PHYSICAL REVIEW B VOLUME 24, NUMBER 6 15 SEPTEMBER 1981

Calculation of diffusion coefficients at any temperature and pressure from a single measurement. II. Heterodiffusion

K. Alexopoulos and P. Varotsos
Department of Physics, University of Athens, Solonos Str. 104, Athens 144, Greece

(Received 11 August 1980)

In a former paper [Phys. Rev. B 22, 3130 (1980)] the authors developed a method that allowed the prediction of self-diffusion coefficients at any temperature and pressure from a single diffusion measurement and from the values of the expansivity and the isothermal bulk modulus. In this paper the study is extended to heterodiffusion. Applications are presented for carbon diffusing in α-iron, antimony diffusing in copper, and zirconium diffusing in niobium. Furthermore, from a single diffusion measurement the activation enthalpy for various temperatures can be succesfully calculated.

In a recent paper[1] a method was developed that allowed the prediction of the self-diffusion coefficient at any temperature and pressure from a single diffusion measurement and from the values of the isothermal bulk modulus B and the thermal volume-expansion coefficient β. In this paper heterodiffusion is studied on the same ground. The method is based on the expression[2]

$$g = cB\Omega \tag{1}$$

for the activation Gibbs energy g of a defect; Ω is the mean volume per atom and c is a constant independent of temperature and pressure. By applying Eq. (1) the diffusion coefficient for cubic crystals can be written

$$D = fa^2\nu \exp\left[-\frac{cB\Omega}{kT}\right] , \tag{2}$$

where f is a numerical constant depending on the diffusion mechanism and the structure, a is the lattice constant, and ν for a given matrix and mechanism depends roughly on the mass of the diffusant. Once the diffusion coefficient D_1 is known for a single temperature T_1 the value of c can be determined from

$$c = -\frac{kT_1}{B_1\Omega_1}\ln\frac{D_1}{fa_1^2\nu_1} , \tag{3}$$

where the subscript 1 denotes the value of each quantity measured for $T = T_1$. Equation (2) then allows the prediction of the diffusion coefficient at any temperature. Of course, the values for a, ν, B, and Ω appropriate to each temperature have to be known.

In the application of the above-mentioned method a difficulty arises about the appropriate value of ν which has to be inserted into Eq. (3) in order to obtain the correct value of c. Owing to the lack of better information one can assume roughly that[3] ν is related to the Debye frequency ν_D of the matrix material (m) by [3]

$$\frac{\nu}{\nu_D} = \left[\frac{m_m}{m_i}\right]^{1/2} , \tag{4}$$

where m_m and m_i denote the mass of the matrix (m) and the diffusant (i), respectively. This is a relation that could give with some accuracy only the ratio ν_i/ν_j of the attempt frequencies of two diffusants (i and j) activated with the same mechanism in the same matrix. The value of ν directly given by Eq. (4) may be in error even by a factor of 10. This last inaccuracy reflects, of course, an error in the determination of c. However, in the ususal cases where a D_1 value differs from $a^2\nu_D$ by several orders of magnitude the error in c introduced by the inaccuracy of ν is of the order of a few percent. The method is applied below for carbon diffusing in α-Fe, for Sb diffusing in Cu, and for Zr diffusing in Nb.

Note that once c has been determined from a single measurement the enthalpy h can be directly computed for any temperature from the relation

$$h = c\left[B - T\beta B - T\frac{\partial B}{\partial T}\bigg|_P\right]\Omega , \tag{5}$$

which results form the thermoldynamical equation $h = g - T(\partial g/\partial T)|_P$ by inserting Eq. (1).

One point should be further noted. When applying Eq. (3) for two atoms (i and j) diffusing in the same matrix the values of c resulting in this way are quite different; this is due not only to the different values of ν for the two atoms but mainly due to the different values of D_1 (because, for the same temperature T, the diffusion coefficients of the two diffusants may differ by orders of magnitude). Therefore Eq. (2) cannot give the same value of the ratio $D_i/D_j = (m_j/m_i)^{1/2}$ for each temperature.

Carbon in α-Fe. Dever[4] has measured the adiabatic (B^s) bulk modulus in the region 298 – 1173 K. By using the known lattice constants[5] and specific-heat data[5] one converts B^s to B in the standard thermodynamical manner. The resulting B values are given in Table I along with those of ν_D extracted from the paper of Killean and Lisher.[6] We see that the temperature variation of ν_D is small and therefore could be disregarded in view of the other uncertainties introduced in our calculation.

