Table I: Thermal Expansion[a] and Linear Compression Coefficients[b] for Tin

α_c, deg.$^{-1}$	κ_c, atm.$^{-1}$	$\Delta\kappa_c$, deg.$^{-1}$ atm.$^{-1c}$	$\delta_c{}^{25}$, atm.$^{-2}$	$\Delta\delta_c$, deg.$^{-1}$ atm.$^{-2d}$
36.4×10^{-6}	6.693×10^{-7}	0.0053×10^{-7}	4.09×10^{-12}	-0.0037×10^{-12}
α_a, deg.$^{-1}$	κ_a, atm.$^{-1}$	$\Delta\kappa_a$, deg.$^{-1}$ atm.$^{-1c}$	$\delta_a{}^{25}$, atm.$^{-2}$	$\Delta\delta_a$, deg.$^{-1}$ atm.$^{-2d}$
16.7×10^{-6}	6.008×10^{-7}	0.0027×10^{-7}	4.19×10^{-12}	0.0013×10^{-12}

[a] S. Lee and W. Raynor, *Proc. Phys. Soc.*, **B67**, 739 (1954). [b] Ref. 14, p. 169; $\Delta l/l_0 = \kappa P - \delta P^2$. [c] $\Delta\kappa = d\kappa/dT$. [d] $\Delta\delta = d\delta/dT$.

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°, 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 μ thick were grouped in threes; each group was weighed to ±10 μg., 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.[15] The relative error in the diffusion coefficients is close to ±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. 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%.

Table II: Diffusion Data

P, kg./cm.^{2}	T, °C.	$D_a \times 10^{11}$, cm.^{2}/sec.	$D_c \times 10^{11}$, cm.^{2}/sec.	$\frac{D_a}{D_c}$
000	160.4	0.2113	...	...
000	162.6	0.249	...	...
000	160.8	...	0.0986	...
000	176.3	0.557	0.255	2.184
000	191.7	1.400	0.563	2.487
000	207.7	3.583	1.558	2.300
000	225.8	10.09	4.82	2.093
2158	189.6	0.918	0.471	1.949
1640	207.9	2.893	1.360	2.127
1992	225.6	7.363	3.403	2.164
1932	228.8	7.892	4.378	1.803
4116	190.1	0.800	...	...
3988	192.0	...	0.360	...
3907	211.3	2.748	1.293	2.125
4007	225.1	5.124	2.876	1.782
3977	235.9	10.029	4.866	2.062
6089	190.0	0.5495	...	...
6035	192.6	0.679	0.272	2.496
6017	208.1	1.557	0.701	2.221
6104	224.6	4.883	2.300	2.123
6020	239.8	10.769	4.196	2.567
7999	191.9	0.400	0.1834	2.181
7909	207.8	...	0.471	...
7959	208.8	1.389	0.664	2.092
7970	224.8	3.642	1.507	2.417
8079	239.8	7.691	3.100	2.451
10090	192.0	0.3467	0.159	2.181
10120	207.6	0.9839	0.422	2.331
10105	225.3	2.910	1.368	2.127
10134	244.8	7.765	2.727	2.847

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

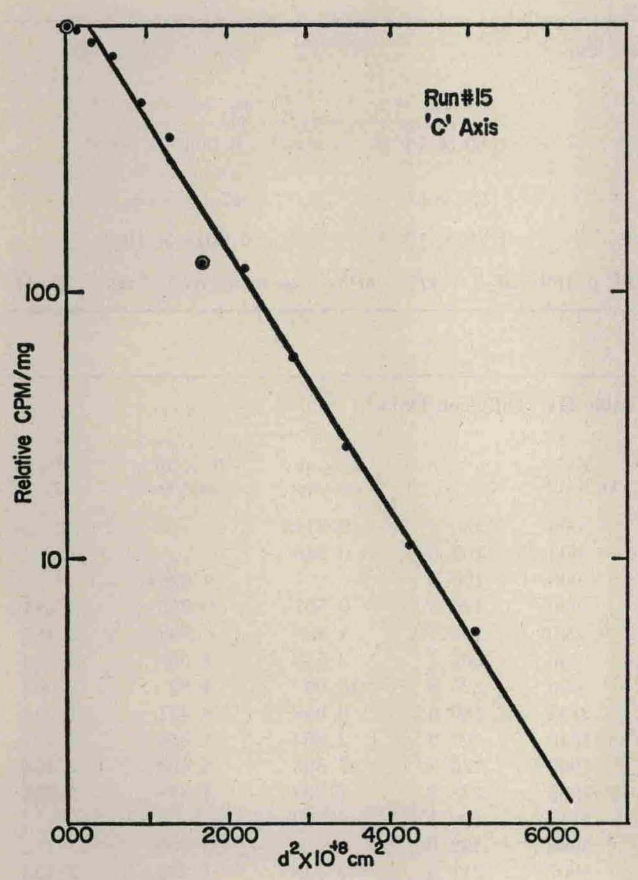

Figure 1. Typical *c*-axis penetration profile.

Table III: Activation Energies and D_0 Values

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

The trend toward higher ΔH 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 ΔS by Keyes[16] (neglecting the pressure variation of thermal expansion, α) we have

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

where γ is the Gruneisen constant. Combining (4) and (5)

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

Thus, a positive change in ΔH with pressure assures that ΔV is greater than zero. This is consistent with previous high pressure diffusion studies.[2]

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

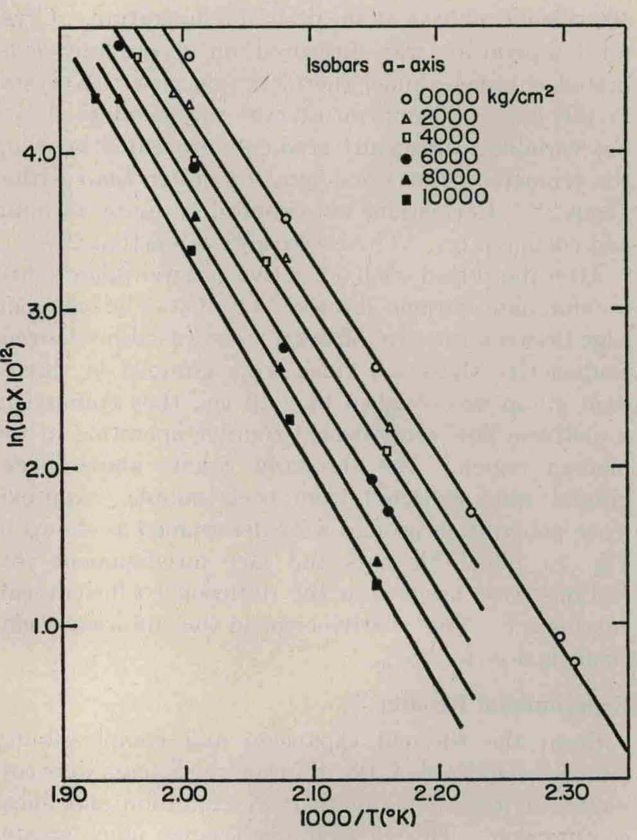

Figure 2. *a*-Axis diffusion isobars.

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[10] observed considerable diffusion anisotropy in their work on tin. This discrepancy is discussed more fully in a later section. The similarity of activa-

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[16] 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