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DEFECT MOBILITY AND REACTION: DIFFUSIONAL AND RATE THEORY FORMULATIONS IN ONE AND THREE DIMENSIONS*

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ABSTRACT

The migration of defects, leading to eventual reaction, is analyzed on the basis of diffusion theory and compared with chemical rate theory. A diffusional treatment is carried out in detail and in special cases of particular interest. Correlations between interstitials and vacancies, typical of metals following electron irradiation, are examined. Trapping by impurities and dislocations, thermal conversion, and high temperature bombardment are also treated.

In each case, formulations are developed along both one- and three-dimensional diffusion models. These alternative results are compared with experiments, particularly annealing in copper irradiated by electrons at low temperature. The results support the conclusion that the defect which migrates in Stage I diffuses in three dimensions.

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I. INTRODUCTION

In the analysis of experiments in which lattice defects diffuse through a crystal enroute to a reaction site, it is generally assumed that the defects are randomly distributed initially and, therefore, that a formulation based on chemical kinetics will adequately describe the situation. In this context, chemical kinetics is taken to designate reaction processes in which bulk concentration, time, etc., are variable but in which spatial positions are not considered explicitly. Even in the case of defect distributions which are completely random initially, the use of chemical kinetics is not fully justified, but, following some initial time transient, may provide a suitable model.(1)

In the case of radiation damage in metals and semiconductors, the inhomogeneity in defect distributions is a salient feature of the damage state. Following neutron or positive ion bombardment, it is recognized that some regions of the material possess high defect (interstitial and vacancy) concentrations whereas others are sparsely populated by defects. In electron irradiation, the distribution of interstitial-vacancy pairs approaches complete randomness; however, a variation in the separation between the two members of a single pair introduces a non-randomness into the damaged state. Clearly the neglect of spatial considerations in such problems may give rise to apparent discrepancies or, more significantly, exclude an opportunity to extract information from available data.

The concern of this paper centers on problems in which spatial considerations are of major importance. Accordingly, we shall discuss defect migration and interactions based on a diffusional analysis. We shall concentrate on the situation which is produced generally by electron irradiation. With this specific orientation, it is our intention to treat a number of relevant features of the problem. These are best presented in the context of an analysis of I_d-I_e recovery--a topic central to the theory of post-irradiation recovery in metals. As presented by Corbett, Smith, and Walker(2) who first designated the nomenclature, substage I_d is produced by the recombination of interstitials with their original vacancies. This recombination is presumed to display the effects of close spatial correlation without energy correlation; that is, atomic jumps are postulated to occur with equal probability in any allowed direction but pair recombination is favored by proximity. For those interstitials which effectively escape the environs of their vacancies despite this spatial correlation, recombination (and other processes) may occur in a more random manner following (on the average) considerably more diffusion by interstitials, giving rise to substage I_e.

1. The analysis presented by Corbett et al. was based on the analytical development of Waite.(1) In order to effect a comparison with experiment, Waite introduced a particular distribution function which described the spatial separations between vacancies and interstitials within pairs. This function was taken over intact by Corbett et al. in their analysis. Subsequently, other forms of this distribution function have been introduced.(3,4) We here discuss the analytic significance of these distribution functions in the analysis of substage I_d and introduce a generalization.

2. The data of Corbett et al., for recovery of irradiated copper, appeared to show a smooth progression in each of the substages, I_d and I_e. Subsequently, it has been reported(5-13) that a closer examination of this

recovery revealed "fine structure," which might invalidate the model proposed by Corbett et al. In particular, such fine structure might indicate the presence of a conglomerate of processes, each characterized by a particular activation energy. The most obvious underlying physical basis for such substructure would lie in "bound close pair" configurations, described in the next section. The analysis of Corbett et al. invokes only one value of migration energy.(2,14) We shall discuss this question of fine structure and attempt to delineate the extent to which fine structure may be observed under reasonable experimental conditions.

3. From the above discussions, concerned mainly with I_d, we will continue into I_e and attempt to establish how the connection between the two substages occurs; that is, we shall be concerned with the ease with which a single diffusional model can account for the entire I_d-I_e recovery region, taking into account the nature of the assumptions made concerning distribution functions and processes which compete with interstitial-vacancy recombination.

