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Impurity-Delayed Diffusion*

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An exact solution is given to a particular model for the problem in which a reactant (vacancies) diffuses to an absorbing boundary (sinks) but is occasionally delayed by traps. The solution is compared with a second solution developed using a rate-theory approach with dispersed sinks.

I. INTRODUCTION

THE manner in which point defects in excess of the equilibrium concentration are removed from a lattice is a major area of investigation. The details of a given process will depend on a number of factors—concentration and mobility of the defects, concentration and configuration of annihilation sites, and concentration of traps. As a result, no general formulation of such processes is feasible.

Under these circumstances, it has been natural to seek an analytic solution of a particular problem by emphasizing the dominant reaction, either ignoring side reactions or treating these as perturbations. This approach has been exploited very effectively by Damask and Dienes[1] (DD) in a series of calculations based on chemical rate theory. A second approach is typified by the calculations of Koehler *et al.*[2] Here, the "exact" equations were presented, including diffusion terms, but the solution was based on approximation techniques.

In this paper we present "exact" solutions for a particular problem in which generalization follows easily. The problem we consider is the migration of vacancies to sinks, in which further interactions perturb the migration. The choice of vacancies as the defect under study is arbitrary. We present solutions of this problem using, alternately, diffusion theory and chemical rate theory. A comparison of the solutions is then made.

We consider a particular model in order to obtain solutions which are more easily examined and because we believe that this model is appropriate to a number of actual physical cases. As an example, in the following paper we apply the solution to the recovery of electrical resistivity in stage IV in platinum. The recovery can be accounted for by the diffusion of vacancies with concurrent trapping by impurities.

This problem has been considered within the framework of chemical rate theory by DD and Sosin.[3] The results described in the DD work bear close qualitative agreement with ours. However, DD assumed that an impurity atom could no longer trap a second vacancy when it had already trapped one. With this assumption, the resulting differential equations are nonlinear. We take the impurity concentration to be a constant. This assumption is reasonable if the impurity concentration exceeds the vacancy concentration sufficiently. In addition, it may be possible that impurities trap more than one vacancy. The assumption is valuable in that the resulting differential equations are linear and may be solved analytically.[4] The problem of diffusion in the absence of impurities has been discussed by Blandin and Friedel.[5]

II. THEORY

A. Diffusion Theory

The problem we have defined is specified by the equations

$$\partial v/\partial t = D\nabla^2 v - \lambda v + \mu c\,, \qquad (1)$$

$$\partial c/\partial t = \lambda v - \mu c\,, \qquad (2)$$

where v and c are the concentration (atomic fraction) of vacancies, and vacancy impurity complexes, respectively. The term $D\nabla^2 v$ is related to the migration of vacancies under a concentration gradient. Trapping of vacancies by impurities is represented in Eq. (1) by $(-\lambda v)$ and release from these traps, by (μc). The rate constants, λ and μ, are defined by[1]

$$\lambda = 84 I\nu \exp(-E/kT)\,, \qquad (3)$$

and

$$\mu = 7\nu \exp[-(E+B)/kT]\,. \qquad (4)$$

Here I is the concentration of impurities (assumed constant, as discussed above); ν, the atomic attack frequency ($\approx 10^{13}$ sec^{-1}); E, the activation energy of

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[1] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, Science Publishers, Inc., New York, 1963); Phys. Rev. **120**, 99 (1960).

[2] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

[3] A. Sosin, Phys. Rev. **122**, 1112 (1961).

[4] Upon completion of this work we have been made aware of a calculation by D. G. Hurst of the problem dealt with below in Sec. IIA. [Atomic Energy Commission, Limited report AECL 1550, 1962 (unpublished)]. Hurst's work should be consulted for a larger number of numerical examples.

