all determinations of critical currents for thin films[18–23] are in disagreement (an exception is reference 20) with the theoretically expected temperature dependences [see reference 9, p. 114, Eq. (18-11); reference 10, p. 183, Eq. (4.38); and reference 22, Eq. (2)]. In the theoretical calculations it has not been taken into account that the transition might go via a domain structure. (For very thin films the transition usually proceeds almost instantaneously from complete superconductivity to complete normal conductivity; see, however, reference 23.) Such a coagulation into a domain structure (and subsequent complete breakdown of superconductivity) might completely change the criteria to be applied for the breakdown of superconductivity.

It should be noted that von Laue (see reference 9) and Ginsburg (see reference 10) apply different criteria for the breakdown of superconductivity under the influence of an externally supplied current. von Laue's treatment (as well as our simple "droplet" model above) is objectionable because the transition is treated by equilibrium thermodynamics while the thermodynamics of irreversible processes should be used. The treatment by Ginsburg seems to be free of such an objection. Both von Laue and Ginsburg use a local theory of superconductivity, while it is now certain that a nonlocal theory is necessary to properly describe superconductivity.[11,12]

X. ACKNOWLEDGMENTS

The authors are indebted to Professor G. H. Dieke for the provision of the liquid helium. They wish to thank the National Science Foundation for supporting this work by a grant. Thanks are also due Mr. R. Sarup for the help with the drawings of this report.

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PHYSICAL REVIEW VOLUME 113, NUMBER 6 MARCH 15, 1959

Influence of Solutes on Self-Diffusion in the Face-Centered Cubic Lattice

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(Received July 16, 1958; revised manuscript received November 13, 1958)

A theory is given for the influence of substitutional solutes on self-diffusion in the face-centered cubic lattice. The theory is limited to cases in which the concentration of solute is low enough so that only one solute atom at a time can interact with a given tracer atom.

Two different kinds of approximation are employed, one in which the processes of association and dissociation of vacancies and solute atoms do not themselves contribute to transport, and one in which they do but the frequency of exchange between solute and vacancy is considered to be infinite.

From data on the diffusion coefficient of the solute as well as on the self-diffusion coefficient in its dependence on solute concentration the ratio of the frequency with which a vacancy exchanges with a solute atom to that with which it exchanges with a host atom in the first coordination shell of a solute can be estimated. This ratio appears to lie between 0.1 and 0.5 for solutes in silver which increase self-diffusion and for which experimental data are available.

An analysis is given which shows that a good estimate of the influence of a given solute on self-diffusion can be made when only the diffusion coefficient of that solute is known.

Finally the effect which Pd in silver has on the self-diffusion coefficient (Pd reduces the self-diffusion coefficient) is calculated on the basis of the theory. Agreement between theory and experiment is satisfactory.

1. INTRODUCTION

A NUMBER of investigations dealing with the influence of solutes on self-diffusion in silver have recently been published.[1–6] Although the experimental work is very thorough no truly detailed theoretical analysis of the data has been given. The present article represents an attempt to supply such an analysis.

Our investigation will be concerned with the more or less correlated motion of three *lattice* particles:

(1) a tracer atom isotopic to the host lattice;
(2) a solute atom occupying a substitutional position in the lattice;
(3) a lattice vacancy.

It will be assumed that the diffusion of both the tracer and the solute involves a vacancy mechanism. In general the vacancy will exhibit different perferences for different sites, e.g., in the neighborhood of a solute atom or otherwise and we shall eventually treat the general situation. However, the problem is very

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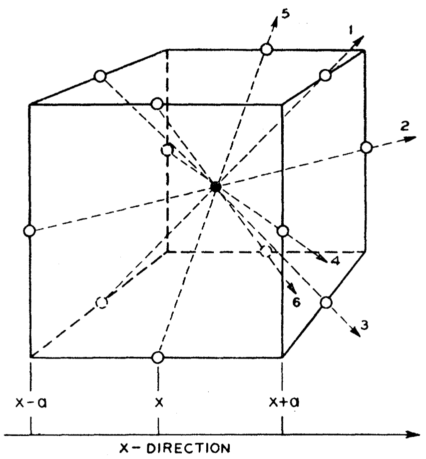

FIG. 1. Cell indicating tracer (filled circle) in face-centered cubic lattice and its first shell of coordinated sites. The important directions are numbered.

complex and it is better to begin with the simplest case. Therefore our inquiry will be limited at first to the circumstance in which the vacancy exhibits so great a preference for a site adjacent to a solute atom that for all intents and purposes it may be regarded as permanently bound to the solute. Furthermore we shall assume that every solute has a vacancy. This means that the concentration of vacancies just equals the concentration of solute atoms.

With these restrictions we shall really deal with the correlated motion of but two lattice particles; tracer atoms and solute-vacancy complexes, the latter facilitating not only its own motion but the motion of the tracer as well.

2. APPLICATION OF LIDIARD'S METHOD

The problem will be attacked using an extension of a method devised by Lidiard[7] for the study of the correlated motion of solute atoms and vacancies. The discussion will be facilitated by reference to Figs. 1 and 2. Figure 1 shows a tracer atom (filled circle) on a site in a face-centered cubic lattice surrounded by its first coordination shell of twelve nearest neighbor sites (open circles). Various directions leading to different nearest neighbors are identified by numbers running from 1 to 6. Although not shown, the reverse of each direction will be specified by the negative of the corresponding number. The x direction is seen to lie along the [100] axis of the crystal and without loss of generality we can choose the x axis to pass through the tracer atom. The interval a is also clearly shown in Fig. 1.

Figure 2 illustrates certain important configurations of tracer atoms and solute vacancy complexes. Tracers are again represented by filled circles while vacancies are symbolized by squares and solute atoms by ×'s. Figure 2(a) depicts a configuration which can facilitate the motion of the tracer, for here the tracer can exchange with the vacancy without requiring the latter to dissociate from the solute; a process which for the time being is forbidden by hypothesis. The configuration illustrated in Fig. 2(b) cannot promote movement of the tracer since the vacancy does not occupy a position adjacent to the former. However, it will prove important in our development because it is the precursor of a configuration which can promote tracer diffusion. Thus the vacancy can move to a position adjacent to the tracer without dissociating from the solute.

If in Fig. 2(b) the vacancy and solute atom are interchanged, the vacancy would then be adjacent to the tracer but the resulting configuration would still be unable to cause motion of the tracer. In this case, place exchange between the tracer and vacancy would require dissociation of the complex. Nevertheless, the configuration in question is still of interest because by place exchange between the solute and vacancy the arrangement shown in Fig. 2(a) is achieved and this can be the precursor of a configuration which can promote motion.

The symbolism $V_{1,6}$ and $S_{2,1}$ appearing in Fig. 2 requires explanation. We adopt the convention that any configuration which places the *vacancy* on one of the twelve nearest neighbor sites is described by V with certain subscripts, while a configuration which places the *solute* (but not the vacancy) on a nearest neighbor site is described by S with certain subscripts. (Note that a configuration having *both* the solute atom and vacancy on nearest neighbor sites has the symbol V.) The subscripts refer in order to the directions traversed in going from the tracer to the vacancy to the solute

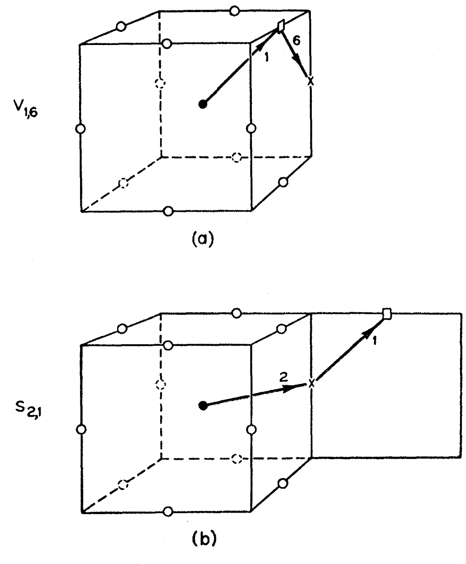

FIG. 2. Drawings showing two configurations required for the discussion of correlation in the bound vacancy problem. Tracers are represented by filled circles, vacancies by squares, and solute atoms by ×'s.

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in case of V configurations and from the tracer to the solute to the vacancy in the case of S configurations. The directions are specified in Fig. 1.

Thus it is obvious why the configuration in Fig. 2(a) is $V_{1,6}$ while in Fig. 2(b) it is $S_{2,1}$. Notice that inversion through the center of symmetry at the tracer produces the configuration described by merely taking the negatives of the subscripts in the original. Thus inversion of $V_{1,6}$ through the center of symmetry would produce $V_{-1,-6}$. Similarly inversion, say of $V_{2,-6}$, would produce $V_{-2,6}$.

In the preceding discussion two different elementary processes have been mentioned. These are:

(1) An exchange between a tracer and a vacancy both of which lie in the first coordination shell of a solute atom. The frequency with which this process occurs will be denoted by ω_T. Notice that ω_T may be, and probably is, different from the frequency ω which characterizes an exchange between a tracer and vacancy when both particles are far from a solute atom. The frequency ω determines the self-diffusion coefficient in the absence of solute.

(2) An exchange between a solute atom and its bound vacancy. The frequency associated with this process will be denoted by ω_S.

We have seen that certain configurations such as $V_{1,6}$ are able to facilitate the motion of tracer atoms. It is, therefore, obvious that the flux of tracers depends in some way upon the probabilities of occurrence of the relevant configurations. In fact it is not difficult to see that if all the probabilities were known, the flux and hence the diffusion coefficient of the tracer could be computed by multiplying each by the corresponding frequency with which the configuration it pertains to is able to promote tracer motion, and summing the separate contributions. If it were imagined that in the neighborhood of a diffusing tracer the solute-vacancy complexes were randomly distributed, the computation of the required probabilities would be greatly simplified. In this circumstance, each probability would be simply proportional to the known uniform concentration of complexes.

Unfortunately the assumption of randomness is invalid in view of correlation. To understand this effect consider configuration $V_{1,6}$ in Fig. 2(a) and $V_{-3,6}$, its mirror image (not shown) in the plane normal to the x axis. If it is assumed that the concentration gradient lies along the x axis, so that the flow of tracer is in the positive x direction, then $V_{-3,6}$ may be referred to as an "upstream" configuration, while $V_{1,6}$ is a "downstream" configuration. One method by which $V_{-3,6}$ could have arisen is to have had the tracer originally in the position occupied by the vacancy in $V_{-3,6}$ and to have had place exchange between the two. In this way the tracer would have jumped in the downstream direction. On the other hand, $V_{1,6}$ could have occurred because the tracer was originally at the site of the vacancy and exchanged places with the latter by jumping upstream. Since the concentration gradient lies in the downstream direction, at any instant, more tracers will have jumped downstream to produce $V_{-3,6}$ than upstream to produce $V_{1,6}$. As a result, the chance of finding $V_{-3,6}$ will be greater than the chance of finding $V_{1,6}$. If these chances had been computed from considerations of randomness, they would have appeared equal.

It is evident that the exact computation of the required probabilities must be a fairly difficult task in view of the several different ways in which a given configuration can be produced, and the over-all interaction of many configurations resulting from this fact. Nevertheless, progress can be made by use of the method introduced by Lidiard,[7] which we are now in a position to describe.

We begin by formulating the flux $j(x)$ associated with a *single* lattice site located at x. In accomplishing this, it is necessary to compute the net flux to the site at x (for example the one shown in Fig. 1) from all contributing sites at $x-a$, as well as the net flow from the site at x to all receiving sites at $x+a$, and to average the two fluxes so obtained. In what follows, the symbol which has been used to denote a configuration will also be used to designate its probability. For example, $V_{1,6}(x)$ indicates the probability of finding configuration $V_{1,6}$ with its tracer located on a site in the plane at x. Similarly, $V_{1,6}(x+a)$ stands for the chance of finding the same configuration shifted a distance a in the positive x direction, i.e., with its tracer in the plane at $x+a$. No confusion should result from this usage.

