Calculated Isotope Effect for Diffusion in Solid Argon

J. J. BURTON
Henry Krumb School of Mines, Columbia University, New York, New York 10027
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The isotope effect was calculated for diffusion in solid argon using a formalism developed by Glyde. The computed values of ΔK are 0.99 for self-diffusion via a single-vacancy mechanism, 0.88 for self-diffusion via a divacancy mechanism, 0.999 for neon impurity diffusion via single vacancies, and 0.94 for krypton impurity diffusion via single vacancies. These calculated values are compared with experimental data and suggest that diffusion in solid argon may be via either a single-vacancy or divacancy mechanism; neither the calculations nor the experiments are sufficiently precise to establish the mechanism with certainty.

I. INTRODUCTION

The mass dependence of the diffusion coefficient is generally expressed as[1]

$$f\Delta K=\frac{D_\alpha/D_\beta-1}{(m_\beta/m_\alpha)^{1/2}-1}, \tag{1}$$

where D_α and D_β are the experimental diffusion coefficients in the same solvent of two tracers of different masses m, but of the same element. f is the correlation factor; it is determined by the diffusion mechanism and has been calculated from first principles.[2,3] ΔK is a correction term originally introduced by Mullen,[4] who related it to the kinetic energy of the diffusing atom. LeClaire[5] subsequently related ΔK to the formation volume of the diffusing defect. Glyde[6] has recently derived an expression for ΔK in terms of the relaxations of the lattice during the diffusion jump.

Experimentally, one wishes to determine $f\Delta K$ in order to obtain some clue to the diffusion mechanism. For instance, a value of 0.78 for $f\Delta K$ for self-diffusion in a face-centered-cubic material is a strong indication of a single-vacancy mechanism.[7] However, in general, knowledge of $f\Delta K$ does not uniquely establish the diffusion mechanism as ΔK is not known.

Parker *et al.*[8] recently measured the isotope effect for krypton diffusion in argon. They found

$$f\Delta K=0.48\pm0.25, \tag{2}$$

and interpreted this result as impurity diffusion via a single-vacancy mechanism with $\Delta K\sim0.6$ (f is 0.78 for single-vacancy self-diffusion[2] and has been estimated[8] to be about 0.8–0.9 for krypton diffusion in argon via a single-vacancy mechanism). This author[9] has recently pointed out that Parker's result, Eq. (2), may be interpreted as consistent with a divacancy diffusion mechanism. The self-diffusion mechanism in argon has been discussed recently elsewhere.[10]

In this paper, we use Glyde's expression[6] to calculate ΔK for self-diffusion via single vacancies and divacancies in argon and for neon and krypton impurity diffusion in argon via a single-vacancy mechanism. The calculated values of ΔK suggest that Parker's result,[8] Eq. (2), is consistent with either a single-vacancy or divacancy mechanism.

II. EXPRESSION FOR ΔK

ΔK may be written as[8]

$$\Delta K=\frac{(\Gamma_\alpha/\Gamma_\beta)-1}{(m_\beta/m_\alpha)^{1/2}-1}, \tag{3}$$

where $\Gamma_\alpha/\Gamma_\beta$ is the ratio of the jump rates of the tracer atoms. Glyde[8] used Vineyard's[11] formalism for the diffusion jump frequency and obtained

$$\Gamma_\alpha/\Gamma_\beta=(m_\beta/m_\alpha)^{1/2}\times\left[1+\frac{m_\alpha}{m_s}\sum_{i\neq1}^{n}\left(\frac{d_{ip}}{d_{1p}}\right)^2\right]^{1/2}\Big/\left[1+\frac{m_\beta}{m_s}\sum_{i\neq1}^{n}\left(\frac{d_{ip}}{d_{1p}}\right)^2\right]^{1/2}. \tag{4}$$

Here m_α and m_β are the masses of the tracer atoms, m_s is the mass of the solvent atoms, d_{ip} are the displacements of the solvent atoms in the diffusion direction during the jump process, and d_{1p} is the displacement of the jumping atom.

This expression for ΔK may be readily simplified. Let

$$g=\sum_{i\neq1}^{n}\left(\frac{d_{ip}}{d_{1p}}\right)^2 \tag{5}$$

and

$$m^*=m_\alpha/m_s. \tag{6}$$

Then, if $g\ll1$,

$$\Delta K=1-m^*g. \tag{7}$$

III. CALCULATION OF ΔK

ΔK is readily obtained if the lattice relaxations around the diffusing defect are known. These relaxations have been calculated during computations of diffusion activation energies. The basic procedure of these calculations is to search the atomic configuration space to find the minimum energy subject to some constraints, such as the existence of a vacancy, or the presence of an atom in a diffusion saddle point. These relaxation calculations are straightforward provided that the interatomic potential is known.

