

Semiempirical Approach to the Theory of Thermal Diffusion in Crystals*

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The theory of thermal diffusion is developed by defining two isothermal systems: one at a temperature such that the jump frequency is equal to that in the direction along the temperature gradient in the non-isothermal system, and another at a temperature such that the jump frequency is equal to that in the direction against the gradient. The difference between these two defined temperatures, and the existing temperature gradient, are used to define a distance parameter x_0 . The flux equations in a temperature gradient are then developed in a formal way using x_0 as an expansion parameter for interstitial impurity diffusion, substitutional impurity diffusion by a vacancy mechanism for the two extreme cases of weak binding and tight binding of the vacancy-impurity complex, and for the flux of vacancies in pure metals. x_0 is interpreted in such a way that it defines the region in which the maximum energy is localized in the critical configuration for a jump, and is, therefore, a measure of the spatial distribution of activation energy. The analysis is applied to existing experimental data.

I. INTRODUCTION

ACCORDING to the macroscopic theory of irreversible processes, the flux of matter in any system depends on the temperature gradient as well as the concentration gradient.¹ Thus, when a temperature gradient is imposed on a multicomponent, homogeneous material, a segregation is expected in which some components migrate to hot regions while other components migrate to cold regions. This phenomenon, known as thermal diffusion or the Soret effect, has actually been observed in a number of crystalline systems. Experiments show that a temperature gradient in dilute solutions of carbon or nitrogen in iron results in a motion of the solute towards hot regions²⁻⁴ whereas hydrogen in iron⁴ and hydrogen in zirconium⁵ move toward cold regions. Experiments on impurity thermal diffusion in zinc show that indium and thallium move toward hot regions while silver moves toward cold regions.⁶ Furthermore, the separation factor for the impurity is greater in the direction parallel to the hexagonal axis than in the perpendicular direction for silver in zinc, whereas the reverse is true for thallium in zinc.⁶

It has been pointed out that point defects, such as vacancies, should also exhibit segregation in a temperature gradient.⁷⁻¹¹ If efficient sources and sinks for the defects are present, the migration of defects in a tem-

perature gradient should result in a marker motion similar to that observed in the Kirkendall effect. Thermal diffusion experiments on pure α -iron¹² and zinc,¹³ have failed to reveal any observable marker motion, but marker has been observed in copper and gold.¹⁴

It is clear that the existence of thermal diffusion in crystals implies that the frequency of atomic jumps across a plane is different in the direction of increasing temperature than in the direction of decreasing temperature. Microscopic theories have been proposed in which local temperatures have been assigned to lattice sites, and the jump frequency was assumed to have a value characteristic of an isothermal system at that temperature.^{7-12,14,15} An alternative approach is often used^{2,13,16} in which the activation energy is taken to be spatially distributed about the jumping atom. Thermal diffusion then depends on the details of the spatial distribution. Allnatt and Rice¹⁷ have treated thermal diffusion as a random walk problem in which the mean displacement does not vanish.¹⁸ They were successful in deriving a formal equation for thermal diffusion, but in relating this equation to the kinetics of the atomic jumps, they assumed that the jump frequency of a given atom is the same in both the directions of increasing and decreasing temperature. This amounts to taking the activation energy as concentrated in the plane separating the final and original position of the moving atom, and in this respect their treatment is closely related to those mentioned previously. The Allnatt-Rice treatment predicts that the heat of transport is always positive for interstitial-impurity diffusion, so that

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¹ S. R. DeGroot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951), Chap. VII.

² L. S. Darken and R. A. Oriani, *Acta Met.* **2**, 841 (1954).

³ P. Shewmon, *Acta Met.* **8**, 605 (1960).

⁴ O. D. Gonzalez (private communication) to R. A. Oriani, *J. Chem. Phys.* **34**, 1773 (1961).

⁵ J. M. Markowitz (private communication) to R. A. Oriani, *J. Chem. Phys.* **34**, 1773 (1961).

⁶ F. R. Winter and H. G. Drickamer, *J. Chem. Phys.* **24**, 492 (1956).

⁷ W. Shockley, *Phys. Rev.* **91**, 1563 (1953).

⁸ A. D. LeClaire, *Phys. Rev.* **93**, 344 (1954).

⁹ J. A. Brinkman, *Phys. Rev.* **93**, 344 (1954).

¹⁰ W. Shockley, *Phys. Rev.* **93**, 1389 (1954).

¹¹ R. W. Keyes, *Phys. Rev.* **94**, 1389 (1954).

¹² W. G. Brammer, *Acta Met.* **8**, 630 (1960).

¹³ P. Shewmon, *J. Chem. Phys.* **29**, 1032 (1958).

¹⁴ C. J. Meechan and G. W. Lehman, *J. Appl. Phys.* **33**, 634 (1962).

¹⁵ R. E. Howard and J. R. Manning, *J. Chem. Phys.* **36**, 910 (1961).

¹⁶ K. Wirtz, *Physik Z.* **44**, 221 (1943).

¹⁷ A. R. Allnatt and S. A. Rice, *J. Chem. Phys.* **33**, 573 (1960).

¹⁸ Their treatment is a simple variation of LeClaire's study of random walk in a concentration gradient. [A. D. LeClaire, *Phil. Mag.* **3**, 921 (1958)].

interstitial solutes should always migrate towards colder regions. This prediction is in direct disagreement with experiment.^{2,3}

Oriani¹⁹ has given a qualitative analysis of the problem of Soret diffusion in crystals and has concluded that the phenomenon may be understood in terms of a thermodynamic and a kinetic effect. For diffusion by a vacancy mechanism, the thermodynamic effect arises from the creation of a vacancy as the jumping atom leaves its normal position and jumps to an adjacent vacancy. Thus, the heat of transport contains a positive contribution, which is the energy needed to form the pseudovacancy as the diffusing atom jumps, and this contribution tends to drive atoms to colder regions. For interstitial diffusion, the thermodynamic effect arises simply from the thermal energy absorbed or released on removing a solute atom from its position in the crystal. The kinetic effect always arises from the redistribution of vibrational energy between the two sides of the flux plane as a result of the jump.

