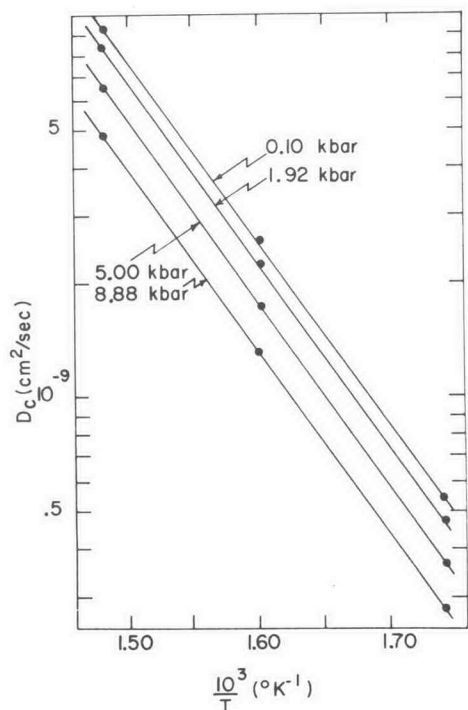
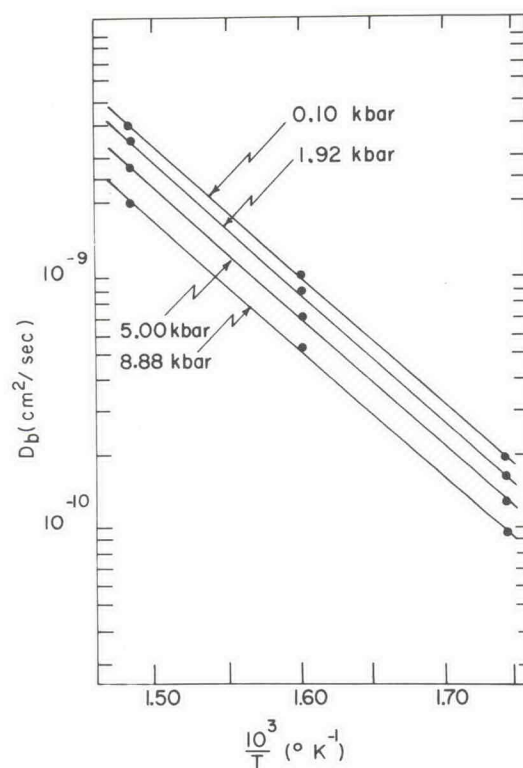


FIG. 3. Variation of activation volume with temperature.

brought to the same common pressure. The activation enthalpies ΔH_c and ΔH_b and the frequency factors D_{0c} and D_{0b} obtained by doing a linear least-squares fit to these plots are given in Table III, together with the zero-pressure values from previous work.¹⁰

The variation of ΔH_c and $\ln D_{0c}$ with pressure is shown in Fig. 6, and that of ΔH_b and $\ln D_{0b}$ with pressure is shown in Fig. 7. Within the experimental limits of error, ΔH_c and ΔH_b are independent of pressure. This can also be seen by considering the variation of activation volume ΔV with temperature T . According to Eq. (7), the intercept

FIG. 4. Arrhenius plots of $\ln D_c$ vs $1/T$ for self-diffusion in zinc at pressures of 0.10, 1.92, 5.00, and 8.88 kbar.FIG. 5. Arrhenius plots of $\ln D_b$ vs $1/T$ for self-diffusion in zinc at pressures of 0.10, 1.92, 5.00, and 8.88 kbar.

of the plot of ΔV vs T in Fig. 5 is simply $(\partial \Delta H / \partial p)_T$. The least-squares fit to the activation-volume data gives $(\partial \Delta H / \partial p)_T = -0.003 \pm 0.3 \text{ cm}^3/\text{mole}$, i. e., $(\partial \Delta H / \partial p)_T \approx 0$.

