proximately similar results have been obtained by Davidson and Brotzen[15] with a different type of calculation. The values of central and noncentral force constants for a pure molybdenum crystal in the force-constant model are 6.005×10^4 g sec^{-2} and -0.418×10^4 g sec^{-2}, respectively. These changes are somewhat higher than those obtained by Davidson and Brotzen. The present situation may be improved if one starts with a more extended perturbation due to a point defect.

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Thermal Coefficient of Expansion of an Activated Vacancy in Zinc from High-Pressure Self-Diffusion Experiments*†

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The coefficient of self-diffusion along the principal axes in zinc was obtained over the temperature range 300–400 °C, and over the pressure range 0–9 kbar. The unusually high precision of 2% in the measurement of the vacancy activation volumes was achieved by means of a novel technique that insured temperature reproducibility in the diffusion zone of ± 0.2 °C at high pressure. The activation volumes for diffusion, associated with the basal and nonbasal vacancy mechanisms are found to be temperature dependent, isotropic, and approximately proportional to T. Hence the thermal coefficient of expansion of an activated vacancy is given by $\alpha_v = T^{-1}$, and is about 15 times larger than the thermal coefficient of expansion of the perfect lattice. The activation entropy is pressure dependent, whereas the activation enthalpy is pressure independent to within the experimental uncertainty.

I. INTRODUCTION

A vacancy in a crystalline lattice is characterized by a set of properties that relate to its formation and motion under conditions of thermodynamic equilibrium. Considered as an entity undergoing reversible thermodynamic processes in both its formation and motion, the vacancy's properties are obviously embodied in a knowledge of the temperature and pressure dependence of $\Delta G_f(T,p)$ and $\Delta G_m(T,p)$, the changes in the Gibbs free energy of the crystal associated with the formation and motion of the vacancy, respectively. Thus, the formation enthalpy ΔH_f and entropy ΔS_f are respectively given by $[\partial(\Delta G_f/T)/\partial(1/T)]_p$ and $-(\partial\Delta G_f/\partial T)_p$, whereas similar temperature derivatives of ΔG_m define the enthalpy and entropy of motion, ΔH_m and ΔS_m. On the other hand, the pressure derivatives $(\partial \Delta G_f/\partial p)_T$ and $(\partial \Delta G_m/\partial p)_T$ give the formation and motional volumes ΔV_f and ΔV_m.

The experiments are by no means trivial to determine precisely the total activation enthalpy $\Delta H(T, 0) = \Delta H_f(T, 0) + \Delta H_m(T, 0)$ from atmospheric radiotracer self-diffusion measurements,[1,2] the quantities $\Delta H_f(T, 0)$ and $\Delta S_f(T, 0)$ directly from combined x-ray and dilatometric measurements,[3,4] and the quantities $\Delta H_f(T, 0)$ and $\Delta H_m(T, 0)$ directly from quenching[5] and annealing kinetics[6] measurements. However, the precision measurement of the total activation volume $\Delta V(T, p) = \Delta V_f(T, p) + \Delta V_m(T, p)$ from self-diffusion measurements at high pressure, and that of $\Delta V_f(T, p)$ and $\Delta V_m(T, p)$ separately from quenching and annealing kinetics measurements under pressure, are indeed formidable owing primarily to the difficulty in making reproducible temperature measurements at pressures up to 10 kbar. Also, various approximations and assumptions regarding the interpretation[7] of quenching data introduce additional uncertainties into the quantities $\Delta V_f(T, p)$ and $\Delta V_m(T, p)$, in marked contrast to the interpretation of self-diffusion data. Thus, one of the most common properties of a thermodynamic system, the coefficient of thermal expansion, has never been measured for a vacancy, prior to the recently reported precision self-diffusion activation-volume measurements in zinc.[8]

The purpose of this paper is to present additional data on activation-volume measurements in zinc to allow a more precise determination of the thermal coefficient of expansion of an activated vacancy, $\alpha_v = (1/\Delta V)\,(\partial \Delta V/\partial T)_p$, and to further test the theory of Gilder and Chhabildas.[8] In addition, the data are used to determine the effect of temperature and pressure on the activation enthalpy for diffusion, as well as to explore the possible anisotropy in the activation volumes associated with the vacancy jumps in the nonideal hcp zinc lattice.

II. THEORY

Self-diffusion and isotope-effect measurements on zinc[9–11] have indicated that basal and nonbasal vacancy mechanisms are responsible for self-diffusion. Accordingly, the activation volume ΔV_c associated with the nonbasal jump and the activation volume ΔV_b associated with the basal jump are given by[12,13]

$$\Delta V_c = \Delta V_f + \Delta V_m^c = -RT\left(\frac{\partial \ln D_c}{\partial p}\right)_T + RT\,\kappa_c\gamma_c \qquad (1)$$

and

$$\Delta V_b = \Delta V_f + \Delta V_m^b = -RT\left(\frac{\partial \ln(D_a - gD_c)}{\partial p}\right)_T + RT\,\kappa_a\gamma_a, \qquad (2)$$

where R is the gas constant, T the absolute temperature, g a geometrical factor, and the ΔV_m's, D's, κ's, and γ's are the motional volumes, diffusion coefficients, isothermal linear compressibilities, and Grüneisen constants, respectively, associated with the a- and c-axis directions.