Oriani's analysis emphasizes the subtle and complex nature of the thermal diffusion problem. In order to arrive at a proper theory of the Soret effect a detailed study of the phonon distribution in nonisothermal crystals, and of the interaction of this distribution with the moving atoms is required. A rigorous program of this sort would encounter great difficulties, since it would require a coupling of the fundamental theories of heat conduction and atomic migration.

In this paper, a much simpler approach is proposed in which the actual jump frequency in a particular direction in a nonisothermal system is used to *define* a temperature that gives the jump frequency the same form it would have in an isothermal system. The jump frequencies along and against the temperature gradient are, therefore, compared to the jump frequencies in two isothermal systems whose temperatures differ by an amount ΔT_e . This temperature difference is then used to define a distance x_e in terms of the temperature gradient in the nonisothermal crystal. A kinetic formalism for thermal diffusion is then constructed containing x_e as a parameter, which represents the empirical content of the theory. x_e can be interpreted in terms of the critical configuration for the atomic jump and, therefore, can be used to extract detailed information about the jump process from thermal diffusion data. This approach also shows that there is no *a priori* reason to expect Soret migration to take place in a particular direction; the direction and magnitude of the Soret effect depends on the nature of the critical configuration of the jump process. The value of x_e also controls the value of the heat of transport, which, in the formalism given in this paper, may be positive, negative, or zero. The parameter x_e , therefore, also provides a link between the mechanism of diffusion and the heat of transport.

If x_e is interpreted as defining the point in the crystal which has the temperature appearing in the rate theory expression for the jump frequency, then the present method is equivalent to a generalization of Wirtz' theory.¹⁶ Wirtz assumes that the energy of activation is accumulated at three sites, the initial site, the saddle point, and the final site, and he assigns three energies and three temperatures to these sites. In the present theory, x_e merely defines the center of a general distribution of activation energy; however, contact can be made between x_e and the Wirtz assumptions, as will be shown later.

II. Soret Effect for Interstitial Solute Diffusion

The simplest example of the Soret effect in crystals is the migration of a dilute interstitial solute in a constant, one-dimensional temperature gradient. We, therefore, consider a system with a constant temperature gradient and a solute concentration gradient in the x direction and calculate the flux across a plane normal to the x axis. Proceeding in the usual way, we find that the flux is

$$J = \beta \lambda [N(L)\Gamma_+ - N(R)\Gamma_-], \quad (1)$$

where $N(L)$ is the solute concentration in the interstitial plane just to the left of the flux plane, $N(R)$ is the concentration in the plane to the right of the flux plane, Γ_+ is the atomic jump frequency from the plane on the left to the plane on the right, and Γ_- is the jump frequency from the plane on the right to the plane on the left. The flux plane is taken to be midway between the left and right interstitial planes. λ is the jump distance and β is a geometric factor.

Expanding $N(R)$ in powers of λ to the first order converts Eq. (1) to

$$J = \beta \lambda [N(L)(\Gamma_+ - \Gamma_-) - \lambda \Gamma_- (dN/dx)]. \quad (2)$$

It would not do to expand the jump frequencies in a similar manner because they involve atoms distributed over several atomic planes. Instead we introduce a formal device by *defining* two temperatures T_+ and T_- by the equations

$$\begin{aligned} \Gamma_+ &= \nu e^{-E_m/kT_+}, \\ \Gamma_- &= \nu e^{-E_m/kT_-}, \end{aligned} \quad (3)$$

where E_m is the energy of motion for diffusion and ν is an atomic frequency factor.²⁰ The significance of the temperatures T_+ and T_- can be understood by referring to Fig. 1. Following Oriani¹⁹ we construct a "coordination sphere" about the midpoint of the line connecting the original position of the jumping atom and the site into which it jumps. The coordination sphere contains all atoms whose motion has a sensible effect on the moving atom. The coordination sphere is sliced into slabs normal to the x direction. For any particular

¹⁹ R. A. Oriani, J. Chem. Phys. **34**, 1773 (1961).

²⁰ G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

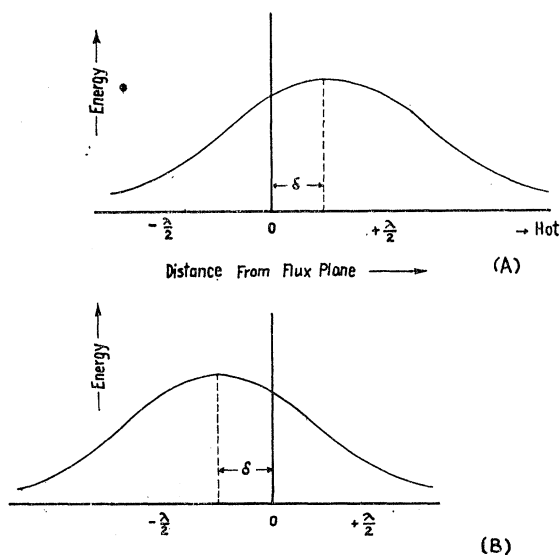


FIG. 1. Spatial energy distribution at the critical configuration for (A), a jump from the left-hand to the right-hand plane; and (B), a jump from the right-hand to the left-hand plane.

configuration, the energy content of each slab can be defined, and a plot of the energy as a function of distance can be constructed. A unique meaning can be given to this plot by considering a statistical ensemble of systems each in a critical configuration required for an atomic jump.¹⁹ For the present problem, we construct an energy plot in this manner for two cases: the critical configuration for an atomic jump from the left-hand plane to the right-hand plane, and the critical configuration for an atomic jump from the plane on the right to the plane on the left. The forms of these two plots are shown in Figs. 1(A) and 1(B), respectively. Since the jump is certain to occur once the critical configuration is reached, the probability of occurrence of this configuration determines the jump frequency.

