

# Effect of Large Vacancy Thermal Expansion on the Pressure Variation of Activation Enthalpy in Pure Metals\*

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The pressure derivative of the activation enthalpy for diffusion,  $(\partial\Delta H/\partial p)_T$ , is a function of the thermal coefficient of expansion  $\alpha_v$  of an activated vacancy, where  $\alpha_v = (1/\Delta V)(\partial\Delta V/\partial T)_p$  and  $\Delta V$  is the vacancy activation volume. Recent measurements of  $\alpha_v$  for zinc and cadmium indicate that  $\alpha_v \gg \alpha_0$ , where  $\alpha_0$  is the ideal lattice thermal-expansion coefficient. The magnitude and functional form of  $\alpha_v$  indicate a value of  $(\partial\Delta H/\partial p)_T \ll \Delta V$ , contrary to previous estimates of  $(\partial\Delta H/\partial p)_T \approx \Delta V$  based on  $\alpha_v = \alpha_0$ .

Prior to recent precision measurements of the temperature dependence of the activation volume in zinc<sup>1</sup> and cadmium,<sup>2</sup> hence the thermal-expansion coefficient of vacancies in these metals, it had been supposed<sup>3-5</sup> that a vacancy expands at the same rate as the undisturbed portion of the host lattice in which it is embedded. In fact, for zinc and cadmium,  $\alpha_v/\alpha_0 \sim 10$ , where  $\alpha_v$  is the thermal-expansion coefficient of the vacancy and  $\alpha_0$  is that of the undisturbed lattice of volume  $V_0$ . As will be shown below, the assumption that  $\alpha_v = \alpha_0$  inevitably precludes the possibility of the activation enthalpy for diffusion  $\Delta H$  being independent of pressure, and, in fact, leads to the generally held belief that  $(\partial\Delta H/\partial p)_T \approx \Delta V > 0$ , where  $\Delta V$  is the vacancy activation volume. It is the purpose of this communication to indicate the profound effect of both  $\alpha_v \gg \alpha_0$  and the functional form of  $\Delta V(T)$  on the value of  $(\partial\Delta H/\partial p)_T$ .

From thermodynamics we know that

$$\Delta G = \Delta H - T\Delta S, \quad (1)$$

$$\Delta V = \left(\frac{\partial\Delta G}{\partial p}\right)_T, \quad (2)$$

and

$$\left(\frac{\partial\Delta V}{\partial T}\right)_p = -\left(\frac{\partial\Delta S}{\partial p}\right)_T. \quad (3)$$

$\Delta G$  and  $\Delta S$  are the changes in Gibbs free energy and entropy, respectively, associated with the formation and motion of the diffusing defect. Differentiating Eq. (1) with respect to pressure  $p$  at constant temperature  $T$ , and making use of Eqs. (2) and (3), we obtain

$$\left(\frac{\partial\Delta H}{\partial p}\right)_T = \Delta V - T\left(\frac{\partial\Delta V}{\partial T}\right)_p. \quad (4)$$

At this point many authors<sup>6-9</sup> make use of the assumption that  $\alpha_v = \alpha_0$ , i.e., that

$$\alpha_v = (1/\Delta V)(\partial\Delta V/\partial T)_p = \alpha_0 = (1/V_0)(\partial V_0/\partial T)_p.$$

Hence, Eq. (4) takes the form

$$(\partial\Delta H/\partial p)_T = \Delta V(1 - \alpha_0 T). \quad (5)$$

Since for most metals<sup>10</sup>  $10^{-2} < \alpha_0 T < 10^{-1}$ ,  $\alpha_0 T \ll 1$ , and Eq. (5) would predict  $(\partial\Delta H/\partial p)_T \approx \Delta V$ . Of course Eq. (5) is

incorrect because  $\alpha_v \neq \alpha_0$ ; Eq. (5) should obviously be replaced by

$$\left(\frac{\partial\Delta H}{\partial p}\right)_T = \Delta V(1 - \alpha_v T). \quad (6)$$

It should be emphasized that Eq. (6) is an exact relation, whereas Eq. (5) is obviously not.

From the high-pressure self-diffusion data for zinc<sup>1</sup> and cadmium,<sup>2</sup> it is found that  $\Delta V = AT$ , where  $A$  is a constant for  $T$  well above the Debye temperature. Under these conditions  $\alpha_v = T^{-1}$ , and according to Eq. (6),  $(\partial\Delta H/\partial p)_T = 0$ . Indeed, the slopes of the isobars of  $\ln D$  vs  $1/T$  are equal, to within the experimental uncertainty of  $\pm 0.3$  kcal/mole, for zinc and cadmium. In those experiments<sup>9,11-14</sup> where a greater variation of enthalpy with pressure is indicated, the experimental uncertainty in  $\Delta H(p)$  is nevertheless large enough to also be consistent with  $(\partial\Delta H/\partial p)_T \approx 0$ .

As the temperature of the solid is lowered,  $(\partial\Delta S/\partial p)_T$  decreases, i.e., according to the third law of thermodynamics,  $(\partial\Delta S/\partial p)_T$  must vanish as  $T$  approaches 0°K. Hence, as the temperature of the solid is lowered well below the Debye temperature, the thermal-expansion coefficient of the vacancy is reduced to such an extent that the quantity  $\alpha_v T$  can indeed become small compared to unity. Thus, in the region where the activation volume  $\Delta V$  has saturated, the quantity  $(\partial\Delta H/\partial p)_T$  attains a maximum value of  $\Delta V(0)$ . Such a variation of  $\Delta H$  with  $p$  would indeed be extremely difficult to observe, in view of the low temperatures at which diffusion would have to be measured.

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