The determination of c is done at the lowest temperature ($T = 234$ K) at which D has been reported. By inserting the appropriate data (for $T = 234$ K) into Eq. (4) and then into Eq. (3) one gets $c = 0.066\,97$. Note that we have assumed that diffusion proceeds by interstitials in octahedral sites, and hence f has been set equal to $\frac{1}{6}$; furthermore, calculation shows that a plausible inacuracy of the value of $fa_1^2\nu_1$ by a factor of 5 results in an error of $\sim 4\%$ in the value of c. By inserting the above value of c into Eq. (2) and using the appropriate data of B, Ω, and ν_D for each temperature we get the values labeled by D_{calc}. The error bars given in the low-temperature range correspond to the uncertainty of c (4%) while the values of B and Ω are assumed without any experimental error. A comparison of the predicted values D_{calc} with the experimental results[7,8] indicates satisfactory agreement if one considers the error bars. Notice that the D value 2.13×10^{-6} predicted for $T = 1058$ K differs by $\sim$ 15 orders of magnitude from the value[7] $D_1 = 5.7 \times 10^{-21}\text{cm}^2/\text{sec}$ for $T_1 = 234$ K.

We proceed to the calculation of the value of the activation enthalpy from Eq. (5). A least-squares fitting to a straight line of the B values close to 234 K gives $(dB/dT)|_P = -0.41$ kbar/K whereas $\beta = 33.6 \times 10^{-6}\ \text{K}^{-1}$ for $T = 234$ K. By inserting these data into Eq. (5) we get $h^{\text{act}} = 0.863$ eV with a plausible uncertainty of at least 4% due mainly to the inaccuracy of c. This value of h compares favorably with the experimental values 0.86 eV (Ref. 4) or 0.81 eV (Ref. 8) quoted for the same temperature range. It is easy to verify that Eq. (5) predicts a value of h that increases with temperature. In order to realize the extent of this increase we repeat its calculation at the other end of the scale, i.e., at $T = 1058$ K. A least-squares fitting to a straight line of the B values[4] between 973 and 1043 K indicates that $(dB/dT)|_P = -0.624$ kbar/K. Accepting this value as appropriate for $T = 1058$ K and considering that, for this temperature, $\beta = 54.9 \times 10^{-6}\ \text{K}^{-1}$, Eq. (5) gives $h^{\text{act}} = 0.988$ eV with an uncertainty of, at least, 4% as mentioned above. This value agrees favorably with the experimental value of 0.97 eV obtained from Silva and McLellan's paper.[8]

Diffusion of Sb into Cu. In Table II we give the experimental D values of Sb diffusing in copper

TABLE I. Calculated and experimental diffusion coefficient of C in Fe.

T (K)	ν_D[a] (10^{12} sec^{-1})	B[b] (kbar)	Ω[c] (Å^3)	D_{calc} (cm^2/sec)	D_{expt}[d] (cm^2/sec)	D_{expt}[e] (cm^2/sec)	h_{calc} (eV)	h_{expt} (eV)
233.9	9.79	1672	11.75	5.70×10^{-21}	5.70×10^{-21}	5.56×10^{-21}	0.863	0.86,[d] 0.18[e]
298	9.72	1647	11.78	$5.24^{+12.5}_{-3.76} \times 10^{-17}$	2.2×10^{-17}	3.2×10^{-17}		
373	9.63	1614	11.81	$4.86^{+7.8}_{-3.1} \times 10^{-14}$	1.8×10^{-14}	2.1×10^{-14}		
573	9.41	1537	11.88	$5.35^{+4.4}_{-2.5} \times 10^{-10}$	4.2×10^{-10}	3.24×10^{-10}		
873	9.06	1390	12.05	2.46×10^{-7}	2×10^{-7}	2.24×10^{-7}		
993	8.92	1322	12.13	1.06×10^{-6}	5.3×10^{-7}	1.05×10^{-6}		
1043	8.86	1277	12.17	1.96×10^{-6}	2.5×10^{-6}	1.81×10^{-6}		
1058	8.84	1275	12.18	2.13×10^{-6}	1.76×10^{-6}	2.11×10^{-6}	0.988	0.97[f]

[a] Reference 6.

