elements into the correlation expression. The systematic investigation of assignments using mixtures of alpha-angular momentum groups involves much computation. None of the cases that involve mixtures of angular momentum groups for the alpha-particle have been computed here; however, Beling[9] has considered a few without finding a convincing fit with the data.

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[9] J. K. Beling, dissertation, Massachusetts Institute of Technology (1951), unpublished.

We are indebted to Professor I. Halpern and his colleagues for communicating to us the results of their investigation. We also wish to thank Professor M. Riou for sending us his most recent unpublished results on the gamma-radiation from the decay of radiothorium.[10]

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[10] *Note added in proof.*—A recent paper by Rosenblum, Valadares, and Guillot (Compt. rend. **235**, 238 (1952)) reports measurements of the internal conversion lines of radiothorium, which confirm the existence of one gamma-ray of 83.4 kev as assumed in the interpretation of our data.

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Entropies of Activation in Metallic Diffusion*

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The various contributions to the entropy of activation for metallic diffusion are examined theoretically. In particular, the entropy contribution arising from the altered vibrational frequencies around the saddle point is estimated. It is concluded that negative over-all entropies of activation are theoretically permissible and are likely to arise when the over-all activation energy is small.

I. INTRODUCTION

THE temperature dependence of volume diffusion is accurately described by the simple exponential relation

$$D=D_0e^{-E/RT},\tag{1}$$

where D = diffusion constant; D_0 = constant; E = activation energy; R = gas constant; T = temperature in °K. The activation energy E may be estimated theoretically in simple cases.[1] It is much more difficult to give a sound theoretical interpretation to D_0, the so-called frequency factor, although many attempts have been made in the past to derive theoretical expressions for this quantity.[2]

This problem was attacked again in the last few years with clarification of some of the puzzling features. The writer proposed an empirical correlation which related D_0 to the quantity E/T_m, where T_m is the melting point in °K, and suggested that E/T_m be identified with the entropy of activation.[3] Zener[4] proposed a theory for D_0, which seemed to account at least partly for the above correlation, in which only positive experimental entropies of activation ΔS, calculated as

$$\Delta S/k=\ln(D_0/\nu a^2),\tag{2}$$

were permitted (ν = Debye frequency, a = lattice parameter). In Zener's theory, the origin of the entropy contribution is traced to the temperature coefficient of the work required to produce a given distortion within the lattice. Finally, this was traced to the temperature coefficient of the elastic moduli, which is negative, yielding a positive ΔS. Zener suggested that experimentally observed negative entropies of activation are to be attributed to experimental inaccuracies or to the presence of short-circuiting diffusion paths.

The writer pointed out[5] that Zener's theory is unable to account for the large negative entropies of activation for self-diffusion in tin as calculated from Fensham's excellent experimental data on single crystals.[6] At about the same time Nowick[7] published an article in which intermetallic diffusion experiments were reinterpreted on the basis of Zener's theoretical expression for D_0. Nowick argues that this theoretical D_0 is correct at least to order of magnitude and suggests that many experimental activation energies are greatly in error at any but the highest temperatures because of diffusion along internal surfaces or "short circuiting paths" and that the writer's earlier correlation reflects essentially this inaccuracy. Nowick is certainly correct in calling attention again to the well-known poor quality of most diffusion data. However, he offers no explanation for the behavior of tin. Further, recent researches by Smoluchowski and co-workers[8,9] indicate strongly that dis-

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* Research carried out under contract with the AEC.

[1] See for example the recent review by F. Seitz in *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951), pp. 77–149.

[2] See for example A. D. LeClaire, section on "Diffusion of Metals" in *Progress in Metal Physics I* (Interscience Publishers, Inc., New York, 1949), pp. 306–379.

[3] G. J. Dienes, J. Appl. Phys. **21**, 1189 (1950).

[4] C. Zener, J. Appl. Phys. **22**, 372 (1951); *Theory of Diffusion*, "Imperfections in Nearly Perfect Crystals," (John Wiley and Sons, Inc., New York, 1952), pp. 289–314.

[5] G. J. Dienes, J. Appl. Phys. **22**, 848 (1951).

[6] P. J. Fensham, Australian J. Sci. Res. **A3**, 91 (1950); **A3**, 105 (1950).

[7] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[8] R. Smoluchowski, Phys. Rev. **87**, 482 (1952).

[9] R. Flanagan and R. Smoluchowski, J. Appl. Phys. **23**, 785 (1952).