Speaking of $V_{1,6}$ it contributes a component $\omega_T V_{1,6}(x)$ to the flow from x to $x+a$. Inspection reveals that there are seven other configurations $V_{2,-6}$, $V_{1,-5}$, $V_{4,-5}$, $V_{4,-6}$, $V_{3,-6}$ and $V_{2,-5}$ which contribute to the flow from x to $x+a$ and which are symmetrical to $V_{1,6}$ in respect to the x axis. Because of this symmetry, the entire contribution of the class can be represented by $8\omega_T V_{1,6}$. In addition, there are 8 mutually symmetric configurations of the type $V_{1,-4}$ which contribute to the flow from x to $x+a$. Thus we obtain another component $8\omega_T V_{1,-4}$. Further inspection will show that $V_{-1,-6}$ centered at $x+a$ and 7 of its symmetrically equivalent counterparts promote flow from $x+a$ to x. These yield a component $-8\omega_T V_{-1,-6}(x+a)$. Inspection also reveals another component $-8\omega_T V_{-1,4}$. Thus the *net* flow between x and $x+a$ is

$$8\omega_T\{V_{1,6}+V_{1,-4}-V_{-1,-6}(x+a)-V_{-1,4}(x+a)\}. \quad (2.1)$$

An exactly similar analysis yields the net flow between $x-a$ and x. This is

$$8\omega_T\{V_{1,6}(x-a)+V_{1,-4}(x-a)-V_{-1,-6}-V_{-1,4}\}. \quad (2.2)$$

The average of (2.1) and (2.2) is $j(x)$:

$$j(x)=4\omega_T\left\{2[V_{1,6}-V_{-1,-6}]+2[V_{1,-4}-V_{-1,4}]\right.$$
$$\left.=a\frac{\partial}{\partial x}[V_{1,6}+V_{-1,-6}]-a\frac{\partial}{\partial x}[V_{1,-4}+V_{-1,4}]\right\}. \tag{2.3}$$

In deriving (2.3), not only have (2.1) and (2.2) been added and divided by 2, but the functions with arguments $x+a$ and $x-a$ have been expanded in a Taylor's series and the linear terms retained. Since $j(x)$ is the flux per site, to get the flux *density* $J(x)$, it must be multiplied by the number of sites per unit area in the plane normal to the x direction. This number is $1/2a^2$. Thus

$$J=\frac{j}{2a^2}=\frac{2\omega_T}{a^2}\left\{2[V_{1,6}-V_{-1,-6}]+2[V_{1,-4}-V_{-1,4}]\right.$$
$$\left.-a\frac{\partial}{\partial x}[V_{1,6}=V_{-1,-6}]-a\frac{\partial}{\partial x}[V_{1,-4}+V_{-1,4}]\right\}. \tag{2.4}$$

In (2.4) terms like $[V_{1,6}-V_{-1,-6}]$involving differences represent the effects of correlation. Under the condition of pure randomness, $V_{1,6}$ and $V_{-1,-6}$ would be equal by symmetry and such terms would vanish. However, since correlation exists, they do not vanish and in fact they reduce the flow expressed by (2.4).

Further progress depends upon the evaluation of $V_{1,6}$, $V_{-1,-6}$, $V_{1,-4}$, and $V_{-1,4}$. This can be accomplished only by a detailed formulation of the over-all kinetics of the process. Consider, for example, the equation for the rate of change with time of $V_{1,6}$. Configuration $V_{1,6}$ can be made from $V_{2,-6}$ through an exchange of solute and vacancy at the frequency ω_S. Thus, in the expression for the rate of change of $V_{1,6}(x)$ with time, we must include the term $\omega_S V_{2,-6}(x)$. By symmetry, $V_{2,-6}=V_{1,6}$, so that it is possible to write the contribution as $\omega_S V_{1,6}(x)$. $V_{1,6}(x)$ can also be produced from $V_{5,4}(x)$, but at the frequency ω_T. Also, it can be produced from $S_{1,2}(x)$, $S_{1,3}(x)$, and $V_{-1,2}(x+a)$ at the frequency ω_T. It can be destroyed by the inverse processes. Thus the expression must also include the term $-[\omega_S+4\omega_T]V_{1,6}(x)$. Collecting all these terms and writing $V_{-1,2}(x+a)$ as $V_{-1,4}(x+a)$ by symmetry, we have

$$\begin{aligned}\partial V_{1,6}/\partial t=\omega_S V_{1,6}+\omega_T[&V_{5,4}+S_{1,2}+S_{1,3}\\&+V_{-1,4}(x+a)]-[\omega_S+4\omega_T]V_{1,6},\end{aligned} \tag{2.5}$$

where t stands for time.

All in all, 30 simultaneous equations can be written for 30 arbitrarily chosen independent V and S variables. These are derived by methods analogous to those used for obtaining (2.5), and are listed below.

$$\begin{aligned}
\partial S_{5,1}/\partial t&=\omega_S V_{5,1}+\omega_T[S_{5,-6}+V_{1,-4}+S_{5,5}+S_{5,1}]\\&\quad-\theta S_{5,1},\\
\partial S_{-5,-1}/\partial t&=\omega_S V_{-5,-1}+\omega_T[S_{-5,6}+V_{-1,4}\\&\quad+S_{-5,-5}+S_{-5,-1}]-\theta S_{-5,-1},\\
\partial S_{1,5}/\partial t&=\omega_S V_{1,5}+\omega_T[S_{1,2}+S_{1,1}+V_{5,4}\\&\quad+S_{1,-3}]-\theta S_{1,5},\\
\partial S_{-1,-5}/\partial t&=\omega_S V_{-1,-5}+\omega_T[S_{-1,-2}+S_{-1,-1}\\&\quad+V_{-5,-4}+S_{-1,3}]-\theta S_{-1,-5},\\
\partial S_{1,-3}/\partial t&=\omega_S V_{1,-3}+\omega_T[V_{5,4}+S_{1,5}+S_{1,5}\\&\quad+V_{5,4}]-\theta S_{1,-3},\\
\partial S_{-1,3}/\partial t&=\omega_S V_{-1,3}+\omega_T[V_{-5,-4}+S_{-1,-5}\\&\quad+S_{-1,-5}+V_{-5,-4}]-\theta S_{-1,3},\\
\partial V_{1,2}/\partial t&=\omega_S S_{1,2}+\omega_T[V_{1,2}+(3/12)p_iN_S]\\&\quad-\theta V_{1,2},\\
\partial V_{-1,-2}/\partial t&=\omega_S S_{-1,-2}+\omega_T[V_{-1,-2}+(3/12)p_iN_S]\\&\quad-\theta V_{-1,-2},\\
\partial S_{1,1}/\partial t&=\omega_S V_{1,1}+\omega_T[S_{1,5}+S_{1,2}+S_{1,5}+S_{1,2}]\\&\quad-\theta S_{1,1},\\
\partial S_{-1,-1}/\partial t&=\omega_S V_{-1,-1}+\omega_T[S_{-1,-5}+S_{-1,-2}\\&\quad+S_{-1,-5}+S_{-1,-2}]-\theta S_{-1,-1},\\
\partial V_{1,3}/\partial t&=\omega_S S_{1,3}+\omega_T[V_{1,3}+V_{1,3}\\&\quad+(2/12)p_iN_S]-\theta V_{1,3},\\
\partial V_{-1,-3}/\partial t&=\omega_S S_{-1,-3}+\omega_T[V_{-1,-3}+V_{-1,-3}\\&\quad+(2/12)p_iN_S]-\theta V_{-1,-3},\\
\partial V_{1,6}/\partial t&=\omega_S V_{1,6}+\omega_T[V_{5,4}+S_{1,2}+S_{1,3}\\&\quad+V_{-1,4}(x+a)]-\theta V_{1,6},\\
\partial V_{-1,-6}/\partial t&=\omega_S V_{-1,-6}+\omega_T[V_{-5,-4}+S_{-1,-2}\\&\quad+S_{-1,-3}+V_{1,-4}(x-a)]-\theta V_{-1,-6},\\
\partial V_{1,-4}/\partial t&=\omega_S V_{5,4}+\omega_T[V_{1,-4}+S_{5,-6}+S_{5,1}\\&\quad+V_{-1,-6}(x+a)]-\theta V_{1,-4},\\
\partial V_{-1,4}/\partial t&=\omega_S V_{-5,-4}+\omega_T[V_{-1,4}+S_{-5,6}+S_{-5,-1}\\&\quad+V_{1,6}(x-a)]-\theta V_{-1,4},\\
\partial V_{5,4}/\partial t&=\omega_S V_{1,-4}+\omega_T[V_{1,6}+S_{1,5}\\&\quad+S_{1,-3}+V_{5,4}]-\theta V_{5,4},\\
\partial V_{-5,-4}/\partial t&=\omega_S V_{-1,4}+\omega_T[V_{-1,-6}+S_{-1,-5}\\&\quad+S_{-1,3}+V_{-5,-4}]-\theta V_{-5,-4},\\
\partial S_{1,2}/\partial t&=\omega_S V_{1,2}+\omega_T[V_{1,6}+S_{1,3}+S_{1,5}+S_{1,1}]\\&\quad-\theta S_{1,2},\\
\partial S_{-1,-2}/\partial t&=\omega_S V_{-1,-2}+\omega_T[V_{-1,-6}+S_{-1,-3}+S_{-1,-5}\\&\quad+S_{-1,-1}]-\theta S_{-1,-2},\\
\partial S_{1,3}/\partial t&=\omega_S V_{1,3}+\omega_T[V_{1,6}+S_{1,2}+S_{1,2}+V_{1,6}]\\&\quad-\theta S_{1,3},\\
\partial S_{-1,-3}/\partial t&=\omega_S V_{-1,-3}+\omega_T[V_{-1,-6}+S_{-1,-2}\\&\quad+S_{-1,-2}+V_{-1,-6}]-\theta S_{-1,-3},\\
\partial V_{5,1}/\partial t&=\omega_S S_{5,1}+\omega_T[V_{1,5}+(3/12)p_iN_S]\\&\quad-\theta V_{5,1},
\end{aligned} \tag{2.6}$$

$$
\begin{aligned}
\partial V_{-5,-1}/\partial t &= \omega_S S_{-5,-1}+\omega_T[V_{-1,-5} \\
&\qquad +(3/12)p_iN_S]-\theta V_{-5,-1}, \\
\partial V_{1,5}/\partial t &= \omega_S S_{1,5}+\omega_T[V_{5,1}+(3/12)p_iN_S] \\
&\qquad -\theta V_{1,5}, \\
\partial V_{-1,-5}/\partial t &= \omega_S S_{-1,-5}+\omega_T[V_{-5,-1} \\
&\qquad +(3/12)p_iN_S]-\theta V_{-1,-5}, \\
\partial V_{1,-3}/\partial t &= \omega_S S_{1,-3}+\omega_T[V_{5,6}+(2/12)p_iN_S \\
&\qquad +V_{5,6}]-\theta V_{1,-3}, \\
\partial V_{-1,3}/\partial t &= \omega_S S_{-1,3}+\omega_T[V_{-5,-6}+(2/12)p_iN_S \\
&\qquad +V_{-5,-6}]-\theta V_{-1,3}, \\
\partial V_{1,1}/\partial t &= \omega_S S_{1,1}+\omega_T[(4/12)p_iN_S]-\theta V_{1,1}, \\
\partial V_{-1,-1}/\partial t &= \omega_S S_{-1,-1}+\omega_T[(4/12)p_iN_S]-\theta V_{-1,-1}.
\end{aligned}
$$

In the foregoing equations we have used

$$\theta=\omega_S+4\omega_T. \tag{2.7}$$

At this point, it is important to mention that the Lidiard technique considers correlation between nearest neighbors only. Thus a solute-vacancy complex, neither end of which is on one of the bearest neighbor sites shown in Fig. 1, would be regarded as completely uncorrelated with the tracer. The error committed by neglecting such second order correlations is not large and has been investigated by Lidiard.[7]

Even so, the number of correlated V and S configurations totals 216, as inspection will reveal. Of these 216 variables, we notice that only 30 appear in Eqs. (2.6). These 30 are the collection of operands of the operator $\partial/\partial t$ in (2.6). The reduction has been possible through considerations of symmetry of the sort applied to (2.5). Even so, we would have been left with a set of variables which included $V_{5,-6}$, $V_{-5,6}$, $V_{5,6}$, $V_{-5,-6}$, $S_{5,5}$, $V_{5,5}$, etc., corresponding to configurations lying entirely in the plane perpendicular to x, i.e., perpendicular to the concentration gradient. These variables do not appear in Eqs. (2.6). The reason is that the set included is closed and sufficient for the computation of the V's which appear in (2.5). In any event, $V_{5,-6}$ and $V_{-5,6}$, lying normal to the gradient, would not be subject to correlation effects, and so, besides being calculable from considerations of randomness, would be equal to one another. The same can be said about other pairs of mutual images by inversion through the center of symmetry which lie in the plane normal to x.

