perpendicular or parallel to the tetragonal (001) axis was detected. Once again only the best crystals were retained. Two faces of each cube were oriented on a small goniometer head by X-rays so that the desired crystal axis and the goniometer axis were parallel to 0.5° of arc. The goniometer head was then aligned optically in a microtome to cut the crystal face perpendicular to the desired axis. Microtoming gave a plane basal surface that to within 2  $\mu$ . The crystal was annealed to remove the slight cold work introduced by the microtome.

Sn<sup>113</sup> in carrier metal was vapor deposited on the diffusion faces at pressures less than  $10^{-5}$  mm. Typically, films less than 1  $\mu$  thick and having an activity of close to  $10^{5}$  counts per min. were achieved.

The crystal was sealed in a Pyrex ampoule under vacuum and placed in a wire-wound resistance furnace at the desired temperature for the zero pressure anneals. Temperature was measured with a carefully calibrated iron-constantan thermocouple positioned near the ampoule at the center of an aluminum bronze block which minimized temperature gradients around the ampoule. Temperature was measured to 0.15° and absolute temperature at the crystal was probably correct to within 1°. Correction for finite warm-up rate was applied, in no case being greater than 0.5% of the anneal time. No cooling correction was needed.

High pressure was generated by a liquid hydraulic system of the Bridgman type.<sup>14</sup> Pressure was transmitted by Dow-Corning 200 silicone fluid and measured with a manganin wire coil calibrated against the freezing point of mercury (7640 kg./cm.<sup>2</sup> at 0°). Automatic pressure control, plus a continuous pressure record, was obtained by monitoring the imbalance of a Wheatstone bridge with a recording potentiometer. Pressure was maintained to within 10 kg./cm.<sup>2</sup> of the mean

<sup>(7)</sup> R. A. Hultsch and R. G. Barnes, Phys. Rev., 125, 1832 (1962).

<sup>(8)</sup> J. B. Hudson and R. E. Hoffman, *Trans. AIME*, 221, 761 (1961).
(9) P. J. Fensham, *Australian J. Sci. Res.*, 3A, 91 (1950); 4, 229 (1951).

<sup>(10)</sup> J. D. Meakin and E. Klokholm, Trans. AIME, 218, 463 (1960)

<sup>(11)</sup> L. A. Girifalco and H. H. Grimes, Phys. Rev., 121, 982 (1961)

<sup>(12)</sup> G. H. Vineyard, J. Phys. Chem. Solids, 3, 121 (1957).

<sup>(13)</sup> Purchased from Vulcan De-Tinning Company.

<sup>(14)</sup> P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1958.

## Self-Diffusion in Tin at High Pressure

Table I: Thermal Expan	sion <sup>a</sup> and Linear Compre	ession Coefficients <sup>b</sup> for Tin	× •	a. 5
$\alpha_c$ , deg1	$\kappa_c$ , atm. <sup>-1</sup>	$\Delta \kappa_c,  \mathrm{deg},  ^{-1}$ atus, $^{-1c}$	$\delta_c$ <sup>45</sup> , atm. <sup>-2</sup>	$\Delta \delta_c$ , deg. $^{-1}$ atm. $^{-2}d$
$36.4 \times 10^{-6}$	$6.693 \times 10^{-7}$	$0.0053 \times 10^{-7}$	$4.09 \times 10^{-12}$	$-0.0037 \times 10^{-12}$
$\alpha_a$ , deg. $^{-1}$	κa, atm. −1	$\Delta \kappa_{\alpha}$ , deg. <sup>-1</sup> atm. <sup>-16</sup>	$\delta_a{}^{25}$ , atm. <sup>-2</sup>	$\Delta \delta_a$ , deg. <sup>-1</sup> atm. <sup>-2d</sup>
$16.7 \times 10^{-6}$	$6.008 \times 10^{-7}$	$0.0027 \times 10^{-7}$	$4.19 \times 10^{-12}$	$0.0013 \times 10^{-12}$
<sup>a</sup> S. Lee and W. Raynor	, Proc. Phys. Soc., B67, 7	<sup>39</sup> (1954). <sup>b</sup> Ref. 14, p. 16	$59; \ \Delta l/l_0 = \kappa P - \delta P^2.$	$^{\epsilon} \Delta \kappa = \mathrm{d}\kappa/\mathrm{d}T.$ $^{d} \Delta \delta = \mathrm{d}\delta/\mathrm{d}T.$

pressure. The bomb was immersed in a Dow-Corning 500 silicone oil bath at the desired temperature. Crystal temperature was measured on a carefully calibrated chromel-alumel thermocouple near the crystal in the bomb. Temperature was measured to  $0.25^{\circ}$ , but variable temperature gradients prevented knowing the temperature at the crystal to better than within about 2°. Corrections were applied for finite warming and cooling rates. These were always less than 2%.