[5] A. Blandin and J. Friedel, Acta Met. **8**, 384 (1960).

motion of vacancies; k, the Boltzmann constant; T, the temperature; B, the vacancy-impurity binding energy; and D, the diffusion coefficient for a free vacancy, given by

$$D=a^2\nu\exp(-E/kT)\,. \qquad (5)$$

Equation (5) is appropriate for diffusion of a vacancy in a cubic crystal where a is the lattice constant.

The boundary and initial conditions imposed on Eqs. (1) and (2) are

$$\begin{aligned} v&=v_0 \quad \text{for} \quad r<R \quad \text{at} \quad t=0,\\ v&=0 \quad \text{for} \quad r=R \quad \text{all} \quad t,\\ c&=c_0 \quad \text{for} \quad r<R \quad t=0. \end{aligned}$$

With these conditions, Eq. (1) describes the diffusion of vacancies with initially uniform distribution to unsaturable sinks which we take to be located on the surface of a sphere of radius R. A physical situation which corresponds to this model is the annihilation of vacancies at grain boundaries or mosaic boundaries.

The solution to this problem may be obtained through the direct application of Laplace transformation methods. However, it is more informative to proceed differently, resorting to Laplace transforms later. We assume that the spatial and time dependences of v and c are separable and, further, that they possess the same spatial dependence:

$$v(r,t)=\rho(r)T^v(t)\,, \qquad (6)$$

and

$$c(r,t)=\rho(r)T^c(t)\,, \qquad (7)$$

where r is a radial coordinate. Then

$$D\nabla^2\rho=K\rho\,, \qquad (8)$$

$$dT^v/dt+dT^c/dt=KT^v\,, \qquad (9)$$

and

$$dT^c/dt=\lambda T^v-\mu T^c. \qquad (10)$$

The eigenfunctions satisfying Eq. (8) are[6]

$$\rho_n(r)=\frac{2}{\pi}v_0\frac{R}{r}\left[\frac{(-1)^{n+1}}{n}\sin\frac{n\pi r}{R}\right], \qquad (11)$$

with

$$K_n=-n^2\pi^2D/R^2\,, \qquad (12)$$

where n is a positive integer and K_n are the eigenvalues of Eq. (8).

Equations (9) and (10) become, under Laplace transformation,

$$p_n\bar{T}_n^v-1+p_n\bar{T}_n^c-f=K_n\bar{T}_n^v\,, \qquad (13)$$

and

$$p_n\bar{T}_n^c-f=\lambda\bar{T}_n^v-\mu\bar{T}_n^c. \qquad (14)$$

The overbars indicate transformed functions in the Laplace variable, p. Here f is defined as c_0/v_0 (the initial ratio of trapped to untrapped vacancies). The inverse transformations to Eqs. (13) and (14) may be evaluated by the method of residues to yield

$$T_n^v=\frac{p_n^++\mu(1+f)}{p_n^+-p_n^-}\exp(p_n^+t)+\frac{p_n^-+\mu(1+f)}{p_n^--p_n^+}\exp(p_n^-t)\,. \qquad (15)$$

Here p_n^+ and p_n^- are the solutions to the quadratic equation,

$$p_n^2+p_n(\lambda+\mu-K_n)-\mu K_n=0. \qquad (16)$$

Similarly,

$$T_n^c=\frac{\lambda[p_n^++\mu(1+f)]}{(p_n^+-p_n^-)(p_n^++\mu)}\exp(p_n^+t)+\frac{\lambda[p_n^-+\mu(1+f)]}{(p_n^--p_n^+)(p_n^-+\mu)}\exp(p_n^-t)\,. \qquad (17)$$

Combining the spatial and temporal parts of the solutions through Eqs. (6) and (7), we have

$$v(r,t)=\frac{2}{\pi}v_0\frac{R}{r}\sum_{n=1}^{\infty}\left\{\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi r}{R}\right)T_n^v(t)\right\}, \qquad (18a)$$

and

$$c(r,t)=\frac{2}{\pi}v_0\frac{R}{r}\sum_{n=1}^{\infty}\left\{\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi r}{R}\right)T_n^c(t)\right\}. \qquad (18b)$$