Relaxation calculations have been performed on

argon[12–14] using a Lennard-Jones potential to represent the atomic interactions. It is well known that this potential is not exact.[15–17] The relaxations for self-diffusion via a single-vacancy mechanism have been reported.[18] We have used these relaxations to compute g, Eq. (5). The results of this computation are in Table I. The computed g is quite small for single-vacancy self-diffusion because the distortions of the argon lattice are small. As a result, the value of ΔK computed from Eq. (7) is nearly 1 (see Table I). In addition, we have previously calculated the relaxations of the argon lattice during impurity diffusion via a single-vacancy mechanism and during divacancy self-diffusion.[18] No other authors have examined impurity or divacancy diffusion in argon. In the earlier work, the activation energies were published but the relaxations themselves were not, as the individual relaxations have no particular significance. We have used our unpublished relaxations to evaluate g, Eq. (5), and ΔK, Eq. (7). The calculated results are in Table I.

We have used the theoretical values of f for self-diffusion via a single-vacancy mechanism[2] and via a divacancy mechanism[3] and for krypton impurity diffusion in argon via single vacancies[8] to compute $f\Delta K$. These are also in Table I, as is Parker's[8] experimental result.

There are several sources of error in this calculation. Glyde's expression[6] for ΔK is based on a harmonic lattice. Anharmonic effects may significantly alter ΔK. Glyde's model also neglects local modes due to the mass defect of the heavy tracer; this may also affect ΔK. The distortions used in calculating ΔK were obtained for a static lattice[18] and might be somewhat different were dynamical effects considered. The distortions around a point defect are sensitive to the assumed potential function.[19] The Lennard-Jones pair potential is not exact for argon[15–17] and the distortions might be slightly different for a better potential.

TABLE I. Values of the Glyde displacement factor g [Eq. (5) in the text], ΔK, and $f\Delta K$ for diffusion in solid argon.

Tracer	Mechanism	g	ΔK	$f\Delta K$
Ar	Single vacancy	0.012	0.99	0.78
Ar	Divacancy	0.12	0.88	0.42
Kr	Single vacancy	0.032	0.94	0.75–0.85
Ne	Single vacancy	0.0025	0.999	
Kr	Experiment			0.48±0.25

IV. COMPARISON WITH EXPERIMENT

Parker[8] has measured $f\Delta K$ to be 0.48±0.25 for krypton diffusion in argon. He suggested that this result corresponds to a single-vacancy mechanism with $\Delta K \sim 0.6$. The present calculations indicate that $f\Delta K$ for krypton diffusion in solid argon should be in the range 0.75–0.85. The upper limit of the experimental work is compatible with this calculated result. We note, however, that the computed value of $f\Delta K$ for divacancy diffusion (Table I) is also consistent with the experimental data. The author[14] has suggested that the divacancy mechanism may be important in argon. The calculated values of $f\Delta K$ do not appear to be in conflict with this point of view, but they do not rule out the single-vacancy mechanism.

[1] N. L. Peterson, Solid State Phys. **22,** 409 (1968).
[2] K. Compaan and Y. Haven, Trans. Faraday Soc. **54,** 1498 (1958).
[3] R. E. Howard, Phys. Rev. **144,** 650 (1966).
[4] J. G. Mullen, Phys. Rev. **121,** 1649 (1961).
[5] A. D. LeClaire, Phil. Mag. **14,** 1271 (1966).
[6] H. R. Glyde, Phys. Rev. **180,** 722 (1969).
[7] N. L. Peterson, Phys. Rev. **136,** A568 (1964).
[8] E. H. C. Parker, B. L. Smith, and H. R. Glyde, Phys. Rev. **188,** 1371 (1969).
[9] J. J. Burton, Phys. Rev. B **2,** 3434 (1970).
[10] J. J. Burton, Comments Solid State Phys. (to be published).
[11] G. H. Vineyard, J. Phys. Chem. Solids **3,** 121 (1957).
[12] H. R. Glyde, Rev. Mod. Phys. **39,** 373 (1967).
[13] H. R. Glyde and J. A. Venables, J. Phys. Chem. Solids **29,** 1093 (1968).
[14] J. J. Burton, Phys. Rev. **182,** 885 (1969).
[15] A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. **41,** 429 (1964).
[16] J. H. Dymond and B. J. Alder, J. Chem. Phys. **51,** 309 (1969).
[17] J. J. Burton, Chem. Phys. Letters **5,** 312 (1970).
[18] J. J. Burton and G. Jura, J. Phys. Chem. Solids **28,** 705 (1967).
[19] J. J. Burton and G. Jura, J. Phys. Chem. Solids **27,** 961 (1966).