It is instructive to compute $V_{5,-6}$ say, assuming complete randomness. To do this we denote the atom fraction of "independent" tracer atoms by p_i. By "independent" tracers we mean those, none of whose 12 nearest neighbor sites are occupied by either a vacancy or solute atom. Then part of the probability of $V_{5,-6}$ is accounted for by the product of the chance that the central site is occupied by an independent tracer and the chance that the next nearest neighbor in the sequence of directions 5 and -6 is occupied by a solute atom. If the atom fraction of solute is N_S, then this product is p_iN_S. Now the vacancy associated with the solute atom in question can occupy at random any of the 12 nearest neighbor sites to the solute. But in $V_{5,-6}$ only that site which is nearest to the tracer in the direction 5 from the latter can be occupied. Therefore, the chance of getting the correct configuration is obtained by reducing p_iN_S by 1/12.

$$V_{5,-6}=p_iN_S/12. \tag{2.8}$$

The appearance of $p_iN_S/12$ multiplied by various small integers in (2.6) has its origin in this type of argument. It represents the probability or probabilities of uncorrelated configurations. These are uncorrelated either because they lie in the 5,6 plane, like $V_{5,-6}$ above, or because they are arrangements in which the solute-vacancy complex does not occupy a nearest neighbor site to the tracer.

Following Lidiard, we expand the variables which contain $x+a$ and $x-a$ as arguments in (2.6) and set the time derivative on the left of each equation equal to zero.[8] We then subtract the equations in pairs, subtracting from a given equation the one corresponding to what is obtained by inverting each of its variables through the center of symmetry. Thus the equation for $V_{-1,-6}$ is subtracted from the one for $V_{1,6}$. In the end, the following set of 15 equations in the 15 unknowns A, B, C, etc., is obtained:

$$
\begin{aligned}
A+B+C-D-4E&=-a(\partial D^*/\partial x),\\
(4+\gamma)B-C-E-G-\gamma I-J&=0,\\
2B-(4+\gamma)C+2E+\gamma K&=0,\\
\gamma A-(3+\gamma)D-E+F&=-a(\partial E^*/\partial x),\\
(3+\gamma)A-\gamma D-E-G-H&=0,\\
D-(3+\gamma)F+\gamma L&=0,\\
A+B-(4+\gamma)G+H+J+\gamma M&=0,\\
2A+2G-(4+\gamma)H+\gamma N&=0,\\
\gamma B-(3+\gamma)I&=0,\\
2B+2G-(4+\gamma)J+\gamma P&=0,\\
\gamma C-(2+\gamma)K&=0,\\
\gamma F-(4+\gamma)L+M&=0,\\
\gamma G+L-(4+\gamma)M&=0,\\
\gamma H-(4+\gamma)N&=0,\\
\gamma J-(4+\gamma)P&=0,
\end{aligned}
\tag{2.9}
$$

$$
\begin{aligned}
A&=V_{5,4}-V_{-5,-4}, & I&=V_{1,2}-V_{-1,2},\\
B&=S_{1,2}-S_{-1,-2}, & J&=S_{1,1}-S_{-1,-1},\\
C&=S_{1,3}-S_{-1,-3}, & K&=V_{1,3}-V_{-1,-3},\\
D&=V_{1,-4}-V_{-1,4}, & L&=V_{5,1}-V_{-5,-1},\\
E&=V_{1,6}-V_{-1,-6}, & M&=V_{1,5}-V_{-1,-5},\\
F&=S_{5,1}-S_{-5,-1}, & N&=V_{1,-3}-V_{-1,3},\\
G&=S_{1,5}-S_{-1,-5}, & P&=V_{1,1}-V_{-1,-1},\\
H&=S_{1,-3}-S_{-1,3}, & &
\end{aligned}
\tag{2.10}
$$

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[8] This is possible because we can always assume that steady-state diffusion is occurring and that the diffusion coefficient possesses only second-order dependence on whether diffusion is steady or time-dependent. Lidiard[7] elaborates on this point.

and

$$\gamma = \omega_S/\omega_T, \tag{2.11}$$

while

$$D^* = V_{1,-4} + V_{-1,4}, \quad E^* = V_{1,6} + V_{-1,-6}. \tag{2.12}$$

From (2.10) it is evident that the variables without asterisks are the differences between the probabilities corresponding to configurations related by inversion through the center of symmetry while from (2.12) it is clear that the variables with asterisks involve the sums. The 30 sums and differences so obtained represent a transformation of variables which is particularly convenient, for it is easy to show by writing down the equation for $\partial p_i/\partial t$, in addition to (2.6), that when all time derivatives are set equal to zero, the 15 quantities with asterisks (the sums) can be assigned their proper values. This leaves only the differences, so that from 216 variables initially, the problem is reduced to one involving 15, i.e., the ones listed in (2.10).

The rule for a sum is that its value is that which would be obtained if each component term, e.g., $V_{1,-4}$ and $V_{-1,4}$ in D^*, were evaluated on the assumption of randomness. Thus, by the argument leading to (2.8), we find

$$V_{1,-4} = V_{-1,4} = p_i N_S/11, \tag{2.13}$$

assuming, of course, complete randomness. This time the product $p_i N_S$ is divided by 11 rather than 12 as in (2.8). The reason is that in the $V_{1,-4}$ configuration one of the 12 neighbors to the solute atom is already occupied by a tracer atom so that the vacancy only has 11 positions to choose from.

Of course, due to correlation neither $V_{1,-4}$ or $V_{-1,4}$ is given by (2.13) *but their sum* is still given by twice the quantity at the right of (2.13). Thus

$$D^* = V_{1,-4} + V_{-1,4} = 2p_i N_S/11. \tag{2.14}$$

By similar reasoning one can show that

$$E^* = V_{1,6} + V_{-1,-6} = 2p_i N_S/11. \tag{2.15}$$

Both (2.14) and (2.15) can be used in (2.5) and (2.9).

The set (2.9), can be solved for D and E, which, along with D^* and E^*, are required for use in (2.5). This is best accomplished by using determinantal methods. However, since fifteenth order determinants are involved, it is desirable to have the assistance of a large computer.

In view of the fact that only $a\partial D^*/\partial x$ and $a\partial E^*/\partial x$ appear on the right of (2.9), and that these derivatives are both equal, according to (2.14) and (2.15), to the same quantity as follows:

$$a\frac{\partial D^*}{\partial x} = a\frac{\partial E^*}{\partial x} = \frac{2aN_S}{11}\frac{\partial p_i}{\partial x}, \tag{2.16}$$

the sum $D+E$ must have the form

$$D+E = \frac{2aN_S}{11}\Omega(\gamma)\frac{\partial p_i}{\partial x}, \tag{2.17}$$

where $\Omega(\gamma)$ is some constant depending on γ which is derived from the proper solution of (2.9). Substituting (2.16) and (2.17) into (2.5), after taking notice of the definitions of D, E, D^*, and E^* in terms of the V's, leads to the expression

$$J = -\frac{8\omega_T N_S}{11a}[1-\Omega(\gamma)]\frac{\partial p_i}{\partial x}. \tag{2.18}$$

Until now, only configurations involving at the most one solute-vacancy complex have been considered. This restriction is valid only when the solid solution is dilute in respect to solute, so that the chance of a given tracer interacting simultaneously with more than one solute atom is small. We are therefore computing the limiting dependence of the self-diffusion coefficient on solute concentration when the latter goes to zero.

If the solid solution is dilute with respect to solute, then we expect that p_i, the chance of finding an *independent* tracer on a site at x, is substantially the same as p, the chance of finding *any* tracer at x. In the first approximation,

$$p_i = p(1-13N_S), \tag{2.19}$$

which shows that $p_i = p$ for small N_S. The origin of (2.19) is simple. Each solute, together with its first coordination shell, occupies 13 sites. By definition, independent tracers are excluded from these sites. If the fraction of solute atoms is N_S, then the fraction of sites inaccessible to independent tracers must be $13N_S$. The fraction of sites available is $(1-13N_S)$. As a result, p_i is reduced from p by the factor $(1-13N_S)$, which explains (2.19).

To convert from probability p to concentration c of tracer, p must be multiplied by the number of sites per cubic centimeter. For the face-centered cubic lattice this is $1/2a^3$ so that

$$p = 2a^3 c. \tag{2.20}$$

Substitution of (2.20) into (2.19) and the latter into (2.18) yields

$$J = -\frac{16\omega_T a^2 N_S}{11}(1-13N_S)[1-\Omega(\gamma)]\frac{\partial c}{\partial x}, \tag{2.21}$$

from which it is apparent that D, the diffusion coefficient of the tracer, is

$$D = \frac{16\omega_T a^2 N_S}{11}(1-13N_S)[1-\Omega(\gamma)]. \tag{2.22}$$

Now $\Omega(\gamma)$ can be evaluated as a function of γ by the solution of the set of Eqs. (2.9). We have done this for various values of γ using determinantal methods and the IBM 704 computer installation at Bell Laboratories. If the term $1-13N_S$ is taken to be unity, one can list values of $h(\gamma) = D(\gamma)/\omega_T a^2 N_S$. Table I consists of such a listing. As expected, we see that when $\omega_S = 0$, i.e., when $\gamma=0$, then $D=0$. For very small values of γ, i.e., for $\omega_S \ll \omega_T$, it is physically reasonable to expect ω_S to be the rate-controlling frequency, so that

$$D/a^2N_S=K_S\omega_S, \tag{2.23}$$

where K_S is a constant. Dividing both sides of (2.23) by ω_T yields

$$D(\gamma)/\omega_T a^2 N_S=K_S\gamma. \tag{2.24}$$

Comparing (2.24) with the data for small γ in Table I reveals that

$$K_S \approx 6.60. \tag{2.25}$$

Thus, for $\omega_S \ll \omega_T$,

$$D=6.60\ \omega_S a^2 N_S, \quad \gamma \text{ small}. \tag{2.26}$$

When $\omega_T \ll \omega_S$, i.e., for large values of γ, it is expected that ω_T will be rate controlling. Under these circumstances

$$D/a^2N_S=K_T\omega_T. \tag{2.27}$$

Comparison with Table I for large values of γ shows that

$$K_T \approx 0.744, \tag{2.28}$$

so that

$$D=0.744\ \omega_T a^2 N_S, \quad \gamma \text{ large}. \tag{2.29}$$

3. COMPUTATION OF D WHEN ONLY THE DIFFUSION COEFFICIENT OF THE SOLUTE IS KNOWN

The computation of D according to Table I presupposes a knowledge of γ as well as ω_T. This prompts us to seek other measurable variables which are themselves functions of γ and ω_T (or ω_S and ω_T). At least two independent variables will be necessary. One such variable is the diffusion coefficient D_S of the solute, which Lidiard[7] has shown to be (for the case of bound vacancies in the face-centered cubic lattice)

$$D_S=\frac{a^2}{3}\left(\frac{\omega_S\omega_T}{\omega_S+\omega_T}\right)=\frac{a^2}{3}\left(\frac{\omega_T\gamma}{1+\gamma}\right). \tag{3.1}$$