The quantity which is most easily related to experiment is the total concentration of free vacancies and bound vacancies at time t. These quantities, following integration over r in Eq. (18), are

$$M_v(t)=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{\frac{1}{n^2}T_n^v(t)\right\}, \qquad (19a)$$

and

$$M_c(t)=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{\frac{1}{n^2}T_n^c(t)\right\}. \qquad (19b)$$

It is significant to observe the effect of different values of the binding energy B. Changing the value of B changes μ [Eq. (4)], yielding different roots, p_n [Eq. (16)]. This, in turn alters T_n^v and T_n^c [Eqs. (15) and (17)]. As a result, the *time* dependences of $v(r,t)$ and $c(r,t)$ are altered [Eq. (18)]. The *spatial* dependences are unaltered. Thus, there is one-to-one correspondence between the spatial distribution of defects represented by the nth component of the sum for $\rho(r)$ at any particular time with the same component under trapping conditions given by a different value of B (including $B=0$ in the no-trap case) at some different time. The time shift between these two identical complexions of the nth component is reflected in a different time basis in Eq. (19)—an important consideration for later discussion.

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[6] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, England, 1956), p. 86.

The solution developed here may be altered to accommodate different boundary conditions. For example, one may treat the volume diffusion of point defects to internal cylinders, representing isolated dislocations or the volume diffusion of point defects to internal spheres, representing jogs or clusters of vacancies. The solutions in these cases involve a redefinition of the constant K_n in terms of the pertinent physical parameters and of different numerical factors.

The above solution may correspond to the physical case of a quench where an excess concentration of vacancies is frozen into the lattice. During the quench some vacancies may have been trapped at impurities which would correspond to a finite value of f. The appropriate initial conditions for the migration of vacancies created by irradiation with charged particles at low temperatures is $f=0$.

B. Rate Theory

This same problem may be solved within the framework of chemical rate theory. Damask and Dienes have presented numerical solutions taking into account explicitly the change in the impurity concentration I. Within the approximation that I is a constant, the kinetic problem lends itself to an analytic solution, which is identical to the first eigenfunction ($n=1$) of the diffusion equation. Using a notation similar to that of DD, we define the kinetic problem by

$$v+I \underset{K_{\mathrm{II}}}{\overset{K_{\mathrm{I}}}{\rightleftarrows}} c, \tag{20}$$

and

$$v \xrightarrow{K_{\mathrm{III}}} \text{sinks}. \tag{21}$$

Then

$$dv/dt=-K_{\mathrm{I}}Iv-K_{\mathrm{III}}v+K_{\mathrm{II}}c, \tag{22}$$

and

$$dc/dt=K_{\mathrm{I}}vI-K_{\mathrm{II}}c. \tag{23}$$

Here

$$K_{\mathrm{I}}=\lambda/I, \tag{24a}$$

$$K_{\mathrm{II}}=\mu, \tag{24b}$$

and

$$K_{\mathrm{III}}=\nu q^2\exp(-E/kT). \tag{24c}$$

Here q is a constant related to the sink concentration. The solutions to Eqs. (22) and (23) are

$$v(t)=A^+\exp(\alpha^+t)+A^-\exp(\alpha^-t), \tag{25}$$

and

$$c(t)=B^+\exp(\alpha^+t)+B^-\exp(\alpha^-t). \tag{26}$$

Here α^+ and α^- are the roots of the quadratic equation:

$$\alpha^2+\alpha(K_{\mathrm{I}}I+K_{\mathrm{II}}+K_{\mathrm{III}})+K_{\mathrm{II}}K_{\mathrm{III}}=0, \tag{27}$$

and A^+, A^-, B^+, and B^- are constants to be evaluated from the initial conditions:

