

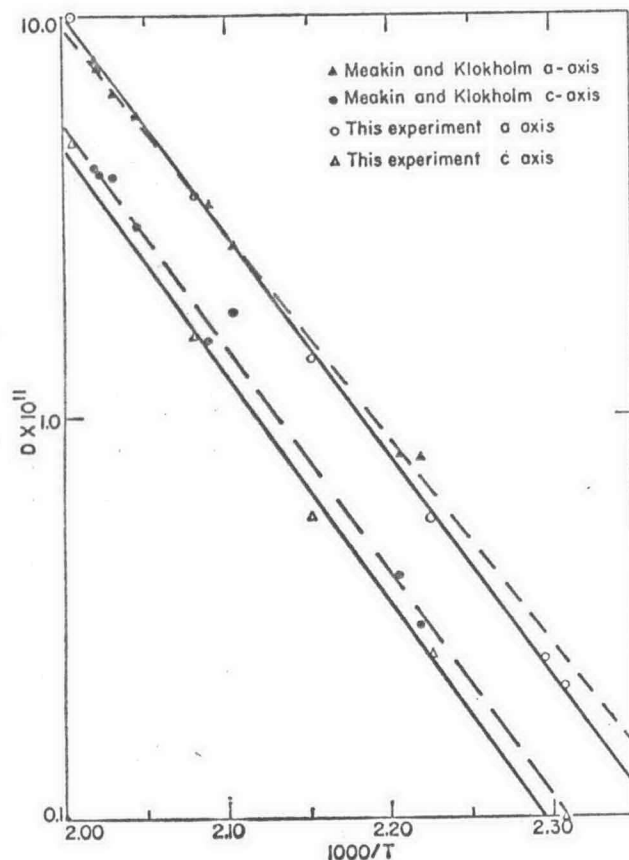


Figure 6. Comparison of *a*- and *c*-axis diffusion coefficients with data of Meakin and Klokholm.

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—	
	<i>a</i> axis	<i>c</i> axis	<i>a</i> axis	<i>c</i> 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).