4. All of the above discussion, particularly that of 3, is based on three-dimensional analyses. We shall also include considerations of one-dimensional analysis since one of the prevailing models of recovery in metals is based on the motion of crowdions in Stage I (which includes I_d-I_e and preceding substages).(15) A crowdion is an interstitial confined to migrate along a straight line--i.e., in one dimension.

II. STATEMENT OF THE PROBLEM

The situation we shall examine is the general state arrived at following an irradiation with energetic electrons at sufficiently low temperatures: interstitial atoms are deposited at various distances from their original vacancies. Due to the discrete nature of the crystal lattice, interstitial-vacancy (i-v) separation distances are also discrete, but this discreteness is generally ignored (see, however, Corbett(16,17)), leading to the concept of a continuous distribution of i-v separation distances. The form of this distribution remains an open question. Clearly it may depend on the bombarding particle (electrons, here), the energy of the particle, the direction of incidence of the particle beam with respect to a frame of reference in the crystal structure, the nature of the interatomic interaction potential, etc. Under controlled experimental conditions, it is apparent that a knowledge of the distribution function would provide important information concerning the interaction potential or vice versa.

In the case of electron irradiation, there are some basic elements of radiation damage theory which indicate some of the general features of the distribution function. As a particularly important point, we note that the distribution of recoil energies, for atoms recoiling from electron-atom collisions, is proportional to T^{-2}, where T is the energy transfer in such collisions. Thus, low energy recoil events are favored, leading to a predominance of small i-v separations. To continue further requires a full appreciation of the displacement kinematics in a crystalline medium.

Kinematic considerations determine the distribution of initial i-v sites, which may be categorized by dividing the lattice into three regions around any vacancy. If the interstitial is deposited too close, the i-v configuration is completely unstable and recombination occurs; in monatomic lattices, such displacement and recombination events are undetectable. If the interstitial is deposited somewhat further--in the intermediate region--the i-v pair is stable; however, with some thermal activation, interstitial migration occurs, but only in the manner to provide simple i-v pair recombination. This gives rise to "close pair recombination" of "bound close pairs." Insofar as each such i-v configuration is identified with a different value of activation energy, each configuration would be expected to lead to a characteristic recovery "peak" which would have the characteristics of a simple first-order process. Substages I_a, I_b, and I_c in copper apparently conform to this pattern.

The most distant region is one in which migration of interstitials is unaffected by the proximity of vacancies. Where the separation between the intermediate and distant regions occurs, or even if such a separation can actually be made, remains obscured somewhat in prevailing controversy. The entire situation is described in the schematic potential energy profile of Figure (1a).

III. CORRELATED RECOVERY

A. Formulation

In this section we shall assume that the separation between intermediate and distant i-v regions may be made in a meaningful manner and concentrate only on the distant region. In this region, there is no correlation based on energy considerations; but, as discussed above, a considerable correlation between i-v separations occurs because of displacement dynamics. If the "free" interstitial performs a relatively small number of jumps in the general direction of its original vacancy, it will penetrate into the intermediate region and subsequently be annihilated readily and almost inevitably. The problem we pose for study is: what is the probability that an interstitial which begins a random walk at a distance r_i from its vacancy will return to that vacancy in time t? Random walk calculations have been performed by Fletcher and Brown,(18) by Streetman,(19) and more recently, by Corbett.(16,17) Although the random walk solutions are exact, Flynn has shown that it is quite reasonable to approximate random walk by free diffusion.(20,21) By passing to a diffusion problem, analytic forms can usually be obtained to help illuminate the basic physical processes involved in correlated recovery. In the spirit of a diffusional analysis our problem* has the following characteristics:

1. There exists around each vacancy a sphere of radius r_o containing "unstable sites"--sites in which an interstitial, following arrival, will

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*As stated in the Introduction, we shall be concerned with analyses in one and three dimensions. The explicit presence of the distance variables x and r will indicate the dimension of the space under consideration: x for one dimension, r, for three.

move in an essentially instantaneous time interval into the vacancy; we restrict our attention here to the three-dimensional case.