TABLE I. Dependence of $h(\gamma)$ upon γ.[a]

$\gamma=\omega_S/\omega_T$	$h(\gamma)=D(\gamma)/\omega_T a^2N_S$	$\gamma=\omega_S/\omega_T$	$h(\gamma)=D(\gamma)/\omega_T a^2N_S$
0.00	0.00	1.10	0.6173
0.00001	0.0000659	1.20	0.6241
0.0001	0.000654	1.30	0.6301
0.001	0.00648	1.40	0.6355
0.002	0.01282	1.50	0.6404
0.003	0.01905	1.60	0.6448
0.004	0.02513	1.70	0.6488
0.005	0.03109	1.80	0.6525
0.006	0.03693	1.90	0.6559
0.008	0.04828	2.00	0.6590
0.01	0.0592	3.00	0.6810
0.03	0.1491	4.00	0.6937
0.05	0.2142	5.00	0.7021
0.08	0.2845	8.00	0.7159
0.10	0.3197	10.00	0.7209
0.20	0.4267	50.00	0.7386
0.30	0.4828	100.00	0.7410
0.40	0.5184	1000.00	0.7432
0.50	0.5437	10 000.00	0.7435
0.60	0.5628	100 000.00	0.7437
0.70	0.5780	1 000 000.00	0.7442
0.80	0.5903		
0.90	0.6007		
1.00	0.6096		

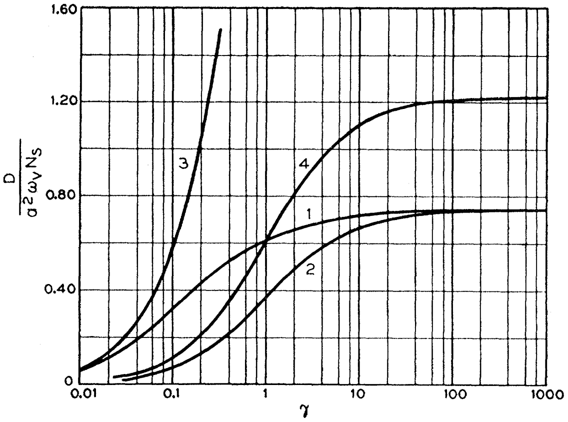

FIG. 3. Plot of the tracer diffusion coefficient against γ calculated on the basis of various approximations. Curve 1 shows the true curve, curve 2 corresponds to the assumption $\gamma=\infty$, curve 3 to $\gamma=0$, and curve 4 to $\gamma=1$.

Since other easily measurable variables are difficult to find, it is of interest to see how far one can go using knowledge of D_S and some broad assumption concerning γ. The hope is that over wide ranges of γ, D will depend primarily on D_S, and on γ only in a secondary fashion.

Three modes of procedure are suggested:

(1) Assume that $\omega_T \ll \omega_S (\gamma \gg 1)$ so that ω_T becomes the rate-controlling frequency. Then according to (3.1) we have a frequency

$$\omega_T'=3D_S/a^2, \tag{3.2}$$

where we use ω_T' instead of ω_T to indicate that ω_T' is a formal frequency obtained on the basis of the assumption that $\omega_T \ll \omega_S$. Only if the assumption is known to be true can we equate ω_T' with ω_T. On the basis of the same assumption, we are forced to use (2.29) with ω_T' substituted for ω_T. The final result is then

$$D=2.23\ N_S D_S=D_2, \tag{3.3}$$

where D_2 is used for D in the current approximation.

The question arises as to how much error is introduced by the indiscriminate use of (3.3) without concern for the real value of γ. An answer can be given as follows. By substituting $D_S(\gamma)$ from (3.1) into (3.2), the dependence of ω_T' on γ can be expressed:

$$\omega_T'=[\gamma/(1+\gamma)]\omega_T. \tag{3.4}$$

Substituting ω_T' in this form into (2.29), we obtain D_2

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[a] *Note added in proof.*—It has come to the author's attention that Compaan and Haven [Trans. Faraday Soc. **52**, 786 (1956)] have in effect evaluated $h(\gamma)$ for several values of γ by a different method. Their technique involved analog computation and the results are in agreement with those in Table I.

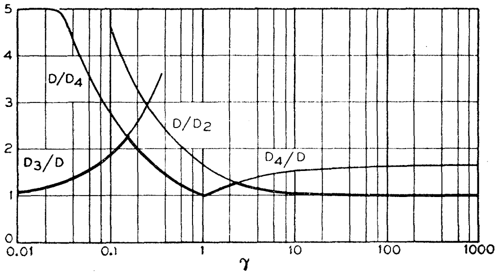


FIG. 4. Curves showing the factors of error inherent in the approximations according to which the curves of Fig. 3 were computed.

expressed in terms of ω_T and γ rather than D_S as in (3.3):

$$D_2(\gamma)/\omega_T a^2 N_S = 0.744\,\gamma/(1+\gamma). \tag{3.5}$$

Thus using (3.5) and Table I, $D_2/\omega_T a^2 N_S$ can be compared with the true value of $D/\omega_T a^2 N_S$ for all values of γ. Curves 1 and 2 of Fig. 3 are plots of $D/\omega_T a^2 N_S$ and $D_2/\omega_T a^2 N_S$ against γ. It should be noted that over quite a range of γ the disparity between the two is not great. This question will be discussed more quantitatively in connection with Fig. 4.

(2) Assume that $\omega_S \ll \omega_T$ ($\gamma \ll 1$) so that ω_S becomes the rate-controlling factor. Now (3.1) suggests the introduction of the formal frequency

$$\omega_S' = 3D_S/a^2, \tag{3.6}$$

and this substituted now into (3.26) rather than (2.29) gives, in place of (3.3),

$$D = 19.8\,N_S D_S = D_3, \tag{3.7}$$

where D_3 indicates D in this approximation. As the counterpart of (3.5), we obtain by the same method

$$D_3(\gamma)/\omega_T a^2 N_S = 6.60\,\gamma/(1+\gamma). \tag{3.8}$$

This ratio is plotted as curve 3 in Fig. 3.

(3) A third assumption which can be made is $\omega_S = \omega_T$ ($\gamma = 1$). With this assumption, (3.1) suggests the formal frequency

$$\omega_T' = 6D_S/a^2. \tag{3.9}$$

Furthermore, according to Table I, for $\gamma = 1$,

$$D = 0.610\,\omega_T a^2 N_S. \tag{3.10}$$

Substituting ω_T' from (3.9) for ω_T in (3.10) gives us

$$D = 3.66\,N_S D_S = D_4, \tag{3.11}$$

where D_4 stands for D in this new approximation. The counterpart of (3.5) and (3.8) is

$$D_4/\omega_T a^2 N_S = 1.22\,\gamma/(1+\gamma). \tag{3.12}$$

This plotted in Fig. 3 as curve 4.

In order to display the errors possible in the three approximations just introduced, we have plotted the ratios D/D_2, D_3/D, D_4/D for $\gamma > 1$, and D/D_4 for $\gamma < 1$ in Fig. 4. The particular form of the ratio (whether D appears in the numerator or the denominator) is chosen so that numbers greater than unity will be involved, giving the factor of error directly. The ratios are obtained from Fig. 3 by taking the ratios of ordinates at the same value of γ.

A heavy line shows the low limit of error possible by assuming that one of the three approximations is valid, and selecting that one which comes closest to experimental result. Thus we see that the error is maximized at $\gamma = 0.15$, but only over a narrow range, and even here it is only about a factor of 2. Over most of the range of γ, only small errors occur.

By referring to the curves for D/D_4 and D_4/D, we see that if one assumes (3.11), then an error of less than a factor of 2 is assured over the entire range $\gamma = 0.2$ to $\gamma = \infty$, and in fact over the *entire range of* γ no more than an error of a factor of 5 could be introduced; this occurring for γ below 0.03. Our later analysis of experimental data will suggest it to be unlikely that γ is much less than 0.2, so that (3.11) may be used as a fairly safe approximation. If we are sure that $\gamma \geq 1$, then (3.3) should be used, for the curve of D/D_2 in Fig. 4 indicates a very small error in this range.

It is clear from Fig. 4 that ω_S exerts less control over D than ω_T, for D_3/D does not approach unity until ω_S is 0.01 ω_T or $\gamma = 0.01$, while D/D_2 is almost unity when ω_T is only 0.1 ω_S or $\gamma = 10$.

Finally, we note that given D and D_S as experimental values, both ω_S and ω_T, or ω_T and γ, can be computed without any approximation.

4. DISSOCIATING COMPLEXES

The results of the preceding analysis, although useful and instructive, are not general enough to include a wide variety of physical situations. One of the most serious restrictions to which they are subject is the hypothesis of the nondissociating solute-vacancy complex. In this section we shall extend the treatment so as to be applicable to the case of dissociating complexes.

As soon as dissociation is permitted, the analysis becomes far more complex. For example, three more frequencies in addition to ω_S and ω_T, the two already considered, must be dealt with:

(1) The first of these was mentioned in Sec. 2. It is ω, the frequency of exchange between a tracer atom and a vacancy, neither of which is in the first coordination shell of a solute. As mentioned, ω determines the self-diffusion coefficient in the absence of solute. It is the jumping frequency of a free vacancy.

(2) Another is ω_A, the frequency with which a free vacancy associates with a solute atom, i.e., the frequency with which a free vacancy exchanges with a host atom lying in the first coordination shell of a solute atom.

(3) Finally we have ω_D, the frequency with which a solute-vacancy complex dissociates, i.e., the frequency with which a vacancy bound to a solute atom exchanges

with a host atom not lying in the first coordination shell of a solute.

Each of the three new processes to which the above frequencies correspond can be responsible for the transport of tracer. Furthermore, they influence the correlation phenomenon in such a way that the number of configurations, and hence, simultaneous equations, which must be dealt with increases astronomically. As a result an exact solution, although possible in principle, is impractical. Fortunately certain reasonable approximations can be introduced which greatly lessen the complexity of the problem. One such approximation is useful if processes taking place with some frequencies are rare events compared to those associated with other frequencies.

For example, if a solute-vacancy complex persists as a recognizable unit over a period large compared to ω_S^{-1} and ω_T^{-1} (i.e., over many jumps for the complex as a whole), then it may be possible to ignore the process of dissociation and the corresponding frequency ω_D. Similarly ω_A can be ignored if the lifetime of a free vacancy is long compared to ω^{-1}. Both these conditions can be met simultaneously. Thus the fact that the lifetime of a complex (bound vacancy) is long, need not imply that every solute atom binds a vacancy and that therefore the lifetime of a free vacancy is short. The degree of association into complexes depends upon two factors, (1) the binding energy, and (2) the concentration of free vacancies and solute atoms. If the binding energy is high, any solute atom and vacancy which encounter one another will remain together for a long time, but if the concentrations are simultaneously low, the chance of such an encounter is small and the equilibrium fraction of vacancies which are bound may still be small. Thus the lifetime of a free vacancy may also be long.