In general, the maximum energy need not be at the flux plane (labeled O in Fig. 1). The flux plane is located in an atomic plane of the solvent, so that if the energy maximum is at the flux plane, the most important contribution to the critical configuration is an out-of-phase motion in which the solvent atoms open up and allow the solute to fall through to the new position. If the energy maximum is near the original site of the moving atom, the critical configuration corresponds to an accumulation of energy in the solute atom, which then punches its way through the shell of solute atoms at O . If the energy maximum is close to the final site of the moving atom, solute atoms beyond the final site are active in the critical configuration, perhaps by exerting attractive forces on the solute atom as the out of phase motion takes place. In Fig. 1(A), these possibilities are represented by different values of δ , the distance between the energy maximum and the flux plane. If $\delta < 0$, atoms to the left of $-\lambda/2$ impart a great

deal of energy to the solute atom which is pushed through the flux plane. If $\delta > 0$, atoms to the right of $\lambda/2$ exert an attractive force on the solute and pull it through the flux plane. In both cases, of course, the opening of the shell of solvent atoms must play a role, and the actual value of δ depends on the balance among the repulsion experienced by the solute atom from atoms on the left, the attraction from atoms on the right and the out of phase motions of the atoms at O . For $\delta = 0$, the repulsive and attractive contributions to the critical configuration are equally important. Certainly, it is a great simplification to describe this complex process by a single parameter δ , but such a description does lead to a fruitful interpretation of thermal diffusion experiments.

The qualitative interpretation of the temperature T_+ and T_- follow from this discussion in a natural way. Actually, what is important is the difference $\Delta T_c = T_+ - T_-$. If $\delta < 0$, then $\Gamma_+ < \Gamma_-$, since the probability of a jump in the forward direction is controlled by an energy fluctuation on the left of the flux plane, while a jump in the reverse direction is controlled by a fluctuation on the right of the flux plane. Since the left side is "cold" and the right side is "hot," jumps to the left are more frequent than jumps to the right. Thus, for $\delta < 0$, $\Delta T_c < 0$. Similarly for $\delta > 0$, $\Gamma_+ > \Gamma_-$ and $\Delta T_c > 0$, since jumps to the right are controlled by an energy fluctuation on the "hot" side, while jumps to the left are controlled by fluctuations on the cold side. If $\delta = 0$, we expect, of course, that $\Delta T_c = 0$, since then the jump frequency is determined by a fluctuation at the flux plane and is, therefore, the same for both directions. We now define a "critical configuration separation distance" x_c by

$$\Delta T_c = x_c dT/dx. \quad (4)$$

T_+ and T_- are the temperatures of two isothermal systems for which the jump frequencies are Γ_+ and Γ_- , respectively. A less rigorous, but more useful, interpretation is that T_+ and T_- are average temperatures of a coordination sphere centered on the energy maximum in the critical configuration energy plots for a forward and a reverse jump, respectively. In the spirit of this interpretation, we can identify x_c with 2δ . Although somewhat lacking in rigor, this procedure is at least qualitatively correct and x_c then becomes a very convenient parameter for interpreting the Soret effect in terms of atomic mechanisms.

Expanding Γ_+ in powers of ΔT_c to the first order and substituting into Eq. (2) gives

$$J = \beta \lambda \Gamma (x_c (E^m/kT^2) N (dT/dx) - \lambda dN/dx), \quad (5)$$

where we have dropped the subscripts of Γ and the arguments of N , and the quantities T , Γ , and N are interpreted in the usual macroscopic sense as averages over regions containing many atoms but small compared to the dimensions of the specimen. At equilibrium, $J = 0$, and integration of (5) then gives for the stationary

distribution

$$\ln\left(\frac{N}{N_0}\right) = \left(\frac{x_c}{\lambda}\right)\left(\frac{E_m}{k}\right)\left(\frac{T-T_0}{T_0T}\right), \quad (6)$$

where N and N_0 are concentrations at two temperatures T and T_0 . Comparison of these results with macroscopic theory (e.g., reference 17) shows that the heat of transport Q^* is given by

$$Q^* = -(x_c/\lambda)E_m. \quad (7)$$

This analysis shows that the heat of transport is closely related to the activation energy for motion, but is equal to it only when $x_c = -\lambda$; i.e., only when the energy of the critical configuration is centered on the original site of the moving atom. Equation (7) shows that Q^* can be positive, negative or zero, and its magnitude can be less than or greater than E_m depending on the detailed nature of the diffusion mechanism. Equation (6) shows that if $x_c = 0$ there is no preferential segregation of interstitial solutes in a temperature gradient. If $x_c < 0$, the solute collects in the colder regions while if $x_c > 0$, the solute migrates to the hot regions.

III. DIFFUSION BY A VACANCY MECHANISM—WEAK BINDING CASE

The qualitative substructure of the theory presented in the previous section is applicable to all diffusion mechanisms, but the quantitative form of the flux equation varies from one mechanism to another. We now consider thermal diffusion of a substitutional impurity by a vacancy mechanism for the special case of weak binding between a vacancy and an impurity atom. That is, the probability of finding a vacancy at a particular site is not affected by the presence of an impurity atom at an adjacent site. We now let $N(L)$ be the concentration of impurity atoms in the plane to the left of the flux plane and $N(R)$ be the concentration of impurity atoms in the plane to the right of the flux plane. Also, let $n_v(L)$ and $n_v(R)$ be the atomic fraction of vacancies in the plane to the left and the plane to the right, respectively. Then the flux across the plane midway between the left and right planes is

$$J = \beta\lambda[N(L)n_v(R)\Gamma_+ - N(R)n_v(L)\Gamma_-], \quad (8)$$

where Γ_+ and Γ_- are the jump frequencies for an impurity atom moving from the left to a vacancy on the right, and from the right to a vacancy on the left, respectively. Expanding $n_v(R)$ and $N(R)$ in powers of λ , the jump distance, to the first order gives

$$J = \beta\lambda[N(L)n_v(L)(\Gamma_+ - \Gamma_-) + N(L)\Gamma_-(dn_v/dx) - n_v(L)\lambda\Gamma_-(dN/dx)], \quad (9)$$

and expanding Γ_+ in powers of the critical configuration separation distance x_c gives

$$J = \beta\lambda\left(N(L)n_v(L)\Gamma_-x_c\frac{E_m}{kT^2}\frac{dT}{dx} + N(L)\Gamma_-\lambda\frac{dn_v}{dx} - n_v(L)\Gamma_-\lambda\frac{dN}{dx}\right), \quad (10)$$

where E_m is the energy of motion for the impurity atom jumping into a vacancy. At equilibrium, $J=0$ and (10) reduces to

$$\frac{d \ln(N/n_v)}{dx} = \frac{x_c}{\lambda} \frac{E_m}{kT^2} \frac{dT}{dx}. \quad (11)$$