$$v=v_0 \quad \text{at} \quad t=0,$$

$$c=c_0 \quad \text{at} \quad t=0,$$

and from two compatibility conditions which demand that

$$B^{\pm}=q^{\pm}A^{\pm}, \tag{28}$$

where

$$q^{\pm}\equiv K_{\mathrm{I}}I/(\alpha^{\pm}+K_{\mathrm{II}}). \tag{29}$$

Accordingly,

$$A^+=v_0(\alpha^++K_{\mathrm{II}}(1+f))/(\alpha^+-\alpha^-), \tag{30a}$$

$$A^-=v_0(\alpha^-+K_{\mathrm{II}}(1+f))/(\alpha^--\alpha^+), \tag{30b}$$

$$B^+=v_0K_{\mathrm{I}}I\frac{\alpha^++K_{\mathrm{II}}(1+f)}{(\alpha^+-\alpha^-)(\alpha^++K_{\mathrm{II}})}, \tag{31a}$$

and

$$B^-=v_0K_{\mathrm{I}}I\frac{\alpha^-+K_{\mathrm{II}}(1+f)}{(\alpha^--\alpha^+)(\alpha^-+K_{\mathrm{II}})}. \tag{31b}$$

C. Comparison of Rate and Diffusion Theory

In order to facilitate the comparison of the solutions, we compare the *first* eigenfunctions of the diffusion theory

$$\frac{6}{\pi^2}v_0\left[\frac{p_1^++\mu(1+f)}{p_1^+-p_1^-}\exp(p_1^+t)+\frac{p_1^-+\mu(1+f)}{p_1^--p_1^+}\exp(p_1^-t)\right], \tag{32a}$$

and

$$\frac{6}{\pi^2}v_0\lambda\left[\frac{p_1^++\mu(1+f)}{(p_1^+-p_1^-)(p_1^++\mu)}\exp(p_1^+t)+\frac{p_1^-+\mu(1+f)}{(p_1^--p_1^+)(p_1^-+\mu)}\exp(p_1^-t)\right], \tag{32b}$$

with

$$v(t)=v_0\left[\frac{\alpha^++\mu(1+f)}{(\alpha^+-\alpha^-)}\exp(\alpha^+t)+\frac{\alpha^-+\mu(1+f)}{(\alpha^--\alpha^+)}\exp(\alpha^-t)\right], \tag{33a}$$

and

$$c(t)=v_0\lambda\left[\frac{\alpha^++\mu(1+f)}{(\alpha^+-\alpha^-)(\alpha^++K_{\mathrm{II}})}\exp(\alpha^+t)+\frac{\alpha^-+\mu(1+f)}{(\alpha^--\alpha^+)(\alpha^-+K_{\mathrm{II}})}\exp(\alpha^-t)\right]. \tag{33b}$$

Now, $p_1^{\pm}$ are the roots of the quadratic equation (16) which is the *same* equation as is satisfied by $\alpha^{\pm}$, namely, (27) *if* $-K_{\mathrm{I}}=K_{\mathrm{III}}$. The only remaining difference between Eqs. (32) and (33) is the numerical factor $6/\pi^2$. This factor arises from the fact that we have singled out for comparison only the first eigenvalue solution. Note that

$$\sum_{n=1}^{\infty}n^{-2}=\tfrac{1}{6}\pi^2.$$

On the basis of this comparison, the limitations of the rate-theory approach may be appreciated. The primary effect of ignoring the concentration gradient term in the diffusion equation is to suppress the higher eigenvalue terms in the solution of the diffusion equation. Accordingly, an exact comparison between diffusion-theory and rate-theory approaches is not possible. At long times, however, the higher order eigenfunctions diminish in importance. A comparison between approaches is then more meaningful. In particular, we may relate q, the sink density, to the appropriate sink dimension of the diffusion problem.

III. NUMERICAL EVALUATION

The concentration of free and bound vacancies as expressed in Eq. (19) was studied as a function of time for various values of λ and μ on an analog computer. In the following numerical examples, we always take

$$K_n = -n^2 \times 10^{-4}.$$

This choice effectively determines a value for $\nu \exp[-E/kT]$. Also a^2/R^2 is a constant for any one material. Then we note from Eqs. (1), (3), and (4) that λ reflects the impurity concentration I and μ the binding energy B, respectively.

