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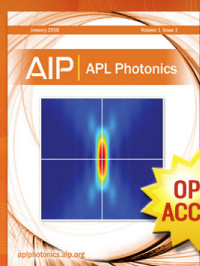
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Calculation of Activation Volumes for Self-Diffusion and Creep at High Temperature*

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It is shown that the activation volume for diffusion or steady-state creep at high temperature ($>0.5T_m$) can be estimated for all crystalline solids if the crystal structure, valence, entropy of melting, and volume change on melting are known. The calculated results agree well with the available experimental data for metals and compounds. Calculations performed for a number of crystalline materials show that the activation volume is a function of the crystal structure and that negative activation volumes are obtained for those materials that contract on melting. These results suggest that diffusion in the solid state occurs by a mechanism similar to the "relaxion" mechanism as originally proposed by Nachtrieb and Handler. In our proposed model the thermally activated process in diffusion involves the cooperative formation of a liquid-like cluster of atoms surrounding a vacant lattice site. Such a model predicts negative activation volumes and satisfactorily explains the influence of different crystal structures on the magnitude of the activation volume obtained.

INTRODUCTION

Numerous studies have been performed to determine activation volumes for creep and self-diffusion in a number of pure metals and compounds.¹⁻³³ A major objective of many of these studies was to relate the activation volume values with mechanisms for diffusion and creep. Results obtained to date indicate that the activation volume for creep above $0.5T_m$ (T_m is the absolute melting temperature) is about equal to the activation volume for lattice self-diffusion, giving additional evidence to the suggestion that the creep rate is controlled by a diffusion mechanism. These results are tabulated in Table I. A number of years ago several investigators³⁴⁻³⁶ calculated activation volumes from certain proposed relations. Experimental data, however, were available then for only a few elements. Accordingly, proper assessment of the relations proposed by these authors could not be made. The purpose of this paper is to show a very simple method of calculating activation volumes for creep and self-diffusion for any pure crystalline solid. Calculations will then be made to compare the predicted values with those obtained experimentally. Calculations will also be made for a number of other pure elements in order to determine if some pattern exists between the activation volumes and the characteristics of the material, and to draw attention to the need to interpret the meaning of negative activation volumes.

METHOD OF CALCULATION

Expressions for Activation Volumes

The activation volumes for diffusion and creep are generally calculated by the following expressions:

$$\Delta V_D = -RT(\partial \ln D / \partial P)|_T, \quad (1)$$

$$\Delta V_C = -RT(\partial \ln \dot{\epsilon} / \partial P)|_{\sigma, T}, \quad (2)$$

where R is the gas constant, T is the absolute temperature, P is the hydrostatic pressure, D is the lattice self-

diffusion coefficient, $\dot{\epsilon}$ is the steady-state creep rate, and σ is the superimposed uniaxial creep stress.

Equation (1) is derived from two basic expressions. One is given by the thermodynamic relation³⁷

$$\partial G / \partial P|_T = V, \quad (3)$$

and the other by the diffusivity expression³⁸

$$D = \gamma a^2 \nu \exp(-\Delta G / RT). \quad (4)$$

Equation (3) can be expressed as

$$\partial \Delta G / \partial P|_T = \Delta V. \quad (5)$$

On the assumption that diffusion occurs by a lattice defect mechanism, ΔG and ΔV represent the difference in Gibbs free energy and the excess volume per mole of lattice defects, respectively, between the activated and normal states. In Eq. (4) γ is a geometrical factor, a is the lattice spacing, and ν is the vibrational frequency of atoms usually taken to be the Debye frequency. Taking the logarithm of Eq. (4) gives

$$-RT \ln(D / \gamma a^2 \nu) = \Delta G. \quad (6)$$

Substituting ΔG from Eq. (6) into Eq. (5) gives

$$-RT(\partial \ln D / \partial P) + RT(\partial \ln \gamma a^2 \nu / \partial P) = \Delta V. \quad (7)$$

Neglecting the pressure dependence of $\gamma a^2 \nu$, which is generally small,¹⁰ and letting ΔV equal ΔV_D , the activation volume for diffusion, Eq. (7) then becomes Eq. (1). Equation (2) is used to calculate ΔV_C from pressure dependence of the creep rate utilizing the form of Eq. (1). The relationship between ΔV_C and ΔV_D will be presented later.