If we assume that local equilibrium is established for the vacancies so that $n_v = c \exp(-E^f/kT)$ for all temperatures, where E^f is the energy of vacancy formation, Eq. (11) integrates to

$$\ln\left(\frac{N}{N_0}\right) = \frac{1}{k}\left(\frac{x_c}{\lambda}E_m + E^f\right)\left(\frac{T-T_0}{TT_0}\right), \quad (12)$$

N and N_0 being the impurity concentrations in two regions of the specimen at temperature T and T_0 . In this case we see that the direction and magnitude of the impurity migration does not depend merely on x_c , but also on the relative values of E_m and E^f .

The equations derived in this section are also valid for diffusion in ionic crystals with the sodium chloride structure if E^f is interpreted as one half the energy of formation of a Frenkel pair.

IV. DIFFUSION BY A VACANCY MECHANISM—TIGHT BINDING CASE

If the energy of interaction between a vacancy and a substitutional impurity atom is very high, the impurity atoms will all exist bound to vacancies, and diffusion will take place by motion of the atom-vacancy pair, provided the impurity concentration is small. The atom-vacancy pair can move by two elementary processes: the impurity atom can jump into the vacancy, or a solute atom that is a nearest neighbor to both the impurity atom and the vacancy can jump into the vacancy.

The flux equation for this case can be derived by a modification of the method of Lidiard²¹ which takes into account the asymmetry of the jump frequencies. With Lidiard, we choose an atomic plane at x as the flux plane and define three concentrations $N_a(x)$, $N_b(x)$, and $N_c(x)$ which are the concentration of impurity vacancy complexes for which the impurity atom is in the plane at x , and the vacancy is in the plane $(x+\lambda)$, x , and $(x-\lambda)$, respectively. The N_a , N_b , and N_c thus give the concentrations of the differently oriented complexes whose atom is in the flux plane. The flux is then

$$J = \frac{1}{2}\beta\lambda\Gamma_2^+(x)N_a(x) - \Gamma_2^-(x+2)N_c(x+\lambda) - \Gamma_2^-N_c(x) + \Gamma_2^+(x-\lambda)N_2(x-\lambda), \quad (13)$$

²¹ A. B. Lidiard, Phil. Mag. **46**, 1218 (1955).

where $\Gamma_2^+(x)$ is the jump frequency for an impurity atom at x jumping into a vacancy at $(x+\lambda)$ and $\Gamma_2^-(x)$ is the jump frequency for an impurity atom at x jumping into a vacancy at $(x-\lambda)$. We now calculate the time derivatives of N_a , N_b , and N_c , restricting ourselves to diffusion along a cubic axis in a face-centered cubic structure:

$$\dot{N}_a(x) = 2\Gamma_1^-(x+\lambda)N_b(x) + \Gamma_2^-(x+\lambda)N_c(x+\lambda) - \Gamma_2^+(x)N_a(x) - 2\Gamma_1^+(x)N_a(x), \quad (14)$$

$$\dot{N}_b(x) = 2\Gamma_1^+(x)N_a(x) + 2\Gamma_1^-(x)N_c(x) - 2\Gamma_1^-(x+\lambda)N_b(x) - 2\Gamma_1^+(x-\lambda)N_b(x), \quad (15)$$

$$\dot{N}_c(x) = 2\Gamma_1^+(x-\lambda)N_b(x) + \Gamma_2^+(x-\lambda)N_a(x-\lambda) - \Gamma_2^-(x)N_c(x) - 2\Gamma_1^-(x)N_c(x), \quad (16)$$

where $\Gamma_1^+(x)$ is the jump frequency for a solvent atom at x jumping into a vacancy at $(x+\lambda)$, and $\Gamma_1^-(x)$ is the jump frequency for a solvent atom at x jumping into a vacancy at $(x-\lambda)$. Equations (13)–(16) are identical to those of Lidiard except that we have taken care to distinguish between jumps in the forward and reverse directions. Now expand the concentrations about x to the first order in λ and the jump frequencies to the first order in the critical configuration separation distances.

$$\begin{aligned} N_c(x+\lambda) &= N_c(x) + \lambda dN_c/dx, \\ N_a(x-\lambda) &= N_a(x) - \lambda dN_c/dx; \end{aligned} \quad (17)$$

$$\begin{aligned} \Gamma_2^-(x+\lambda) &= \Gamma_2^-(x) [1 + (E_2^m/kT^2)x_c^{(2)}dT/dx], \\ \Gamma_2^-(x) &= \Gamma_2^-(x) [1 - (E_2^m/kT^2)(\lambda - x_c^{(2)})dT/dx], \\ \Gamma_2^+(x-\lambda) &= \Gamma_2^+(x) [1 - (E_2^m/kT^2)\lambda dT/dx], \\ \Gamma_1^-(x+\lambda) &= \Gamma_1^-(x) [1 + (E_1^m/kT^2)x_c^{(1)}dT/dx], \\ \Gamma_1^-(x) &= \Gamma_1^-(x) [1 - (E_1^m/kT^2)(\lambda - x_c^{(1)})dT/dx], \\ \Gamma_1^+(x-\lambda) &= \Gamma_1^+(x) [1 - (E_1^m/kT^2)\lambda dT/dx], \end{aligned} \quad (18)$$

where E_1^m and E_2^m are the activation energies for a solvent-vacancy interchange and a solute-vacancy interchange, respectively. $x_c^{(1)}$ and $x_c^{(2)}$ are the critical configuration separation distances for a solvent vacancy and a solute-vacancy interchange, respectively, defined as in Sec. II. Equations (18) are easily verified by drawing figures similar to Fig. 1 for each type of jump. Substitution of (17) and (18) into Eqs. (13)–(16) gives the result

