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March 15, 1963

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ABSTRACT

A model of self-diffusion is developed in which the activation energy to form a vacancy  $Q_v$  is correlated with the heat of sublimation  $L_s$ , and the activation energy to move a vacancy  $Q_m$ , is correlated with either the melting temperature  $T_m$  or with the product of the bulk modulus  $B_s$  and the atomic volume  $V_o$ . The resulting equations for the activation energy for diffusion  $Q_D$  in face-centered metals are

$$Q_D = 22.6 B_s V_o + 0.27 L_s$$

and

$$Q_D = 16.0 T_m + 0.27 L_s$$

with similar equations for BCC elements. The results of these equations are compared to the experimental results for  $Q_m$ ,  $Q_v$ , and  $Q_D$  and the agreement is found to be better than that obtained with previous correlations. Desirable features of the correlation equations are that they employ only readily measured parameters, that they predict not only  $Q_D$  but also  $Q_m$  and  $Q_v$ , and that they can be readily generalized to describe diffusion in substitutional alloys.

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## 1. INTRODUCTION

Previous correlations of the activation energy  $Q_D$  for diffusion in pure metals can be grouped into two classes: Those that have used thermodynamic parameters such as the heat of fusion, heat of sublimation, and melting temperature; and those that have used mechanical parameters such as the shear moduli.

Johnson<sup>(1)</sup> pointed out that the activation energy for self-diffusion is nearly proportional to the melting temperature  $T_m$  or to the sublimation energy  $L_s$ . According to LeClaire,<sup>(2)</sup>  $Q_D/T_m$  has a mean value of 38 and  $Q_D/L_s$  a mean value of 0.64. Nachtrieb and Handler<sup>(3)</sup> found that  $Q_D$  was equal to approximately  $16.5 L_f$ , where  $L_f$  is the heat of fusion, and proposed a local melting or relaxation of atoms about a vacancy to explain the diffusion process.

These one-parameter thermodynamic correlations can be reduced to roughly equivalent forms. At the melting point  $L_f = \Delta S_f T_m$ . But the change in entropy upon melting is approximately a constant  $2.2 \text{ cal mole}^{-1} \text{ deg}^{-1}$  (Richards' rule).<sup>(4)</sup> LeClaire's rule that  $Q_D/T_m = 38$  is equivalent on the average, therefore, to  $Q_D = 17.3 L_f$ . One parameter correlations of  $Q_D$  with heats of sublimation will often give very different predicted values of  $Q_D$  than will correlations in terms of the heat of fusion or the melting temperature, however, because ratios of the heats of sublimation at 298°K to the heats of fusion vary for common metals from as low as 18 for zinc to as high as 42 for sodium and lead.

The thermodynamic correlations so far cited all have equated  $Q_D$  to a single parameter. For self-diffusion proceeding by a vacancy mechanism  $Q_D$  is generally accepted to be the sum of the activation energy for

the formation of a vacancy  $Q_v$  and the activation energy for motion of the vacancy  $Q_m$ .<sup>(1)</sup> The reasonably good agreement between experimental and calculated values with the use of these one-parameter equations implies that  $Q_v$  and  $Q_m$  are approximately proportional to each other. Treating  $Q_v$  and  $Q_m$  as separate terms, however, should improve the agreement between experimental and calculated values of  $Q_D$  and should give better insight into the nature of diffusion.

Recently Sherby and Simnad<sup>(5)</sup> have introduced the valence,  $V$ , of the element as an additional parameter. In their correlations, the activation energy is given as

$$Q_D = R(K + V)T_m$$

where  $K$  is a constant dependent on the crystal structure. The correlation gives remarkably good agreement with the experimental data. Since valence and melting temperatures vary differently across the periodic table, this expression represents a two-term correlation which probably reflects the different variations in  $Q_v$  and  $Q_m$ . But neither term of the Sherby-Simnad equation can be directly equated to  $Q_v$  or  $Q_m$ . Furthermore, to obtain good agreement with experimental values of  $Q_D$  requires assignment of some rather dubious valences. In particular a valence of zero is assumed for platinum. A variety of evidence supports belief that the valence is, in fact, 5 to 6 for this element.<sup>(6)</sup>