The activation volumes calculated by Eqs. (1) and (2) are not to be confused with the activation volumes calculated by various thermally activated creep theories. As pointed out by Li,³⁹ the latter should more correctly be called activation areas, and the values calculated are usually not related in any way to the activation volumes determined experimentally by Eqs. (1) and (2).

TABLE I. Experimentally determined activation volumes.

Element or compound	$\Delta V/\Omega^a$	Ω (cm ³ /mole)	Remarks	References
A. Body-centered cubic metals				
K	0.55	46	Creep at $\dot{\epsilon} < 7 \times 10^{-7} \text{ sec}^{-1}$	1
K	0.97		Creep at $\dot{\epsilon} > 10^{-6} \text{ sec}^{-1}$	1
K	0.53		Creep	2
K	0.56		Creep	3
Li	0.28	13.0	Self-diffusion	4
Li	0.39		Self-diffusion	5
Li	0.26		Self-diffusion	6
Na	0.53	24	Creep at $\dot{\epsilon} < 3 \times 10^{-7} \text{ sec}^{-1}$	7
Na	1.04		Creep at $\dot{\epsilon} > 3 \times 10^{-7} \text{ sec}^{-1}$	7
Na	0.41		Creep	8
Na	0.52		Self-diffusion	9
Na	0.41		Self-diffusion	4
γ -U	0.44	13.5	Self-diffusion	10, 11
B. Hexagonal close-packed metals				
Cd	0.65	13.0	Creep	12
Zn	0.63	9.6	Creep	12
Zn	1.75		Self-diffusion <i>c</i> axis	13
Zn	0.52		Self-diffusion \perp <i>c</i> axis	13
C. Face-centered cubic metals				
Ag	0.90	10.3	Self-diffusion	14
Ag	0.88		Self-diffusion	10, 11
Ag	0.93		Self-diffusion	15
Al	1.36	10.0	Creep	16
Al	0.74		Creep at 0.3–0.5 T_m	17
Al	0.87		Creep at 0.5–0.6 T_m	17
Al	0.44–0.87		Self-diffusion (dislocation loop annealing) at 0.2–0.6 T_m	18
Al	1.29		Self-diffusion at $> 0.6T_m$	11, 19
Au	0.71	10.2	Self-diffusion	20
Au	0.72		Self-diffusion	11, 19
Cu	0.91	7.0	Self-diffusion	11, 19
Pb	0.80	18.2	Creep	21
Pb	0.70		Creep	22
Pb	0.71		Self-diffusion	23
Pb	0.64		Self-diffusion	24
D. Other crystal structures				
In	0.76	15.7	Single crystal creep	8
P ₄	0.44	68.0	Creep	25
P ₄	0.44		Self-diffusion	26
Sn	0.32	16.2	Creep	27
Sn	0.33		Self-diffusion	28
E. Compounds				
AgBr	1.31	29.0	Creep	29
	1.51		Bromine diffusion	30
F. Materials that contract on melting				
ϵ -Pu	−0.42	14.5	Self-diffusion	31
ϵ -Pu	−0.33		Self-diffusion	32
H ₂ O	−0.64	18.0	Creep	33

^a ΔV is the experimentally determined activation volume and Ω is the molar volume at room temperature; γ -U and ϵ -Pu are exceptions where Ω was calculated at the melting temperature.

We will now demonstrate how it is possible to estimate ΔV_D and ΔV_C from a knowledge of some of the basic properties of materials.