$$\begin{aligned} J = \beta\lambda \left[\Gamma_2(N_a - N_c) - \frac{1}{2}\lambda\Gamma_2 \frac{d(N_a + N_c)}{dx} \right. \\ \left. + \frac{1}{2}\Gamma_2 \frac{E_2^m}{kT^2} \lambda (N_c - N_a) \frac{dT}{dx} \right], \end{aligned} \quad (19)$$

$$\begin{aligned} \dot{N}_a = 2\Gamma_1(N_b - N_a) + \Gamma_2(N_c - N_a) + \lambda\Gamma_2 \frac{dN_c}{dx} \\ + 2N_b\Gamma_1 x_c^{(1)} \frac{E_1^m}{kT^2} \frac{dT}{dx} + N_c\Gamma_2 x_c^{(2)} \frac{E_2^m}{kT^2} \frac{dT}{dx}, \end{aligned} \quad (20)$$

$$\begin{aligned} \dot{N}_b = 2\Gamma_1(N_a + N_c - 2N_b) \\ + 2\Gamma_1 \frac{E_1^m}{kT^2} (x_c^{(1)} - \lambda)(N_c - N_b) \frac{dT}{dx}, \end{aligned} \quad (21)$$

$$\begin{aligned} \dot{N}_c = 2\Gamma_1(N_b - N_c) + \Gamma_2(N_a - N_c) \\ + 2\Gamma_1 \frac{E_1^m}{kT^2} \frac{dT}{dx} [N_c(\lambda - x_c^{(1)}) - N_b\lambda] \\ + \Gamma_2 \frac{E_2^m}{kT^2} \frac{dT}{dx} [N_c(\lambda - x_c^{(2)}) - N_a\lambda] - \lambda\Gamma_2 \frac{dN_a}{dx}. \end{aligned} \quad (22)$$

In these equations, the $+$ superscript on the jump frequencies has been dropped for convenience.

The total impurity concentration N is given by

$$N = N_a + N_b + N_c, \quad (23)$$

and in the absence of any gradients,

$$N_a = N_b = N_c = \frac{1}{3}N, \quad (24)$$

since all orientations of the complex are equally probable. If we stay within the limits of the linear theory, then we can use (24) in all terms in which concentrations are multiplied by a temperature gradient. Also, when (19)–(22) are used to derive a flux equation for the total concentration, the only time derivative that appears in the final equation is $(\dot{N}_a - \dot{N}_c)$. Since N_a and N_c differ only through gradients, this term represents a time derivative of gradients and can be neglected if the system is not too far from steady state.²¹ The algebra is considerably simplified if we take advantage of these approximations at this point by using (24) in all terms containing the temperature gradient and taking $\dot{N}_a = \dot{N}_b = \dot{N}_c = 0$. Then Eqs. (19) to (22) become

$$J = \beta\lambda \left[\Gamma_2(N_a - N_c) - \frac{\lambda\Gamma_2}{2} \frac{d(N_a + N_c)}{dx} \right], \quad (25)$$

$$\begin{aligned} 2\Gamma_1(N_b - N_a) + \Gamma_2(N_c - N_a) + \lambda\Gamma_2 \frac{dN_c}{dx} \\ + \frac{N}{3} \frac{dT}{dx} \frac{1}{kT^2} [2\Gamma_1 E_1^m x_c^{(1)} + \Gamma_2 E_2^m x_c^{(2)}] = 0, \end{aligned} \quad (26)$$

$$N_a + N_c - 2N_b = 0, \quad (27)$$

$$\begin{aligned} 2\Gamma_1(N_b - N_c) + \Gamma_2(N_a - N_c) \\ - \frac{1}{3} \frac{dT}{dx} \frac{N}{kT^2} [2\Gamma_1 E_1^m x_c^{(1)} + \Gamma_2 E_2^m x_c^{(2)}]. \end{aligned} \quad (28)$$

Subtracting (28) from (26) and solving for $(N_c - N_a)$ gives

$$N_c - N_a = \frac{\lambda \Gamma_2}{2(\Gamma_1 + \Gamma_2)} \frac{d(N_a + N_c)}{dx} - \frac{N}{3(\Gamma_1 + \Gamma_2)} \frac{dT}{dx} [2\Gamma_1 E_1^m x_c^{(1)} + \Gamma_2 E_2^m x_c^{(2)}] \frac{1}{kT^2}. \quad (29)$$

Also, from (27) and (23)

$$N_a + N_c = \frac{2}{3}N. \quad (30)$$

Substituting (29) and (30) into (25) gives

$$J = -\frac{\beta \lambda^2}{3} \frac{\Gamma_1 \Gamma_2}{(\Gamma_1 + \Gamma_2)} \frac{dN}{dx} + \frac{\beta \lambda \Gamma_2 N}{3(\Gamma_1 + \Gamma_2)} \frac{dT}{dx} [2\Gamma_1 E_1^m x_c^{(1)} + \Gamma_2 E_2^m x_c^{(2)}] \frac{1}{kT^2}. \quad (31)$$

This is the flux equation for tightly bound impurity-vacancy complexes in a face-centered cubic crystal. It is identical to Lidiard's Eq. 3.8,²¹ except for the second term, which comes about because of the temperature gradient. If we write D for the ordinary diffusion coefficient and D_T for the thermal diffusion coefficient, so that

$$J = -D dN/dx - D_T dT/dx, \quad (32)$$

then

$$D = \frac{\beta \lambda^2}{3} \frac{\Gamma_1 \Gamma_2}{(\Gamma_1 + \Gamma_2)}, \quad (33)$$

and

$$D_T = -(DN/\lambda) [2E_1^m x_c^{(1)} + (\Gamma_2/\Gamma_1) E_2^m x_c^{(2)}] (1/kT^2). \quad (34)$$