[b] Reference 4; see text.

[c] Reference 5.

[d] Reference 7.

[e] Reference 8.

[f] From Eq. (1) of Ref. 8.

TABLE II. Calculated and experimental diffusion coefficient of Sb in Cu.

T (K)	a^{a} (Å)	Ω^{a} (Å^3)	B^{b} (kbar)	D_{calc} (cm^2/sec)	D_{expt} (cm^2/sec)	h_{calc} (eV)	h_{expt} (eV)
800	3.64869	12.1437	1202	1.16×10^{-12}	1.16×10^{-12}	$1.79\pm4\%$	1.82 ± 0.03
1000	3.66416	12.2988	1135	$2.12^{+0.84}_{-0.61}\times10^{-10}$	2.27×10^{-10}		
1200	3.68111	12.4703	1071	$6.59^{+2}_{-1.56}\times10^{-9}$	7.68×10^{-9}		
1300	3.69038	12.5647	1039	$2.47^{+0.66}_{-0.53}\times10^{-8}$	2.98×10^{-8}		

[a] R. O. Simmons and R. W. Balluffi, Phys. Rev. 129, 1533 (1963).

[b] Y. A. Chang and L. Himmel, J. Appl. Phys. 37, 3568 (1966); they report B^s values up to 800 K and from their values, we have made linear extrapolation. The conversion of B^s to B has been done with the help of C^p data reported by C. R. Brooks, J. Phys. Chem. Solids 29, 1377 (1968) and the expansivity data of Ref. a.

from 800 up to 1300 K as measured by Inman and Barr.[9] We determine c from the lowest temperature, i.e., from $T_1 = 800$ K. For this temperature we have $a = 3.648\,69$ Å, $\Omega = 12.1437$ Å^3, $B = 1202$ kbar, and $D_1 = 1.16\times10^{-12}$cm^2/sec; furthermore, we have $\nu_D = 6.52\times10^{12}$ sec^{-1} and by assuming diffusion via monovacancies we set $f = 0.78$. The insertion of these data into Eq. (3)—and consideration of Eq. (4)—leads to $c = 0.1676$. This value of c has two main sources of uncertainty, 2% due to an eventual experimental error of B and another due to the arbitrary selection of the frequency ν. An error in the estimation of ν by a factor of 5 leads to $\sim$ 7% variation of the resulting value of c. Once c has been determined, the D_{calc} value can be calculated, for any temperature, from Eq. (2). The values obtained in this way are given in Table II for a number of temperatures. For each temperature we state the uncertainty that results from a 2% variation of c (due to the experimental error of B). In spite of the fact that we have not considered any error resulting from a bad estimation of ν and further that D varies by 4 orders of magnitude we see that calculated values agree with the experimental ones within the error bars.

The calculation of the activation enthalpy h is now straightforward. By inserting into Eq. (5) the values $T = 800$ K, $(dB/dT)|_P = -0.33$ kbar/K, $B = 1202$ kbar, $\beta \simeq 6\times10^{-5}\,\text{K}^{-1}$, and $\Omega = 12.1437$ Å^3, one gets $h = 1.79$ eV which agrees well with the experimental value[9] 1.82 ± 0.03 eV. If one repeats the calculation of h at temperatures close to 1300 K a value higher by some percent is obtained; this relatively small change of h predicts a slight deviation from linearity in the diffusion plot. Hence if the measurements were either more numerous or extended to lower temperatures, an upward curvature should become detectable. Unfortunately the limited existing existing diffusion data do not permit any systematic study of the slight curvature predicted from the small increase of h with temperature.

Zirconium diffusing in niobium. The diffusion of Zr in Nb has been recently studied by Einziger and Mundy[10] for tempertures between 1900 and 2523 K. Their results are given in Table III. One should note that for each temperature (1900, 2068, 2391, and 2523 K) they give two values which differ by 18%, 30%, 47%, and 30%, respectively.

We determine c at the lowest temperature, i.e.,

TABLE III. Calculated and experimental diffusion coefficient of Zr in Nb.