2. All i-v pairs are isolated; effectively an i-v pair is contained in an infinite volume devoid of other interstitials or vacancies. This restriction is lifted in a subsequent section.

3. All i-v separation distances can be described by an initial distribution function. A number of continuous functions have been suggested and we shall examine them shortly. Obviously, such functions must approximate to discrete ones.

To incorporate the above concepts into a mathematical framework, we proceed as follows. Let $P(\vec{r},t)dV$ be the probability that an interstitial is in the volume element dV at $\vec{r}$ at time t. The origin is placed at the position of the vacancy. This probability obeys the microscopic diffusion equation

$$\frac{\partial P(\vec{r},t)}{\partial t} = D\nabla^2 P(\vec{r},t) \tag{3.1}$$

where

$$D = D_o \exp(-E_m/kT) \tag{3.2}$$

Here D is the diffusion coefficient for defect (interstitial) migration, composed of a pre-exponential constant, D_o, and the standard Arrhenius factor displaying the energy of migration, E_m, the temperature, T, and Boltzmann's constant, k. Note that Equation (3.1) describes the explicit time-dependence of $P(\vec{r},t)$. The boundary conditions placed on Equation (3.1) are

$$P(r \leq r_o, t) = 0 \tag{3.3}$$

and

$$P(r > r_o, t=0) = g(r) \quad , \tag{3.4}$$

the initial distribution.

We shall make the simplifying assumption of spherical symmetry. Then the probability that the interstitial is in the range dr about r, is given by

$$\rho(r)\,dr = 4\pi g(r) r^2 dr \tag{3.5}$$

with the normalization condition that

$$4\pi \int_{r_o}^{\infty} g(r)\, r^2\, dr = 1 \tag{3.6}$$

In addition, we have that

$$n(t)/n_o = \int_{\infty} P(\vec{r},t)\, dV \tag{3.7}$$

where n(t) is the defect concentration present at time t; n_o is the initial concentration and the integral is taken over all space.

To obtain the time-rate of decay of interstitial concentration, we evaluate the flux of interstitials through the capture sphere of radius r_o around the vacancies, given by

$$\frac{dn}{dt} = -4\pi\, n_o\, r_o^2\, D \left.\frac{\partial P(r,t)}{\partial r}\right|_{r = r_o} \tag{3.8}$$

Following customary notation,(1) we define the fractional recovery as

$$\phi(t) = \frac{n_o - n(t)}{n_o} \tag{3.9}$$

so that

$$\phi\ (t) = 4\pi\ r_o^{\ 2}\ D \int_o^t \frac{\partial P(r,t')}{\partial r}\Bigg|_{r = r_o} dt' \tag{3.10}$$

Equivalently,

$$\phi\ (t) = 1 - \int_\infty P(\vec{r},t)\ dV \tag{3.11}$$

In three dimensions, there is a finite chance for an interstitial to escape its vacancy entirely. Thus, we calculate the asymptotic value of recovery as

$$\phi(\infty) = 4\pi\ r_o^{\ 2}\ D \int_o^\infty \frac{\partial P(r,t')}{\partial r}\Bigg|_{r = r_o} dt' \quad . \tag{3.12}$$

The general solution to the diffusion problem posed above is(22)

$$P(r,t) = (4\pi Dt)^{-1/2} \int_o^\infty (\xi+r_o)\ g(\xi+r_o)\ r^{-1}\ \{\exp\ [-\frac{(r-r_o-\xi)^2}{4Dt}] - \exp\ [-\frac{(r-r_o+\xi)^2}{4Dt}]\}\ d\xi \tag{3.13}$$

This gives the fractional recovery as

$$\phi(t) = 4\pi\ r_o \int_{r_o}^\infty r\ g(r)\ \mathrm{erfc}\ (\frac{r-r_o}{\sqrt{4Dt}})\ dr \tag{3.14}$$

From Equation (3.14), letting t→∞, we may obtain an alternative form to Equation (3.12)

$$\varphi(\infty) = 4\pi \int_{r_o}^\infty (\frac{r_o}{r})\ r^2\ g(r)\ dr \tag{3.15}$$

demonstrating a well-known result: the probability of capture of an interstitial by a vacancy at an initial distance r_i, given a capture radius, r_o, is $\left(\frac{r_o}{r_i}\right)$.

