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 $\Delta V = 5.7\ \text{cm}^3/\text{mole}$, whereas we presently measure $\Delta V \simeq 4\ \text{cm}^3/\text{mole}$. 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 $\Delta V_c = 4.7 \pm 0.7\ \text{cm}^3/\text{mole}$ and $\Delta V_a = 4.3 \pm 0.2\ \text{cm}^3/\text{mole}$. 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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