Many physical situations (and we shall have reference to these later) meet the conditions just enunciated. In such instances the total self-diffusion problem can be solved by a linear superposition of two simpler problems, one dealing with free vacancies and the frequency ω, and the other only with bound vacancies, as in the preceding sections, and the frequencies ω_S and ω_T. In this way an approximate solution for the case of dissociating complexes can be arrived at.

Assume that dynamic equilibrium exists between free and associated vacancies, so that the chance N_v' that a site adjacent to a solute is occupied by a vacancy is given by Boltzmann's law

$$N_v'=N_v e^{-W/kT}. \tag{4.1}$$

Here N_v is the chance that a site not adjacent to a solute is occupied by a vacancy while W is the potential energy of a vacancy on a site next to a solute. The zero of energy is referred to a site removed from a solute. In the present model we assume this zero to occur at the next nearest neighbor site so that next nearest neighbors do not interact. It should be noted that N_v is merely the equilibrium atom fraction of vacancies found in pure host crystal at the temperature in question.

Since each solute atom has 12 nearest neighbors, the fraction of solute atoms bound to vacancies is

$$\alpha=12N_v'. \tag{4.2}$$

In accordance with the plan enunciated above, the problem for the case of dissociable complexes will be solved by approximating the diffusion flux by summing the contributions due to bound and free vacancies after both have been evaluated separately. The conditions under which this procedure is valid are as follows: (1) the complex is long-lived compared to its jump time $\sim\omega_T^{-1}$, and (2) the free vacancy is long-lived compared to its jump time ω^{-1}. Actually condition (2) can be relaxed if the lifetime of the complex is so long and the concentration so high that most of the diffusion involves bound vacancies; but then we have the bound case which has been solved exactly. The lifetime of a complex is essentially ω_D^{-1}, so that condition (1) becomes

$$\omega_T \gg \omega_D. \tag{4.3}$$

The lifetime of a free vacancy is $(N_S\omega_A)^{-1}$, so that condition (2) becomes

$$\omega \gg (N_S\omega_A)^{-1}. \tag{4.4}$$

Now detailed balance requires

$$N_v\omega_A=N_v'\omega_D. \tag{4.5}$$

We digress here for a moment to describe an approximation, which although not assuredly good, will be used in a later discussion where the explicit effects of association-dissociation are treated. We do this here in order to be able to compare the formulas of this treatment with those of the later one. It is emphasized that the approximation is not necessary for the current development nor does the latter depend upon it. The approximation is illustrated by Fig. 5.

This figure shows the region about a part of the potential well near a solute atom. For simplicity the well is viewed as a square well of depth W. The drop occurs midway between the first and second nearest neighbor sites. We assume that this drop is merely superposed upon the normal activation energy picture for the jumping of a free vacancy with activation energy E_ω. Thus as the figure makes clear the activation energy for association is $E_{\omega A}$ and equals $E_\omega - W$. Thus,

$$\omega_A=\omega \quad \text{and} \quad \omega_D=\omega\exp(W/kT). \tag{4.6}$$

According to (4.1) and (4.2)

$$\exp(W/kT)=12N_v/\alpha=12/\beta, \tag{4.7}$$

where

$$\beta=\alpha/N_v, \tag{4.8}$$

so that

$$\omega_A=\omega, \quad \omega_D=12\omega/\beta. \tag{4.9}$$

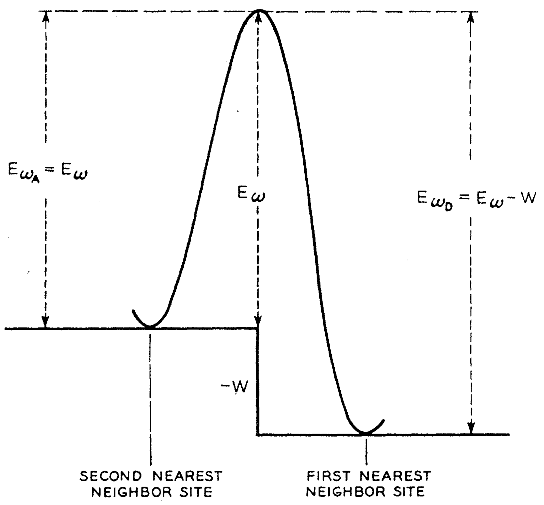


FIG. 5. The energy barrier between second and first nearest neighbor sites to a solute atom.

If we use the first of relations (4.9) in (4.4) and (4.5) and use (4.4) in (4.3), then (4.5) yields in place of (4.2) and (4.4)

$$N_v'\omega_T/N_v\omega\gg 1, \tag{4.10}$$

$$N_S\ll 1. \tag{4.11}$$

The second of these is almost always satisfied. When it is not, and (4.10) is, we have the case of bound vacancies which has been solved exactly. Now the contribution of free vacancies to diffusion in the face-centered cubic lattice has been derived by Lidiard.[7] He finds the diffusion coefficient due to free vacancies to be

$$D_*=36\,\omega a^2N_v/11, \tag{4.12}$$

when N_S is zero. When N_S is not zero, the atom fraction of free vacancies referred to the whole crystal is not N_v as assumed in (4.12), but some smaller number which can be arrived at in the following way. For every solute atom 13 sites are removed as possible locations for free vacancies. One of these 13 is the site occupied by the solute itself, while the other 12 are the nearest neighbors of the solute, for any vacancy ceases to be free when it becomes a nearest neighbor to a solute atom. Since N_S represents the chance that a given site is occupied by a solute, it follows that in place of N_v in (4.12) we should use

$$N_v(1-13N_S), \tag{4.13}$$

which now represents the atom fraction of free vacancies.

Thus the contribution to the total diffusion coefficient due to free vacancies is

$$D_f=36\omega a^2N_v(1-13N_S)/11. \tag{4.14}$$

The contribution due to bound vacancies is obtained from Table I as follows. We write

$$D(\gamma)=h(\gamma)\omega_Ta^2N_S, \tag{4.15}$$

where $h(\gamma)$ is the number appearing at the appropriate value of γ in Table I. However, the atom fraction of solutes bound to vacancies is no longer N_S but, according to (4.2), is $12N_v'N_S$. Substituting this for N_S in (4.15), we obtain for the contribution due to bound vacancies

$$D_b(\gamma)=h(\gamma)\omega_Ta^2(12N_v'N_S). \tag{4.16}$$

The diffusion coefficient of the tracer is then the sum of D_f and D_b,

$$\begin{aligned}D&=[36\omega a^2N_v(1-13N_S)/11]\\&\qquad+[h(\gamma)\omega_Ta^2(12N_v'N_S)]\\&=D_*\{1+N_S[0.306\,h(\gamma)\beta\omega_T/\omega-13]\},\end{aligned} \tag{4.17}$$

in which we have utilized (4.7) and (4.12) in passing to the final form on the right. Defining b as the quantity multiplying N_S, we have

$$D=D_*[1+bN_S], \tag{4.18}$$

where

$$b=0.306\,h(\gamma)\beta\omega_T/\omega-13. \tag{4.19}$$

5. ANALYSIS OF EXPERIMENTAL DATA

Equation (4.19) is only valid when condition (4.10) holds. The latter can be transformed with the aid of (4.2) and (4.8) into

$$\beta\omega_T/\omega\gg 12. \tag{5.1}$$

Since, according to Table I, $h(\gamma)$ never exceeds unity, comparison of (5.1) with (4.19) shows that the former tends to become valid for positive values of b. We therefore restrict the initial analysis of experimental data to systems in which this is the case.

The literature contains several examples of data in which b is positive. Hoffman, Turnbull, and Hart[2] have measured the self-diffusion coefficient of silver in the presence of various concentrations of the solutes Pb, Ge, Al, Cu over a range of temperatures. Sonder[5] has done the same using Sb as a solute. Furthermore, Hoffman[4] has investigated Tl as a solute. In all these cases, D at any one temperature is an increasing function of solute atom fraction N_S.

The limiting slope of the plot of D *versus* N_S as $N_S\to 0$ is the value of b sought. The various authors represent D in the form

$$D=D_0\exp(-Q/RT), \tag{5.2}$$

where R is the gas constant and both D_0, the pre-exponential factor, and Q the activation energy are functions of N_S. From (4.18) and (5.2), we have

$$\begin{aligned}b&=\left\{\frac{D(N_S)}{D_*}-1\right\}\Big/N_S\\&=\left\{\frac{D_0(N_S)}{D_{0*}}\exp\left(\frac{Q(N_S=0)-Q(N_S)}{RT}\right)-1\right\}\Big/N_S.\end{aligned} \tag{5.3}$$

From the various available data for each solute, we have chosen for $D_0(N_S)$ and $Q(N_S)$ the values quoted at the smallest value of N_S so that the best approximation to the limiting slope would be achieved. This was the case in all instances, except for Sb where data at the next to lowest value of N_S were used because it was felt that not enough data existed in the most dilute case to yield reliable values of D_0 and Q. Values of b computed by using (5.3) are to be found in Table II. There exists a certain discrepancy between the values of D_* for Ag measured by different authors. The discrepancy, however, is not prohibitive and whenever possible the value of D_* used is that measured by the author who measured the D leading to a given b.

To proceed further it is necessary to have measurements of D_S, the diffusion coefficient of the solute. If the contribution of association and dissociation to transport is ignored (in keeping with the spirit of the superposition of effects embodied in the previous analysis), then Lidiard[7] has effectively shown that

$$D_S=\beta N_v\left(\frac{a^2}{3}\right)\frac{\omega_T\gamma}{1+\gamma}. \tag{5.4}$$

Solving for $\beta\omega_v$ from (5.4) and for ω in (4.12) and substituting these into (4.19) yields

$$\frac{(b+13)}{3}\left(\frac{D_*}{D_S}\right)=h(\gamma)\left(\frac{1+\gamma}{\gamma}\right). \tag{5.5}$$

From Table I we obtain values of $h(\gamma)$, and are therefore able to plot in Fig. 6 the quantity $h(\gamma)[(1+\gamma)/\gamma]$ against γ. Using experimental values of b, D_*, and D_S, the left side of (5.5) can be evaluated. This quantity can then be used in connection with Fig. 6 to locate γ.

The quantity D_S has been measured for Pb by Hoffman *et al.*,[2] and for Ge and Tl by Hoffman.[4] It has been measured for Sb by Sonder, Slifkin, and Tomizuka[9] and for Cu by Sawatsky and Jaumot (according to Hoffman in reference 4). These values of D_S also appear in Table II.

Values of γ determined through use of (5.5) and Fig. 6 appear after the corresponding values of b, D_*, and D_S in Table II. In our later discussion it will be shown that the neglect of associative and dissociative processes is justifiable only when the first term on the right of (4.19) is large compared to a number of the order of 16. From (4.19) it is evident that this first term is given by $(b+13)$. For this reason, the last column of Table II lists the value of $(b+13)/16$ in each case.