Estimation of Activation Volume for Diffusion

Experimentally, the diffusion coefficient is given by

$$D = D_0 \exp(-Q/RT), \quad (8)$$

where Q is the experimentally determined activation energy and D_0 is the preexponential diffusion constant. Equation (8) can be considered equal to Eq. (4) with $D_0 = \gamma a^2 \nu \exp(\Delta S/R)$ and $Q = \Delta H$, where $\Delta G = \Delta H - T\Delta S$. Here, ΔH and ΔS are the differences in enthalpy and entropy, respectively, between the activated and the normal states. The activation energy Q has been shown to be primarily a function of the absolute melting temperature T_m .^{40,41} Values reported for Q can be approximated by $36 \cdot T_m$ ⁴¹ (or $18 \cdot R \cdot T_m$). A more precise relation which takes into account crystal structure and valence⁴² is given as

$$Q = RT_m(k_0 + v), \quad (9)$$

where k_0 is a crystal structure factor (14 for bcc, 16 for hcp, 17 for fcc, and 20 for diamond-cubic elements), and v is the valence of the element. Substituting the value for Q given by Eq. (9) into Eq. (8) gives

$$\ln D = \ln D_0 - (T_m/T)(k_0 + v). \quad (10)$$

Assuming that D_0 , k_0 , and v are independent of the hydrostatic pressure and substituting the value of $\ln D$ given by Eq. (10) into Eq. (1) results in

$$\Delta V_D = R(k_0 + v)(dT_m/dP). \quad (11)$$

From the Clausius-Clapeyron equation it is possible to relate the change in melting temperature with pressure to other thermodynamic constants,⁴³ namely

$$dT_m/dP = \Delta V_m / \Delta S_m, \quad (12)$$

where ΔV_m is the volume change upon melting and ΔS_m is the entropy of melting. By substituting Eq. (12) into Eq. (11) one obtains

$$\Delta V_D = R(k_0 + v)(\Delta V_m / \Delta S_m). \quad (13)$$

If we let χ equal the fractional volume change upon melting, i.e., $\chi = \Delta V_m / \Omega$, where Ω is the molar volume in the solid state, Eq. (13) becomes

$$\Delta V_D = R(k_0 + v)(\chi / \Delta S_m)\Omega. \quad (14)$$

On the basis of Eq. (14) the activation volume can be determined in relation to the molar volume if the crystal structure, valence, fractional volume change on melting, and entropy of melting of the element are known. We will make a calculation to illustrate an expected value of ΔV_D for a typical fcc metal. The crystal structure factor k_0 is 17, and ΔS_m for most fcc metals is about 2.3 entropy units.⁴⁴ A typical value of χ for many close-packed metals is +0.04 and letting v equal 2, we obtain

$\Delta V_D = 0.66 \Omega$. The calculated result is typical of those obtained experimentally (see Table I).

Since χ and ΔS_m values are readily available for a number of crystalline materials, it is a simple matter to calculate ΔV_D for these materials. The results of such calculations are given in Table II (using Refs. 30, 45-64).

Estimation of Activation Volume for Creep

The activation volume for creep can be calculated if a precise relation is known between the creep rate and other fundamental constants of the material. Phenomenologically, it has been shown that the creep rate of pure polycrystalline metals can be given by

$$\dot{\epsilon} = S(\lambda, \gamma) D(\sigma/E)^n. \quad (15)$$

In the equation, $S(\lambda, \gamma)$ has been shown to be a function of subgrain size λ ^{65,66} and of the stacking fault energy γ .^{67,68} σ is the creep stress, E is the average unrelaxed elastic modulus at the temperature of test T , and n is a constant typically equal to about five or seven (see Ref. 65). Substituting $\dot{\epsilon}$ from Eq. (15) into Eq. (2), and making the reasonable assumption that $S(\lambda, \gamma)$ is independent of hydrostatic pressure, one obtains

$$\Delta V_C|_{\sigma, T} = -RT(d \ln D/dP)|_{\sigma, T} + nRT(d \ln E/dP)|_T. \quad (16)$$