After the anneal, each nonactive face was microtomed to eliminate surface diffusion effects. The common edge between the two diffusion faces was also removed. Radioactive slices 2  $\mu$  thick were grouped in threes; each group was weighed to  $\pm 10 \ \mu$ g., then counted in a methane flow proportional counter operating in the plateau region. Ten thousand counts above background were collected from each sample. Approximate penetration profiles were determined as shown in Fig. 1. Slice thickness and face misalignment corrections were applied to the diffusion coefficient calculations.<sup>15</sup> The relative error in the diffusion coefficients is close to  $\pm 5\%$ .

## **Experimental Results**

From the thermal expansion and compressibility data given in Table I, the diffusion coefficients were corrected for the effects of thermal expansion and linear compression. This effect is small, never much greater than 1%. At the highest pressures it was occasionally negative or zero. The corrected diffusion coefficients, as well as other pertinent quantities, are given in Table II.

Isobars. A temporary value of  $(\partial \ln D/\partial P)_T$  was taken from a plot of the data as approximate isobars, and this value was used to correct each diffusion coefficient to the nominal (*i.e.*, 000, 2000, etc.) pressure of the run. Corrections were never greater than 3%, so that a more accurate correction procedure is unnecessary. The corrected isobars for *a*- and *c*-axis diffusion are shown in Fig. 2 and 3. The lines shown are not least-squares lines, but are instead intuitive lines which show more clearly the trends in the data. Table II: Diffusion Data  $D_a$ P.  $D_a \times 10^{11}$ ,  $D_c \times 10^{11}$ , kg./cm.2 T, °C. - cm.2/sec. cm.2/sec.  $D_c$ 000 160.4 0.2113 . . . 000 162.6 0.249. . . 000 160.8 0.0986 176.3 0.557 0.255000 2.184 000 191.7 1.400 0.563 2.487000 207 7 3.583 1.558 2.300000 225.8 10.09 4.82 2 093 2158189.6 0.918 0.471 1.949 2.893 1640 207.9 1.360 2.127 7.363 1992 225.6 3.403 2.164 1932 228.8 7.892 4.378 1.803 4116 190.10.800 0.360 3988 192.03907 211.3 2.748 1.293 2.125 225.1 5.124 2.876 4007 1.782 3977 235.9 10.0294.866 2.062 0.5495 6089 190.00.2726035 192.6 0.679 2.496 208.1 1.557 0.701 2.221 6017 2.3006104 224.6 4.883 2.123 10.769 2.567 6020 239.8 4.1960.1834 7999 191.9 0.400 2.181 7909 207.8 0.471 . . . 1.389 2.092208.8 0.664 7959 7970 224.8 3.642 1.507 2.417 8079 239.8 7.691 3.100 2.451 0.3467 0.15910090 192.02.181 10120 207.6 0.9839 0.422 2.33110105 225.32.9101.368 2.127 10134 244.8 7.765 2.7272.847

This is justified since four points are inadequate for a meaningful least-squares treatment, particularly in view of the scatter in the data. Activation energies and  $D_0$  values derived from these isobars are given in Table III. A reasonable mean value of the standard deviations for the activation energies is 1.25 kcal., or 5%, while the relative error of the  $D_0$  values is close to 10%.

<sup>(15)</sup> G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta Met., 1, 514 (1953).



Figure 1. Typical c-axis penetration profile.

Table III: Activation Energies and Do Values

	Pressure, kg./cm.2					
	000	2000	4000	6000	8000	10,100
$\Delta H_a$ , kcal./mole	25.12	25.57	25.61	26.33	27.24	27.90
$\Delta H_e$ , kcal./mole	25.55	25.81	26.70	27.48	28.06	28.48
$D_0^{a}$ , cm. <sup>2</sup> /sec.	9.06	10.7	9.40	15.2	29.9	42.1
$D_9^{c}$ , cm. <sup>2</sup> /sec.	6.23	7.16	13.4	21.7	28.8	35.2

The trend toward higher  $\Delta H$  values with increased pressure implies an activation volume greater than zero since thermodynamics gives

$$\left(\frac{\partial\Delta H}{\partial P}\right)_{T} = T \left(\frac{\partial\Delta S}{\partial P}\right)_{T} + \Delta V \qquad (4)$$

