

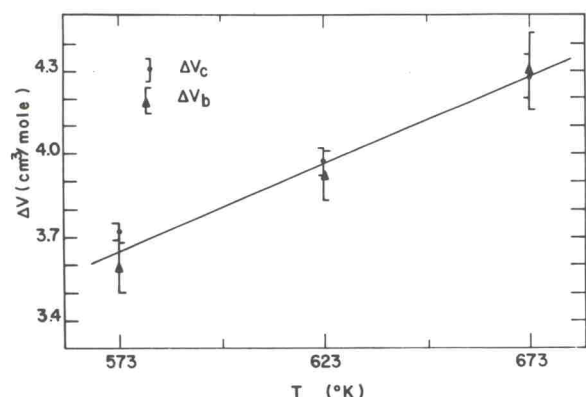
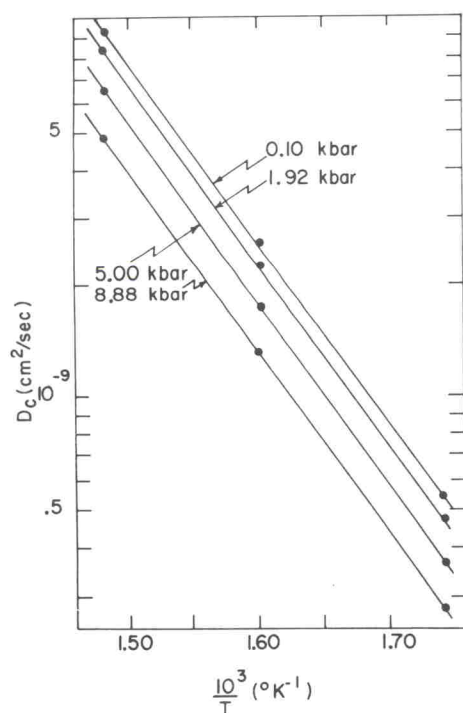
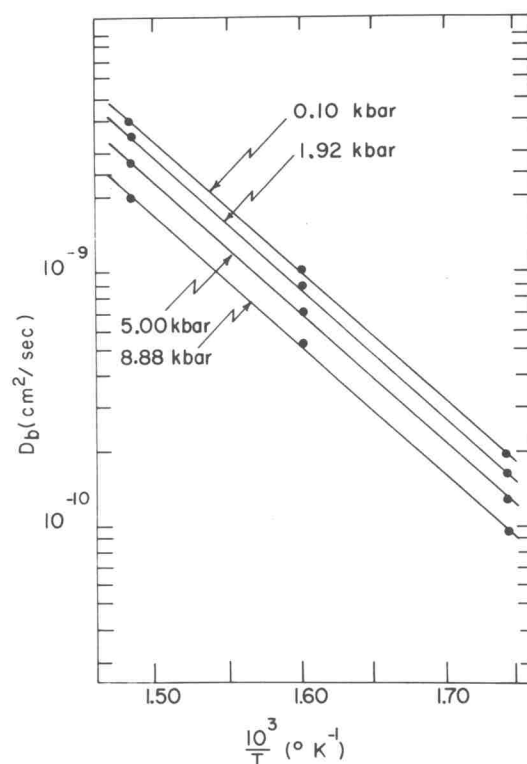


FIG. 3. Variation of activation volume with temperature.

brought to the same common pressure. The activation enthalpies  $\Delta H_c$  and  $\Delta H_b$  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.<sup>10</sup>

The variation of  $\Delta H_c$  and  $\ln D_{0c}$  with pressure is shown in Fig. 6, and that of  $\Delta H_b$  and  $\ln D_{0b}$  with pressure is shown in Fig. 7. Within the experimental limits of error,  $\Delta H_c$  and  $\Delta H_b$  are independent of pressure. This can also be seen by considering the variation of activation volume  $\Delta V$  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  $\Delta V$  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,  $\nu$  is the barrier attack frequency (comparable to the Debye frequency), and  $\Delta S$  is the activation entropy. Differentiating  $\ln D_0$  with respect to pressure and realizing<sup>13</sup> 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.

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

<sup>a</sup>Obtained from Ref. 10.