Combining Eqs. (1) and (16) yields the relationship between the two activation volumes

$$\Delta V_C|_{\sigma} = \Delta V_D + nRT(d \ln E/dP). \quad (17)$$

The elastic moduli of normal metals would be expected to increase slightly with increase in pressure; hence, the term $nRT(d \ln E/dP)$ in Eq. (17) should be positive. Thus, we would expect that in general ΔV_C should be larger than ΔV_D . The limited experimental data given in Table I do not necessarily suggest that this conclusion is borne out. It should be pointed out, however, that the second term in Eq. (17) is generally very small³ so that ΔV_C should about equal ΔV_D .

RESULTS AND DISCUSSION

The values of ΔV_D calculated by means of Eq. (14) for a number of elements and compounds are listed in Table II. The materials evaluated are listed according to their crystal structure prior to melting. Those solids that contract upon melting, i.e., those that exhibit negative activation volumes, are listed at the bottom of the table. The major source of error in estimating values of ΔV_D is in the accuracy of the data available for χ , the fractional volume change on melting. For example, the reported values of χ for Ag vary by a factor of almost two. Furthermore, no data are available for many elements. The χ values used are listed in Table II.

TABLE II. Activation volumes for various metals and compounds calculated from $\Delta V = R(k_0 + v)(\chi/\Delta S_m)\Omega$.

Element or compound	Crystal structure factor, k_0	Valence v	Entropy of melting, ΔS_m	Fractional volume change on melting, χ	Activation volume Molar volume, Ω
A. Body-centered cubic metals					
Li	14	1	1.58 ^h	0.0165 ⁱ	0.31
Na	14	1	1.68 ^h	0.025 ⁱ	0.44
K	14	1	1.67 ^h	0.0255 ⁱ	0.46
Rb	14	1	1.73 ^h	0.025 ⁱ	0.43
Cs	14	1	1.72 ^h	0.026 ⁱ	0.45
δ -Fe	14	3	2.01 ^h	0.030 ⁱ	0.50
β -Tl	14	3	1.69 ^h	0.022 ⁱ	0.44
γ -U	9.5 for $(k_0 + v)^a$		2.2 ^h	0.05 ⁱ	0.43
B. Hexagonal close-packed metals					
Mg	16	2	2.32 ^h	0.041 ⁱ	0.63
Zn	16	2	2.55 ^h	0.042 ⁱ	0.59
Cd	16	2	2.46 ^h	0.040 ⁱ	0.58
C. Face-centered cubic metals					
Al	17	3	2.75 ^h	0.060 ⁱ	0.85
Cu	17	1	2.30 ^h	0.051 ⁱ	0.79
Ag	17	1	2.31 ^h	0.038 ⁱ	0.59
Ag	17	1	2.31 ^h	0.050 ^k	0.77
Ag	17	1	2.31 ^h	0.059 ⁱ	0.91
Au	17	1	2.21 ^h	0.051 ⁱ	0.83
Pb	17	4	1.89 ^h	0.035 ⁱ	0.77
Ar	17	0	3.35 ⁱ	0.144 ⁱ	1.45
Kr	17	0	3.37 ⁱ	0.151 ⁱ	1.51
Xe	17	0	3.40 ⁱ	0.151 ⁱ	1.50
D. Other crystal structures					
In (face-centered tetragonal)	17	3	1.82 ^h	0.020 ⁱ	0.44
Sn (body-centered tetragonal)	14	4	3.31 ^h	0.028 ⁱ	0.30
Hg (rhombohedral)	16	2	2.37 ^h	0.037 ^h	0.56
P ₄ (cubic)	14.9 for $(k_0 + v)^b$		1.88 ^h	0.035 ^h	0.28
E. Compounds					
AgBr (complex fcc)	32.2 for $(k_0 + v)^a$		3.16 ^m	0.089 ⁿ	1.80
F. Materials that contract on melting					
ϵ -Pu (bcc)	10 for $(k_0 + v)^a$		-0.016 for $\chi/\Delta S_m^e$		-0.32
δ -Pu (fcc)	14 for $(k_0 + v)^a$		1.68 ^f	-0.0439 ^g	-0.88
Ge (diam)	20	4	6.0 ⁱ	-0.050 ⁱ	-0.40
Si (diam)	20	4	7.17 ^h	-0.096 ⁱ	-0.64
Sb (rhom)	25 for $(k_0 + v)^d$		5.19 ^h	-0.0095 ⁱ	-0.09
Bi (rhom)	28.5 c for $(k_0 + v)^d$		4.77 ^h	-0.0335 ⁱ	-0.40
Bi (rhom)	129.5 $\perp c$ for $(k_0 + v)^d$		4.77 ^h	-0.0335 ⁱ	-1.81
Ga (fcc)	17	3	4.41 ^h	-0.032 ⁱ	-0.29
Ice (hex)	16	2	5.26 ^p	-0.091 ^q	-0.62