Clearly to proceed further it is necessary to specify the form of g(r). The forms of g(r) that we shall consider here are:

$$g_1(r) = N_1 \delta(r - r_i) \tag{3.16 a}$$

$$g_2(r) = \sum_i (N_2)_i \, \delta(r - r_i) \tag{3.16 b}$$

$$g_3(r) = N_3 \exp(-r/\lambda_3 r_o) \tag{3.16 c}$$

$$g_4(r) = N_4 r^{-1} \exp(-r/\lambda_4 r_o) \tag{3.16 d}$$

$$g_5(r) = N_5 \exp[-(r/\lambda_5 r_o)^2] \tag{3.16 e}$$

Obviously, the above functions are defined for $r \geq r_o$. For $r < r_o$, the functions are zero.

It is noted that ϕ depends on time and temperature only through the product of the diffusion coefficient and the time, so that it is convenient to define a characteristic length:

$$z = \sqrt{4Dt} \tag{3.17}$$

The explicit probability distribution function is obtained for the modified exponential ($g_4(r)$) as

$$\psi_4\left(\frac{r}{r_o}, z\right) = \left[2\lambda_4(1+\lambda_4)\right]^{-1} \exp\left(\frac{z}{2\lambda_4 r_o}\right)^2 \left\{\left(\frac{r}{r_o}\right) \exp\left[\frac{1}{\lambda_4}\left(1-\frac{r}{r_o}\right)\right]\right.$$

$$\operatorname{erfc}\left[\frac{z}{2\lambda_4 r_o} - \frac{r_o}{z}\left(\frac{r}{r_o}-1\right)\right] - \exp\left[-\frac{1}{\lambda_4}\left(1-\frac{r}{r_o}\right)\right] \operatorname{erfc}$$

$$\left.\left[\frac{z}{2\lambda_4 r_o} + \frac{r_o}{z}\left(\frac{r}{r_o}-1\right)\right]\right\} \qquad (3.18)$$

Values of this function are plotted in Figure (2) for different values of z. For quite small z, the distribution collapses at $r=r_o$ and gradually approaches a uniform value as z increases. After the existing interstitials have made a considerable number of jumps, the distribution loses much of its rapid variation and is mainly characterized by the area under the curve, i.e., by the fraction of defects which have escaped correlated recovery.

Equation (3.14) was evaluated for the boundary condition represented by Equation (3.16) and the results are:

$$\phi_1(z) = \frac{r_o}{r_i} \operatorname{erfc}\left(\frac{r_i - r_o}{z}\right) \qquad (3.19\ a)$$

$$\phi_2(z) = \sum_i \frac{n_i}{n_o} \frac{r_o}{r_i} \operatorname{erfc}\left(\frac{r_i - r_o}{z}\right) \qquad (3.19\ b)$$

where $\frac{n_i}{n_o}$ is the fraction of interstitials initially at the distance r_i.

$$\phi_3(z) = [\lambda_3^{-1} + 2\lambda_3 + 2]^{-1} \{ (1 + \lambda_3^{-1}) [1 - \exp (\frac{z}{2\lambda_3 r_o})^2 \operatorname{erfc} (\frac{z}{2\lambda_3 r_o})]$$

$$- \frac{z}{\lambda_3 r_o} [\pi^{-1/2} - \frac{z}{2\lambda_3 r_o} \exp (\frac{z}{2\lambda_3 r_o})^2 \operatorname{erfc} (\frac{z}{2\lambda_3 r_o})] \} \tag{3.19 c}$$

$$\phi_4(z) = (1+\lambda_4)^{-1} [1 - \exp (\frac{z}{2\lambda_4 r_o})^2 \operatorname{erfc} (\frac{z}{2\lambda_4 r_o})] \tag{3.19 d}$$