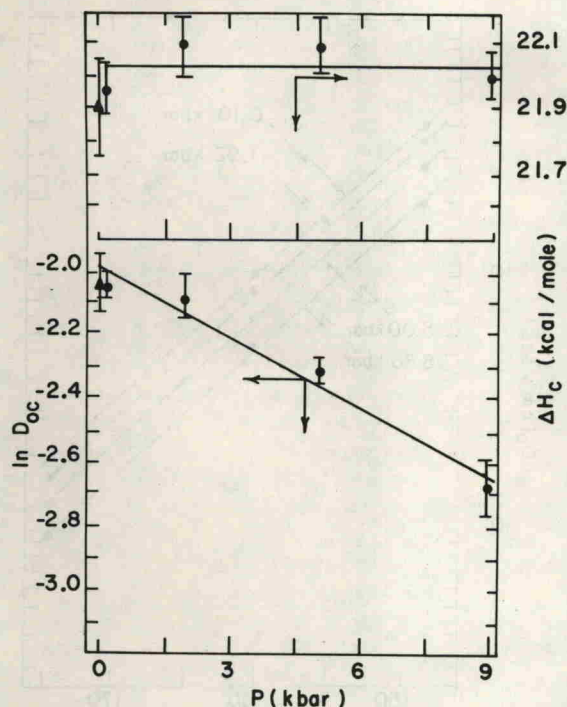


FIG. 6. Variation of  $\Delta H_c$  and  $\ln D_{0c}$  with pressure. The  $\Delta$ 's are data from Ref. 10.

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

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 $\alpha_v$ with Gilder-Chhabildas Model Calculation

According to the model calculation of Gilder and Chhabildas,<sup>8</sup> well above the Debye temperature, the thermal coefficient of expansion of an activated vacancy,  $\alpha_v$ , 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,  $\alpha^{-1}$  is a range parameter in a Morse-like potential, and  $\delta_1$  and  $\delta_2$  are the displacements (assumed to be purely radial) of the first and second nearest neighbors to the vacancy. Using reasonable<sup>8,28</sup> values for  $\alpha$  and  $r_0$ , the presently measured value of  $\Delta V \approx 4 \text{ cm}^3 / \text{mole}$ , and a range for  $\delta_2 / \delta_1$  from 0 to 0.5 and  $\delta_1$  from  $5 \times 10^{-2} r_0$  to  $10^{-1} r_0$ , Eq. (10) places  $\alpha_v$  in the range  $0.5 \times 10^{-3} - 3 \times 10^{-3} ^\circ\text{K}^{-1}$ . In the present experiment (see Table IV),  $\alpha_v$  varies from  $1.7 \times 10^{-3} ^\circ\text{K}^{-1}$  at  $300.9 ^\circ\text{C}$  to  $1.5 \times 10^{-2} ^\circ\text{K}^{-1}$  at  $400.8 ^\circ\text{C}$ . In view of the simplifying assumptions made in the calculation, the agreement between the measured values of  $\alpha_v$  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  $\Delta H_c$  and  $\Delta H_b$  are, to within the experimental uncertainty, independent of pressure. The value obtained for  $(\partial \Delta H / \partial p)_T$  from the intercept of the  $\Delta V$ -vs- $T$  plot in Fig. 3 is  $0.003 \pm 0.3 \text{ cm}^3 / \text{mole}$ . More directly,  $\Delta H_c$  and  $\Delta H_b$  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  $\Delta V = AT$ .

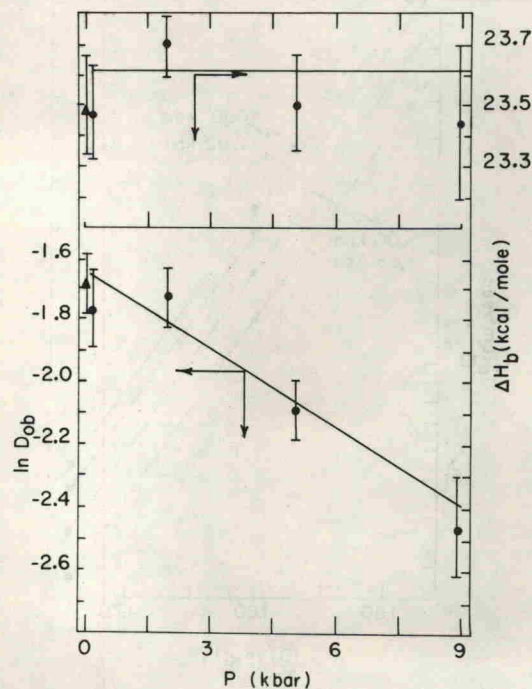


FIG. 7. Variation of  $\Delta H_b$  and  $\ln D_{0b}$  with pressure. The  $\Delta$ 's are data from Ref. 10.