TABLE II. D_*, D_S, b taken from experimental data, and values of γ and γ' computed from them.[a]

Element	Temp. (°K)	D_* (cm²/sec)	D_S (cm²/sec)	b	γ	γ'	$\frac{(b+13)}{16}$
Tl	900	6.74×10^{-12}	9.68×10^{-11}	71	0.34	1.16	5.3
Tl	1100	6.78×10^{-10}	4.56×10^{-9}	41	0.18	0.76	3.4
Pb	973	4.55×10^{-11}	6.57×10^{-10}	120	0.14	0.43	8.3
Pb	1098	6.33×10^{-10}	5.86×10^{-9}	108	0.05	0.28	7.6
Sb	841	1.44×10^{-12}	1.88×10^{-11}	89	0.19	0.62	6.4
Sb	990	7.48×10^{-11}	5.98×10^{-10}	64	0.12	0.52	4.8
Sb	1163	2.11×10^{-9}	1.09×10^{-8}	46	0.08	0.46	3.7
Ge	973	4.55×10^{-11}	5.53×10^{-10}	43	0.57	2.4	3.5
Ge	1098	6.57×10^{-10}	4.7×10^{-9}	35	0.26	1.2	3.0
Cu	1000	9.5×10^{-11}	1.19×10^{-10}	11.4	0.001	0.54	1.5

[a] *Note added in proof.*—The value of γ in Table II is always less than unity. Recently Watkins [Phys. Rev. **113**, 79 and 91 (1959)] showed by spin resonance techniques that γ for Mn in NaCl is less than unity.

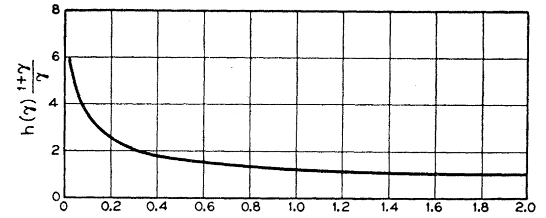


FIG. 6. Plot of the function $h(\gamma)[(1+\gamma)/\gamma]$ against γ.

The values of γ listed in Table II are all less than unity but not very much so. With the exception of Cu, it might be said that all values of γ are of the order of 0.1 or greater. Reference to Fig. 4 then suggests that the approximation $\omega_T=\omega_S$ (i.e., that leading to D_4) is probably the best of the three alternatives.

The exceptional status of Cu ($\gamma=0.001$) must be regarded with caution, since the last column shows $(b+13)/16$ for Cu to be only 1.5, and the neglect of association-dissociation is probably not justified. In fact, later it will be shown that an approximate treatment of association-dissociation yields a value for γ which falls in line with the others.

It will be noted that some values of $(b+13)/16$ are in the neighborhood of 3. It might seem as though this is not very different from 1.5, certainly not large enough to lead to so much more spurious a value of γ for copper. An analysis of the mechanics of getting at γ using (5.5) and Fig. 5 shows that the difference between 3 and 1.5 is sufficient to invalidate the use of the current approximation. This is associated with the sensitivity of $h(\gamma)[(1+\gamma)/\gamma]$ to γ when γ becomes small (see Fig. 6).

In closing, attention is drawn to the fact that the current approximation which depends upon $\beta\omega_T/\omega$ being very large would very likely be well suited to the self-diffusion of something like sodium in sodium chloride, the latter being doped with a divalent cationic impurity. The lattice of sodium ions in this salt is face-centered cubic, and the cation vacancies introduced with the divalent impurities are bound to the latter with energies of the order of $W\approx-0.5$ ev.[10] Introduction of this value into (4.7) at temperatures of 600°K (where Na diffusion can be measured) yields

$$\beta=2\times10^5, \tag{5.6}$$

which is very high. If we assume $\omega_S\approx\omega$, then this is the value of $\beta\omega_T/\omega$ and is to be compared with the

---

[9] Sonder, Slifkin, and Tomizuka, Phys. Rev. **93**, 970 (1954).

[10] Harrison, Morrison, and Rudham, Trans. Faraday Soc. **54**, 106 (1958).

value of just a few hundred typical for the solutes in silver dealt with in Table II.

6. CONTRIBUTION OF ASSOCIATION AND DISSOCIATION

Although it is possible to neglect the associative and dissociative process in many systems, there remain important cases in which this cannot be done. In addition to the example of Cu in silver discussed in the last section, the entire class of systems for which b is negative cannot be treated in the previous approximation. Therefore, in this section, an attempt will be made to take account of association-dissociation.

As discussed in Sec. 4, the exact treatment of association-dissociation is very difficult and approximations will have to be made. The results derived from this approximation will be equally valid for all systems (i.e., to those in which association-dissociation can be neglected as well as to those in which it cannot), but, where it is known that association-dissociation can be ignored, it is more desirable to use the approximation developed earlier in this paper as it is more exact.

The first step involves the assumption that $\omega_S=\infty$ ($\gamma=\infty$). We know from the last section that a typical average for γ is something like 0.3 so that this is not correct. On the other hand, the curve for D/D_2 in Fig. 4 shows that at the most we can expect about a factor of 2 error. An error of this size is acceptable when the reduction in complexity which it permits is considered.

If ω_S is taken to be infinite, then a solute-vacancy complex may be regarded as a short of divacancy, i.e., the solute and vacancy exchange positions so rapidly relative to other occurrences that to all intents and purposes the vacancy may be regarded as permanently smeared over the two sites spanned by the complex. However, the tumbling frequency of the complex must now be taken to be $\omega_T/2$ rather than ω_T because the vacancy spends only half the time at either end of the complex. With this point of view, many S and V configurations can be equated to one another and the number of simultaneous equations of the type (2.6) which need to be solved is reduced.

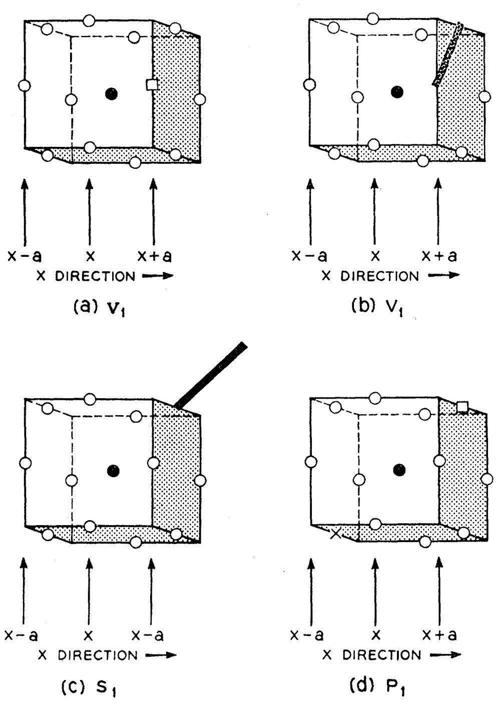
Another assumption which shall be made is the following. Consider all configurations in which a divacancy has one end on a given one of the twelve first shell sites. Then all of the configurations belonging to this cluster will be regarded as equivalent even though they occur in reality with different probabilities. It is evident that this device also reduces the number of simultaneous equations which need to be considered.

Both assumptions act to reduce the effect of correlation, and therefore both introduce errors in the same direction. This means that the total error should be somewhat greater than the factor of 2 quoted above.

The frequencies ω_A and ω_D for association and dissociation must now be included in the development. Figure 7 will be helpful in understanding the various configurations which need to be considered in treating the present problem. Parts (a), (b), (c), and (d) are four different representations of a tracer atom (solid circle) in the face-centered cubic lattice and its 12 nearest neighbors. The tracer concentration gradient is still taken to lie in the x direction which in Fig. 7 is the [100] direction as shown. All configurations which are symmetrical with respect to the x axis can therefore be regarded as equivalent, i.e., they will all have the same probability of occurrence.

In Fig. 7 the open circles are normal host atoms, the squares are free vacancies, the cross is a solute atom, and the thin solid rectangle is a vacancy-solute divacancy of the sort mentioned above. The meaning of a remains the same as before. All the configurations shown in Fig. 7 are capable of promoting the motion of the tracer. Figure 7(a) shows a free vacancy on the plane at $x+a$ into which the tracer atom can jump at the frequency ω. Since all positions on the $x+a$ plane are symmetrical with respect to the x direction, they are all equivalent and shall be denoted by the symbol v. All positions for the free vacancy on the planes at x and $x-a$, respectively, are mutually equivalent for the same reason, and shall be denoted by v_2 and v_3. These are not shown in Fig. 7.

Figure 7(b) shows a divacancy spanning two positions on the $x+a$ plane. In this configuration, motion of the tracer is possible when either end of the divacancy exchanges position with the tracer. The frequency



(a) V_1 (b) V_1

(c) S_1 (d) P_1

FIG. 7. Configurations in the face-centered cubic lattice. The filled circle is a host lattice tracer. Vacancies are represented by squares and solute atoms by **×**'s. Filled-in narrow rectangles are effective divacancies.

associated with this motion is $\omega_T/2$. The factor of $\frac{1}{2}$ appears because, as discussed, the vacancy is regarded as smeared over the two sites of the divacancy, spending half of its time at each end. All positions of the divacancy on the $x+a$ plane are symmetrically equivalent, and are assigned the symbol V_1. Similarly, all positions of the divacancy in which it spans two sites on the $x+a$ and x planes, respectively, are assigned the symbol V_2. Configurations between the x and $x-a$ planes are given the symbol V_3, and configurations on the $x-a$ plane, the symbol V_4.

Figure 7(c) illustrates a configuration in which only one end of a divacancy occupies a site among the tracer's shell of nearest neighbors. In this case the site occupied lies on the $x+a$ plane. Obviously there are 7 other orientations for the divacancy in which it can remain attached to the same first shell site and not have its other end in the first shell also. These 7 orientations are really not symmetrically equivalent but, nevertheless, by our assumption we regard them as so. As the prototype of all seven orientations, we choose the one shown (directed radially away from the tracer) and assign it the symbol S_1. There are 3 other symmetrically equivalent clusters associated with the $x+a$ plane, and all of them are assigned the symbol S_1. When the attachment is on plane at x the symbol S_2 applies, and when it is on plane $x-a$ we use S_3.

Configuration S_1 can facilitate the motion of the tracer only through dissociation of the divacancy, i.e., by escape of the vacancy from the first coordination shell of the solute atom. The frequency ω_D is associated with this motion. The factor $\frac{1}{2}$ must also be included as the vacancy spends half its time at either end of the complex. Thus the equivalent frequency is $\omega_D/2$.

Figure 7(d) illustrates a fourth kind of configuration. Here the vacancy and solute atom both occupy nearest neighbor sites but are not adjacent to one another. Such configurations are denoted by the general symbol P. Independent of where the solute atom is located (except that it cannot be adjacent to the vacancy), the symbol P_1 is given to arrangements which have the vacancy on the $x+a$ plane. P_2 is assigned when the vacancy is on the x plane and P_3 when it is on the $x-a$ plane. To each location of the vacancy there corresponds, as in the case of the S configurations, a cluster of 7 distinct orientations all of which are treated as equivalent. As in the case of the S's, correlation is also lost by this device. The assumed prototype of P_1 is the one shown in the figure, i.e., all three particles lie in a straight line. The prototypes of P_2 and P_3 are determined by the same condition.

Configuration P_1 can contribute to the motion of the tracer by having the vacancy jump to the center of the diagram. In so doing it enters the coordination shell of the solute atom and forms a divacancy. The frequency associated with this motion is ω_A.

From the foregoing it is evident that when we come to discuss the net rates of formation of the various v, V, S, and P configurations, several frequencies are liable to be involved in any one equation. For example, a particular V configuration can be destroyed or created at the tumbling frequency $\omega_T/2$. In addition it can be created at the tumbling frequency $\omega_T/2$. In addition it can be created by association at the frequency ω_A and destroyed by dissociation at the frequency $\omega_D/2$. Similar considerations hold for S and P configurations.