The expressions for the activation enthalpies ΔH_c and ΔH_b associated with the nonbasal and basal vacancy mechanisms are[12]

$$\Delta H_c = -R\left(\frac{\partial \ln D_c}{\partial(1/T)}\right)_p \qquad (3)$$

and

$$\Delta H_b = -R\left(\frac{\partial \ln(D_a - gD_c)}{\partial(1/T)}\right)_p . \qquad (4)$$

From thermodynamics we have

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_T = \left(\frac{\partial(\Delta H - T\Delta S)}{\partial p}\right)_T$$

$$= \left(\frac{\partial \Delta H}{\partial p}\right)_T - T\left(\frac{\partial \Delta S}{\partial p}\right)_T . \qquad (5)$$

But, according to one of Maxwell's thermodynamic equations,

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = -\left(\frac{\partial \Delta V}{\partial T}\right)_p . \qquad (6)$$

Therefore, we have

$$\Delta V = \left(\frac{\partial \Delta H}{\partial p}\right)_T + T\left(\frac{\partial \Delta V}{\partial T}\right)_p . \qquad (7)$$

Hence $(\partial \Delta H/\partial p)_T$ and $(\partial \Delta V/\partial T)_p$ are, respectively, obtained as the intercept and the slope of the plot of ΔV vs T. Equation (7) may be written as

$$\left(\frac{\partial \Delta H}{\partial p}\right)_T = \Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_p$$

$$= \Delta V\left[1 - T\frac{1}{\Delta V}\left(\frac{\partial \Delta V}{\partial T}\right)_p\right]$$

$$= \Delta V(1 - \alpha_v T). \qquad (8)$$

Equation (8) is an exact relation, and does not involve the assumption[14–20] that $\alpha_v = \alpha_0$, where α_0 is the coefficient of thermal expansion for the perfect lattice.

III. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Single-crystal rods of zinc about 6 in. long and 1 cm in dia. were grown by the Bridgman method, from 99.999%-pure zinc obtained from Cominco American Inc. After the rods were cut into 1-cm-length disks on an acid string saw, one end of each sample was polished on successively finer grades of emery paper. The surface was etched between each polishing step, to minimize the cold work in the surface. An optically flat, mirrorlike surface was finally achieved by polishing on a silk cloth impregnated with fine alumina powder.

The samples were then annealed at 380 °C in vacuum for at least five days, to remove any lattice strains that might have resulted from polishing. Those samples that showed any signs of recrystallization were rejected immediately. Furthermore, a back-reflection x-ray photograph of each specimen was taken to determine the extent of residual lattice strain as well as crystallographic orientation. Only those samples that were strain free and had their principal axes to within 15° of the cylindrical axis were used for diffusion anneals.

The flat end of each specimen was then electroplated with Zn^{65} from a standard cyanide solution.[21] The thickness of the radioactive layer was estimated to be of the order of 100 atomic layers.

B. Procedure

As D_b depends on a weighted difference of D_a and D_c, the principal-axis diffusion coefficients were obtained in pairs by annealing a- and c-axis single-crystal specimens simultaneously. The weighted difference is then less subject to errors arising from uncertainties in the temperature and pressure than would be the case if D_a and D_c were obtained separately.

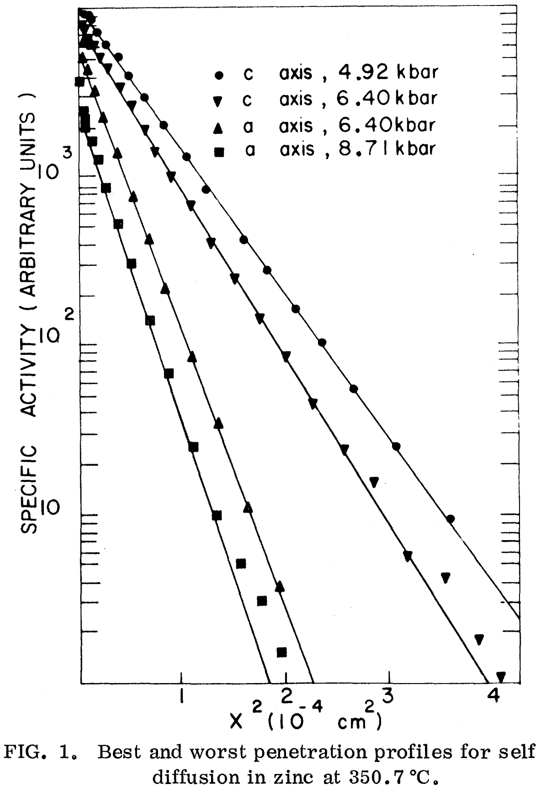

FIG. 1. Best and worst penetration profiles for self-diffusion in zinc at 350.7 °C.

The a- and c-axis samples were wrapped in a molybdenum[22] foil with their active faces separated by a thin molybdenum disk. They were placed in a pressure vessel which was subsequently pressurized and then submerged in a well-stirred molten-tin bath whose temperature could be controlled and reproduced to ± 0.2 °C. A detailed description of the apparatus, including the pressure vessel and the molten-tin bath, is given elsewhere.[23]

For a particular isotherm, the diffusion anneals were run for the same duration, as it was found that the warm-up time was independent of the pressure. Thus, warmup corrections, although affecting the absolute value of the diffusion coefficients by only a few percent, have no effect on the quantity $(\partial \ln D/\partial p)_T$ and hence on the activation volume ΔV.