Table I. Values of γ for different lattices.[a]

Lattice	γ
Face-centered cubic	2
Body-centered cubic	4/3
Hexagonal close packed, $\parallel C$	1.0
Hexagonal close packed, $\perp C$	1.0
Tetragonal tin lattice, $\parallel C$	1/3
Tetragonal tin lattice, $\perp C$	2/3

[a] γ defined here is not quite the same as Zener's γ since the jump distance λ rather than the lattice parameter a is used here. λ is a more convenient quantity whenever noncubic lattices are considered.

locations and mosaic block boundaries cannot serve as short-circuiting paths. Only high angle grain boundaries could act as short circuits.

In view of the rather unsatisfactory state of affairs discussed above, the writer felt that it was worthwhile to investigate in somewhat more detail the various contributions to the entropy of activation. In particular, it is important to find out whether negative entropies of activation be theoretically permissible. The purpose of this note is to describe some of the results of this theoretical study.

II. THE ENTROPY OF ACTIVATION

The vacancy mechanism of diffusion will be assumed as operative throughout since this mechanism is probably the most prevalent one in metals.[1] Rather obvious modifications, which would not influence the final conclusions, are required if other mechanisms are dominant. The complete expression for D as a function of temperature may be written as[4]

$$D=\gamma\nu\lambda^2 e^{\Delta S/R}e^{-(E_v+E_m)/RT}, \tag{3}$$

where γ = geometrical constant, entirely determined by the lattice geometry of the atomic jump; ν = vibrational frequency of atom in the equilibrium position $\cong$ Debye frequency; λ = jump distance; ΔS = over-all entropy of activation; E_v = energy required to create vacancy at 0°K; and E_m = energy required to move vacancy at 0°K. The values of γ for typical lattices are listed in Table I.

Equation (3) is based on the well-known transition state theory of reaction rates. The fundamental assumption of this theory is that the activated complexes are always in equilibrium with the initial reactants.[10] This fundamental assumption, as applied to solid state diffusion, has not yet been critically examined.[11] In this paper the entropies of activation are examined within the framework of the transition state theory.

The value of ΔS in Eq. (3) is a composite quantity. As a first approximation, the following processes contribute to the over-all ΔS.

(1) The variation of the over-all activation energy with temperature. As the lattice expands with increasing temperature, the energies needed to create and move a vacancy will decrease. That is,

$$E=E_v'+E_m'=E_0-\delta T=E_v+E_m-\delta T, \tag{4}$$

where δ is inherently positive. The corresponding entropy $\Delta S_1=\delta/R$ is inherently positive. For convenience it has been assumed that these temperature effects may be expressed through the same δ for both E_v' and E_m'. As long as Eq. (4) is valid one always measures E_0 experimentally. E_0 already includes the contribution to the energy originating in displacements (relaxation) of the atoms around the vacancy and the saddle point, respectively.

(2) The altered vibrational frequencies around a vacancy. The neighboring atoms of a vacancy possess vibrational frequencies different from normal atoms. This effect introduces a constant factor in Eq. (3) which shows up as a contribution to the entropy ΔS_2.

(3) The altered vibrational frequencies around the saddle point. The atoms constituting the configuration of the saddle point possess vibrational frequencies different from normal atoms. As in (2) a constant factor is introduced which appears as an entropy contribution ΔS_3.

In the following, an attempt is made to estimate theoretically each of these contributions to the entropy.

(1) Mott and Gurney[12] and Frenkel[11] have made estimates of ΔS_1. A derivation somewhat different in technique but not in concept is given here. From the rapid decrease of interatomic forces with increasing atomic separation, one may assume that E of Eq. (4) depends on the interatomic distance r in an exponential manner. Thus

$$E(r)=Ae^{-\alpha r}. \tag{5}$$

Then

$$\begin{aligned} dE/dT&=Ae^{-\alpha r}(-\alpha)dr/dT\\ &=-\alpha(dr/dT)E. \end{aligned} \tag{6}$$

Letting $dr/dT=r_0\beta$, where β = coefficient of linear expansion, gives

$$dE/E=-\alpha r_0\beta dT. \tag{7}$$

Integration gives

$$E=E_0e^{-\alpha r_0\beta T}, \tag{8}$$

or within the range of linearity of Eq. (4), certainly valid over limited temperature ranges,

$$E=E_0(1-\alpha r_0\beta T), \tag{9}$$

which corresponds to an entropy contribution

$$\Delta S_1=\alpha r_0\beta E_0. \tag{10}$$

ΔS_1 is inherently positive and may be quite large depending on the magnitude of the various quantities in Eq. (10). Further, ΔS_1 may vary a great deal from material to material, primarily through E_0 and α.

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[10] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 184–201, 477–552.

[11] In this connection see the qualitative discussion in reference 2 and that by J. Frenkel in *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), pp. 17–37.

[12] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1946), pp. 26–36.