Working with mechanical parameters LeClaire<sup>(7)</sup> has proposed that

$$Q_v = k_1 L_s$$

and that

$$Q_m = k_2 M \mu / \rho$$

where  $k_1$  and  $k_2$  are constants dependent only on the crystal structure,  $M$  is the atomic weight,  $\mu$  is an appropriate shear modulus of the crystal, and  $\rho$  is the density. A similar approach was proposed by Buffington and Cohen.<sup>(8)</sup> We will show later in this paper that the term  $k_2 M \mu / \rho$  given by LeClaire for  $Q_m$  is related to the thermodynamic terms above and to another expression which we formulate. We consider that LeClaire's expression for  $Q_v$  is entirely satisfactory, but that alternate expressions for  $Q_m$  can be formulated which have advantages over the expression that he proposed.

## 2. DETERMINATION OF THE ENERGY OF MOVEMENT $Q_m$

Buffington and Cohen evaluated  $Q_m$  in terms of the shear modulus that acts in the direction necessary to spread atoms on sites adjacent to a vacancy. These atoms are assumed to occupy the same positions that they would occupy if they were not adjacent to a vacancy.

The atoms surrounding a vacancy will relax into the vacant site, however, so that the positions of the atoms and the direction of their movement may not be the same as initially assumed for the model. Furthermore, as was pointed out by Swalin<sup>(9)</sup> for alloy diffusion, the migrating atom is compressed in an undefinable manner during the migration process and its energy of compression should be added to the energy required to compress the atoms adjacent to the path of migration. To avoid the difficulty of assigning positions to the atoms surrounding a vacancy, of fixing the direction of their movement, and of distributing the strain energy among all the processes contributing to the vacancy migration, a more general model may be used in which the individual



atomic movements are not defined. The only assumptions necessary are that atoms, already displaced from their lattice sites, move in a spherically symmetric potential about the mean relaxed rest positions of the atoms and that the diffusion process in all metals of a given crystal structure is the same.

When an atom and a vacancy exchange positions, or when a group of atoms coordinate their motions to allow a vacancy to migrate, the individual bonds are compressed or extended. The energy of compression is

$$E_c = - \int P dV.$$

Expressing  $P$  in terms of the bulk modulus  $B_s$

$$dP = -B_s / V dV$$

or 
$$P = -B_s \ln V/V_0,$$

we obtain upon integration

$$E_c = V_0 B_s [V_f/V_0 \ln V_f/V_0 + 1 - V_f/V_0]. \quad (1)$$

Here  $V_0$  is a generalized initial volume of all the atoms involved in a particular vacancy migration and  $V_f$  is a generalized volume of the same atoms at the time of maximum distortion. The ratio of  $V_f/V_0$  should simply reflect the local change in volume necessary to move an atom through the position of maximum distortion in the diffusion process. This ratio should be essentially a function of the crystal geometry and should be constant for a given crystal structure type. Thus we can write

$$Q_m = E_c = K_2 V_0 B_s. \quad (2)$$

The proportionality constant  $K_2$  is dependent upon crystal structure and is adjusted so that  $V_0$  is now the atomic volume.

Another expression for  $Q_m$  can be obtained from a correlation with  $T_m$ . An atomic model based on the concept of localized melting as first proposed by Nachtrieb and Handler<sup>(3)</sup> may be used to explain the correlation. Atoms in the liquid state possess very little resistance to shear, hence it may be assumed that in a solid the activation energy for movement  $Q_m$  is equal to the energy which must be imparted to the exchanging atoms to make their total energy equal to that of atoms in the liquid. This energy is proportional to  $L_f$ .

Since we argue that  $Q_m$  should be proportional both to  $V_0 B_s$  and to  $T_m$ , we should demonstrate a proportionality between values of  $V_0 B_s$  and of  $T_m$ . We can do so by means of the following arguments.

According to Debye,<sup>(10)</sup>  $\mu_T$ , the average displacement of an atom from its rest position is related to the temperature by the following formula:

$$\mu_T^2 = \frac{6}{4\pi^2} \frac{h^2 T}{MK_B \Theta_D^2} [\phi(y) + y/4].$$

Here  $M$  is the atomic mass,  $K_B$  = Boltzmann's constant,  $\Theta_D$  the Debye temperature,  $\phi(y)$  the Debye integral, and  $y = \Theta_D/T$ . At temperatures above the Debye temperature  $[\phi(y) + y/4]$  is very nearly one. Furthermore, according to Lindemann<sup>(11)</sup> the ratio of  $\overline{u_T^2}/r_0^2$  ( $r_0$  = atomic radius) is nearly constant at the melting temperature for all metals, although the proportionality constant depends slightly on the structural type.