After the specimens were run for a time appropriate to obtain a penetration depth of ~50 μ, the self-diffusion coefficients were obtained by the usual radiotracer lathe-sectioning techniques.[24]

IV. EXPERIMENTAL RESULTS

A. Penetration Profiles

Typical penetration profiles for self-diffusion in zinc at 350.7 °C are shown in Fig. 1. It is quite evident that they are Gaussian over at least $2\frac{1}{2}$ orders of magnitude in tracer specific activity. However, some of these penetration profiles do exhibit a tail, indicative of short circuiting at deep penetration distances. In such cases, the bulk diffusion coefficient was determined by considering only the linear segment of the penetration profile, ignoring the tail. The principal-axis self-diffusion coefficients $D_c(T, P)$ and $D_a(T, P)$ are listed in Table I.

B. Isotherms

The variation of $\ln D_c$, $\ln D_a$, and $\ln D_b$ with pressure at temperatures of 400.8, 350.7, and 300.9 °C are shown in Fig. 2. These isotherms are obviously linear over a pressure range of 0 to 9 kbar. The zero-pressure data of Peterson and Rothman[10] and Batra[11] are in excellent agreement with the present data, while those of Shirn *et al.*[9] do not agree nearly as well. More significantly, the zero-pressure data of the present experiment taken in the same way as those of the high-pressure runs, are obviously consistent with the rest of the present data.

Least-squares-fit lines were used to obtain the slopes of these isotherms and hence the activation volumes ΔV_c and ΔV_b in accordance with Eqs. (1) and (2). The $\kappa_c \gamma_c$ term in Eq. (1) is of the order of 3% of the first term and cannot be ignored, as

TABLE I. Self-diffusion coefficients for zinc.

p (kbar)	T (°C)	D_c (10^{-9} cm^2/sec)	D_a (10^{-9} cm^2/sec)
0.131	400.8	9.449	5.846
1.938	400.8	8.381	5.174
3.495	400.8	7.300	...[a]
3.895	400.8	7.133	4.503
5.107	400.8	...[a]	4.135
6.863	400.8	5.812	3.586
7.028	400.8	5.792	3.574
8.910	400.8	4.872	2.963
0.133	350.7	2.550	1.505
1.380	350.7	2.286	1.360
1.860	350.7	2.200	...[b]
3.380	350.7	1.968	1.146
4.920	350.7	1.750	...[b]
4.990	350.7	...[b]	1.047
6.400	350.7	1.580	0.933
8.710	350.7	1.345	0.789
0.100	300.9	0.5443	0.2953
0.913	300.9	0.5119	0.2746
1.916	300.9	0.4728	0.2542
5.093	300.9	0.3696	0.2032
6.564	300.9	0.3340	0.1779
8.349	300.9	0.2907	0.1579

[a] Samples recrystallized during run.
[b] Samples destroyed while sectioning.

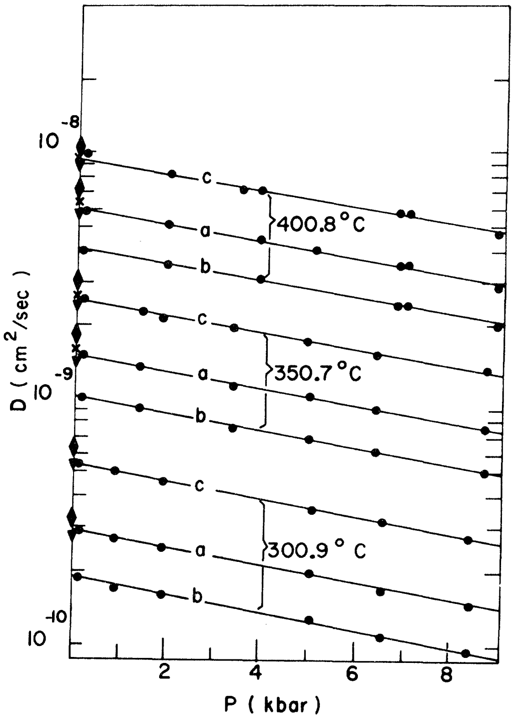

FIG. 2. Isotherms of $\ln D_c$, $\ln D_a$, $\ln D_b$ vs p for temperatures of 400.8, 350.7, and 300.9 °C. The ♦, ▼, and ×, are data from Refs. 9–11, respectively.

the activation volumes are measured to the unusually high precision of a few percent. On the other hand, in Eq. (2) the $\kappa_a\gamma_a$ term is only of the order of 0.3% of the first term, and therefore makes a negligible contribution. The values of the linear compressibilities and Grüneisen constants were obtained from the data of Alers and Neighbors[25] and Grüneisen and Goens,[26] respectively. The activation volumes $\Delta V_c(T)$ and $\Delta V_b(T)$ are given in Table II.

C. Variation of Activation Volume with Temperature

The activation volumes ΔV_c and ΔV_b, listed in Table II, show a systematic linear decrease with decreasing temperature. This dependence is a result of the constancy of the terms $(\partial \ln D_c/\partial p)_T$ and $[\partial \ln(D_a - gD_c)/\partial p]_T$, which then become proportionality factors between ΔV and T in Eqs. (1) and (2).