From the development of  $\Delta S$  by Keyes<sup>16</sup> (neglecting the pressure variation of thermal expansion,  $\alpha$ ) we have

$$\left(\frac{\partial\Delta S}{\partial P}\right)_{\tau} = 2\left(\gamma - \frac{1}{3}\right)\alpha\Delta V \tag{5}$$

where  $\gamma$  is the Gruneisen constant. Combining (4) and (5)

$$\Delta V = \left[1 + 2\left(\gamma - \frac{1}{3}\right)\alpha T\right]^{-1} \left(\frac{\partial\Delta H}{\partial P}\right)_{T} \quad (6)$$

Thus, a positive change in  $\Delta H$  with pressure assures that  $\Delta V$  is greater than zero. This is consistent with previous high pressure diffusion studies.<sup>2</sup>

An approximate value of  $(\partial \Delta H/\partial P)_T = 12.5$  cm.<sup>3</sup>/ mole leads to the value  $\Delta V = 12.0$  cm.<sup>3</sup>. This result does not agree with the value obtained from the usual method of determining  $\Delta V$  and undoubtedly reflects the uncertainty in higher pressure isobar slopes (Fig. 2 and 3).



Figure 2. a-Axis diffusion isobars.

The most striking feature of the data in Table III is that the activation energies for both *a*- and *c*-axis diffusion are the same to well within experimental error. This is surprising, in view of the definite anisotropy in thermal expansion and compressibility shown in Table I. More important, Meakin and Klokholm<sup>10</sup> observed considerable diffusion anisotropy in their work on tin. This discrepancy is discussed more fully in a later section. The similarity of activa-

<sup>(16)</sup> R. W. Keyes, "Solids Under Pressure." W. Paul and D. M. Warschauer, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p. 71



Figure 3. c-Axis diffusion isobars.

1.90

tion energies for diffusion in intrinsically different directions plays an important role in the discussion of possible diffusion mechanisms in tin.

2.10

1000/T(°K)

2.20

Isotherms. Values of  $(\partial \ln D/\partial T)_P$  from the isobars were used to correct the data to the appropriate nominal temperatures (225.6, 208.8, 192.0°). Corrections were generally less than 5%. The least-squares isotherm at 2.5.6° is shown in Fig. 4. Activation volumes derived from these isotherms via the usual formula<sup>2</sup>

$$\left(\frac{\partial \ln \left(D/\gamma a^2 \nu\right)}{\partial P}\right)_T = -\Delta V/RT \qquad (7)$$

are given in Table IV, along with their standard deviations.

As for  $\Delta H$  values, the activation volumes are essentially equal for both a- and c-diffusion directions. The apparent variation in a-axis  $\Delta V$  values may or may not

Figure 4. Diffusion isotherms  $(225.6^{\circ})$  for a and c axes.

be real since it is just outside the limits of experimental error. For the purposes of this discussion,  $\Delta V$  can be considered constant, equal to 5.3 cm.<sup>3</sup>/mole for both a- and c-axis diffusion. This result is central in the discussion of possible diffusion mechanisms.

Corresponding States Test. The isobar data and the change in melting temperature of tin with pressure are sufficient to test the corresponding states relation (2) of Rice and Nachtrieb.<sup>5</sup> The most accurate determination of the melting curve to 10 kbars has been made by Babb.<sup>17</sup> From his results,  $T_m/T$  was found for each value of D. Figure 5 is a plot of  $\ln D$  against  $T_{\rm m}/T$  for diffusion along each axis. The lines shown are least-squares lines for the respective axis. Apparently the corresponding states relation is quite closely satisfied.

It is interesting to compare a- and c-axis values of

(17) S. E. Babb, J. Chem. Phys., 37, 922 (1962).

192.0



Figure 5. *a*- and *c*-axis diffusion coefficients as a function of reciprocal reduced temperature.

several quantities derived from the data in Fig. 5. Since  $T_{\rm m}$  is a function of pressure, eq. 2 may be written

$$\left(\frac{\partial \ln (D/\gamma a^2 \nu)}{\partial T_{\rm m}/T}\right)_{T_{\rm m}} = \frac{1}{T_{\rm m}} \left(\frac{\partial \ln (D/\gamma a^2 \nu)}{\partial 1/T}\right)_{P} = -\frac{\Delta H}{RT_{\rm m}}$$
(8)

or

$$\Delta H = -RT_{\rm m}({\rm constant}) \tag{9}$$

Hence, if the corresponding states law holds, the activation enthalpy should vary linearly with  $T_{\rm m}$ . Slopes of the  $T_{\rm m}/T$  curves and representative values of  $\Delta II$  at three pressures from eq. 9 are given in Table V. Comparison with similar  $\Delta H$  values from Table III supports the conclusion that the slopes of the isobars as drawn in Fig. 2 and 3 are probably too steep at higher pressures.