$$\phi_5(z) = [1 + \frac{1}{2} \lambda_5 \pi^{1/2} \exp (\lambda_5^{-2}) \operatorname{erfc} (\lambda_5^{-1})]^{-1}$$

$$\{ 1 - [1 + \frac{z^2}{r_o^2 \lambda_5^2}]^{-1} \exp [z^2/r_o^2 \lambda_5^4 (1 + z^2/r_o^2 \lambda_5^2)]$$

$$\operatorname{erfc} [z/r_o \lambda_5^2 (1 + z^2/\lambda_5^2 r_o^2)^{1/2}] \} \tag{3.19 e}$$

For crowdion-vacancy annihilation (i.e., one dimensional diffusion), the recovery is

$$\phi(t) = \int_{x_o}^{\infty} \{g(x)\} \operatorname{erfc} \left(\frac{x - x_o}{\sqrt{4Dt}}\right) dx \tag{3.20}$$

where $\{g(x)\}$ is the initial distribution of crowdions about their vacancies. Equation (3.20) will be similar to Equation (3.14) provided

$$g(r) \rightarrow x\, g(x) = \{g(x)\} \tag{3.21}$$

The evaluation of Equation (3.20) for infinite time gives the result

$$\phi(\infty) = 1 \tag{3.22}$$

i.e., we have the well-known result that <u>all</u> interstitials eventually return to their own vacancies. This proves to be the most significant difference between the one and three dimensional formulations of correlated recovery. Examples resulting from the evaluation of Equations (3.20) and (3.21) are

$$\phi_1(z) = \operatorname{erfc} \left(\frac{x_i - x_o}{z}\right) \tag{3.23 a}$$

$$\phi_4(z) = \left[1 - \exp \left(\frac{z}{2\lambda_4 r_o}\right)^2 \operatorname{erfc} \left(\frac{z}{2\lambda_4 r_o}\right)\right] \tag{3.23 b}$$

with expressions similar to Equations (3.19c) and (3.19e) for the exponential and Gaussian distributions.

B. Discussion

Again note that the fraction of defects which escape correlated recovery is determined only by the value $\sum_i \frac{n_i}{n_o} \frac{r_o}{r_i}$ or by λ_i. The result of using expressions ϕ_3, ϕ_4, and ϕ_5 are given in Figure (3). The value of λ_i was selected so that $\phi_i(\infty)$ would be the same for each function. The solid dots on this figure represent experimental data$^{(3)}$ for isochronal recovery of aluminum irradiated by 0.40 MeV electrons. In each case, the value of $\frac{D_o}{r_o^2}$ and E_m were the same. Note that all three functions give closely the same curve. This is perhaps fortuitous for aluminum, since the Gaussian (i.e., $g_5(r)$) is different from the other function in that the peak of this distribution occurs at $\lambda_5 = \frac{r}{r_o}$. A slight adjustment of $\frac{D_o}{r_o^2}$ for each of the functions ϕ_3, ϕ_4, and ϕ_5 would give almost perfect coincidence between the experimental data and the theoretical curves.

It should be noted that, insofar as these formulations which take account only of i-v annihilation in I_d are correct, it seems reasonable to compare concentrations, calculated analytical, with electrical resistivity data. In the comparison, it is implicitly assumed that there is a simple constant which connects these concentrations with resistivity--the specific resistivity of a Frenkel (i-v) defect. The success of the fit between analysis and experiment is evidence that the Frenkel resistivity depends weakly, if at all, on the separation distance between an interstitial and a vacancy.

Plots of the normalized initial distribution functions assumed for Figure (3), are given in Figure (4). As expected, these curves lie very close together. This indicates that, at least for low energy electron irradiated aluminum, all three distributions are adequate. However, this may not be the case for other metals, especially for higher energy irradiations. Although the exact shape of the initial distribution function has only limited physical significance at this time, the gross features of the distribution do appear to be important. For example, the modified exponential distribution has a maximum at $\frac{r}{r_o} = 1$ whereas the Gaussian has a maximum at $\frac{r}{r_o} = \lambda_5$ and the straight exponential at $\frac{r}{r_o} = 2\lambda_3$. In addition, the width of the distributions determine the gross features of the recovery behavior. These features must be determined by the energy of irradiation and by the crystal properties of the material.