Also, as can be seen from Table II, the slopes of the isotherms and hence the basal and nonbasal activation volumes at a particular temperature are equal to within the experimental uncertainty. Thus in Fig. 3, both ΔV_b and ΔV_c have the same variation with temperature. A linear least-squares fit to the six data points of ΔV vs T gives

$$\left(\frac{\partial \Delta V}{\partial T}\right)_p = (6.4 \pm 0.5)\times 10^{-3} \text{ cm}^3/\text{mole}\,°\text{K}.$$

D. Variation of Activation Enthalpy and Entropy with Pressure

Arrhenius plots of $\ln D_c$ vs $1/T$ and $\ln D_b$ vs $1/T$ at pressures of 0.10, 1.92, 5.00, and 8.88 kbar are given in Figs. 4 and 5, respectively. By choosing these pressures, the chosen experimentally measured diffusion coefficients for a particular isobar were corrected by no more than 2% in being

TABLE II. Isotherm slopes and activation volumes in zinc.

T (°C)	$-\left(\frac{\partial \ln D_c}{\partial p}\right)_T$ (kbar)$^{-1}$	$-\left(\frac{\partial \ln (D_a - gD_c)}{\partial p}\right)_T$ (kbar)$^{-1}$	ΔV_c (cm^3/mole)	ΔV_b (cm^3/mole)
400.8	0.074 029 ± 0.0015	0.076 718 ± 0.0024	4.28 ± 0.08	4.30 ± 0.14
350.7	0.073 953 ± 0.0010	0.074 666 ± 0.0015	3.97 ± 0.05	3.92 ± 0.09
300.9	0.076 061 ± 0.0006	0.075 345 ± 0.0017	3.72 ± 0.03	3.59 ± 0.09

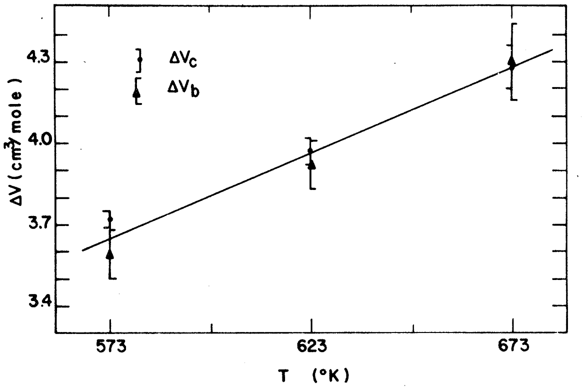

FIG. 3. Variation of activation volume with temperature.

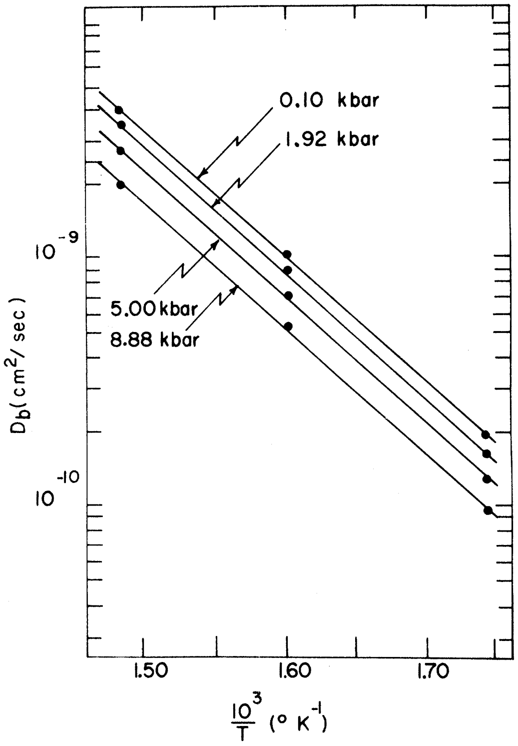

FIG. 5. Arrhenius plots of $\ln D_b$ vs $1/T$ for self-diffusion in zinc at pressures of 0.10, 1.92, 5.00, and 8.88 kbar.

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 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 $(\partial \Delta H/\partial p)_T = -0.003 \pm 0.3$ cm³/mole, i.e., $(\partial \Delta H/\partial p)_T \simeq 0$.

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 realizing[13] that the self-diffusion coefficients are determined by serial sectioning at room temperature and pressure, we then have

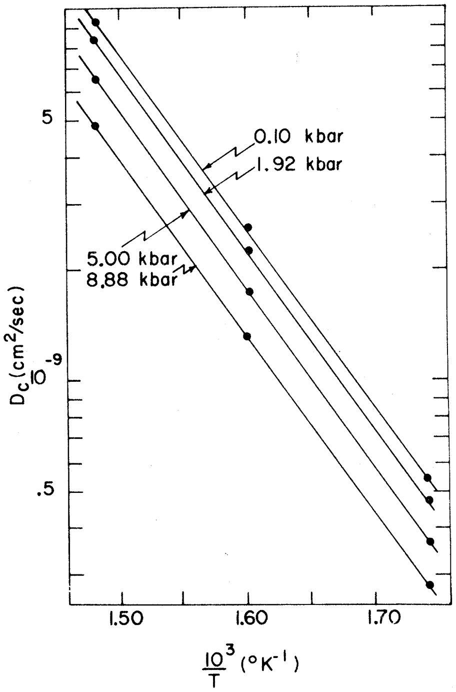

FIG. 4. Arrhenius plots of $\ln D_c$ vs $1/T$, for self-diffusion in zinc at pressures of 0.10, 1.92, 5.00, and 8.88 kbar.

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

[a] Obtained from Ref. 10.