T (K)	B (kbar)	Ω (Å^3)	D_{calc} (cm^2/sec)	D_{expt} (cm^2/sec)
1900	1395.52	18.56	$3.82-4.51\times10^{-11}$	$3.82-4.51\times10^{-11}$
2068	1364.84	18.776	$2.26^{+0.88}_{-0.65}\times10^{-10}$	$2.23-2.89\times10^{-10}$
2391	1305.86	18.955	$3.61^{+1.15}_{-0.9}\times10^{-9}$	$3.68-5.41\times10^{-9}$
2523	1281.76	19.034	$9.12^{+2.68}_{-2}\times10^{-9}$	$9.59-12.5\times10^{-9}$

$T_1 = 1900$ K, where Einziger and Mundy give $D_1 = 4.51 \times 10^{-11}$ or 3.82×10^{-11}cm^2/sec. The adiabatic bulk modulus B^s of niobium at high temperatures has been measured by Talmor, Walker, and Steineman[11]; we have extracted the B^s values from their Fig. 2 and corrected them in order to obtain the isothermal bulk modulus. The correction needed specific-heat data[6] and lattice constants.[6,12] In view of the lack of specific-heat and expansivity data for the higher temerature, the trend of C_p and β was extrapolated linearly. Of course, C_p and β should show, at very high T, a stronger upward increase, which means that the correction of B^s to B should be higher than those considered here. In other words, the actual B values should be slightly smaller than those used in our calculation. For the preexponential factor we use $f = 0.727$ and for the frequency ν α^a value that corresponds to $\Theta_D = 275$ K after correction with the help of Eq. (4). By inserting the appropriate data into Eq. (3), for $T_1 = 1900$ K, one gets $c = 0.1884$ or 0.1867 for $D_1 = 3.82$ or 4.51×10^{-11} cm^2/sec, respectively. By using Eq. (2) now, one calculates the values of D at higher temperatures. For the calculation we have used the mean value $c = 0.1875$ and the results are given in Table III. For each case we give the errors introduced by an uncertainty of 2% in the value of c. If one now recalls that possibly the B values used in our calculation are 0.5% to 1% higher than the actual ones, the calculated self-diffusion coefficients become slightly higher, thus giving better agreement with the experimental points.

The calculation of h for $T = 1900$ K through Eq. (5) can be made by using the values $\beta = 2.9 \times 10^{-5}$ K^{-1}, $B = 1395.5$ kbar, $\Omega = 18.56$ Å^3, and $(dB/dT)|_P \simeq -0.183$ kbar/K; furthermore, by using the two values of c mentioned above one finds $h = 3.61$ or 3.64 eV. These values are about 8% lower than the experimental value[10] of 3.93 eV; this small difference was expected because, for reasons explained above, the real absolute value of $(dB/dT)|_P$ is expected to be slightly higher than that used in our calculation so that Eq. (5) should give a slightly greater value of h. However, the above result lies within the uncertainties of our calculation because, as mentioned, the arbitrary selection of ν reflects errors to the value of c—and hence to h through Eq. (5)—of the order of some percent.

---

[1] P. Varotsos and K. Alexopoulos, Phys. Rev. B 22, 3130 (1980).

[2] P. Varotsos and K. Alexopoulos, Phys. Rev. B 24, 904 (1981); it contains a theoretical background for the validity of Eq. (1).

[3] D. L. Decker, R. A. Ross, W. E. Evenson, and H. B. Vanfleet, Phys. Rev. B 15, 507 (1977).

[4] D. J. Dever, J. Appl. Phys. 43, 3293 (1972).

[5] *Metals Handbook: Properties and Selection of Metals,* 8th ed., edited by Lydon Taylor (American Society for Metals, Cleveland, 1961), Vol. I.

[6] R. C. G. Killean and E. J. Lisher, J. Phys. C 8, 3510 (1975).

[7] A. E. Lord and D. N. Beshers, Acta Metall. 14, 1659 (1966).

[8] J. R. G. Silva and R. B. McLellan, Mater. Sci. Eng. 26, 83 (1976).

[9] M. C. Inman and L. W. Barr, Acta Metall. 8, 112 (1960)

[10] R. E. Einziger and J. N. Mundy, Phys. Rev. B 17, 449 (1978).

[11] Y. Talmor, E. Walker, and S. Steinemann, Solid State Commun. 23, 649 (1977).

[12] V. A. Petukhov, V. Ya. Chekhovskoi, and A. G. Mozgovoi, Teplofiz. Vys. Temp. 16, 421 (1978).