The gross features of the initial distribution function should be influenced by the focusson efficiency of a particular material. For example, in aluminum all three functions are maximum at $\frac{r}{r_o} \approx 1$, whereas for electron irradiated copper, the Gaussian maximizes at $\frac{r}{r_o} = 1.25$. Since the focusson efficiency is low for aluminum,(23) one would expect the distribution to fall off gradually, beginning at $\frac{r}{r_o} = 1$. However, for copper, which has a high focusson efficiency,(24) the distribution could be shifted away from the r_o due to long range displacements. Clearly this result needs to be investigated for copper in terms of a complete energy dependent study.

Figures (3) and (4) have been concerned either directly with the continuous distribution functions of Equations (3.16c-e) or calculations based on these functions. Yet it is clear that continuous functions are approximations to the real situation which should be described instead by the function of Equation (3.16b). When the problem is framed in terms of this distribution function, the need for the ad hoc adoption of a particular functional form vanishes: the function of Equation (3.16b) is entirely arbitrary. The price of relinquishing continuous functions in favor of a sum of delta functions lies in the need to select actual values of r_i. This poses mathematical difficulty since the number of values of r_i, let alone the actual values, is largely unknown. It remains to be seen whether this approach, a delta function approach, will allow a unique deduction of the distribution function. Experiments directed toward this end are presently in progress in our laboratory.

IV. FINE STRUCTURE

A. Formulation

The introduction of a delta function distribution of close pair separations raises the possibility that the isochronal rate of recombination of i-v pairs (or the rate of isothermal recovery when plotted against the logarithm of time) may show an uneven progress, with several maxima and minima. Indeed, some recent experimental observations for the low temperature recovery of radiation-induced damage in Al and Cu have indicated such "structure" within the I_d recovery region.(5-13)

There are two distinct manners in which this structure might arise. The first arises from the considerations of distinct lattice positions, with only a single governing migration energy, as noted above. The alternative to this is to speculate that a spectrum of activation energies should be considered, a different energy for each type of i-v separation. Clearly these alternatives are extreme cases and blending is likely.

The significance of the energy spectrum lies in a well-established observation concerning the nature of activated processes. Consider Figure (1) again, As stated previously in Figure (1a), we have presented the schematic potential energy versus distance diagram which formed the basis for discussion in Section III. Figure (1b) differs in that the transition from bound close pairs, A, B, and C in Figure (1a), occurs more slowly over a wide range of lattice distances. Now, if the potential barrier structure surrounding a lattice position is significantly asymetric, it is almost as though the defect were constrained to jumps only in the direction leading to recombination and, equally important, that the time of stay in sites lying between the initial site and the vacancy is negligible.(25) Under these conditions, the diffusional aspects of the problem vanish and we revert to a consideration of the first order processes:

$$\frac{dn_j}{dt} = -A_j n_j \exp(-E_j/kT) \tag{4.1}$$

The observations in which fine structure has been reported have generally originated in isochronal annealing experiments, although the recent work of Bauer(26)--which failed to reveal such fine structure in copper--consisted of a linear-heating method. For analytic simplicity, we treat the latter with no loss of generalization. If the heating rate, assumed constant, is $\beta \doteq dT/dt$,

$$\frac{dn_j}{dT} = -\frac{A_j}{\beta} n_j \exp(-E_j/kT) \tag{4.2}$$

The "peak" temperature of such a process is defined by the condition that

$$\left.\frac{d^2 n_j}{dT^2}\right|_{T=T_c} = 0 \tag{4.3}$$

and the relationship between activation energy and peak temperature, T_c, is

$$\frac{A_j}{\beta} \exp(-E/kT_c) = E/kT_c^{\,2} \tag{4.4}$$

Thus, the separation in temperature of two neighboring peaks, each identified by its own activation energy, is

$$\frac{\Delta T}{\bar{T}_c} \cong \frac{\Delta E}{\bar{E}} \tag{4.5}$$

where $\bar{T}_c$ and $\bar{E}$ are the average peak temperatures and energies, respectively.