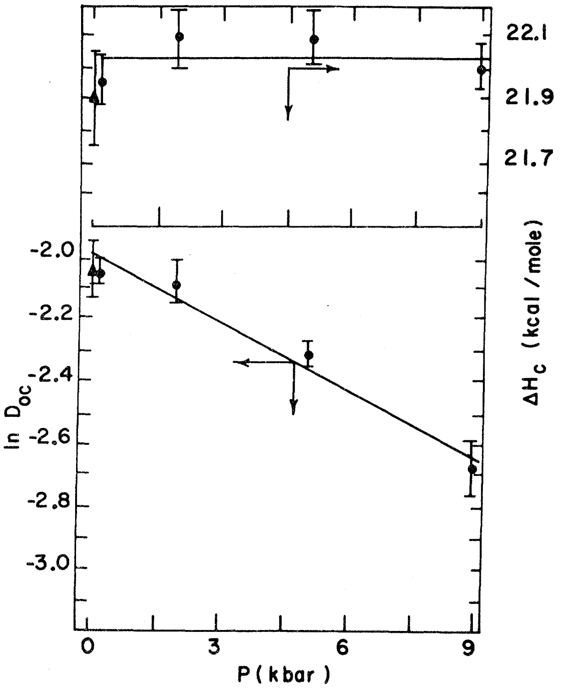

FIG. 6. Variation of ΔH_c and $\ln D_{0c}$ with pressure. The ▲'s are data from Ref. 10.

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

$$\simeq \frac{1}{R}\left(\frac{\partial \Delta S}{\partial p}\right)_T . \qquad (9)$$

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 $(\partial \Delta S_c/\partial p)_T = -(6.0 \pm 0.6)\times 10^{-3}$ cm^3/mole °K and $(\partial \Delta S_b/\partial p)_T = -(6.90\times 1.0)\times 10^{-3}$ cm^3/mole °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 $-(6.5 \pm 0.8)\times 10^{-3}$ cm^3/mole °K and is in good agreement with the value $-(6.4 \pm 0.5)\times 10^{-3}$ cm^3/mole °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 Chhabiluas,[8] well above the Debye temperature, the thermal coefficient of expansion of an activated vacancy, α_v, is given by the following expression:

$$\alpha_v \simeq (Rr_0/3\Delta V)(2\kappa_a + \kappa_c)\,\alpha^3\delta_1^2 \times[545 + (36\sqrt{2}\,\alpha\delta_1)(\delta_2/\delta_1) + 270(\delta_2/\delta_1)^2 - (30/\alpha\delta_1)] , \qquad (10)$$

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 $\Delta V \simeq 4$ cm^3/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 0.5×10^{-3}–3×10^{-3} °K^{-1}. In the present experiment (see Table IV), α_v varies from 1.7×10^{-3} °K^{-1} at 300.9 °C to 1.5×10^{-2} °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 ± 0.3 cm^3/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 ±0.2 kcal/mole. According to Eq. (8), this result is consistent with $\alpha_v = T^{-1}$, and hence $\Delta V = AT$.

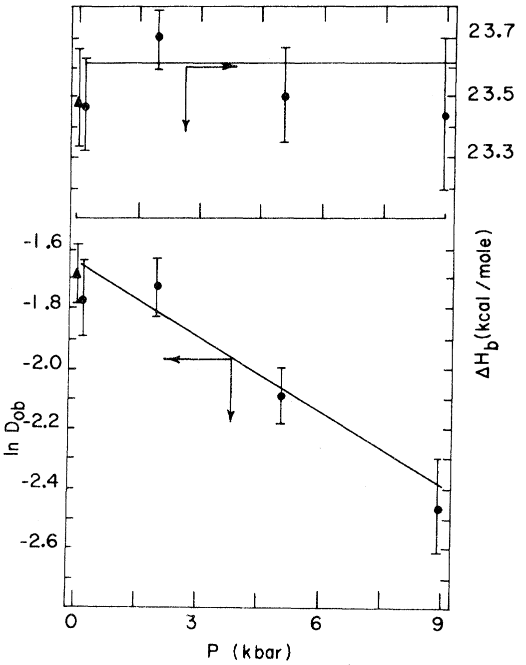

FIG. 7. Variation of ΔH_b and $\ln D_{0b}$ with pressure. The ▲'s are data from Ref. 10.

TABLE IV. Comparison of α_v to α_0.

T (°C)	$\alpha_v = \frac{1}{\Delta V}\frac{\partial \Delta V}{\partial T}$ (10^{-4}/°K)	α_0[a] (10^{-4}/°K)	α_v/α_0
400.8	14.92 ± 1.6	1.02 ± 0.06	14.6 ± 0.2
350.7	16.20 ± 1.6	1.04 ± 0.06	15.6 ± 0.3
300.9	17.49 ± 1.7	1.04 ± 0.06	16.8 ± 0.5

[a] Obtained from Ref. 27.