The increase in  $\Delta H$  with pressure, taken from Table V, may be used in eq. 6 to calculate a mean activation volume of 6.1 cm.<sup>3</sup>, in satisfactory agreement with the value of 5.3 cm.<sup>3</sup> derived more directly from the isotherms. Since the latter give  $\Delta V$  more directly, the lower value is considered more reliable.

Table V: Quantities Derived from Corresponding States Test

	Quantity	a axis	c axis
	Slope	-25,686	-25.413
	Standard deviation <sup>a</sup>	0.142	0.148
	$\Delta H \left( P = 0 \right)^b$	25,780 cal.	25,500 cal.
	$\Delta H (P = 5000)^{b}$	26,570 cal.	26,290 cal.
	$\Delta H \left( P = 10, 100 \right)^b$	27,350 cal.	27,060 cal.
	$\Delta V$	6.1 cm. <sup>3</sup>	6.1 cm.3
a	This corresponds to a	a difference in D	values of ~15%
P	is in kg./cm. <sup>2</sup> .		

The corresponding states relation (3) may be tested using the values  $\Delta H = 25.3$  kcal. and  $\Delta V = 5.3$  cm.<sup>3</sup> (derived from this study),  $\Delta H_{\rm m} = 1690$  cal.,<sup>18</sup> and  $\Delta V_{\rm m}$ = 0.454 cm.<sup>3</sup>.<sup>19</sup> The right-hand side of (3) predicts that  $\Delta H = 19.75$  kcal., only 80% of the observed 25.3 kcal. The discrepancy is outside of the accumulated experimental error, and hence this relation does not seem to hold well for tin. This is surprising in view of the agreement observed for a large number of other metals.<sup>7</sup>

 $D_a/D_c$  Ratio. Examining the isotherms (Fig. 4) more closely shows that the isotherm points tend to deviate in pairs from their "best" positions, being both high or both low at each pressure. This variation is probably the result of uncertainty in temperature at the position of the crystal, as mentioned previously. Figure 5 shows that *a*- and *c*-axis diffusion coefficients differ by only a constant factor close to 2.2 over the entire temperature and pressure range, and that no significant difference in  $\Delta H$  exists for the two directions. Table V gives the spread in the data for this plot. Deviations from this plot, too, are pairwise, and the most meaningful comparison between a- and c-axis diffusion rates is not found here. Instead, the  $D_a/D_c$ ratios given in Table II for those runs in which both quantities were determined successfully have been used to calculate a mean value  $\langle D_a/D_c \rangle_{av} = 2.20 \pm 0.15$ . The ratio of diffusion rates in fundamentally different crystal directions evidently varies little over the temperature and pressure range used in this study. This is truly a remarkable result. Furthermore, the large spot X-rays used to determine crystal quality are indistinguishable in terms of crystal perfection for either axis. The explanation of the remarkable sameness then must lie in the nature of the fundamental diffusion process in tin.

<sup>(18)</sup> U. S. National Bureau of Standards Circular 500, F. Rossini, Ed., U. S. Government Printing Office, Washington, D. C., 1952, p. 649.

<sup>(19)</sup> S. G. Kubaschewski, Trans. Faraday Soc., 45, 931 (1949).



Figure 6. Comparison of *a*- and *c*-axis diffusion coefficients with data of Meakin and Klokholm.

#### Discussion

The zero pressure results of this experiment are compared with the previous results of Meakin and Klokholm in Fig. 6. Evidently, the absolute values of D agree very well between the two studies, though the D values of the present experiment are generally slightly smaller, particularly at lower temperatures for *a*-axis values.  $\Delta H$  and  $D_0$  values derived from each study are given in Table VI.

Table VI:	able VI: Comparison of Zero Pressure Results			
$\sim$	—-Meakin and a axis	Klokholm		study
D <sub>0</sub> , cm. <sup>2</sup> / sec.	$1.4 \pm 0.5$	$8.2 \pm 0.6$	$10.7 \pm 1$	$7.7 \pm 3$
$\Delta H$ , kcal./ mole	$23.3 \pm 0.5$	$25.6 \pm 0.8$	$25.2 \pm 1.0$	$25.6 \pm 1.2$

The differences in  $\Delta H$  and  $D_0^{-1}$  values in Table VI seem outside experimental error. In view of the con-

stant  $D_a/D_c$  ratio found in this study, the present authors cannot but feel that their *a*-axis results are more closely correct than the earlier values. The greater temperature range of this experiment increases the accuracy of the isobar slope, and hence  $\Delta H$ , which supports this conclusion.