We now want to derive the counterpart of Eq. (2.4), i.e., the equation for the flux density $J(x)$ at the central site on plane x shown in all four parts of Fig. 7. Considerations of the same sort as those leading to (2.4) yield the following result, in which the necessary Taylor's expansions have been carried out and in which the symbols denoting the various configurations have also been used to denote the probabilities of their occurrence.

$$
\begin{aligned}
J(x)=&\frac{2\omega}{a^2}\left[(v_1-v_3)-\frac{ag}{N_S}\right]\\
&+\frac{2\omega_T}{a^2}\left[(V_1-V_4)+(V_2-V_3)-\frac{4\alpha ag}{11N_v}\right]\\
&+\frac{7\omega_D}{2a^2}\left[(S_1-S_3)-\frac{4\alpha ag}{11N_v}\right]\\
&+\frac{14\omega_A}{a^2}[(P_1-P_3)-ag], \qquad (6.1)
\end{aligned}
$$

where α, N_S, and N retain the same significances they had before and

$$g=(\partial/\partial x)(p_iN_SN_v), \qquad (6.2)$$

where, as before, p_i is the fraction of sites occupied by independent tracers.

Some discussion as to the manner in which g finds its way into (6.1) is worthwhile. Consider $-ag/N_S$ which appears in the first brackets. By the earlier arguments of this paper, the sum of the probabilities of a given downstream configuration and its upstream counterparts is the sum of the probabilities of each computed from considerations of randomness, as though no correlation existed. Thus,

$$v_1+v_3=2p_iN_v, \qquad (6.3)$$

since p_iN_v is the random probability of v_1 or v_3. As in (2.4), the terms in $J(x)$ contain differences between the probabilities of upstream and downstream counterparts less a times the derivatives of the sums of these respective probabilities. On this basis it is understandable that in (2.1) the first brackets contain the derivative

$$-\tfrac{1}{2}a(\partial/\partial x)(v_1+v_3). \qquad (6.4)$$

Upon using (6.3) and (6.2), this is obviously

$$
\begin{aligned}
-\frac{a}{2}\frac{\partial}{\partial x}(v_1+v_3)&=-\frac{a}{2}\frac{\partial}{\partial x}(2p_iN_v)\\
&=-\frac{a}{N_s}\frac{\partial}{\partial x}(p_iN_sN_v)=-\frac{ag}{N_s}. \qquad (6.5)
\end{aligned}
$$

The appearance of g in other brackets of (6.1) is based on similar considerations. The further counterparts of (6.3) are

$$\begin{aligned} V_1+V_4&=(4/11)p_iN_s\alpha,\\ V_2+V_3&=(4/11)p_iN_s\alpha,\\ S_1+S_3&=(4/11)p_iN_s\alpha,\\ P_1+P_3&=2p_iN_sN_v. \end{aligned} \tag{6.6}$$

The factor 4/11 appears for reasons similar to those for the appearance of 1/12 in Eq. (2.8). The chance of one end of a divacancy being placed on a given site equals the fraction of associated solutes. This is obviously $N_s\alpha$ The other end of the divacancy has a choice of 11 other sites (one of the 12 neighbors is occupied by a tracer), so the chance of having the divacancy in just the required orientation is $N_s\alpha/11$. But the orientation could have been achieved starting with either end of the divacancy, so that its probability is $2N_s\alpha/11$. Summing two such probabilities leads to $4N_s\alpha/11$.

Closer inspection will reveal that the sum S_1+S_3 in (6.6) should really be set equal to $(2/11+2/12)N_s\alpha$, because in starting with one end of the divacancy rather than the other, in this case, a site already occupied by a tracer does not appear. However, in the interest of symmetry and in view of the smallness of the error in comparison to those created by the approximations already made, we have elected to ignore this refinement.

Careful inspection now leads to a set of kinetic equations similar to (2.6). The resulting equations are

$$\begin{aligned}
\partial v_1/\partial t&=\omega[7p_iN_v+2v_1+2v_2+v_3(x+a)-12v_1],\\
\partial v_3/\partial t&=\omega[7p_iN_v+2v_3+2v_2+v_1(x-a)-12v_3],\\
\partial V_1/\partial t&=\tfrac{1}{2}\omega_T[2V_2+2V_3(x+a)+4S_1-8V_1]\\
&\quad+\omega_A(2P_1+2P_2+10p_iN_sN_v)-\tfrac{1}{2}\omega_D(14V_1),\\
\partial V_4/\partial t&=\tfrac{1}{2}\omega_T[2V_3+2V_2(x-a)+4S_3-8V_4]\\
&\quad+\omega_A(2P_3+2P_2+10p_iN_sN_v)-\tfrac{1}{2}\omega_D(14V_4),\\
\partial V_2/\partial t&=\tfrac{1}{2}\omega_T[V_1+2V_2+V_4(x+a)+2S_1\\
&\quad+2S_2-8V_2]+\omega_A(10p_iN_sN_v+P_1+P_2\\
&\quad+2P_3)-\tfrac{1}{2}\omega_D(14V_2),\\
\partial V_3/\partial t&=\tfrac{1}{2}\omega_T[V_4+2V_3+V_1(x-a)+2S_3\\
&\quad+2S_2-8V_3]+\omega_A(10p_iN_sN_v+P_3\\
&\quad+P_2+2P_1)-\tfrac{1}{2}\omega_D(14V_3),\\
\partial S_1/\partial t&=\tfrac{1}{2}\omega_T[4S_1+(8/12)p_iN_s\alpha-8S_1]\\
&\quad+\omega_A[9p_iN_sN_v+2v_1N_s+2v_2N_s\\
&\quad+P_3(x+a)]-\tfrac{1}{2}\omega_D(14S_1),\\
\partial S_3/\partial t&=\tfrac{1}{2}\omega_T[4S_3+(8/12)p_iN_s\alpha-8S_3]\\
&\quad+\omega_A[9p_iN_sN_v+2v_3N_s+2v_2N_s\\
&\quad+P_1(x-a)]-\tfrac{1}{2}\omega_D(14S_3),\\
\partial P_1/\partial t&=\omega(2P_2+2P_1+7p_iN_sN_v-11P_1)\\
&\quad+\tfrac{1}{2}\omega_DS_3(x+a)-\omega_1P_1,\\
\partial P_3/\partial t&=\omega(2P_2+2P_3+7p_iN_sN_v-11P_3)\\
&\quad+\tfrac{1}{2}\omega_DS_1(x-a)-\omega_1P_3.
\end{aligned}\tag{6.7}$$

The time derivatives are set equal to zero and the functions with arguments $x+a$ and $x-a$ are expanded in a Taylor's series about x, only the linear term being retained. Then the second equation is subtracted from the first, the fourth from the third and so on. The results are

$$\begin{aligned}
&v_1-v_3=2ag/11N_s,\\
&-(4\omega_T+7\omega_D)(V_1-V_4)+2\omega_T(S_1-S_3)\\
&\qquad+2\omega_A(P_1-P_3)=-4\omega_1\alpha ag/11N_v,\\
&-(3\omega_T+7\omega_D)(V_2-V_3)+\omega_T(S_1-S_3)\\
&\qquad-\omega_A(P_1-P_3)=-2\omega_1\alpha ag/11N_v,\\
&-(2\omega_T+7\omega_D)(S_1-S_3)-\omega_A(P_1-P_3)\\
&\qquad+2\omega_AN_s(v_1-v_3)=-2\omega_Aag,\\
&\tfrac{1}{2}\omega_D(S_1-S_3)-(9\omega+\omega_A)\\
&\qquad\times(P_1-P_3)=-2\omega_D\alpha ag/11N_v.
\end{aligned}\tag{6.8}$$

The frequencies ω_D and ω_A refer to processes which are the inverse of one another, and since no gradient of solute exists, the net process must be in equilibrium. Thus ω_D and ω_A are related by the principle of detailed balance. The rate at which vacancies jump into a site in the coordination shell of an impurity is $\omega_iN_vN_s$ while the rate at which they leave this shell is $\omega_D\alpha N_s/12$. Equating these rates gives

$$\omega_A/\omega_D=\alpha/12N_v=\beta/12, \tag{6.9}$$

which is contained in (4.9). However, (4.9), being two equations, says more than (6.9). It is based on the barrier scheme shown in Fig. 5. The same scheme will be employed in the current problem. Only the part of (4.9) contained in (6.9) is exact. We accept the remaining part because no further information is available and because it is a more or less traditional approximation. Besides it is consistent with detailed balancing.

If, as seems to be the case, the main force between a solute and vacancy is that due to the screened Coulomb potential,[11] the approximation in Fig. 5 will have more validity. In any event, since it enters only into that part of the argument dealing with association and dissociation and since the latter process is only responsible for part of the over-all phenomenon, it can only introduce a partial error.

Upon using (4.9) in (6.8) and defining

$$B=2\beta N_v\omega_Ta^2, \tag{6.10}$$

$$G=2N_v\omega a^2, \tag{6.11}$$

$$\lambda=ag/11, \tag{6.12}$$

Eqs. (6.8) can be solved for (V_1-V_4), (V_2-V_3), (S_1-S_3), and (P_1-P_3). The results are

$$\frac{V_1-V_4}{\beta\lambda}=\frac{[(5B+6G)(B+84G)+(5B-3G)(B+13G)]}{(B+21G)(10B+417G)}, \tag{6.13}$$

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[11] L. C. R. Alfred and N. H. March, Phil. Mag. 2, 985 (1957).

$$\frac{V_2-V_3}{\beta\lambda}=\frac{2[(5B-6G)(3B+84G)+(5B+3G)(13G-B)]}{(3B+84G)(10B+417G)},\tag{6.14}$$

$$\frac{S_1-S_3}{\beta\lambda}=\frac{118G}{10B+417G},\tag{6.15}$$

$$\frac{P_1-P_3}{\lambda}=\frac{6[4B+155G]}{10B+417G}.\tag{6.16}$$

Furthermore, using (6.10), (6.11), and the first of equations (6.8), it is possible to express (6.1) as

$$J(x)=-\left(\frac{9}{11}\right)\left(\frac{G}{a^3}\right)\left\{1+N_s\left[\frac{B}{9G}\left(4-\frac{(V_1-V_4)}{\beta\lambda}-\frac{(V_2-V_3)}{\beta\lambda}\right)+\frac{7}{3}\left(4-\frac{2(S_1-S_3)}{\beta\lambda}\right)+\frac{7}{9}\left(11-\frac{(P_1-P_3)}{\lambda}\right)\right]\right\}\frac{\partial p_i}{\partial x}.\tag{6.17}$$

Also, using (4.12), we get

$$D_*=(18/11)G.\tag{6.18}$$

Using (2.19), (2.20), and (6.18) in (6.17) yields finally

$$J(x)=-D_*\left\{1+N_s\left[\frac{B}{9G}\left(4-\frac{(V_1-V_4)}{\beta\lambda}-\frac{(V_2-V_3)}{\beta\lambda}\right)+\frac{7}{3}\left(4-\frac{2(S_1-S_3)}{\beta\lambda}\right)+\frac{7}{9}\left(11-\frac{(P_1-P_3)}{\lambda}\right)-13\right]\right\}\frac{\partial C}{\partial x},\tag{6.19}$$

where terms in N_s^2 have been neglected. It is evident from (6.19) that the diffusion coefficient D of the tracer is given by D_* multiplied by the expression in curly brackets preceding the concentration gradient. Thus, comparing with (4.18), we have

$$b=\left[\frac{B}{9G}\left(4-\frac{(V_1-V_4)}{\beta\lambda}-\frac{(V_2-V_3)}{\beta\lambda}\right)+\frac{7}{3}\left(4-\frac{2(S_1-S_3)}{\beta\lambda}\right)+\frac{7}{9}\left(11-\frac{(P_1-P_3)}{\lambda}\right)-13\right].\tag{6.20}$$

The terms in (6.20) which do not contain B/G as a factor are those in which the influence of ω_A and ω_D appear. These will obviously be a small part of the whole when

$$B/G=\beta\omega_T/\omega\gg 1,\tag{6.21}$$

a condition which merits comparison with (5.1) which also specifies the conditions under which association-dissociation can be ignored.