An alternative derivation may be carried through for the case of correlated process in which the activation energies are the same, but the i-v separation distances are r_1 and r_2; the derivation is given in Appendix 1. Here the separation is given by

$$\frac{\Delta T}{T_c} \cong \frac{2k\overline{T}_c}{E_m} \ln \left[\frac{r_2 - r_o}{r_1 - r_o}\right] \tag{4.6}$$

The question we seek to answer is the following: under which conditions can two peaks be resolved, separated as given by either conditions of Equations (4.5) or (4.6). As a condition of resolution, we impose the condition that the peak half widths of the two processes, treated as first order processes, is of the order of the peak separation. The peak width of such processes is (Granato and Nilan$^{(5)}$),

$$\frac{\Delta T_{1/2}}{T_c} \cong 2.4 \frac{kT_c}{E} \tag{4.7}$$

This condition clearly applies to the energy spectrum case; it is a minimal condition in the correlated processes case in that each process is actually wider than given by this criterion.

Consider first the correlated processes case, using this criterion. From Equations (4.6) and (4.7), we require approximately that

$$r_2 - r_o > 3(r_1 - r_o) \tag{4.8}$$

or

$$1/2\ (r_2 - r_1) > r_1 - r_o \tag{4.9}$$

Now it is reasonable to assume that $r_1 - r_o$ should be of the order of one lattice constant (1b) even for the very closest separations. Therefore, at the best, we require that

$$\Delta r \equiv r_2 - r_1 > 2\,b \tag{4.10}$$

Our conclusion is, then, that resolution of peaks in the correlated case can only be expected for the most close pairs and indeed for few of these. This is equivalent to the conclusion that fine structure may only be observed in the early portion of I_d recovery.

Consider the energy spectrum case. In order to relate the condition of Equations (4.5) and (4.7) to i-v separations, we make the ad hoc assumption that the activation energy-distance relation may be expressed as

$$E = E_m - \frac{\alpha}{r} \tag{4.11}$$

where the constant α is determined from the condition that the migration energy at the capture radius, r_c, is equal to the observed value of the I_c substage, E_c=0.09 eV (See Figure 1b). Then

$$E = E_m - (E_m - E_c)\,\frac{r_c}{r} \tag{4.12}$$

and taking differentials, with E_m=0.12 eV,

$$\frac{\Delta T}{T} \simeq \frac{\Delta E}{E} \sim \frac{r_c}{r}\left(\frac{\Delta r}{4r - r_c}\right) \tag{4.13}$$

Also, as a very general rule,

$$\frac{2.4\ kT}{E} \sim 5 \times 10^{-2} \tag{4.14}$$

Combining, we require that

$$\Delta r \gtrsim 5 \times 10^{-2} \left(\frac{r}{r_c}\right) (4r - r_c) \tag{4.15}$$

The condition of Equation (4.15) is somewhat less restrictive than that of Equation (4.10) but the main conclusion made after Equation (4.10) remains essentially intact; see the following discussion.

B. Discussion

The main conclusion to be made from the preceding analysis is the following: within the framework of correlated diffusion (no variation in migration energy), it is possible to observe fine structure in substage I_d. This structure, however, should be most highly resolved in the lower temperature portion of I_d, corresponding to recombination of the closer i-v pairs. These conclusions are supported by direct applications of Equation (4.2) with judicious choices of parameters r_j and n_j. In Figure (5) we display an example of structure predicted by this procedure, but this structure was introduced only by our choice of parameters. A more arbitrary choice of parameters fails to introduce any significant structure into I_d and, even in the most artificial cases, no resolvable structure can be resolved in the latter portion of I_d or at higher temperature (i.e. in I_e).