These equations are also correct for body-centered cubic crystals, and for hexagonal crystals when the diffusion takes place in a direction perpendicular to the c axis. For diffusion parallel to the c axis of a hexagonal crystal, however, a solvent-vacancy interchange can take place in three ways on each side of the flux plane, and (33) and (34) must be replaced by

$$D_{11} = 2/9 \beta \lambda^2 [\Gamma_1 \Gamma_2 / (\Gamma_1 + \Gamma_2)], \quad (35)$$

$$D_T^{11} = -\frac{2}{3} (D_{11} N / \lambda) \times [3E_1^m x_c^{(1)} + (\Gamma_2/\Gamma_1) E_2^m x_c^{(2)}] (1/kT^2). \quad (36)$$

Integrating (32) for the case of zero flux gives, for the equilibrium distribution of tightly bound complexes in a temperature gradient,

$$\ln \frac{N}{N_0} = \frac{2x_c^{(1)}}{\lambda} \frac{E_1^m}{k} \left(\frac{T - T_0}{TT_0} \right) + \frac{x_c^{(2)}}{\lambda} \frac{E_2^m}{\Delta E} \frac{\nu_2}{\nu_1} (e^{\Delta E/kT} - e^{\Delta E/kT_0}), \quad (37)$$

where $\Delta E = E_1^m - E_2^m$ and ν_2 and ν_1 are the vibration frequencies in the jump frequency equations

$$\Gamma_1 = \nu_1 e^{-E_1^m/kT}, \quad \Gamma_2 = \nu_2 e^{-E_2^m/kT}. \quad (38)$$

Equation (37) is valid for diffusion in face-centered, body-centered, and hexagonal crystals in which diffusion is perpendicular to the c direction. For diffusion parallel to the c direction,

$$\ln \frac{N}{N_0} = \frac{3x_c^{(1)}}{\lambda} \frac{E_1^m}{k} \left(\frac{T - T_0}{TT_0} \right) + \frac{3}{2} \frac{E_{2m}}{\Delta E} \frac{\nu_2}{\nu_1} (e^{\Delta E/kT} - e^{\Delta E/kT_0}). \quad (39)$$

V. FLUX OF VACANCIES IN PURE METALS

We now calculate the flux of vacancies in a pure metal having a one dimensional temperature gradient. If $N_v(L)$ is the vacancy concentration just to the right, then the flux is

$$J_v = \beta \lambda (N_v(L) \Gamma_- - N_v(R) \Gamma_+), \quad (40)$$

where Γ_- is the jump frequency for an atom to the right of the flux plane moving into a vacancy to the left, while Γ_+ is the jump frequency for an atom moving from the left into a vacancy on the right. Expanding $N(R)$ to the first order in λ , and Γ_+ to the first order in x_c , gives

$$J_v = -\beta \lambda^2 \Gamma \frac{dN_v}{dx} - \beta \lambda x_c \frac{E^m}{kT^2} \Gamma \frac{dT}{dx} N_v. \quad (41)$$

If the crystal is free of sources and sinks, an equilibrium is eventually established for which $J=0$, and integration of (41) then gives for the vacancy distribution

$$\ln(N_v/N_v^0) = (x_c/\lambda) (E^m/k) [(T - T_0)/TT_0]. \quad (42)$$

If the crystal contains large numbers of efficient sources and sinks, so that the vacancies are in local thermodynamic equilibrium, then since $N_v \propto e^{-E^f/kT}$, where E^f is the formation energy for a vacancy,

$$dN_v/dx = N_v (E^f/kT^2) (dT/dx), \quad (43)$$

and the flux becomes

$$J_v = -\beta \lambda N_v (1/kT^2) (x_c E^m + \lambda E^f) (dT/dx), \quad (44)$$

so that zero vacancy flux cannot be established unless $x_c = -\lambda E^f/E^m$.

VI. CONNECTION WITH THE THEORY OF WIRTZ

The theory of Wirtz¹⁶ states that the jump frequency in the forward direction is given by

$$\Gamma_+ = \nu \exp[-(1/k)(E_1/T_1 + E_2/T_2 + E_3/T_3)], \quad (45)$$

where E_1 , E_2 , and E_3 are the parts of the activation energy accumulated at the initial site, the saddle point, and the final site during a diffusive jump. T_1 , T_2 , and T_3 are the temperatures at the initial site, saddle point, and final site, respectively. The sum of the energies is the energy of motion,

$$E^m = E_1 + E_2 + E_3, \quad (46)$$

and the temperatures are related, to the first order, by

$$\begin{aligned} T_3 &= T_2 + \frac{1}{2}\lambda dT/dx, \\ T_1 &= T_2 - \frac{1}{2}\lambda dT/dx. \end{aligned} \quad (47)$$

We now establish a connection between x_c and the theory of Wirtz by requiring that Γ_+ defined by Eq. (3) must be equal to Γ_+ defined by Eq. (45), i.e., the Wirtz assumptions are incorporated in the present theory. The temperature T_+ in Eq. (3) is related to T_2 by the first-order relation,

$$T_+ = T_2 + \frac{1}{2}x_c dT/dx. \quad (48)$$

Equating (3) and (45), and using (47) and (48) gives

$$\begin{aligned} E_m \left(1 + \frac{x_c}{2T_2} \frac{dT}{dx}\right)^{-1} &= E_1 \left(1 - \frac{\lambda}{2T_2} \frac{dT}{dx}\right)^{-1} + E_2 \\ &+ E_3 \left(1 + \frac{\lambda}{2T_2} \frac{dT}{dx}\right)^{-1}. \end{aligned} \quad (49)$$

Expanding the parentheses in (49) to the first order, making use of (46) and solving for x_c/λ gives

$$x_c/\lambda = (E_3 - E_1)/E_m. \quad (50)$$

Equation (50) shows that, within the limits of the Wirtz theory, x_c/λ can only take values between ± 1 . If $x_c/\lambda < 0$, then the energy of the moving atom is the more important factor in the critical configuration for diffusion, while if $x_c/\lambda > 0$, the local expansion of the site receiving the moving atom is more important.

If $x_c/\lambda = 0$, then $E_1 = E_3$ and the two factors are equally important. The value of x_c/λ has nothing to say about the contribution E_2 to the critical configuration. This is to be expected, since the saddle point is at a symmetry plane between the initial and final jumps and, therefore, E_2 has no effect on the asymmetry of Γ implied by thermal diffusion.

