

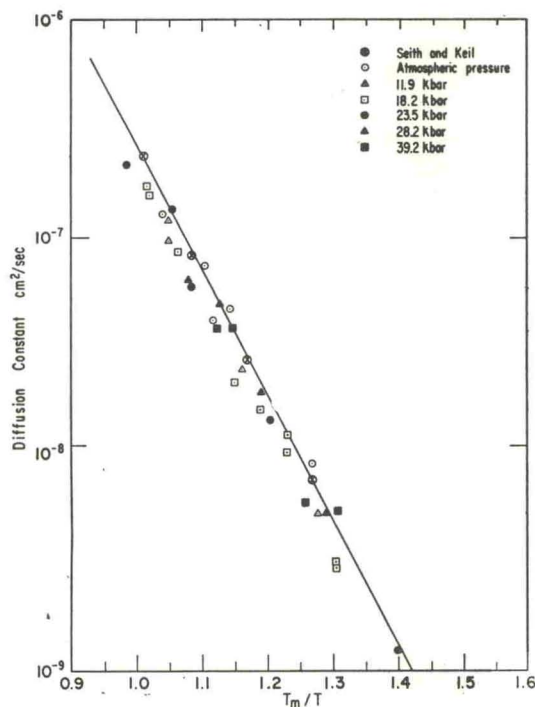


FIG. 4. The diffusion coefficient as a function of the ratio of the melting to the annealing temperature for all of the data.

However, the correction $(\gamma - \frac{2}{3})RTK_T$ to the activation volume, in Eq. (4), ranged from about 3 to 5% for temperatures between 556 and 769°K for all pressures between 0 and 40 kbar. The correction terms in Eqs. (4) and (5) were approximated using $\gamma = 3.0$, the coefficient of thermal expansion as tabulated in standard tables²⁰ for atmospheric pressure and 100°C, and Bridgman's²¹ isothermal-compressibility data extrapolated to the temperatures of interest.

The logarithm of the diffusion coefficient is plotted in Fig. 4 as a function of the ratio of the melting temperature at the annealing pressure to the annealing temperature. The values for the melting temperature of lead were obtained from work performed in this laboratory by Dudley and Millet,²² and subsequently pressure corrected for thermal expansion using the correction obtained by Decker and Vanfleet¹⁹ on their work with gold.

IV. DISCUSSION

The activation energies ΔH shown in Table I increase monotonically with pressure from 15.2 kcal/mole at atmospheric pressure to 21.9 kcal/mole at 39.2 kbar. This is in accord with the interpretation of ΔH being an energy of activation, it being expected that the

energy required to form a vacancy and/or move a defect from one equilibrium position to an adjacent one should increase with increasing pressure.

The activation volume ΔV as can be seen from the slopes of the curves of Fig. 3 is independent of the pressure for each temperature above 11.9 kbar. Below 11.9 kbar, however, it is evident that ΔV increases with decreasing pressure. This effect can be explained if one assumes that at some pressure both the vacancy and interstitial mechanism contribute significantly to the diffusion. The ratio of the diffusion constant D_v for vacancy diffusion to that for interstitial diffusion D_i is proportional to $\exp[-(\Delta G_v - \Delta G_i)/RT]$, where ΔG_v and ΔG_i are the free energies for diffusion by the vacancy and interstitial mechanism, respectively. If the activation volume for the vacancy mechanism ΔV_v is large in comparison to ΔV_i for an interstitial, it is evident that D_v/D_i will decrease rapidly with increasing pressure. A calculation has been made assuming that the linear portions of the $\ln D$ versus pressure curves of Fig. 3 are characteristic of interstitial diffusion. These curves were extrapolated to atmospheric pressure for each isotherm. The resulting values of D were taken to represent the interstitial contribution to the diffusion at atmospheric pressure for each temperature. By subtracting the interstitial contribution from Seith and Keil's¹⁵ data the vacancy contribution at atmospheric pressure is obtained. Analysis of these data gave atmospheric pressure activation energies of 15.4 and 15.7 kcal/mole for the interstitial and vacancy contributions to the diffusion. Good agreement with the isotherms of Fig. 3 was made by using Hudson and Hoffman's⁵ low-pressure activation volumes for ΔV_v and the high-pressure activation volume from this experiment for ΔV_i in conjunction with the atmospheric-pressure values of D_i and D_v as discussed above. Hence, if the diffusion mechanism changes with pressure, as it is seen that it may do, one would expect the observed decrease in the measured activation volume. However, since the proposed mechanism involves a diffusion constant with two terms with different temperature dependency some curvature in the $\ln D$ versus $1/T$ curves for pressures below about 10 kbar should be apparent. Data in this pressure range would do much to confirm or refute the proposed mechanism.

Hudson and Hoffman⁵ observed a decrease in the activation volume for self diffusion in lead at about 30 kbar which is probably similar to the effect at atmospheric pressure observed in this experiment.

It has been proposed by Braune²³ and Van Liempt²⁴ using Lindemann's theory of melting that

$$\Delta H(P)/T_m(P) = \Delta H(0)/T_m(0), \quad (6)$$

where $\Delta H(P)$ and $T_m(P)$ are the activation energy and melting temperature of the solvent at the pressure P .

²⁰ Landolt-Börnstein Tables, edited by H. Borchers and E. Schmidt (Springer-Verlag, Berlin, 1964), Vol. IV, Part 2a, p. 934.

²¹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), p. 161.

²² J. D. Dudley and L. E. Millet (private communication).

²³ H. Braune, *Z. Physik Chem.* **110**, 147 (1924).

²⁴ J. A. M. Van Liempt, *Rec. Trav. Chim.* **51**, 114 (1932).