Several significant observations can be directly deduced from the calculated values of ΔV_D . With just a few exceptions, the calculated activation volumes are nearly equal to those obtained from diffusion and creep experiments. This rather good correlation obtained can be seen in Fig. 1. Of major significance is the excellent agreement shown for H₂O and epsilon plutonium where negative activation volumes were obtained.

From the viewpoint of considering diffusion mechanisms it might be thought that ΔV_D , being representative of a configuration factor in diffusion, should be related to the nature of the crystal structure within which the atom migration process occurs. It is thus not entirely surprising that ΔV_D is a function of the crystal structure and quite independent of the melting temperature. This trend is clearly seen in Table II where ΔV_D is about 0.4 Ω for most bcc crystals, about 0.6 Ω for hcp crystals and about 0.8 Ω for fcc crystals (except the inert gases). Perhaps an additional important clue to determining diffusion mechanisms in solids is to assess the meaning of the negative activation volumes that are calculated for a number of materials listed at the bottom of Table II. These values were obtained, of course, because the specific volume on melting of these materials decreased instead of increased.

A very attractive approach to explaining the above results is to consider a diffusion mechanism similar to the "relaxion" mechanism as proposed by Nachtrieb and Handler.⁶⁹ These authors proposed that diffusion occurs through the cooperative action of a group of atoms in a liquid-like state. Instead of having a discrete vacancy movement, they assume that the vacancy dissolves locally in the lattice to form a complex of disordered atoms which then move through the lattice. It was assumed that the basic diffusive unit corresponds to the 12 nearest-neighbor atoms for fcc structures and to the 14 nearest- and next-nearest-neighbor atoms for bcc structures, respectively. A "relaxion"-type mechanism explains in a rather straightforward way, the results tabulated in Table II. For crystalline solids that contract on melting (such as Pu, H₂O, Ge, Si, and Ga), the volume of the activated state, which we would relate to the molten state, should be smaller than the state

before the thermal activation process occurred, thus leading to negative activation volumes. Similarly, for normal crystalline materials where expansion occurs on melting, the volume of the activated state should be larger than the state before thermal activation occurs in the diffusion process and positive activation volumes should result. In our diffusion model, however, we do not envision the continuous existence of a "relaxion" region as suggested by Nachtrieb and Handler. Rather, we believe that the vacancy, once created, exists at a discrete lattice site. It is only during its motion that atoms surrounding the vacancy are disturbed and a liquid-like region (i.e., "relaxion") is created. We would also envision the same type of activated state in the process of vacancy formation. The difference in activation volumes observed between normal bcc and fcc metals can also be explained by our proposed mechanism. In general, the volume increase on melting is smaller for bcc metals than for fcc metals (see Table II). Thus, the activation volume should generally be smaller for bcc metals than for fcc metals, a prediction in general agreement with the calculated activation volumes.