Prior to the present measurements, it was assumed[14–20] that $\alpha_v = \alpha_0$, i.e., that $\alpha_v = (1/\Delta V) \times (\partial \Delta V/\partial T)_p = \alpha_0 = (1/V_0)(\partial V_0/\partial T)_p$, where V_0 is the volume of the perfect lattice. Hence, Eq. (8) has been incorrectly written as

$$\left(\frac{\partial \Delta H}{\partial p}\right)_T = \Delta V(1 - \alpha_0 T) . \tag{11}$$

Since for most metals,[29] $10^{-2} < \alpha_0 T < 10^{-1}$, $\alpha_0 T \ll 1$, and Eq. (11) has predicted $(\partial \Delta H/\partial p)_T \simeq \Delta V$. Of course, Eq. (11) is obviously incorrect in view of the present data for zinc, and those for cadmium[30] as well. Thus, the "physically intuitive" view that the diffusive jump becomes more difficult to make as the pressure is increased owing to an increase in the activation enthalpy with pressure through the addition of a "$p\Delta V$" term is incorrect, at least for the cases of self-diffusion in zinc and cadmium. In fact, in those experiments[20,31–34] where a variation of enthalpy with pressure is indicated, the experimental uncertainty in $\Delta H(p)$ is nevertheless large enough to be also consistent with $(\partial \Delta H/\partial p)_T \simeq 0$. The crucial requirement is that the change in Gibbs free energy, ΔG, increase with pressure. This occurs through $(\partial \Delta S/\partial p)_T < 0$, as seen in Figs. 6 and 7, even though $(\partial \Delta H/\partial p)_T \simeq 0$.

C. Variation of Activation Enthalpy with Temperature

Nowick and Dienes,[15] Levinson and Nabarro,[14] and Girifalco[16] have all attempted to estimate the maximum possible variation of activation enthalpy with temperature for a vacancy jump, and hence the extent of the inherent curvature of an Arrhenius plot for the case of self-diffusion by means of a monovacancy mechanism. Their analyses all involve the assumption that $\alpha_v/\alpha_0 = 1$. This results in $(\partial \Delta H/\partial T)_p = \Delta c_p \le \frac{1}{2}R$, where Δc_p is the difference in specific heat (at constant pressure) between a lattice containing a vacancy in the activated state and one containing no vacancy. Instead, if one uses $\alpha_v/\alpha_0 \simeq 16$, as is indicated by the data for zinc and cadmium, the previous analyses then yield $(\partial \Delta H/\partial T)_p \le 8R$.

This corrected value of $(\partial \Delta H/\partial T)_p$ is consistent with the value of $(\partial \Delta H/\partial T)_p$ calculated by Gilder and Chhabildas.[8] According to their model calculation

$$\left(\frac{\partial \Delta S}{\partial T}\right)_p = \frac{\alpha_0}{\kappa}\left(\frac{\partial \Delta V}{\partial T}\right)_p . \tag{12}$$

Consequently,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \frac{\alpha_0}{\kappa}\left(\frac{\partial \Delta V}{\partial T}\right)_p T . \tag{13}$$

Equations (12) and (13) are integrated to obtain

$$\Delta S(T) - \Delta S(T_0) = \frac{\alpha_0}{\kappa}\left(\frac{\partial \Delta V}{\partial T}\right)_p (T - T_0) \tag{14}$$

and

$$\Delta H(T) - \Delta H(T_0) = \frac{\alpha_0}{2\kappa}\left(\frac{\partial \Delta V}{\partial T}\right)_p (T^2 - T_0^2) , \tag{15}$$

where T_0 is some reference temperature above the Debye temperature. As the right-hand side of Eq. (12) varies by no more than 10% over a wide temperature range, it was assumed to be constant for the integrations. With $\alpha_0 = 10^{-4}$ °K^{-1},[27] $\kappa = 18 \times 10^{-13}$ cm^2/dyn,[26] and our experimentally measured value of $(\partial \Delta V/\partial T)_p = 6.4 \times 10^{-3}$ cm^3/mole °K, the change in ΔH, as calculated from Eq. (15), is 0.8 kcal/mole over the temperature range 250–400 °C. The change in ΔS, according to Eq. (14), is about 1.3 cal/mole °K. Atmospheric self-diffusion data for zinc,[10] however, show no change in ΔH to within the experimental uncertainty of 0.2 kcal/mole, and no change in ΔS to within the experimental uncertainty of 0.3 cal/mole °K. The apparent discrepancy between the atmospheric data and the changes in ΔH and ΔS predicted from Eq. (14) and (15) can be explained in the following way. Writing diffusion coefficient $D(T)$ as

$$D(T) = f a_0^2 \, \nu \, e^{\Delta S(T)/R} \, e^{-\Delta H(T)/RT} , \tag{16}$$

and using Eqs. (14) and (15) in Eq. (16), we obtain

$$D(T) = f a_0^2 \nu \exp\left(\frac{\Delta S(T_0)}{R} + \frac{2\rho(T - T_0)}{R}\right) \times \exp\left(\frac{-\Delta H(T_0)}{RT} - \frac{\rho(T^2 - T_0^2)}{RT}\right) , \tag{17}$$

where $\rho = (\alpha_0/2\kappa)(\partial \Delta V/\partial T)_p = 4.23 \times 10^{-3}$ cal/mole °K^2. Equation (17) can be rearranged into the form

$$D(T) = D^I(T) e^{\rho(T - T_0)^2/RT} , \tag{18}$$

where

$$D^I(T) = f a_0^2 \nu \, e^{\Delta S(T_0)/R} \, e^{-\Delta H(T_0)/RT} . \tag{19}$$

