

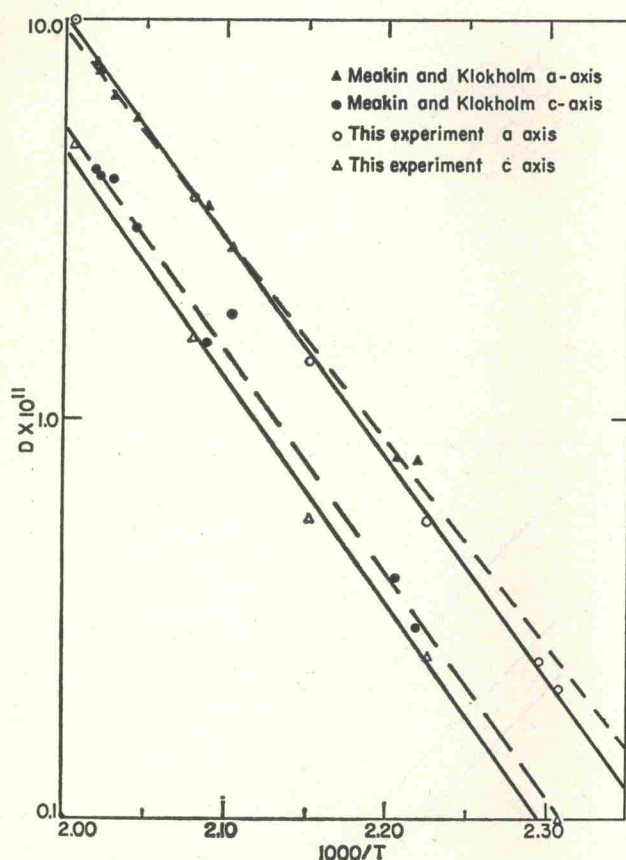


Figure 6. Comparison of a - and c -axis diffusion coefficients with data of Meakin and Klokholm.

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. ΔH and D_0 values derived from each study are given in Table VI.

Table VI: Comparison of Zero Pressure Results

	Meakin and Klokholm		This study	
	a axis	c axis	a axis	c axis
D_0 , cm. ² /sec.	1.4 ± 0.5	8.2 ± 0.6	10.7 ± 1	7.7 ± 3
ΔH , kcal./mole	23.3 ± 0.5	25.6 ± 0.8	25.2 ± 1.0	25.6 ± 1.2

The differences in ΔH and D_0 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 ΔH , 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.² 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.⁷ 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 quench-resistance studies of vacancies in gold. From the rate of annealing under pressure of quenched-in resistivity, Emrick²⁰ 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 Homan²¹ 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

(20) R. M. Emrick, *Phys. Rev.*, **122**, 1720 (1961).

(21) R. P. Heubener and C. G. Homan, *ibid.*, **129**, 1162 (1963).

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

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

$$\frac{D_c}{D_a} = \frac{\gamma_c' c^2 \nu_c' e^{+\Delta S_c'/R} e^{-\Delta H_c'/RT}}{\gamma_a a^2 \nu_a e^{+\Delta S_a/R} e^{-\Delta H_a/RT}} \quad (10)$$

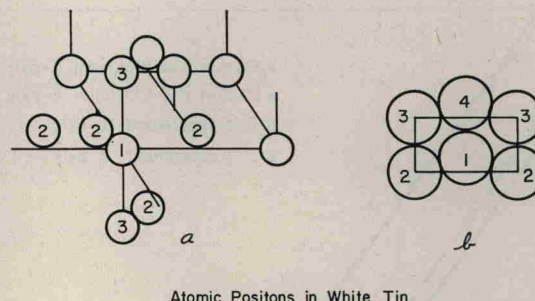
where all terms have their usual meaning. If only "a" jumps are assumed then $\Delta H_a = \Delta H_c'$, $\Delta S_a = \Delta S_c'$, and $\nu_a = \nu_c'$, and (10) becomes

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

The component of an "a" jump in the a -axis direction is one-half the length of an 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 γ -values.²² Since $D_a/D_c = 2.20$, we have

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

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 two-thirds of the observed rate must be assigned to "c"-type jumps, so that c -axis diffusion is a combination of both elementary jumps.



Atomic Positions in White Tin

Figure 7. Atomic positions in tin.

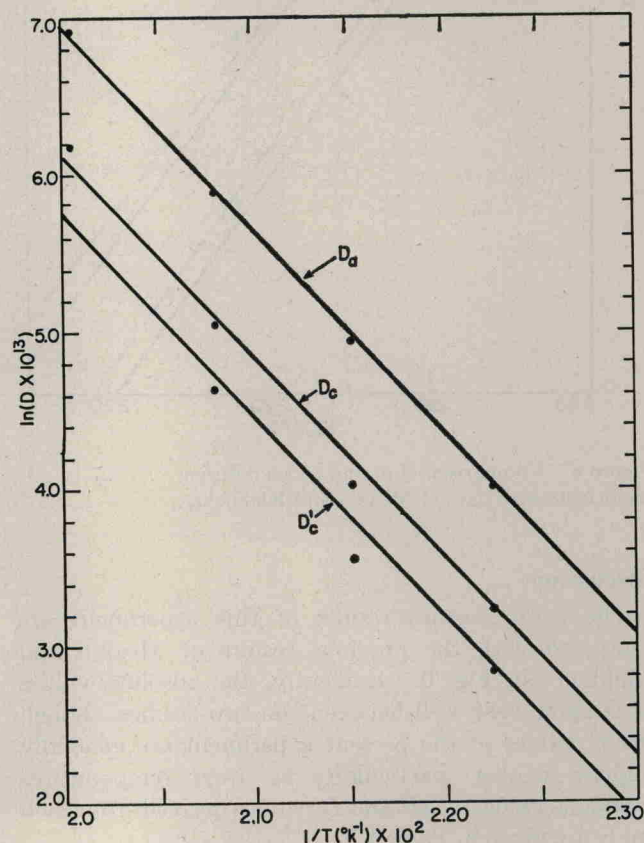


Figure 8. Contributions of a - and c -type jumps.

Similar to Meakin and Klokholm,¹⁰ 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 $D_0' = 4.64 \text{ cm}^2/\text{sec}$. and $\Delta H_c' = 25.6 \text{ kcal}$., essentially unchanged in

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