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

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

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 $(\partial \Delta H/\partial T)_p = \Delta c_p \leq \frac{1}{2}R$, 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 $(\partial \Delta H/\partial T)_p \leq 8R$.

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

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

Consequently,

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

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

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

and

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

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

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

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

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

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

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

where

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

$D^I(T)$ 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 $T_0 = 598\ ^\circ\mathrm{K}$ (the center of the Arrhenius plot temperature range) and $T=673\ ^\circ\mathrm{K}$, $\rho(T-T_0)^2/RT = 2\times 10^{-2}$, 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 $T=623\ ^\circ\mathrm{K}$, 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 $\alpha_0 = 100\times 10^{-6}\ ^\circ\mathrm{K}^{-1}$, 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