Over a moderate temperature range the Einstein characteristic temperature  $\Theta_E$  may be taken proportional to the mean frequency of vibration or

$$\Theta_E = \frac{h}{K} \int v^3 dv / \int v^2 dv = 3/4 \Theta_D.$$

Einstein<sup>(12)</sup> was the first to relate the compressibility,  $X$ , of a solid to the characteristic temperature of the atoms by the formula:

$$\Theta_E = \frac{1}{M^{1/3} \rho^{1/6} X^{1/2}}$$

$\rho$  is the atomic density. Combining these equations and assuming Lindemann's equation we obtain

$$\frac{Mr_0^2}{M^{2/3} \rho^{1/3} X} \propto T_m$$

or  $B_s V_0 \propto T_m$ .

For isotropic cubic systems  $1/\mu$  is proportional to  $B_s$  and thus LeClaire's and Buffington and Cohen's equation for  $Q_m$  are shown to be equivalent in special cases to the thermodynamic equation. The above result was first shown by Leibfried<sup>(13)</sup> in a slightly more elaborate manner.

### 3. RELATIONSHIP BETWEEN $Q_m$ , $Q_v$ , and $Q_D$

The entire expression for the activation energy of diffusion can now be written as

$$Q_D = k_2 V_0 B_s + k_1 L_s \quad (3a)$$

and  $Q_D = k_2 T_m + k_1 L_s$  . (3b)

In order to determine  $k_1$ ,  $k_2$ , and  $k_2^I$  independent measurements of  $Q_v$  and  $Q_m$  should be used. The best available experimental values are listed in Table I. From the ratio of the experimental values of  $Q_v/L_s$  a mean value of 0.27 is found for face-centered cubic (FCC) and hexagonal close-packed (HCP) elements treated as one class; and the same value is found for the body-centered cubic (BCC) elements. For the FCC elements  $k_2^I$  was evaluated from the experimental values of  $Q_m/T_m$  and a mean value of 16.0 was found. As no experimental values for  $Q_m$  in BCC elements were available,  $k_2^I$  for these elements was evaluated from the experimental values of  $(Q_D - 0.27 L_s)/T_m$ . A mean value of 14.7 was obtained. Similarly, the experimental values of  $(Q_D - 0.27 L_s)/B_s V_o$  were used to determine  $k_2$  for FCC(HCP) and BCC elements, and mean values of 22.6 and 23.8 were found, respectively, with  $V_o$  taken as the atomic volume expressed in units  $\text{cm}^3/\text{mole}$  and  $B_s$  in  $\text{kg}/\text{cm}^2 \times 10^{-7}$ . The final equations for the activation energies for formation and movement of vacancies may now be written as

$$Q_v = 0.27 L_s \quad (4a)$$

$$\text{FCC(HCP)} \quad Q_m = 16.0 T_m \quad (4b)$$

$$\text{BCC} \quad Q_m = 14.7 T_m \quad (4c)$$

The equations for the activation energy for diffusion are:

$$\text{FCC(HCP)} \quad Q_D = 16.0 T_m + 0.27 L_s \quad (5a)$$

$$\text{BCC} \quad Q_D = 14.7 T_m + 0.27 L_s \quad (5b)$$

$$\text{FCC(HCP)} \quad Q_D = 22.6 B_s V_o + 0.27 L_s \quad (6a)$$

$$\text{BCC} \quad Q_D = 23.8 B_s V_o + 0.27 L_s \quad (6b)$$

Table I. Comparison of experimental and calculated values of  $Q_v$  and  $Q_m$  (all values in kcal)

Element	$Q_v$ experimental	$Q_v$ Eq. 4a	$Q_m$ experimental	$Q_m$ Eq. 4b
Li	9.4 <sup>a</sup>	9.6		
Na	9.2 <sup>b</sup> 6.0 <sup>c</sup> 4.6 <sup>d</sup> }	6.5		
K	9.2 <sup>b</sup> 9.0 <sup>a</sup> 5.5 <sup>c</sup> }	5.4		
Al	17.5 <sup>e</sup>	19.4	15.0 <sup>f</sup>	14.9
Cu	21.9 <sup>g</sup>	20.2	24.9 <sup>h</sup>	21.7
Ag	24.4 <sup>i</sup> 25.1 <sup>j</sup> }	17.1	20.3 <sup>h</sup>	19.7
Au	23.5 <sup>k</sup>	21.8	19.1 <sup>h</sup>	21.4
Pt	32.6 <sup>l</sup>	33.3	31.2 <sup>l</sup>	32.7

