

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 α_v of an activated vacancy, where $\alpha_v = (1/\Delta V)(\partial \Delta V / \partial T)_p$ and ΔV is the vacancy activation volume. Recent measurements of α_v for zinc and cadmium indicate that $\alpha_v \gg \alpha_0$, where α_0 is the ideal lattice thermal-expansion coefficient. The magnitude and functional form of α_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 zinc¹ and cadmium,² hence the thermal-expansion coefficient of vacancies in these metals, it had been supposed³⁻⁵ 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 α_v is the thermal-expansion coefficient of the vacancy and α_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 ΔH 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 ΔV 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

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

ΔG and ΔS 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 authors⁶⁻⁹ 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 metals¹⁰ $10^{-2} < \alpha_0 T < 10^{-1}$, $\alpha_0 T \ll 1$, 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 zinc¹ and cadmium,² 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 ± 0.3 kcal/mole, for zinc and cadmium. In those experiments^{9,11-14} 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 ΔV has saturated, the quantity $(\partial \Delta H / \partial p)_T$ attains a maximum value of $\Delta V(0)$. Such a variation of ΔH 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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