Lack of agreement between the *a*-axis results of the two studies is puzzling, particularly in view of the excellent *c*-axis fit. The only significant divergence of the experimental techniques involved cutting out the diffusion specimen. Meakin and Klokholm used a fine jeweler's saw, while a spark cutter was employed in this study. Greater long-range crystal damage results from sawing than spark erosion, which might account for the lower D values for most of this study. The crossover for *a*-axis diffusion is not explained on this basis.

The conclusion that bulk diffusion is observed rests primarily on the linearity of the penetration profiles obtained (Fig. 1) over more than an order of magnitude change in activity. Assuming that this conclusion is valid, we inquire into the nature of the diffusive process.

In close-packed metals, activation volumes on the order of half the molar volume are assumed to indicate vacancy diffusion.<sup>2</sup> A smaller  $\Delta V/V$  (=26%) in the nonclose-packed metal lithium has led to speculation that interstitial diffusion might be operating in that metal.<sup>7</sup> The present study has observed a relative activation volume of very similar size (33%), hence interstitial diffusion should be considered. That it is not likely may be seen by considering the quenchresistance studies of vacancies in gold. From the rate of annealing under pressure of quenched-in resistivity, Emrick<sup>20</sup> concluded that the motional activation volume of vacancies in gold was only 15% of the atomic volume. The resistivity quenched into gold at high pressures by Heubener and Homan<sup>21</sup> indicates that the formation volume of vacancies is 53% of an atomic volume. It is difficult to see how in tin a larger relative volume would be needed for motion than in the close-packed gold structure. Hence, an upper limit of  $\Delta V_{\text{mob}}/V = 0.15$  implies a lower limit of  $\Delta V_{\text{form}}/V =$ 0.18, and this positive formation volume implies a vacancy diffusion mechanism. A similar analysis leads to vacancy diffusion for lithium.

A more complete description of the white tin structure is necessary before discussing the proposed jump mechanism. Two interpenetrating body-centered tetragonal lattices give a unit cell with atoms at

<sup>(20)</sup> R. M. Emrick, Phys. Rev., 122, 1720 (1961).

<sup>(21)</sup> R. P. Heubener and C. G. Homan, ibid., 129, 1162 (1963).

(000),  $(1/2 \ 0 \ 1/4)$ ,  $(1/2 \ 1/2 \ 1/2)$ , and  $(0 \ 1/2 \ 3/4)$  with unit cell dimensions at 25° of a = 5.820 Å., c = 3.175 Å., so that c/a = 0.5456. Each atom has four nearest neighbors at a distance of 3.016 Å., directed  $\sim 15^{\circ}$  out of the *a*-axis plane, and two next nearest neighbors along the *c*-axis at 3.175 Å.

In this structure two distinct kinds of jump are possible for bulk diffusion via vacancies. If in Fig. 7a the vacancy is at the site labeled 1, it may exchange with either of four nearest neighbors labeled 2 or two next-nearest neighbors labeled 3. Only these jumps are considered; other jumps are essentially blocked by the atoms neighboring the vacancy. For convenience, a vacancy jump from site 1 to site 2 shall be called an "a" jump, not exactly in the *a*-axis direction, and a "c" jump will be the vacancy jump from site 1 to site 3. Note that the "a" jump contains a component in the *c*-axis direction which contributes to *c*-axis diffusion, while "c" jumps do not contribute to *a*-axis diffusion.

In view of the essentially identical energies and volumes associated with diffusion along the different axes, it is attractive to postulate that only one jump, the "a" type, might satisfactorily account for the results of this study. We check this possibility by forming the ratio

$$\frac{D_e}{D_a} = \frac{\gamma_e' c^2 \nu_e' e^{+\Delta S e'/R} e^{-\Delta H e'/RT}}{\gamma_a a^2 \nu_a e^{+\Delta S a/R} e^{-\Delta H a/RT}}$$
(10)

where all terms have their usual meaning. If only "a" jumps are assumed then  $\Delta H_a = \Delta H_c'$ ,  $\Delta S_a = \Delta S_c'$ , and  $\nu_a = \nu_c'$ , and (10) becomes

