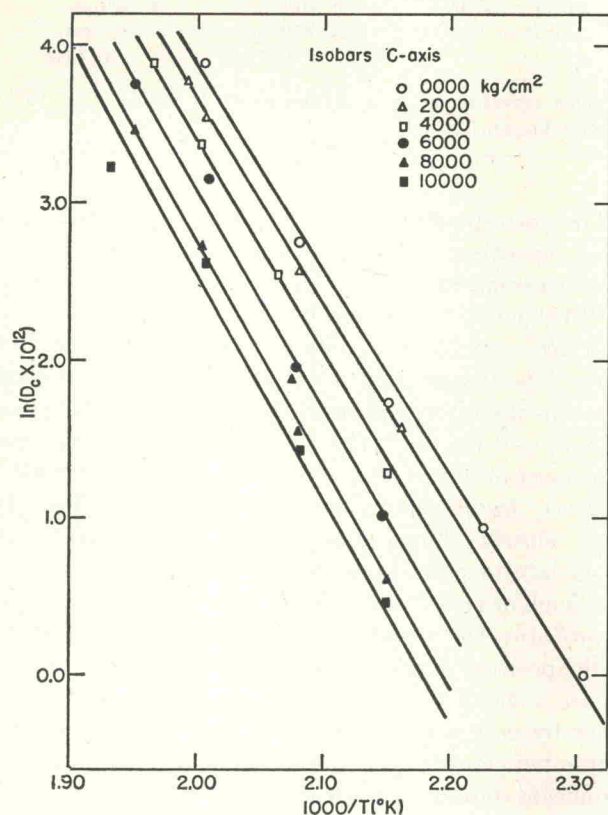


Table IV: Activation Volumes

$T, ^\circ\text{C.}$ $\Delta V, \text{cm.}^3$	a axis			c axis		
	225.6	208.8	192.0	225.6	208.8	192.0
	4.96 ± 0.38	5.20 ± 0.25	5.91 ± 0.50	5.31 ± 0.38	5.23 ± 0.30	5.36 ± 0.30

Figure 3. c -Axis diffusion isobars.

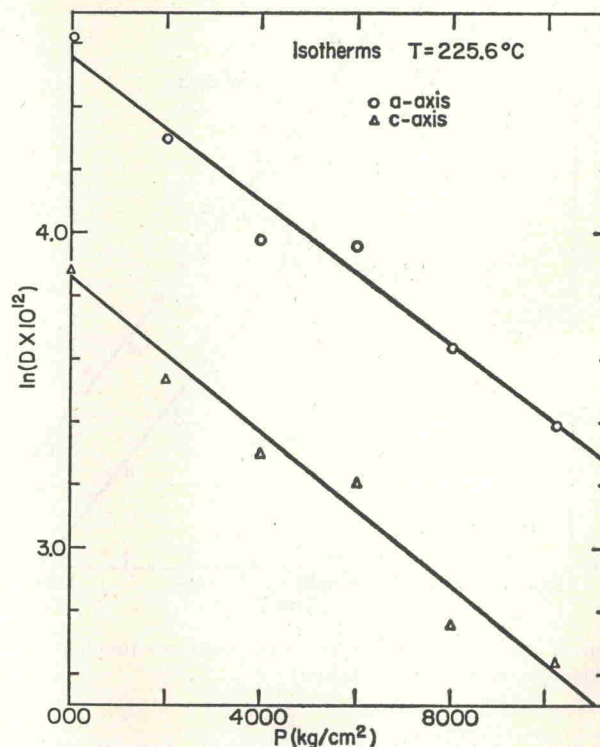
tion energies for diffusion in intrinsically different directions plays an important role in the discussion of possible diffusion mechanisms in tin.

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 225.6° is shown in Fig. 4. Activation volumes derived from these isotherms *via* the usual formula²

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

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

As for ΔH values, the activation volumes are essentially equal for both a - and c -diffusion directions. The apparent variation in a -axis ΔV values may or may not

Figure 4. Diffusion isotherms (225.6°) for a and c axes.

be real since it is just outside the limits of experimental error. For the purposes of this discussion, ΔV can be considered constant, equal to 5.3 cm.³/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.⁵ The most accurate determination of the melting curve to 10 kbars has been made by Babb.¹⁷ From his results, T_m/T was found for each value of D . Figure 5 is a plot of $\ln D$ against T_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).