VII. DISCUSSION AND COMPARISON WITH EXPERIMENTS

From the point of view of the theory of thermal diffusion, the simplest type of system is the interstitial impurity diffusing in an otherwise pure metal by an interstitial mechanism. As shown by Eqs. (5) and (6), thermal diffusion in such systems depends only on the critical configuration separation distance, and the activation energy for motion of the interstitial. If the latter is known from ordinary diffusion experiments, the former can be calculated from thermal diffusion

TABLE I. Critical configuration separation distances.

System	x_c/λ
α -Fe (C)	1
γ -Fe (C)	0.056
α -Fe (N)	1
α -Fe (H)	<0
α -Zr (H)	-0.5
Zn (Ag)	~ -0.5
Zn (Th, In)	~ -0.3
Au	-1.6
Cu	-1
KCl (K ⁺)	-0.21
KCl (Cl ⁻)	+0.53

data. Table I includes values of x_c/λ for interstitial diffusion calculated from a compilation of heats of transport by Oriani.¹⁹ We see that x_c is positive for carbon and nitrogen diffusion in iron, while x_c is negative for hydrogen diffusion in iron or zirconium. According to the interpretation of x_c that is proposed in this paper, the negative value of x_c for hydrogen diffusion suggests that the accumulation of energy in the hydrogen atom itself is of great importance in the critical configuration for the jump. This is to be expected, since the hydrogen atom has such a small mass that it acts as an Einstein oscillator when in its interstitial position, and can probably find its way through the interstices of the metal rather easily. However, the fact that $x_c = -0.5$ for hydrogen in zirconium, indicates that some cooperative motion of the zirconium atoms that surround the final positions of the hydrogen must occur during the jump. If the hydrogen atom could jump whenever it acquired the activation energy without any help from the zirconium atoms, we would expect $x_c = -1$.

The critical configuration distance has the value unity for both nitrogen and carbon in α -iron. This indicates that the local expansion around the site receiving the diffusing atom is the most important contribution to the critical configuration. Since $x_c = 0.06$ for carbon diffusing in γ -iron, we conclude that, in this case, nearly equal parts of the activation energy are spent in moving the carbon atom and in expanding the group of iron atoms around the final position of the diffusing carbon. This difference in x_c between α - and γ -iron is reasonable in view of the fact that γ -iron is more closely packed than α -iron.

The data and analysis of Rosolowsky²² suggest that silver in zinc provides a good example of a substitutional impurity that is not bound to a vacancy while indium in zinc is a good example of a substitutional impurity strongly bound to a vacancy. Therefore, in analyzing thermal diffusion data for zinc,⁶ it will be assumed that silver in zinc corresponds to the weak binding case while indium and thallium correspond to the tight case. The data of Winter and Drickamer⁶ are given in terms of a

²² J. H. Rosolowsky, Phys. Rev. **124**, 1828 (1961).

"separation constant" α defined by

$$\ln(N/N_0) = \alpha \ln(T/T_0). \quad (51)$$

Since, for their experiments $(T - T_0) = 45^\circ\text{C}$, it is sufficiently accurate for our purposes to expand the logarithm on the right side of (51) and write

$$\ln(N/N_0) = \alpha(T - T_0)/T_0. \quad (52)$$

Comparing this with Eq. (12), we see that x_c/λ is given by

$$x_c/\lambda = \alpha kT/E^m - E_f/E^m. \quad (53)$$

A rough estimate of E^m and E_f can be made by taking E^m to be one-half the activation energy of diffusion for the impurity atom and E_f to be one-half the activation energy of self-diffusion of the solvent. Using the data of Rosolowsky²¹ and of Shirn, Wajda and Huntington²² for the diffusion activation energies, this suggests that E_f/E^m is approximately unity for silver diffusing in zinc. Since the absolute magnitude of α is less than unity,⁶ and $kT/E^m \approx 0.1$, this approximation gives $x_c/\lambda \approx -1$. We interpret this result to mean that the centroid of the distribution of energy in the critical configuration is at the original site of the diffusing silver atom. Since the silver atom and the vacancy act as screened negative charges,²³ a repulsion is set up between them that must be overcome by the moving silver atom, in addition to the ion-core interactions. The screened charge repulsions cannot be greatly diminished by local expansion around the vacancy, so it is reasonable that the activation energy is concentrated in the moving atom.

Equations (37) and (39) show that for the tight-binding case, thermal diffusion of a substitutional impurity depends on two critical configuration distances and two energies of motion so that even approximate calculations of $x_c^{(1)}$ and $x_c^{(2)}$ cannot be made from the available data with any degree of reliability. However, a rough correlation between the x_c 's and experiment can be made by expanding $e^{\Delta E/kT}$ about T_0 to the first order in $\Delta T = T - T_0$ and comparing the result to (52). This gives

$$\alpha = 2 \frac{x_c^{(1)} E_1^m}{\lambda kT} + \frac{x_c^{(2)} E_2^m}{\lambda kT_0} \frac{\nu_2}{\nu_1} \quad (54)$$

for diffusion perpendicular to the hexagonal axis, and

$$\alpha = 3 \frac{x_c^{(1)} E_1^m}{\lambda kT} + \frac{3 x_c^{(2)} E_2^m}{2 \lambda kT_0} \frac{\nu_2}{\nu_1} \quad (55)$$

for diffusion parallel to the hexagonal axis. Now if we take $E_1^m/kT = E_2^m/kT \approx 10$, then we have

$$\begin{aligned} 2x_c^{(1)}/\lambda + x_c^{(2)}/\lambda &= 0.1\alpha, & (\perp) \\ 3x_c^{(1)}/\lambda + \frac{3}{2}x_c^{(2)}/\lambda &= 0.1\alpha. & (\parallel) \end{aligned} \quad (56)$$

Unfortunately, we have no way of evaluating $x_c^{(1)}$ and $x_c^{(2)}$ separately. However, it will be shown later that x_c/λ is of the order of -1 for self-diffusion in copper and gold. Assuming this is also true for $x_c^{(2)}/\lambda$ gives

$$\begin{aligned} x_c^{(1)}/\lambda &= 0.05\alpha - 0.5, & (\perp) \\ x_c^{(1)}/\lambda &= 0.033\alpha - 0.5, & (\parallel) \end{aligned} \quad (57)$$

and using the appropriate values⁶ for α gives $x_c^{(1)}/\lambda = -0.3$ to -0.4 for diffusion of indium or thallium in zinc, and $x_c^{(1)}/\lambda \approx -0.5$ for the diffusion of silver in zinc. We would conclude, therefore, that the critical configuration is one in which both an opening of the shell of atoms around the vacancy, and a large kinetic energy of the moving atom is important. The maximum in the spatial distribution of activation energy is somewhere between the original site and the plane separating the impurity from the vacancy. It would be interesting to compare $x_c^{(1)}/\lambda$ for the parallel and perpendicular directions of diffusion, but the calculations are not accurate enough for this purpose.