$$\frac{D_c}{D_a} = \frac{\gamma_c' c^2}{\gamma_a a^2} \tag{11}$$

The component of an "a" jump in the *a*-axis direction is one-half the length of an *a* edge of the unit cell. There are four possible jumps of this type, only two of which contribute to diffusion along a given *a*-axis, so  $\gamma_a a^2 = \frac{1}{2}(2)(a/2)^2 = a^2/4$ . All *a* jumps contain components in the *c*-axis direction of magnitude c/4, so  $\gamma_c'c^2 = \frac{1}{2}(4)(c/4)^2 = c^2/8$ . The factor  $\frac{1}{2}$  in front of each product arises from the definition of the  $\gamma$ values.<sup>22</sup> Since  $D_a/D_c = 2.20$ , we have

$$\frac{1}{2.20} = 0.454 \neq (1/8)c^2/(1/4)a^2 = (1/2)(c^2/a^2) = 0.15 \quad (12)$$

since the ratio  $(c^2/a^2)$  is 0.298. Hence, the observed rate of *c*-axis diffusion is a factor of three too high to be explained by only "*a*" jumps. The missing twothirds of the observed rate must be assigned to "*c*"type jumps, so that *c*-axis diffusion is a combination of both elementary jumps.



Atomic Positons in White Tin

Figure 7. Atomic positions in tin.



Figure 8. Contributions of a- and c-type jumps.

Similar to Meakin and Klokholm,<sup>10</sup> we compare the diffusion coefficients for "a" and "c" jumps separately by subtracting  $0.15D_a$  from each  $D_c$  value at the same temperature. This removes the "a"-jump contribution to *c*-axis diffusion. Figure 8 shows the zero-pressure isobars for  $D_a$ ,  $D_c$ , and  $D_c'$ , where  $D_c' =$  $D_c - 0.15D_a$ . Least squares gives  $D_0' = 4.64$  cm.<sup>2</sup>/ sec. and  $\Delta H_c' = 25.6$  kcal., essentially unchanged in

(22) C. Zener, J. Appl. Phys., 22, 372 (1952).

 $\Delta H$  and somewhat lower in  $D_0$  than the uncorrected isobar results.

Since the isobars in Fig. 8 are essentially parallel, we can determine the relative jump frequencies, defined<sup>4</sup> as  $\Gamma_i = \nu_i e^{\Delta S_i/R} e^{-\Delta H_i/RT}$  for the *i*th jump type, by substituting  $\gamma_a a^2 = 1/_4 a^2$ ,  $\gamma_c c^2 = 1/_2(2)(c)^2 = c^2$ , and  $D_c/D_a = 0.306$  into eq. 10. Thus

$$0.306 = \frac{c^2}{\frac{1}{4a^2}} \frac{\Gamma_e}{\Gamma_a} = 1.19 \frac{\Gamma_e}{\Gamma_a}$$
(13)

or

$$\Gamma_c = 0.257\Gamma_a \tag{14}$$

Hence, the jump frequency for direct vacancy motion along the *c*-axis is only roughly 25% of the frequency of "*a*" jumps. This result provides considerable information about the details of the jump mechanism in tin.

Rice and co-workers<sup>4-6</sup> have analyzed the conditions for a diffusive jump. Briefly, the atom must have a critical amplitude in the direction of the vacancy, and simultaneously, and also most restrictively, all blocking atoms must move aside with a breathing mode of sufficient amplitude to allow the diffusing atom to pass. These criteria may be visualized for tin in terms of Fig. 7a and 7b. Figure 7b is a view of the a-c plane looking along the *a*-direction in the tin crystal. Suppose that in Fig. 7b the site labeled 1 is vacant. If a "c" jump is to occur (exchange with the site labeled 3), then both atoms labeled 4, plus the two body-centered atoms not shown, must move aside. Thus, both the conditions of sufficient amplitude of the diffusing atom and a suitable breathing mode of the four blocking atoms must be satisfied. But from Fig. 7a it is evident that any one of the atoms labeled 2 may move into the vacancy at 1 without interference from blocking atoms. Hence, the only condition for "a" jumps is that the diffusing atom have sufficient amplitude to effect the jump. Relaxation of the atoms toward the vacancy will modify this picture only slightly, since now a breathing motion is required for the other atoms labeled 2 in Fig. 7a if one of these is to jump. But the required amplitude is small, and should be easily achieved. Thus, "a" jumps are greatly favored, since the frequency of occurrence of the necessary breathing mode in both pairs of blocking atoms involved in "c" jumps is expected to be much lower than the frequency with which the amplitude conditions are fulfilled for either jump. This agrees with (14).

