$$\Delta S = R \ln (D_0/\gamma a^2 \nu) \qquad (15)$$

The choice of ν is difficult and has been related to a normal mode analysis of lattice vibrations by several authors.[4,12] In practice, the Debye frequency is used as the best available estimate. In this experiment the jump rates differing by a factor of 4 can only be the result of differences in ΔS and ν, and the uncertainty in ν is compounded further. Consider three cases: $\nu_a = \nu_c$ and the D_0 differences are reflected in ΔS; $\nu_a = 4\nu_c$, the jump rate difference being almost entirely due to ν differences; $\nu_a = 2\nu_c$, an intermediate case. These cases are presented in Table VII, with calculations based on $\nu_a = \nu_\theta$, where $\theta_D = 142°K$.[27] It is interesting that $\Delta S_a = \Delta S_c$ if $\nu_a = 2\nu_c$. The ΔS values do not agree well with Meakin and Klokholm, who apparently used a much different Debye temperature.

Table VII: Activation Entropies

Case	ΔS_a, e.u.	ΔS_c, e.u.	Relationships
1	16.6	17.8	$\nu_a = 4\nu_c$
2	16.6	15.1	$\nu_a = \nu_c$
3	16.6	16.4	$\nu_a = 2\nu_c$

Keyes[16] has used continuum theory to write

$$\Delta S = 2(\gamma - {}^1/_3)\alpha\Delta G \qquad (16)$$

where α and γ are the thermal expansion coefficient and the Grüneisen constant. To a first approximation, this study gives $\Delta G \simeq \Delta H = 25.3$ kcal. and $\Delta S = 5.2$ e.u. From this estimate $\Delta G = \Delta H - T\Delta S = 23.0$ kcal., and $\Delta S = 4.75$ e.u. This is much lower than the observed ΔS values and seems to cast doubt on the applicability of the theory.

Volume. It is interesting to note that DeVries, Baker, and Gibbs,[28] in a preliminary report, have found an activation volume for creep in tin of about 30% of the molar volume, in close agreement with the 33% observed in this study. Their results have not been fully published to date so further comment is difficult.

Keyes[16] has also developed the relation

$$\Delta V = 2\left(\gamma - \frac{1}{3}\right)\kappa\Delta G \qquad (17)$$

where κ is the compressibility. Using $\Delta G = 23.0$ kcal., we have $\Delta V = 5.1$ cm.^{3}, in excellent agreement with the observed 5.3 cm.^{3}. Hence, the strain energy approach gives quite good agreement for ΔV, though the predicted ΔS is not good.

We can get some indication as to why no anisotropy in ΔV was observed in this study from considering eq.

12a in the Appendix. The S_i are sums of elastic constants, the same for all k directions, so anisotropy comes only from the $M_i{}^k$ (the $\gamma RT s_{ij}\delta_{ik}$ term is small, so anisotropy from this source is negligible). But the $M_i{}^k$ are defined by eq. 8a in terms of a formation and a motion contribution, w_i and $m_i{}^k$; only the latter can be anisotropic. But we have seen that in gold this term is only 22% of the total activation volume, and in general $w_i \geqslant m_i{}^k$ is probably valid. Therefore, any anisotropy in $m_i{}^k$ for different k is largely masked by the isotropic w_i contribution.

Probably the largest contribution to anisotropy in ΔV_{mob} arises because the blocking atoms must assume a breathing mode before the diffusing atom may exchange with the vacancy. But the previous comments about vibration amplitudes in tin show that this effect will be small at best, since little or no "excess" volume is required. Hence, ΔV_a should be almost equal to ΔV_c.

From eq. 10a we can get some idea of the magnitude of the $M_i{}^k$. The tin elastic moduli were taken from Mason and Bommel.[29] For the a-axis isotherm at $225.6°$ we have

$$4.82 \text{ cm.}^3 = (M_1{}^1 + M_2{}^1)(10.3 \times 10^{-13}) +$$
$$M_3{}^1(7.8 \times 10^{-13}) \qquad (18)$$

so that an upper limit for $M_i{}^k$ is $\sim 5 \times 10^{12}$ ergs $= 10^3$ kcal. The work of Liu and Drickamer[30] on the effect of uniaxial compression on diffusion in zinc can be used in a consistent way[31] to evaluate some individual $M_i{}^k$ values. From the elastic data for zinc of Hearmon,[32] we find that $M_1{}^3 = 35 \times 10^3$ kcal. and $M_3{}^3 = 190 \times 10^3$ kcal. These values are up to two orders of magnitude greater than the upper bounds found for tin and also exceed similar upper limits determined from the hydrostatic pressure results for zinc by the same margins. Two possible explanations of this difficulty are: (1) the effect of pressure is not adequately accounted for by a sum over the individual stress components of the form of eq. 10a; (2) some gross difficulty exists in the experiments. Neither alternative is favored; indeed both may be partially correct.

(27) R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.*, **131**, 529 (1963).

(28) K. L. DeVries, G. S. Baker, and P. Gibbs, *Bull. Am. Phys. Soc.*, [II] **6**, 169 (1961).

(29) W. P. Mason and W. E. Bommel, *J. Acoust. Soc. Am.*, **28**, 930 (1956).

(30) T. Liu and H. G. Drickamer, *J. Chem. Phys.*, **22**, 312 (1954).

(31) See A. W. Lawson, *ibid.*, **22**, 1948 (1954). However, if the stress range is great enough, $\partial \ln D_k/\partial P_j$ may be evaluated using only uniaxial stress data. This avoids the inconsistency.

(32) R. F. S. Hearmon, *Rev. Mod. Phys.*, **18**, 409 (1946).