Figure 1.   Typical c-axis penetration profile.

Table III: Activation Energies and D_0 Values

	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

(Pressure, kg./cm.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 $\Delta V = 12.0$ 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).
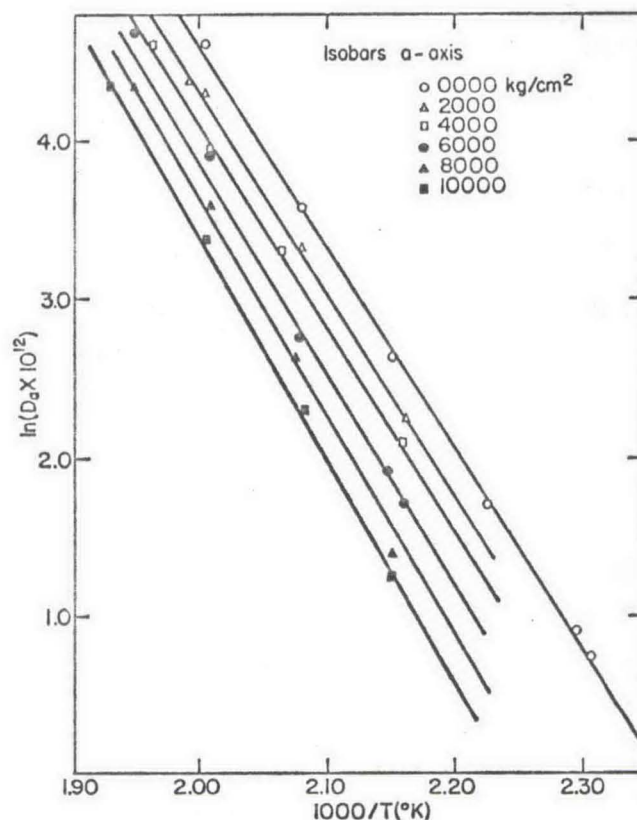
Figure 2.   a-Axis diffusion isobars.

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-

(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