But the activation energies should be different for these jumps, since the jump conditions are different. We use eq. 1 to compare the relative importance of various contributions to  $\Delta H$ .  $\Delta H_f$  is the same for each jump type, since all vacancies are presumed equivalent. The sums  $\sum_{k>l} \Delta H_{kl}$  should be very nearly the same for both jump types. The terms  $U_0$  will be close to equal for each jump type, though perhaps slightly larger for "c" jumps. At first the energy contributions from  $\sum_{j} U_j$  appear quite anisotropic, since the sum is zero for "a" jumps, but finite for "c" jumps into an unrelaxed vacancy. Relaxation should increase this contribution nearly equally for each type. To determine the anisotropy in  $\Delta H$ , it is necessary to form some estimate of  $\sum U_j$  for "c" jumps.

The dynamical theory, as developed by Manley,<sup>23</sup> identifies as the critical variable for each atom j the difference  $\Delta q_j$  between the maximum attainable amplitude,  $q_{jmax}$ , and the necessary amplitude to just permit the jump,  $q_{jmin}$ . In tin the geometry is such that  $q_{jmin}$  is 0.106 Å. at 25°, and it decreases slightly with temperature. But from Mössbauer measurements in tin<sup>24</sup> the root mean squared vibrational amplitudes of atoms in the (100) direction at 300°K. is  $\sim 0.150$  Å, and increases to 0.178 Å, at 400°K, and to 0.204 Å. at 500°K. Apparently, at the diffusion temperatures the root mean squared amplitudes are nearly a factor of two larger than  $q_{imin}$ , and the atoms j do not need to acquire extra energy for a diffusive jump. Obviously, they must still satisfy the breathing mode requirement, and this will limit the jump rate. But anisotropy in  $\Delta H$  due to different contributions from  $\sum U_j$  will be small, since both jump types require little or no increase over the mean thermal energies for the interfering atoms.

It can still be argued that the activation energies could be quite unequal if the admittedly nonidentical factors  $U_0$  and  $\sum_{j} U_j$  of (1) were dominant. It has been estimated<sup>6</sup> that the various terms for a simple model have the approximate weights  $\Delta H_t = 20-40\%$ ,  $U_0 =$ 30-60%,  $U_j = 15-25\%$ , and  $\sum_{k>l} \Delta H_{kl} = 5-10\%$ . Recent results of quenching measurements and lattice dilatation studies in Ag,<sup>25</sup> Au,<sup>26</sup> and Cu<sup>3</sup> show that a more probable weight for  $\Delta H_t$  for the noble metals is close to 60\%. While tin is far from a noble metal, it seems likely that the formation enthalpy is still close to 50\% of the total effect. Thus, anisotropy in the activation energies must be small as observed.

Entropy. The activation entropy,  $\Delta S$ , was calculated from the usual relation<sup>1</sup>

- (23) O. P. Manley, J. Phys. Chem. Solids, 13, 244 (1960).
- (24) A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, *Proc. Phys. Soc.* (London), A77, 129 (1961).
- (25) M. Dovama and J. S. Koehler, Phys. Rev., 127, 21 (1962).
- (26) J. E. Bauerle and J. S. Koehler, ibid., 107, 1493 (1957).

$$\Delta S = R \ln \left( D_0 / \gamma a^2 \nu \right) \tag{15}$$

The choice of  $\nu$  is difficult and has been related to a normal mode analysis of lattice vibrations by several authors.<sup>4,12</sup> In practice, the Debye frequency is used as the best available estimate. In this experiment the jump rates differing by a factor of 4 can only be the result of differences in  $\Delta S$  and  $\nu$ , and the uncertainty in  $\nu$  is compounded further. Consider three cases:  $\nu_a = \nu_e$  and the  $D_0$  differences are reflected in  $\Delta S$ ;  $\nu_a = 4\nu_e$ , the jump rate difference being almost entirely due to  $\nu$  differences;  $\nu_a = 2\nu_e$ , an intermediate case. These cases are presented in Table VII, with calculations based on  $\nu_a = \nu_{\theta}$ , where  $\theta_D = 142^{\circ}$ K.<sup>27</sup> It is interesting that  $\Delta S_a = \Delta S_e$  if  $\nu_a = 2\nu_e$ . The  $\Delta S$  values do not agree well with Meakin and Klokholm, who apparently used a much different Debye temperature.

able VII:	Activation Ent	ropies	
Case	$\Delta S_a$ . e.u.	$\Delta S_c$ , e.u.	Relationships
1	16.6	17.8	$\nu_a = 4\nu_c$
2	16.6	15.1	$\nu_a = \nu_c$
3	16.6	16.4	$\nu_a = 2\nu_c$

Keyes<sup>16</sup> has used continuum theory to write

$$\Delta S = 2(\gamma - \frac{1}{3})\alpha\Delta G \tag{16}$$

where  $\alpha$  and  $\gamma$  are the thermal expansion coefficient and the Grüneisen constant. To a first approximation, this study gives  $\Delta G \simeq \Delta H = 25.3$  kcal. and  $\Delta S = 5.2$ e.u. From this estimate  $\Delta G = \Delta H - T\Delta S = 23.0$ kcal., and  $\Delta S = 4.75$  e.u. This is much lower than the observed  $\Delta S$  values and seems to cast doubt on the applicability of the theory.