The inequality (6.21) can be subjected to more quantitative consideration as follows. Numerical inspection of the values of $(V_1-V_4)/\beta\lambda$, etc., given by (6.13) to (6.16) shows that they are quite insensitive to the choice of B and G when the latter are in the range of interest for the present phenomenon. Thus, when B varies from 10^{-10} to 10^{-7} and G from 10^{-13} to 10^{-9}, the variables $(V_1-V_4)/\beta\lambda$, etc., hardly vary. In fact the following is an excellent approximation:

$$\begin{aligned}(V_1-V_4+V_2-V_3)/\beta\lambda&\approx 1.5,\\ 2(S_1-S_3)/\beta\lambda&\approx 0.10,\\ (P_1-P_3)/\beta\lambda&\approx 2.36.\end{aligned}\tag{6.22}$$

Introduction of (6.22) into (6.12) yields

$$b\approx[0.28(\beta\omega_T/\omega)+16]-13.\tag{6.23}$$

The terms in square brackets are the ones which need to be compared, since the 13 is merely a consequence of geometry. It can be seen that if $\beta\omega_T/\omega$ begins to exceed 100 by very much, the 16 begins to be unimportant. Results computed using Table II and (4.19) indicate that $\beta\omega_T/\omega$ usually lies between 200 and 400.

If the 16 in (6.23) can be neglected, e.g., when (5.1) holds, then (6.23) reduces to a form identical with (4.19). In fact, if we set $\gamma=\infty$ in (4.19) [since (6.23) has been derived on this assumption], the numerical coefficient becomes

$$0.306\,h(\infty)=0.23,\tag{6.24}$$

which compares favorably with the 0.28 in (6.23). The difference between the two is a result of the loss of correlation inherent in the approximation made in (6.23) that the various configurations of a cluster are equally probable. Loss of correlation leads to a higher value of D and hence of b.

The origin of the factor $(b+13)/16$ used in Table II should also be clear from (6.23).

7. TREATMENT OF EXPERIMENTAL DATA USING THE RESULTS OF SEC. 6

Using our notation, Lidiard's result[7] for D_S including association-dissociation can be put in the form

$$D_S=\frac{\gamma B}{8}\left[\frac{B+42G}{(\gamma+1)B+42G}\right].\tag{7.1}$$

From this, we have

$$\gamma=\frac{6D_S(B+42G)}{B^2+6B(7G-D_S)}.\tag{7.2}$$

The procedure now involves determining G from D_* and (6.18), and then B from measured values of b and (6.20). These values of B and G are then to be inserted in (7.2) along with the values of D_S for the determination of γ. In connection with (6.23), the point was made that the values of $(V_1-V_4)/\beta\lambda$, $(V_2-V_3)/\beta\lambda$, $(S_1-S_3)/\beta\lambda$, and $(P_1-P_3)/\lambda$ were insensitive to change over the range of B and G, typical of the phenomenon. The almost steady values of $(V_1-V_4)/\beta\lambda$, etc., given in (6.22) are very helpful in solving for B in (6.20) when b and G are known. One merely substitutes them in that equation and calculates an approximate B, and then substitutes the latter in (6.13) through (6.16) to get refined values of $(V_1-V_4)/\beta\lambda$, etc. These can be used again in (6.2) to produce a more exact value of B. Then (7.2) can be used to obtain γ. The results of γ obtained this way are listed in Table II as γ'.

The values of γ' are about three times as great as those for γ. Our previous discussion had estimated an error of this sort due to the neglect of correlation in the current approximation. The average value of γ' seems to be about 0.5. It is to be noticed that now the value for Cu falls into line with the others. This lends support to the thesis that its exceptional behavior in the original γ column was due to the inapplicability of the approximation neglecting association-dissociation.

8. SOLUTES WITH NEGATIVE VALUES OF b

Nachtrieb, Petit, and Wehrenberg[6] have measured the self-diffusion coefficient of silver using Pd as a solute. They discovered that D satisfied a relation of the kind (4.18) with

$$b=-8.2, \tag{8.1}$$

apparently without any dependence on temperature. In addition, they noticed as an experimental fact that D could be expressed in a form independent of N_S as

$$D=D(T_M/T), \tag{8.2}$$

where T_M is the melting temperature of the alloy of Ag and Pd for which the atom fraction of Pd is N_S. Nachtrieb *et al.* suggest that this relation stems from the fact that the same energetic considerations must be applied to those processes which loosen or tighten the lattice to produce greater or lesser concentrations of vacancies as apply to the loosening or tightening which hastens or hinders melting. In this case the solute provides the tightening in both instances.

The present author is inclined to agree with this view, and as a matter of fact a fairly quantitative argument can be given on the basis of special models for the solution. The pursuit of this topic is not however within the domain of the present paper. It suffices to notice that if the conclusion is true, the key to the mechanism by which D is reduced with increasing N_S must lie mainly with the manner in which $\beta/12=e^{-W/kT}$ differs from unity, rather than upon the ratio ω_T/ω. That is, the phenomenon must be controlled by W, which is the work required for the formation of a vacancy next to a solute atom relative to the work required for its formation far from a solute. This quantity is an equilibrium parameter, and is connected at least qualitatively to the heat of melting. On the other hand, ω_T/ω depends on kinetic considerations and need not have any thermodynamic relevance.

We therefore assume that

$$\omega_T\approx\omega, \tag{8.3}$$

and that

$$\beta/12<1. \tag{8.4}$$

The first relation is necessary if the addition of solute is not to change D by frequency considerations, and the second is demanded in view of (8.3) if b is to be negative, i.e., the addition of solute must reduce the concentration of vacancies. Equation (8.3) as indicated is to be regarded as approximate. No very significant change in our conclusions would occur if it failed to be exact by as much as 50%.

In view of (8.4), W is now positive, so that the coordination shell of a solute is now the region of a potential plateau for vacancies rather than a well. Instead of (4.9) we must now use (on the basis of the same addition of energies) the relations

$$\omega_D=\omega,\quad \omega_A=\omega\beta/12. \tag{8.5}$$

This invalidates (6.13) to (6.16); returning to (6.8) and inserting (8.5), we obtain

$$\frac{V_1-V_4}{\beta\lambda}=\frac{2\{24[108\omega_T+\beta(\omega+\omega_T)](\omega_T+7\omega)+[216\omega_T+\beta(2\omega_T-\omega)](12\omega_T+\beta\omega)\}}{(24\omega_T+42\omega)[(4\omega_T+14\omega)(108+\beta)-\beta\omega]}, \tag{8.6}$$

$$\frac{V_2-V_3}{\beta\lambda}=\frac{\{12[216\omega_T+2\beta(\omega_T-\omega)](3\omega_T+7\omega)+[216\omega_T+\beta(2\omega_T-\omega)](13\omega-12\omega_T)\}}{(18\omega_T+42\omega)[4\omega_T+14\omega)(108+\beta)-\beta\omega]}, \tag{8.7}$$

$$\frac{S_1-S_3}{\beta\lambda}=\frac{(1404\omega+\beta\omega)}{(12\omega_T+42\omega)(108+\beta)-3\omega\beta}, \tag{8.8}$$

$$\frac{P_1-P_3}{\beta\lambda}=\frac{2[48\omega_T+155\omega]}{[4\omega_T+14\omega][108+\beta]-\beta\omega}. \tag{8.9}$$

Because of (8.8), Eq. (6.20) must also be changed. The first term in brackets remains unchanged because it stemmed from a term in ω_T. However, here we write $\beta\omega_T/\omega$ in place of B/G since we are not using B, G terminology. The second term arose from a term in ω_D and, since ω_D has now gone from $12\omega/\beta$ to ω, it must be multiplied by $\beta/12$. In the same way the third term, since it arose from a term in ω_A, must be multiplied by $\beta/12$ since ω_A has gone from ω to $\omega\beta/12$. As a result, we obtain

$$b=\frac{\beta\omega_T}{9\omega}\left[4-\frac{(V_1-V_4)}{\beta\lambda}-\frac{(V_2-V_3)}{\beta\lambda}\right]+\frac{7\beta}{36}\left[4-\frac{2(S_1-S_3)}{\beta\lambda}\right]+\frac{7\beta}{108}\left[11-\frac{\beta(P_1-P_3)}{\beta\lambda}\right]-13. \tag{8.10}$$

The use of (8.5) in Lidiard's[7] expression for D_S yields

$$D_S=\frac{\beta N_v a^2}{3}\left\{\frac{\omega_S[\omega_T+7\omega/2]}{\omega_S+[\omega_T+7\omega/2]}\right\}. \tag{8.11}$$

If in this relation we use (8.3) and, furthermore, make use of the information available in Table II which places $\omega_S\approx\omega_T/2$[12] on the average, (8.11) can be reduced to

$$D_S=3\beta N_v a^2\omega_T/20. \tag{8.12}$$

This relation is hardly dependent on the validity of (8.3), because $\omega_T+7\omega/2$ is in any event considerably larger than ω_S, and this almost exactly cancels out of (8.11). In that case, the 3/20 in (8.12) would simply be replaced by 1/6, which is almost the same number.

Combining (8.12) and (4.12) leads to the relation

$$\beta\omega_T/\omega=(21.8)D_S/D_*. \tag{8.13}$$

Nachtrieb[13] has measured the ratio D_S/D_* between 1124°K and 1169°K for Pd in Ag and finds it to be 0.123 with no apparent dependence on temperature. Introducing this figure into (8.13) gives us

$$\beta\omega_T/\omega=2.68. \tag{8.14}$$

Upon this assumption (8.3), this yields

$$\beta\approx 2.68. \tag{8.15}$$

Equations (8.6) through (8.9) can now be evaluated using (8.3) and (8.15). As a matter of fact, since β is so small, negligible error is introduced by ignoring all terms in (8.6) through (8.9) which contain it as a factor. In passing, it should be remarked that in the present instance also, $(V_1-V_4)/\beta\lambda$, etc., are not too sensitive to the values of ω_T and ω, just as in the case of Sec. VI where insensitivity to B and G was illustrated. Thus, any approximation contained in (8.3) will not quickly invalidate the following evaluation of $(V_1-V_4)/\beta\lambda$, etc. We obtain

$$\begin{aligned}(V_1-V_4)/\beta\lambda&=0.41,\\(V_2-V_3)/\beta\lambda&=0.22,\\(S_1-S_3)/\beta\lambda&=0.24,\\(P_1-P_3)/\beta\lambda&=0.21.\end{aligned} \tag{8.16}$$

Substitution of (8.16), (8.15), and (8.14) into (8.10) yields

$$b=-8.3, \tag{8.17}$$

which agrees with (8.1). The apparent lack of temperature dependence of b is partially explained on the basis of the present model. In the first place, most of b comes from the -13 in (8.10) which has no temperature dependence. The remainder of b depends on $\beta=12e^{-W/kT}$. If W is sufficiently small, then β will not change much with temperature over the small range 988–1215°K investigated. Using (8.15) and assuming it, applied to 1000°K, we get

$$W=RT\ln(12/\beta)=3.0\text{ kcal}. \tag{8.18}$$

With this value of W, β at 1200°K would be 3.41 if it were 2.68 at 1000°K, and b would only range from 8.3 at 1000°K to 7.0 at 1200°K.

ACKNOWLEDGMENTS

The author wishes to thank Professor D. Lazarus and Professor J. Bardeen of the University of Illinois for detailed helpful discussion in connection with the foregoing work. Special thanks are due to N. H. Nachtrieb of the University of Chicago for furnishing data, prior to publication, concerned with the diffusion of palladium in silver.

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[12] We use the average of γ' rather than γ although the latter is considered more accurate. This is because in the present section, we are using the same approximation used in deriving γ' from experimental data. Thus, use of γ' may lead to cancellation of errors.

[13] N. H. Nachtrieb (private communication).