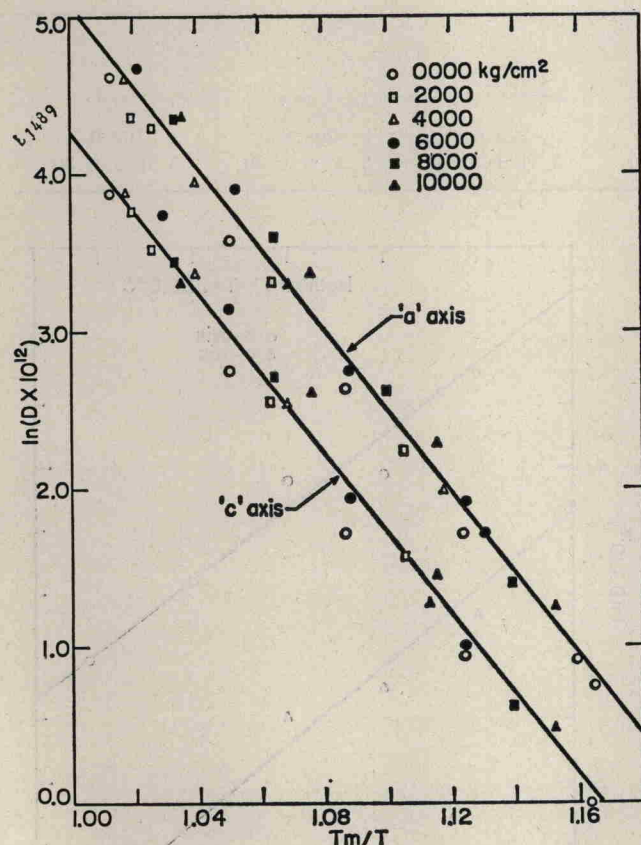


Figure 5. *a*- and *c*-axis diffusion coefficients as a function of reciprocal reduced temperature.

several quantities derived from the data in Fig. 5. Since T_m is a function of pressure, eq. 2 may be written

$$\left(\frac{\partial \ln(D/\gamma a^2 \nu)}{\partial T_m/T} \right)_{T_m} = \frac{1}{T_m} \left(\frac{\partial \ln(D/\gamma a^2 \nu)}{\partial 1/T} \right)_P = -\frac{\Delta H}{RT_m} \quad (8)$$

or

$$\Delta H = -RT_m(\text{constant}) \quad (9)$$

Hence, if the corresponding states law holds, the activation enthalpy should vary linearly with T_m . Slopes of the T_m/T curves and representative values of ΔH at three pressures from eq. 9 are given in Table V. Comparison with similar ΔH 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 ΔH with pressure, taken from Table V, may be used in eq. 6 to calculate a mean activation volume of 6.1 cm.³, in satisfactory agreement with the value of 5.3 cm.³ derived more directly from the isotherms. Since the latter give ΔV more directly, the lower value is considered more reliable.

Table V: Quantities Derived from Corresponding States Test

Quantity	<i>a</i> axis	<i>c</i> axis
Slope	-25.686	-25.413
Standard deviation ^a	0.142	0.148
ΔH ($P = 0$) ^b	25,780 cal.	25,500 cal.
ΔH ($P = 5000$) ^b	26,570 cal.	26,290 cal.
ΔH ($P = 10,100$) ^b	27,350 cal.	27,060 cal.
ΔV	6.1 cm. ³	6.1 cm. ³

^a This corresponds to a difference in D values of ~15%.

^b P is in kg./cm.².

The corresponding states relation (3) may be tested using the values $\Delta H = 25.3$ kcal. and $\Delta V = 5.3$ cm.³ (derived from this study), $\Delta H_m = 1690$ cal.,¹⁸ and $\Delta V_m = 0.454$ cm.³.¹⁹ 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.⁷

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 ΔH 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.

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

(19) S. G. Kubaschewski, *Trans. Faraday Soc.*, **45**, 931 (1949).