The absence of marker movement in thermal diffusion^{12,13} cannot be understood unless either $x_c = -\lambda E_f/E^m$, or the vacancy sources and sinks are not operative in thermal diffusion. The former possibility would require an unlikely coincidence, since the negative result has been observed for the quite different structures of α -iron and zinc. The possibility that the sources and sinks are inefficient certainly exists, and further experimentation on thermal diffusion marker motion as a function of dislocation density and grain size is needed to clarify this point. These experiments should be performed on zone refined material since impurity concentrations greater than 10^{-6} – 10^{-7} atomic fraction can have serious effects on experiments involving vacancies.²⁴ The impurity atoms act as vacancy traps: As a vacancy performs its random walk towards a sink, it may combine with an impurity atom and be trapped there for some time before it escapes and continues its walk.²⁴ Such an effect seriously decreases the efficiency of sources and sinks, particularly since impurity atoms are expected to aggregate in the vicinity of dislocations and grain boundaries. Meehan and Lehman¹⁴ have emphasized the great care that must be exercised in interpreting negative marker motions because of experimental difficulties which give rise to spurious results.

Positive marker motions have been observed in copper and gold.¹⁴ If we assume a random distribution of sources and sinks, then x_c/λ can be computed from Eq. (44) using the marker motion data and known values of E^m and E_f .^{25,26} From their data, Meehan and Lehman calculate a quantity ΔE which they interpret as $\Delta E = E^m - E_f$, but in our theory is given by

²⁴ A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960).

²⁵ J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

²⁶ G. Airoldi, G. L. Bacchella, and E. Germagnoli, Phys. Rev. Letters **2**, 145 (1959).

²³ G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta Met. **1**, 513 (1953).

$[(x_c/\lambda)E^m + E^f]$. Using their result of $\Delta E = -0.3$ eV, for gold and $\Delta E = +0.2$ eV, for copper gives $x_c/\lambda = -1.6$ and -1 for gold and copper, respectively. This means that most of the energy of activation is concentrated in the moving atom, and if the value -1.6 is valid, the atoms to the left of the diffusing atom are important in the activated configuration. (Diffusion jump from left to right).

No direct thermal diffusion data are available for ionic crystals. However, the heat of transport has been obtained from thermoelectric measurements for potassium chloride²⁷ with the result that for the potassium ion the heat of transport is $Q_{K^+}^* = 0.99$ eV while for the chloride ion, $Q_{Cl^-}^* = 2.09$ eV. Comparing Eq. (12) with macroscopic theory gives

$$\begin{aligned} Q_{K^+}^* &= (x_c^+/\lambda)E_+^m + E^f, \\ Q_{Cl^-}^* &= (x_c^-/\lambda)E_-^m + E^f, \end{aligned} \quad (58)$$

where now E^f is one-half the formation energy for a Frenkel pair, E_+^m and x_c^+ are the migration energy and critical configuration distance for the cation, and E_-^m and x_c^- are corresponding quantities for the anion. From conductance measurements,²⁸ $E^f = 1.15$ eV for potassium chloride so that Eq. (52) gives $x_c^+/\lambda = -0.21$ and $x_c^-/\lambda = 0.53$. This means that for a cation jump, the energy of the moving ion is more important than the local expansion of the site it jumps into, while the reverse is true for an anion jump. This result is reasonable in view of the relative sizes of the ions.

If the interpretation of x_c given in this paper is correct, we should expect x_c to take on values between $+1$ and -1 . This is, in fact, the case for all systems studied, except for self-diffusion in copper. The values of x_c for copper and gold are not extremely accurate, however, since they depend on the accuracy of forma-

tion and motion energies determined from quenching experiments, as well as on the accuracy of measured marker movements. In fact, the errors are such that x_c/λ for copper could be as high as -1 and as low as -2.5 . More accurate data are needed to establish the self-diffusion x_c values more precisely.

VIII. SUMMARY AND CONCLUSIONS

A theory of thermal diffusion in crystals is presented in which the jump frequencies along and against the temperature gradient are used to define the temperature of two isothermal systems. The difference in these two temperatures determines the asymmetry of the jump frequency in the nonisothermal system, and is used to calculate a parameter x_c , which is a measure of the spatial distribution of energy of the activated state. The analysis was applied to available experimental data, and the results indicate that for diffusion of carbon and nitrogen in α -iron, the activation energy is centered on the site receiving the moving atom; for diffusion of carbon in γ -iron, the activation energy is centered near the plane of atoms separating the initial and final positions of the moving atom, but on the side of this plane nearer to the final position; for diffusion of hydrogen in α -zirconium and α -iron, and of silver, indium, or thallium in zinc, the activation energy is centered on the side of this plane nearer the original site of the moving atom; for self-diffusion in gold and copper, the activation energy is centered on the original site of the moving atom. For diffusion of K^+ in KCl, the activation energy is centered near the flux plane, but closer to the original than to the final site while for diffusion of Cl^- in KCl, the reverse is true.

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²⁷ A. R. Allnatt and P. W. M. Jacobs, Proc. Roy. Soc. (London) **267**, 31 (1962).

²⁸ A. R. Allnatt and P. W. M. Jacobs, Trans. Faraday Soc. **58**, 116 (1962).