Volume. It is interesting to note that DeVries, Baker, and Gibbs,<sup>28</sup> in a preliminary report, have found an activation volume for creep in tin of about 30%of the molar volume, in close agreement with the 33%observed in this study. Their results have not been fully published to date so further comment is difficult.

Keyes<sup>16</sup> has also developed the relation

$$\Delta V = 2\left(\gamma - \frac{1}{3}\right)\kappa\Delta G \tag{17}$$

where  $\kappa$  is the compressibility. Using  $\Delta G = 23.0$  kcal., we have  $\Delta V = 5.1$  cm.<sup>3</sup>, in excellent agreement with the observed 5.3 cm.<sup>3</sup>. Hence, the strain energy approach gives quite good agreement for  $\Delta V$ , though the predicted  $\Delta S$  is not good.

We can get some indication as to why no anisotropy in  $\Delta V$  was observed in this study from considering eq. 12a in the Appendix. The  $S_i$  are sums of elastic constants, the same for all k directions, so anisotropy comes only from the  $M_i^k$  (the  $\gamma RTs_i\delta_{ik}$  term is small, so anisotropy from this source is negligible). But the  $M_i^k$  are defined by eq. 8a in terms of a formation and a motion contribution,  $w_i$  and  $m_i^k$ ; only the latter can be anisotropic. But we have seen that in gold this term is only 22% of the total activation volume, and in general  $w_i \ge m_i^k$  is probably valid. Therefore, any anisotropy in  $m_i^k$  for different k is largely masked by the isotropic  $w_i$  contribution.

Probably the largest contribution to anisotropy in  $\Delta V_{\rm mob}$  arises because the blocking atoms must assume a breathing mode before the diffusing atom may exchange with the vacancy. But the previous comments about vibration amplitudes in tin show that this effect will be small at best, since little or no "excess" volume is required. Hence,  $\Delta V_{\rm a}$  should be almost equal to  $\Delta V_{\rm c}$ .

From eq. 10a we can get some idea of the magnitude of the  $M_4^{\ k}$ . The tin elastic moduli were taken from Mason and Bommel.<sup>29</sup> For the *a*-axis isotherm at 225.6° we have

$$4.82 \text{ cm.}^3 = (M_1^1 + M_2^1)(10.3 \times 10^{-13}) +$$

 $M_{3^{1}}(7.8 \times 10^{-13})$  (18)

so that an upper limit for  $M_1^k$  is  $\sim 5 \times 10^{12}$  ergs = 10<sup>3</sup> kcal. The work of Liu and Drickamer<sup>30</sup> on the effect of uniaxial compression on diffusion in zinc can be used in a consistent way<sup>31</sup> to evaluate some individual  $M_t^k$  values. From the elastic data for zinc of Hearmon,<sup>32</sup> we find that  $M_{1^3} = 35 \times 10^3$  kcal. and  $M_{3^3} =$  $190 \times 10^3$  kcal. These values are up to two orders of magnitude greater than the upper bounds found for tin and also exceed similar upper limits determined from the hydrostatic pressure results for zinc by the same margins. Two possible explanations of this difficulty are: (1) the effect of pressure is not adequately accounted for by a sum over the individual stress components of the form of eq. 10a; (2) some gross difficulty exists in the experiments. Neither alternative is favored; indeed both may be partially correct.

<sup>(27)</sup> R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.*, 131, 529 (1963).

<sup>(28)</sup> K. L. DeVries, G. S. Baker, and P. Gibbs, Bull. Am. Phys. Soc., [II] 6, 169 (1961).

<sup>(29)</sup> W. P. Mason and W. E. Bommel, J. Acoust. Soc. Am., 28, 930 (1956).

<sup>(30)</sup> T. Liu and H. G. Drickamer, J. Chem. Phys., 22, 312 (1954).

<sup>(31)</sup> See A. W. Lawson, *ibid.*, 22, 1948 (1954). However, if the stress range is great enough,  $\partial \ln D_k/\partial P_i$  may be evaluated using only uniaxial stress data. This avoids the inconsistency.

<sup>(32)</sup> R. F. S. Hearmon, Res. Mod. Phys., 18, 409 (1946).