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### 3. DISCUSSION OF RESULTS

Table I shows the experimental data for  $Q_m$  and  $Q_v$  and compares these values with those calculated from Eqs. 4a and 4b. Table II compares the values of  $Q_D$  calculated from Eqs. 5 and 6 with the experimental values. Overall agreement is good. For BCC metals, the model based on compressibilities gives better agreement with experimental values than does the local melting model. But for FCC and HCP metals the values calculated from the local melting model give the better overall agreement. In particular, the agreement of the local melting model is much better for gold and platinum.

The most serious discrepancy between predicted and experimental values of  $Q_D$  is found for zirconium. However, the reported experimental values of  $Q_D$  for both modifications of zirconium are so low compared to values for related metals that it seems inconceivable that the observed self-diffusion in zirconium can take place by the same mechanism that operates for most transition metals, and no single correlation theory is likely to be satisfactory for zirconium and the remainder of the metals discussed in the paper.

Our expression for the activation energy of diffusion is similar in concept to that proposed by LeClaire, but our two alternate expressions for  $Q_m$  appear to have advantages over that which he developed. They can be used without the necessity for assumption of a definite mechanism of slip which is required in application of his expression. Furthermore, as will be demonstrated in a second paper, they can be readily adapted to describe diffusion in substitutional alloys.

Table II. Comparison of experimental and calculated values of  $Q_D$   
(all values in kcal)

Element	$Q_D$ experimental	$Q_D$ (bulk modulus) Eq. 6	$Q_D$ (melting temp.) Eq. 5
Li (BCC)	13.2 <sup>a</sup>	14.0	17.0
Na	10.5 <sup>b</sup>	10.6	12.4
K	9.1 <sup>c</sup>	8.8	10.7
Cr	53.0 <sup>d</sup>	54.3	57.5
$\alpha$ Fe	59.2 <sup>e</sup>	55.5	53.4
Nb	105.0 <sup>f</sup>	93.1	88.3
Ta	110.0 <sup>g</sup>	104.7	98.1
W	120.5 <sup>h</sup>	122.5	105.3
$\beta$ Tl	20.0 <sup>i</sup>	23.5	20.1
$\beta$ Zr	27.0 <sup>j</sup>	70.6	70.7
Mg (FCC HCP)	32.0 <sup>k</sup>	20.3	24.0
Al	32.3 <sup>l</sup>	37.7	35.8
$\gamma$ Fe	64.5 <sup>e</sup>	54.0	55.9
$\beta$ Co	62.0 <sup>m</sup>	55.0	55.7
Ni	66.8 <sup>n</sup>	56.3	54.9
Cu	48.1 <sup>o</sup>	44.0	43.6
Zn	22.7 <sup>p</sup>	20.7	19.5
Ag	44.1 <sup>q</sup>	42.0	38.2
Cd	18.6 <sup>r</sup>	20.3	16.7
In	17.9 <sup>s</sup>	19.6	22.3
Pt	68.0 <sup>t</sup>	93.3	69.1
Au	41.7 <sup>u</sup>	62.7	44.3
$\alpha$ Tl	22.8 <sup>i</sup>	22.9	20.9
Pb	24.2 <sup>v</sup>	30.0	22.2
$\alpha$ Zr	22.0 <sup>j</sup>	68.8	73.4

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We conclude that the correlation developed here for self-diffusion in metals gives better agreement with experimental values of  $Q_D$  than does any other of which we are aware except for the correlation of Sherby and Simnad which gives comparable results. Our approach appears to have two significant advantages for theoretical applications over that of Sherby and Simnad: First, the two terms of our expression for  $Q_D$  can be identified directly with the heats for formation and movement of vacancies. Second, two characteristic parameters for each metal that is used in prediction of  $Q_D$  are both directly measurable and readily available quantities, while one of the parameters used in the Sherby and Simnad approach, the valence, is an inferred quantity with values for many metals that are subject to debate.

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