On the other hand, the frequency factors D_{0c} and D_{0b} decrease with pressure. The frequency factor D_0 is defined as $D_0 = f a_0^2 \nu e^{\Delta S/R}$, where f is the correlation factor, a_0 is the effective jump distance, ν is the barrier attack frequency (comparable to the Debye frequency), and ΔS is the activation entropy. Differentiating $\ln D_0$ with respect to pressure and realizing¹³ that the self-diffusion coefficients are determined by serial sectioning at room temperature and pressure, we then have

TABLE III. Activation enthalpies and frequency factors at various pressures.

p (kbar)	ΔH_c (kcal/mole)	ΔH_b (kcal/mole)	$\ln D_{0c}$	$\ln D_{0b}$
0.10	21.96 ± 0.08	23.47 ± 0.15	-2.06 ± 0.04	-1.77 ± 0.12
1.92	22.10 ± 0.10	23.70 ± 0.11	-2.08 ± 0.07	-1.72 ± 0.09
5.00	22.10 ± 0.08	23.50 ± 0.15	-2.31 ± 0.04	-2.09 ± 0.12
8.88	22.00 ± 0.10	23.44 ± 0.25	-2.68 ± 0.08	-2.47 ± 0.20
0.00 ^a	21.90 ± 0.15	23.48 ± 0.15	-2.04 ± 0.08	-1.68 ± 0.18

^aObtained from Ref. 10.

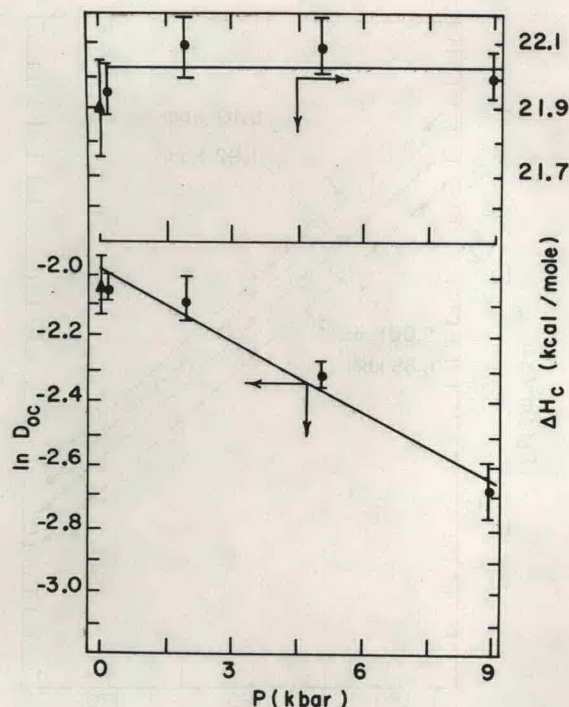


FIG. 6. Variation of ΔH_c and $\ln D_{0c}$ with pressure. The Δ 's are data from Ref. 10.

$$\left(\frac{\partial \ln D_0}{\partial p}\right)_T = \frac{\partial \ln \nu}{\partial p} + \frac{1}{R} \left(\frac{\partial \Delta S}{\partial p}\right)_T = \kappa\gamma + \frac{1}{R} \left(\frac{\partial \Delta S}{\partial p}\right)_T \quad (9)$$

$$\approx \frac{1}{R} \left(\frac{\partial \Delta S}{\partial p}\right)_T$$

Because $\partial \ln D_0 / \partial p$ can be determined to an accuracy of only about 10%, the " $\kappa\gamma$ " term which is approximately 3% of the second term, is neglected. Thus, by determining $(\partial \ln D_{0c} / \partial p)_T$ and $(\partial \ln D_{0b} / \partial p)_T$, one can obtain values for $(\partial \Delta S_c / \partial p)_T$ and $(\partial \Delta S_b / \partial p)_T$. A linear least-squares analysis of the data of Figs. 6 and 7 gives $(\partial \Delta S_c / \partial p)_T = -(6.0 \pm 0.6) \times 10^{-3} \text{ cm}^3 / \text{mole } ^\circ\text{K}$ and $(\partial \Delta S_b / \partial p)_T = -(6.90 \pm 1.0) \times 10^{-3} \text{ cm}^3 / \text{mole } ^\circ\text{K}$. Therefore, $(\partial \Delta S / \partial p)_T$ appears to be isotropic, to within our experimental uncertainty. An average value for $(\partial \Delta S / \partial p)_T$ is $-(6.5 \pm 0.8) \times 10^{-3} \text{ cm}^3 / \text{mole } ^\circ\text{K}$ and is in good agreement with the value $-(6.4 \pm 0.5) \times 10^{-3} \text{ cm}^3 / \text{mole } ^\circ\text{K}$ obtained for $-(\partial \Delta V / \partial T)_p$ from the data of Fig. 3.