In Figs. 1 and 2 we present the results of the computer plots for the fractional free-vacancy concentration (M_v) and bound-vacancy concentration (M_c) as a function of time. A number of observations may be made:

(1) The number of complexes M_c increases rapidly at early times. During this same transient period, the number of free vacancies M_v decreases correspondingly. The length of this transient period depends almost entirely on the value of λ (i.e., concentration of impurities) rather than on the value of μ (i.e., binding energy). That is, the time required to establish a dynamic equilibrium between free and bound vacancies is more sensitively determined by the sink and trap concentrations than by the binding energy, for reasonable values of these parameters.

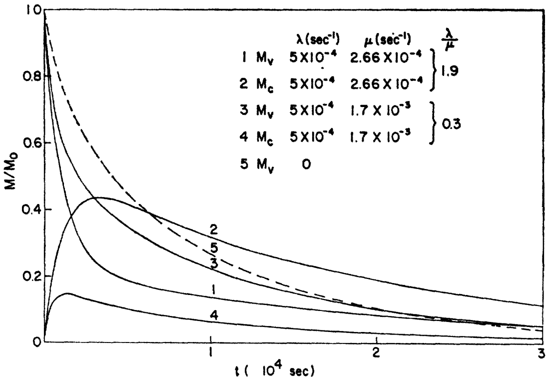

FIG. 1. Plots of free-vacancy (fractional) concentration M_v and bound-vacancy (fractional) concentration M_c as a function of time. The impurity concentration has been kept constant (keeping λ constant) but the binding energy has been varied (varying the value of μ) in plots 1–4. Plot 5 pertains to diffusion in the absence of impurities.

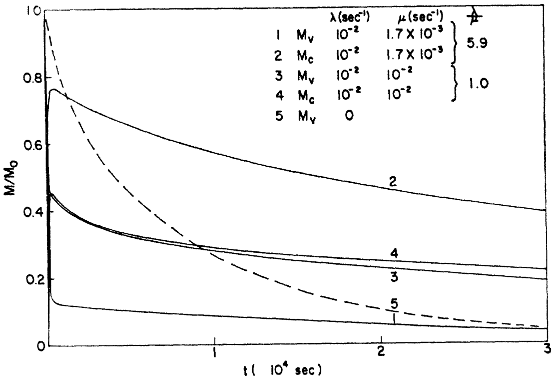

FIG. 2. Same as Fig. 1 with different parameters.

(2) After this initial transient period, both M_c and M_v decay steadily and a dynamic equilibrium between them is followed. This suggests that, to a good approximation, Eq. (2) may be altered to

$$\partial c/\partial t = \lambda v - \mu c \approx 0. \tag{34a}$$

Hence,

$$\frac{\lambda}{\mu} \approx \frac{c(t)}{v(t)} \approx \frac{M_c(t)}{M_v(t)}. \tag{34b}$$

The extent to which this relationship holds can be deduced from the results in Figs. 1 and 2. We have compiled the numerical values of Table I arbitrarily for a time of 2×10^4 sec.

TABLE I. Comparison of Eq. (34) with computer results.

Run	λ/μ	$M_c/M_v(2\times10^4$ sec)
1&2 Fig. 1	1.9	2.3
3&4 Fig. 1	0.3	0.34
1&2 Fig. 2	5.9	8.0
3&4 Fig. 2	1.0	1.1

(3) Figures 1 and 2 represent the calculated results for two different impurity concentrations and each figure represents the results for the same impurity concentration and different binding energies. It is clear that the total vacancy concentration ($M_c + M_v$) at any given time depends on λ and μ in a complicated manner. However, the significant delay in the annihilation of the vacancies by the impurities is apparent when the results are compared with curve 5 in each figure. The magnitude of the delay becomes more pronounced at longer times.

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