(2) Mott and Gurney[12] have estimated the contribution to the entropy ΔS_2 arising from the altered vibrational frequencies around a vacancy. They assume that the vibrational frequencies of the X neighbors of a vacancy are ν as before in the two directions perpendicular to the line joining the neighbor to the vacancy, but some smaller value ν' parallel to this line. Under these conditions the contribution to the entropy of activation ΔS_2 is

$$\Delta S_2 = XR\ln(\nu/\nu'). \tag{11}$$

ΔS_2 is positive if the assumption $\nu' < \nu$ is valid.[13] It is difficult to assign a value to ΔS_2, but Mott and Gurney estimate that it may be of the order of 6 entropy units. This figure may be a considerable overestimate. The atoms surrounding a vacancy tend to move in toward the vacancy.[14,15] It was pointed out to the writer by LeClaire[16] that this relaxation restricts the movement of these atoms tangential to the sphere on which their centers lie. It is probable that ΔS_2 remains positive, but it may be considerably smaller than originally estimated by Mott and Gurney.

(3) The third important factor contributing to the over-all entropy of activation, which has not been considered by previous workers, arises from the altered vibrational frequencies of the atoms constituting the saddle point configuration. Physically, one anticipates that the situation existing at the saddle point is somewhat analogous to that around an interstitial atom. The volume available to the atoms has been decreased by moving an atom to the saddle point, and consequently the vibrational frequencies have been increased. Consequently one expects ΔS_2 to be negative. Any sort of exact calculation is difficult particularly if the relaxation of the atoms is to be taken into account. An order of magnitude calculation is possible, however, and will be described in this section.

It will be assumed that the vibrational frequency, ν, may be expressed as an inverse power function of the volume.[17] Thus

$$\nu = C/V^{\gamma}, \tag{12}$$

where V is the volume, C is a constant and γ is Grüneisen's constant. In terms of the interatomic distance, Eq. (12) may be written

$$\nu = C'/(r)^{3\gamma}, \tag{13}$$

where all constant factors have been absorbed in C'. A change in the vibrational frequency of an atom from ν to ν' corresponds to an entropy change (per mole of that atom) of

$$\Delta S_i = R\ln(\nu_i/\nu_i') = R\ln[r_i'/r_i]^{3\gamma} = 3R\gamma\ln(r_i'/r_i). \tag{14}$$

Analogous to the procedure of Mott and Gurney for vacancies, it is assumed that the neighbors of the atom at the saddle point vibrate with the altered frequency in the direction of the line connecting them to the moving atom, but that their frequencies are not altered in the two directions perpendicular to this line. Thus, each altered vibrational frequency corresponds to one degree of freedom. The contribution to the entropy of activation of N neighbors of an atom at the saddle point is given by

$$\Delta S = 3R\gamma\sum_{i=1}^{N}\ln\frac{r_i'}{r_i}. \tag{15}$$

It is somewhat more difficult to estimate the altered vibrational frequencies of the atom at the saddle point in the two directions perpendicular to the jump direction. As a crude approximation, this contribution may be taken as the average of ΔS in Eq. (15) with two degrees of freedom. The final expression for ΔS_3 is then given by

$$\Delta S_3 = 3R\gamma\sum_{i=1}^{N}\ln\frac{r_i'}{r_i} + \frac{6R\gamma}{N}\sum_{i=1}^{N}\ln\frac{r_i'}{r_i}. \tag{16}$$

Equation (16) forms the basis of the present calculation. The procedure may be illustrated for a simple face centered cubic lattice. Let the vacancy be situated at (110) (in units of $a/2$) and let the diffusing atom be located at (000). Assume that the saddle point is halfway along the line from (000) to (110), i.e., at $(\frac{1}{2}\,\frac{1}{2}\,0)$. If the nearest neighbors around both (000) and (110) are taken into account, care being taken not to count the common neighbors twice, it is found that for these 18 neighbors

$$\sum_{i=1}^{N}\log_{10}\frac{r_i'}{r_i} = -0.286,$$

and ΔS_3 for this system is, therefore,

$$\Delta S_3 = 2.3(3R\gamma)[-0.286-(2/18)(0.286)] = -4.36\gamma.$$

If one takes 2 as a representative value for Grüneisen's constant, this contribution to the entropy of activation amounts approximately to

$$\Delta S_3 \sim -8.7 \text{ eu}.$$

Similar calculations were made for other crystal lattices with the results shown in Table II. The results indicate that in the lattices considered here the effect of decreased interatomic distances outweighs the effect of increased distances leading to a net "tightening" of the lattice and a corresponding net negative contribution to the entropy of activation. It is difficult to say what influence the relaxation of the atoms may have on ΔS_3. In the present order-of-magnitude calculation, this

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[13] It should be pointed out that ΔS_2 is expected to be negative when an interstitial rather than a vacancy is created in the lattice (see reference 12).