V. DISCUSSION AND INTERPRETATION OF DATA

A. Comparison of Data for α_v with Gilder-Chhabildas Model Calculation

According to the model calculation of Gilder and Chhabildas,⁸ well above the Debye temperature, the thermal coefficient of expansion of an activated vacancy, α_v , is given by the following expression:

$$\alpha_v \approx (Rr_0 / 3\Delta V) (2\kappa_a + \kappa_c) \alpha^3 \delta_1^2$$

$$\times [545 + (36 \sqrt{2} \alpha \delta_1) (\delta_2 / \delta_1) + 270 (\delta_2 / \delta_1)^2 - (30 / \alpha \delta_1)] \quad (10)$$

where r_0 is the equilibrium separation of an isolated pair of zinc ions, α^{-1} is a range parameter in a Morse-like potential, and δ_1 and δ_2 are the displacements (assumed to be purely radial) of the first and second nearest neighbors to the vacancy. Using reasonable^{8,28} values for α and r_0 , the presently measured value of $\Delta V \approx 4 \text{ cm}^3 / \text{mole}$, and a range for δ_2 / δ_1 from 0 to 0.5 and δ_1 from $5 \times 10^{-2} r_0$ to $10^{-1} r_0$, Eq. (10) places α_v in the range $0.5 \times 10^{-3} - 3 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$. In the present experiment (see Table IV), α_v varies from $1.7 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$ at 300.9°C to $1.5 \times 10^{-2} \text{ } ^\circ\text{K}^{-1}$ at 400.8°C . In view of the simplifying assumptions made in the calculation, the agreement between the measured values of α_v and those predicted by the theory is indeed satisfactory.

B. Variation of Activation Enthalpy with Pressure

The data of the present experiment indicate that both ΔH_c and ΔH_b are, to within the experimental uncertainty, independent of pressure. The value obtained for $(\partial \Delta H / \partial p)_T$ from the intercept of the ΔV -vs- T plot in Fig. 3 is $0.003 \pm 0.3 \text{ cm}^3 / \text{mole}$. More directly, ΔH_c and ΔH_b obtained from the slopes of the isobars in Figs. 4 and 5, when plotted against pressure, as shown in Figs. 6 and 7, show no variation with pressure to within the experimental uncertainty of about $\pm 0.2 \text{ kcal/mole}$. According to Eq. (8), this result is consistent with $\alpha_v = T^{-1}$, and hence $\Delta V = AT$.

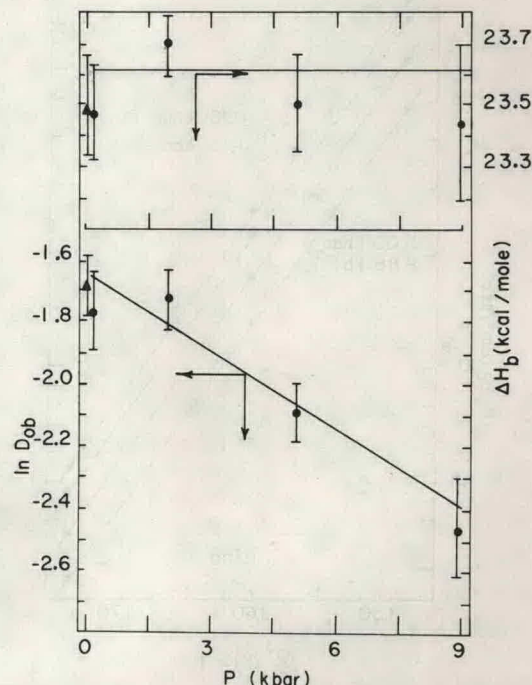


FIG. 7. Variation of ΔH_b and $\ln D_{0b}$ with pressure. The Δ 's are data from Ref. 10.