$D^I(T)$ is nothing more than the usual expression for a diffusion coefficient in which the activation entropy and enthalpy are independent of the temperature. As $\rho(T - T_0)^2/RT \ll 1$ over the range 250–400 °C, Eq. (19) can be cast in the form

$$D(T) \simeq D^I(T)\,[1+\rho(T-T_0)^2/RT] \ . \qquad (20)$$

The "curved" function $D(T)$ and the "straight" function $D^I(T)$ obviously coincide at $T=T_0$. Thus, taking $T_0 = 598$ °K (the center of the Arrhenius plot temperature range) and $T = 673$ °K, $\rho(T-T_0)^2/RT = 2\times10^{-2}$, i.e., Eq. (20) gives a difference between $D(T)$ and $D^I(T)$ at the upper end of the Arrhenius plot of only about 2%. A comparable difference is found at the lower end as well. As the self-diffusion coefficients themselves are measured to a precision of about 2%, it is therefore not surprising that there is no apparent curvature in the atmospheric self-diffusion data, even though the activation enthalpy is estimated to change by about 5% over the range of measurements. Thus, as the temperature is increased, the temperature dependent term in ΔH increases to effect a decrease in D, while that of ΔS increases to effect an increase in D. These two competing effects very nearly compensate each other, thereby making it extremely difficult to detect curvature in the Arrhenius plot.

D. Activation Volumes and Anisotropy

As can be seen by referring to Table II, to within the precision of the measurements, the basal and nonbasal activation volumes ΔV_b and ΔV_c are equal. Since the total activation volume is the sum of the vacancy formation volume ΔV_f and vacancy migration volume ΔV_m, any difference between ΔV_c and ΔV_b would be due to a difference between ΔV_m^b and ΔV_m^c, as

$$\Delta V_c = \Delta V_f + \Delta V_m^c \ , \qquad \Delta V_b = \Delta V_f + \Delta V_m^b \ .$$

Since we might expect that $\Delta V_f \simeq 4\Delta V_m$,[17,20,35,36] it is perhaps not too surprising that we have not detected a difference between ΔV_c and ΔV_b. Accordingly, if we assume that the migration volume for zinc is about 20% of the total volume, as is the case for gold,[17,35] then the present data would indicate a maximum possible difference of about 20% between ΔV_m^c and ΔV_m^b.

E. Activation Volumes and Semiempirical Models

1. *Activation Volumes and Continuum Models*

A number of semiempirical models have been proposed to estimate ΔV. Keyes[37] obtained the relation

$$\Delta V = 4\kappa \Delta H \ ,$$

which relates the compressibility κ and the activation enthalpy ΔH to the activation volume ΔV. Using 18×10^{-13} cm^2/dyn for κ and an average value of 22.5 kcal/mole for ΔH, one obtains 6.8 cm^3/mole for ΔV. Based upon a strain energy model, Keyes[38] obtained the relation

$$\Delta V = 2(\gamma - \tfrac{1}{3})\kappa \Delta G \ .$$

Using 22.5 kcal/mole for ΔH, $3R$ for ΔS, and $T = 623$ °K, one obtains $\Delta G = 19.0$ kcal/mole from the relation $\Delta G = \Delta H - T\Delta S$. With this value for ΔG and an average value of 1.86 for γ, this relation estimates 4.4 cm^3/mole for ΔV. Keyes,[38] Lawson *et al.*[39] and Zener[40] independently obtained the relation

$$\Delta V = (\kappa/\alpha_0)\,\Delta S \ .$$

Taking $\alpha_0 = 100\times10^{-6}$ °K^{-1}, this relation gives $\Delta V = 4.5$ cm^3/mole.

Considering that these models are approximate, the agreement or even the lack of it, should neither be surprising nor taken very seriously. More often, these relations are useful in providing rough guides to the magnitude of ΔV.

2. *Activation Volumes and Isotope Effect*

Barr and Mundy[41] first observed that for several metals $\Delta K = \Delta V/V_M$, where V_M is the molar volume. The parameter ΔK obtained from isotope effect measurements is defined as the fraction of the total translational kinetic energy, possessed by the diffusing atom, associated with the decomposition of the saddle-point configuration. Although the relation agrees very well for most of the metals, in the case of zinc the agreement is rather poor. ΔK for zinc is 0.88–0.93,[10,11] whereas $\Delta V/V_M$ is 0.42.

According to LeClaire,[42] for a vacancy mechanism the total kinetic energy associated with the decomposition of the saddle-point configuration is shared between the diffusing atom and the neighboring host atoms. Thus, during the vacancy-tracer exchange, the neighboring atoms continuously rearrange themselves. After the exchange is completed, they take up new relaxed positions around the site vacated by the diffusing atom. If ΔK is large, then the fraction of energy associated with the rearrangement of the neighboring atoms would be small. In other words, it could be argued that the relaxation around a vacancy would be small, thereby indicating a large activation volume. Based on this argument, LeClaire[42] derived the approximate relation

$$\Delta K = (1+\tfrac{1}{3}n|\,1-\Delta V_f/V_M)^{-1} \ ,$$

where n is approximately the number of atoms that relax during the decomposition of the saddle-point configuration. Using 0.9 for ΔK and 0.4 for $\Delta V_f/V_M$, we get the unrealistic value of $n = 0.5$. Besides, in view of the presently measured temperature dependence of ΔV, the functional form of Barr and Mundy's relation, and also that of LeClaire's relation, would make ΔK temperature dependent by about 15 to 20% over the temperature range 300–400 °C. For zinc, even though ΔV is temperature dependent, $\Delta K^{10,11}$ is found to be temperature independent. Hence it seems that the correlation between ΔV_f and ΔK for zinc as given in the above functional forms is not valid. Both ΔK and ΔV are admittedly quantities that describe the interaction between the diffusing defect and its neighboring atoms. However, the exact form of the relation connecting these two quantities is still not well known. On the other hand, it does not rule out the possibility that a relation between ΔK and ΔV for a monovacancy mechanism could in principle make ΔK temperature dependent, in view of the presently measured temperature dependence of ΔV. The trend and magnitude of this temperature dependence would of course depend on the form of the functional relation between ΔK and ΔV.