[14] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[15] G. J. Dienes, Phys. Rev. **86**, 228 (1952).

[16] A. D. LeClaire (private communication, May, 1952).

[17] See for example J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 215–221.

Table II. Contribution to the entropy of activation from altered vibrational frequencies of atoms in the saddle point configuration. Vacancy mechanism.

Crystal lattice	Vacancy at	Saddle point at	No. of neighbors considered	$\sum_{i=1}^{N} \log_{10} \frac{r_i'}{r_i}$	$\frac{2}{N} \sum_{i=1}^{N} \log_{10} \frac{r_i'}{r_i}$	ΔS_3	ΔS_3 in entropy units for $\gamma = 2$
Face-centered cubic	110	$\frac{1}{2}\ \frac{1}{2}\ 0$	18	−0.286	−0.032	-4.36γ	−8.72
Body-centered cubic	111	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	20	−0.269	−0.027	-4.06γ	−8.12
Hexagonal close packed, $\parallel C$ $C/a = 1.633$	$0\ \frac{1}{\sqrt{3}}\ \frac{1}{2}$	$0\ \frac{1}{2\sqrt{3}}\ \frac{1}{4}$	18	−0.286	−0.032	-4.36γ	−8.72
Hexagonal close packed, $\perp C$ $C/a = 1.633$	100	$\frac{1}{2}\ 0\ 0$	18	−0.286	−0.032	-4.36γ	−8.72
Hexagonal, Zn $C/a = 1.862$, $\parallel C$	$0\ \frac{1}{\sqrt{3}}\ \frac{1}{2}$	$0\ \frac{1}{2\sqrt{3}}\ \frac{1}{4}$	18	−0.308	−0.034	-4.69γ	−9.38
Hexagonal, Zn $C/a = 1.862$, $\perp C$	100	$\frac{1}{2}\ 0\ 0$	18	−0.272	−0.030	-4.14γ	−8.28
Tetragonal, Sn lattice, $\parallel C$	0 0 1	$0\ 0\ \frac{1}{2}$	26	−0.309	−0.012	-4.40γ	−8.80
Tetragonal Sn lattice, $\perp$C	$\frac{1}{2}\ 0\ \frac{1}{4}$	$\frac{1}{4}\ 0\ \frac{1}{8}$	26	−0.298	−0.011	-4.23γ	−8.46

effect was neglected. In one respect the magnitudes given in Table II have been probably underestimated. The initial frequencies were assumed to be the normal frequencies corresponding to the normal interatomic distance, r_i. If the decreased frequencies around the vacancy had been used, the relative change, and therefore ΔS_3, would have been greater in magnitude. The total entropy of activation is given by

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3. \tag{17}$$

The first two terms are positive while the last term is negative according to the calculations presented in this section. The final sign and magnitude of ΔS is determined by the relative importance of these three factors.

III. DISCUSSION

The results described in the previous section seem to indicate that negative entropies of activation are theoretically permissible. ΔS_1 in Eq. (17), the contribution arising from a decrease in activation energy with increasing temperature due to the expansion of the lattice, is always positive. It is proportional to the energy of activation and for small energies of activation may become quite small. Thus, it is precisely for low energies of activation that the negative contribution to ΔS is expected to outweigh the positive contribution leading to a net negative ΔS. This trend is in agreement with experimental observations.[3,5] ΔS_2 is probably positive but may, in many cases, be considerably smaller than the 6 eu estimated by Mott and Gurney. The results of Table II indicate that in many cases ΔS_3 may be considerably larger than ΔS_2. ΔS, therefore, may be negative for small values of ΔS_1.

It is concluded that, contrary to Zener's views,[4] negative entropies of activation for solid state diffusion are theoretically permissible. It also follows that, at least in some cases, Nowick's[7] reinterpretation of activation energies for intermetallic diffusion based on Zener's theory for D_0 may be incorrect.

It must be re-emphasized, as many have pointed out before, that for further progress accurate diffusion data over wide ranges of temperature are required so that the various critical quantities may be evaluated with a high degree of reliability. Fortunately, new techniques are coming into use,[18,19] following the work of Zener and co-workers,[20,21] which will permit diffusion measurements at much lower temperatures than hitherto possible. Further, since solid state diffusion is not a single process but depends on the creation and motion of vacancies, it is important that the energies and entropies of activation of each process be established independently. Anelasticity studies offer some hope of accomplishing this.[18]

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[18] A. S. Nowick, Phys. Rev. **82**, 551 (1951).

[19] A. D. LeClaire, Phil. Mag. **42**, 672 (1951).

[20] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[21] C. Wert, Phys. Rev. **79**, 601 (1950).