Anisotropic metals should exhibit different values of activation volumes depending on the direction of measurement. From Eq. (14), the different activation volumes would be associated with the crystal structure factor k_0 . A method of calculating k_0 for a given anisotropic metal would be by means of Eq. (9) which gives $(k_0 + v) = Q/RT_m$. If the activation energy for diffusion Q is known as a function of crystallographic direction then $(k_0 + v)$ is readily calculated. Most hcp metals show some anisotropy in their diffusion behavior and yield different values of Q depending on crystallographic direction. The differences in Q are generally small, however, and we would predict only minor differences in activation volumes for most hcp metals. For example, calculations can be made from the diffusion data reported by Liu and Drickamer¹³ on zinc (see Table I). Using their activation energies for diffusion ($Q_{||c} = 19.6$ kcal per mole and $Q_{\perp c} = 25.9$ kcal/mole), we obtain $(\Delta V_D)_{||c} = 0.47 \Omega$ and $(\Delta V_D)_{\perp c} = 0.63 \Omega$. These values, however, may not reflect the true activation volumes since Liu and Drickamer show,

TABLE II (Continued)

^a Abnormally low activation energies are observed for γ -U, ϵ -Pu and δ -Pu. Accordingly, the $(k_0 + v)$ values were obtained from Eq. (9), i.e., $(k_0 + v) = Q/RT_m$. The Q values were obtained from Refs. 54, 56, respectively, and the melting temperature for δ -Pu was calculated by the method of Ardell.⁵⁷

^b Values for both k_0 and v cannot reasonably be assigned to phosphorus. Accordingly, the $(k_0 + v)$ value was calculated by the method described in (a). Q was obtained from Ref. 58.

^c Values for both k_0 and v cannot reasonably be assigned to AgBr. Accordingly, the $(k_0 + v)$ value was calculated by the method described in (a). Q was obtained from Ref. 30.

^d Since k_0 is not known for the rhombohedral crystal structures associated with Sb and Bi, the $(k_0 + v)$ values for these elements were calculated by the method described in (a). Q values were obtained from Refs. 59 and 60.

^e The χ value for ϵ -Pu is not well established. Values have been quoted from -0.01 to -0.25 (Refs. 61-63). $\chi/\Delta S_m$ was, therefore, calculated from the relationship given by Eq. (12), i.e., $\Delta V_m/\Delta S_m = dT_m/dP$. The

value for dT_m/dP was obtained from the T - P phase diagram published by Stephens⁶⁴; the molar volume, Ω , used to convert ΔV_m to χ is 14.68 and was obtained from the density of Pu of 16.28 (Ref. 61).

^f Obtained by the method of Ardell.⁵⁷

^g Obtained by extrapolation of the densities in the δ and ϵ phases⁶⁵ to T_m of the δ phase. T_m of the δ phase was calculated by the method of Ardell.⁵⁷

^h Reference 45.

ⁱ Reference 46.

^j Reference 47.

^k Reference 48.

^l Reference 49.

^m Reference 50.

ⁿ Reference 51.

^o Reference 52.

^p Reference 53.