3. *Activation Volumes and Nachtrieb's "Law of Corresponding States"*

Nachtrieb, based on the assumption that the diffusion coefficient is a function only of the melting temperature $T_m(p)$, derived the relation[32]

$$\Delta V = \frac{\Delta H}{T_m^0}\,\frac{dT_m}{dp}\ ,$$

where $T_m(p)$ is the melting temperature of the metal at pressure p. $T_m(p)$ can be approximated by a linear equation of the form

$$T_m(p) = T_m^0 + \frac{dT_m}{dp}\,p\ .$$

T_m^0 is the melting point of the metal at zero pressure. For most metals, dT_m/dp is a constant, over the range 0–10 kbar. Taking $\Delta H = 22.5$ kcal/mole, $T_m^0 = 693$ °K, and $dT_m/dp = b = 4.2$ °C/kbar,[43] this relation gives $\Delta V = 5.7$ cm^3/mole, whereas we presently measure $\Delta V \simeq 4$ cm^3/mole. Nachtrieb theorized that a plot of $\ln D$ vs $T_m(p)/T$ should be a straight line. This is equivalent to assuming that the diffusion coefficient is a function of the melting temperature $T_m(p)$ only. Therefore, according to Nachtrieb,

$$\left(\frac{\partial \ln D}{\partial (T_m/T)}\right)_T = \left(\frac{\partial \ln D}{\partial (T_m/T)}\right)_p = \left(\frac{\partial \ln D}{\partial (T_m/T)}\right)_{p=0}\ .$$

Thus,

$$\Delta V/Rb = \Delta H(p)/R(T_m^0 + bp) = \Delta H(0)/RT_m^0\ . \qquad (21)$$

To obtain a straight line, Eq. (21) has to be valid. Equation (21) would indeed be valid if ΔV were temperature independent. However, in this investigation we obtain $(\partial \Delta V/\partial T)_p \neq 0$. Thus, the condition for Nachtrieb's law of corresponding states to hold is not fulfilled for zinc. It is therefore not surprising that when a trial plot of $\ln D$ vs T_m/T was attempted a series of straight-line segments of different slopes with discontinuous jumps resulted. In a later paper,[34] Nachtrieb mentions that Eq. (21) is only approximate and will be in error to the extent that the entropy of activation is strongly pressure dependent. This is equivalent to saying that it is in error to the extent that the activation volumes are temperature dependent.

F. Discussion of Experimental Precision

According to Eq. (1), ΔV is experimentally determined by measuring the slope of an isotherm of $\ln D$ vs p. Since D has an exponential dependence on the temperature T, the quantity $(\partial \ln D/\partial p)_T$ can only be measured to a precision of approximately 1% by reproducing, under high pressure, diffusion-zone temperature, and hence the temperature of points constituting a particular isotherm, to within 0.2 °C. This corresponds to a relative error in D for points on the same isotherm of about 0.5%. Since the "$\kappa\gamma$" term is only about 3–4% of ΔV, an uncertainty of 10% in its calculated value introduces an uncertainty of only a few tenths of a percent in ΔV. Similarly, the "RT" factor can easily be determined to within a fraction of a percent by simply knowing the absolute temperature T to about a degree. Additional random errors encountered in lathe sectioning, weighing, and counting of the radiotracer activity contribute a total uncertainty to D of about another 0.5%. A random error of about 0.5% in the measurement of pressure due to hysteresis effects in the manganin resistence coil of the pressure cell, when added to the aforementioned errors, gives a cumulative uncertainty in ΔV of about 1.5%. This is in agreement with the uncertainty of 2% obtained from the least-squares estimate of the slopes of the isotherms.

Previous measurements of Norton and Tomizuka,[44] of activation volumes in zinc at 410 °C, give $\Delta V_c = 4.7 \pm 0.7$ cm^3/mole and $\Delta V_a = 4.3 \pm 0.2$ cm^3/mole. These values are in good agreement with the results of the present experiment.

VI. SUMMARY

The results of the present experiment can be summarized as follows: (i) The activation volumes are temperature dependent and are of the form $\Delta V = AT$. Hence, the thermal coefficient of expansion of an activated vacancy in zinc is given by $\alpha_v = 1/T$, and is approximately equal to $15\alpha_0$. (ii) The activation entropy is pressure dependent, and to within the experimental uncertainty, one of the Maxwell's thermodynamic equations; namely,

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = -\left(\frac{\partial \Delta V}{\partial T}\right)_p ,$$

is well obeyed for a diffusing defect. (iii) The activation enthalpy ΔH, to within the experimental uncertainty, is found to be pressure independent, i.e., $(\partial \Delta H/\partial p)_T \simeq 0$.

The results that are found in this investigation and for those in cadmium,[30] are significantly different from those in previous experiments. Obviously, much more refined measurements have to be made for other metals to establish the generality of the above results.

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