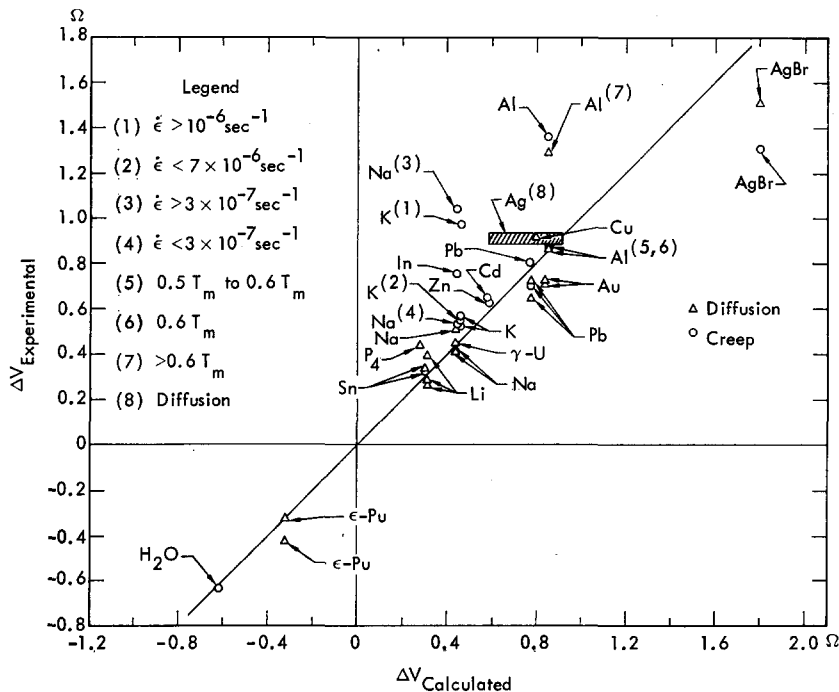


FIG. 1. Plot showing the general agreement between experimental and calculated activation volumes for diffusion and creep as shown by the data relative to the straight line curve drawn for a 1:1 relationship. Data plotted for values obtained above $0.5T_m$. Due to large anisotropy, diffusion data for Zn (from Tables I and II) are not plotted.

contrary to the generally observed behavior, that D_0 for Zn is a strong function of the pressure. True activation volumes can be calculated by means of Eq. (7) rather than Eq. (1). Through Eqs. (7) and (10) it can be shown that

$$\Delta V = R(k_0 + v)(dT_m/dP) - T(\partial \Delta S / \partial P). \quad (18)$$

Thus a knowledge of the change in entropy with pressure and the temperature of measurement is needed. Liu and Drickamer show irregular but large changes of the entropy of activation with pressure and therefore the true activation volumes, based upon Eq. (18), may be difficult to interpret. In our opinion, further studies on the pressure dependence of diffusion in zinc should be initiated, especially since D_0 (from which ΔS can be calculated) seems to be generally insensitive to pressure for other metallic systems.^{9,10}

It would appear from the above discussion that there is considerable uncertainty regarding the values of the activation volumes for a material that is crystallographically anisotropic. Further experimental work is clearly needed to determine the influence of such anisotropies. Using a "relaxation"-type mechanism as a physical model for diffusion, we would expect the activation volume to vary with crystallographic direction. The diffusing specie should experience volume changes upon thermal activation that are crystallographically dependent, since the bonds that are broken on "localized melting" would be highly directional in anisotropic materials.

The activation volume for creep or diffusion should be a function of pressure if the method of calculation proposed herein [Eq. (14)] is correct. This is because the volume change on melting will be a function of pres-

sure (ΔS_m is a factor associated with configuration changes and should not, therefore, be a function of pressure). Since the compressibility of liquids is usually greater than that of solids,⁷⁰ it follows that, in general, ΔV_m would decrease with an increase in pressure. Hence, ΔV_D and ΔV_C should also decrease with increasing pressure. This predicted trend has been observed for sodium,⁹ zinc and cadmium,¹² and aluminum.¹⁷

While we agree that the previously described diffusion process which led to our calculated activation volume is related to the latent heat of melting through a "relaxation" type mechanism as proposed by Nachtrieb and Handler, it is difficult to theoretically ascribe values to the two components—activation volume of formation ΔV_F , and activation volume of motion ΔV_M —which comprise the total activation volume. We do believe that both of these terms are related to a melting-like process and to the crystal structure, although, as mentioned earlier, we consider the liquid-like cluster of atoms to exist only during the thermally activated state. One can gain some insight into the relative contributions of these formation and migration terms to the total activation process. Namely, if Eq. (9) also describes the activation energy for formation and motion of vacancies (with a different value of k_0) then the following equations enable one to calculate ΔV_F and ΔV_M from previously determined experimental data on the activation energies of formation Q_F and migration Q_M , for diffusion

$$\Delta V_F = (Q_F/T_m)(\chi/\Delta S_m)\Omega, \quad (19)$$

and

$$\Delta V_M = (Q_M/T_m)(\chi/\Delta S_m)\Omega. \quad (20)$$

For example, the average activation energies for forma-

tion and migration in gold, as determined from the data compiled in Refs. 71 and 72, yield calculated activation volumes of 0.40 and 0.27 Ω for formation and migration, respectively. The relative contributions to the total activation volume, as given by these two values, are reasonably consistent with the experimentally determined values of 0.57 Ω (see Ref. 73) and 0.14 Ω (see Ref. 74). Unfortunately, the formation and migration activation volumes have only been determined for gold⁷⁵ so comparisons with experiment for other metals cannot be made at this time.

Attempts by other investigators have been made to calculate the activation volume for thermally activated processes.³⁴⁻³⁶ Lawson³⁴ indicated that the ratio of the entropy of activation ΔS to the activation volume ΔV was about equal to α/β where α is the volumetric thermal expansion coefficient and β is the isothermal compressibility. Thus $\Delta V \simeq \beta \Delta S / \alpha$. Since data of ΔS are not readily available, calculation of ΔV is difficult. A simpler relation for ΔV was developed and proposed by Keyes.³⁵ He showed that $\Delta V \simeq 4\beta \Delta H$ where ΔH is the enthalpy of activation (essentially the same as Q). Keyes showed the relation to work reasonably well for a number of elements; however, since ΔH and β are both positive it is not possible to obtain negative activation volumes using his approach. Thus, this equation cannot be used to explain the negative activation volume values found for ice and epsilon plutonium. Rice and Nachtrieb³⁶ calculated activation energies for self-diffusion using the formula $\Delta H = (\Delta H_m / \Delta V_m) \Delta V$, where ΔH_m and ΔV_m are the latent heat of melting and volume change on melting, respectively. The formula they used to calculate activation energies is similar to the formula we have used to calculate activation volumes except that we have utilized Eq. (9) to describe the factors influencing the activation energy.

SUMMARY AND CONCLUSIONS

It is shown that the activation volume for diffusion or steady-state creep can be estimated for crystalline solids. The specific relation developed is given by

$$\Delta V_D = R(k_0 + v)(\chi / \Delta S_m) \Omega.$$

In this expression R is the gas constant (1.987 cal/mole/deg), k_0 is a crystal structure factor (14 for bcc metals, 16 for hcp metals, 17 for fcc metals, and 20 for diamond-cubic metals), v is the valence, χ is the fractional volume change on melting, ΔS_m is the entropy of melting, and Ω is the molar volume.

Activation volumes calculated by means of the above equation correlate very well with those for self-diffusion and high-temperature creep that have been determined experimentally from hydrostatic pressure experiments (data are now available for seventeen elements and compounds).

It is shown that the activation volume is a function

of the crystal structure and quite independent of melting temperature (but, not of dT_m/dP at moderate to high pressures); ΔV is calculated to be about 0.4 Ω for most bcc crystals, 0.6 Ω for hcp crystals, and 0.8 Ω for most fcc crystals. In addition, it is shown that negative activation volumes are obtained for metals and compounds that contract on melting. These observations suggest that diffusion in the solid state occurs by a mechanism similar to the "relaxion" process as originally proposed by Nachtrieb and Handler. In our proposed model the thermally activated state in diffusion involves the cooperative formation of a liquid-like cluster of atoms surrounding a vacant lattice site.

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