The next conclusion that we draw from the analysis is: little additional structure is allowed in the formulation based on an energy spectrum, assuming an energy versus distance relationship of the form of Equation (4.11). A "typical" recovery curve for this case (i.e., based on an energy spectrum) is presented in Figure 6. Although such an expression is entirely ad hoc, the dependence on distance is characteristic of defect field dependence generally predicted in defect calculations. A stronger dependence on r (e.g., r^{-2}) would lead to predictions of even less structure.

From these conclusions we derive our final conclusion: if any significant amount of structure is indeed present in the higher temperature portions of I_d or in I_e, the origin of this structure lies in one or more of three sources: (a) competing processes (e.g., trapping of interstitials by impurity atoms). This seems unlikely based on considerations of relative distances between an interstitial and its vacancy, on the one hand, and between an interstitial and an impurity atom, on the other hand. However, if displacements are significantly easier near an impurity atom, some interaction might be expected. Nevertheless, experiment speaks against this possibility since it has been observed that substage I_d is almost completely identical (on a normalized basis provided by Equation (3.9), for example) in samples in which the radiation doses have differed by a factor of 20.(2) (b) anomolous separations. In examining the two formulations above, it was implicitly assumed that stable interstitial sites occur in an essentially consecutive manner, proceeding outward from the vacancy. Abrupt discontinuities in this progression might introduce additional structure. There is no reason to anticipate such discontinuities. (c) peculiar energy-distance spectrum. Despite our arguments concerning the reasonableness of a relationship similar to Equation (4.11), it remains possible that the energy profile is considerably more complex than suggested.(27) In this case, further structure can be induced by additional judicious choices of parameter. Obviously, we are disposed to doubt the significance of explanation (c) by virtue of its lack of intuitive appeal and, more concretely, on the following consideration. Even in models based on an energy-distance spectrum, it is reasonable to cut off the interaction at some i-v separation distance. For example, we might cut off the distribution when the r^{-1} term in Equation (4.11) becomes of the order of kT. Then $r \sim 12\ r_c$. Whereas the implied capture volume is rather large, the distance to an impurity atom, on the average, in pure materials is still considerably larger so that spatial correlation effects must still remain. Thus correlated recovery, as discussed in the correlated diffusion framework, must still be an important factor.

Finally, there is the possibility that an unusually high potential energy barrier exists at some appropriate i-v separation, giving rise to an effective repulsion. This, too, strikes us as an unlikely factor of importance. If this barrier occurs at small i-v separations, little structure could be observed; if it occurs at larger i-v separations, the barrier should be reasonably small and unimportant.

Turning again to experiment, it appears to be well established that I_e is concentration-dependent,(2,28) as expected from diffusional models, so that the presence of structure in this substage is questionable. In fact, as the experimental techniques have improved, the amount of structure seems to decrease. This is particularly evident in the constant rate of heating experiments performed by Bauer(26) and in the high resolution isochronal experiments of Simpson et al.(29) Indeed, Schilling et al.(30) have gone so far as to completely dismiss the significance of structure. We concur with the observation that a small amount of structure is not incompatible with models based on correlated recovery.

V. FULL DIFFUSIONAL TREATMENTS

A. Formulation

We consider the case of three-dimensional diffusion first. When $\frac{Dt}{r_o^2}$ becomes much greater than 1, the probability for an interstitial to escape the environs of its vacancy becomes significant and the chance encounter of an interstitial with another interstitial, an impurity atom or a vacancy other than its original one becomes appreciable. Thus, the supposition of isolated defects becomes invalid and one must resort to a full diffusional treatment. Such diffusion-limited reactions have been treated by Waite,(1) Monchick et al.,(31) and recently by K. Schroder.(32) The following development parallels the work of these authors in many respects, with particular emphasis on Waite's work. Waite investigated the case of interstitial-vacancy annihilation without specifically allowing the reactants to proceed further; i.e., no interstitial clustering or impurity trapping. Schroder treats all cases, but he separates the case of correlated recovery from the other reaction processes. Clearly, a need exists for a unified treatment of diffusion-limited reactions, since experimental data show that numerous processes occur within the I_d and I_e recovery regions. We outline such a treatment here.

We note again that in moderate energy electron irradiation experiments, it is generally agreed that Frenkel defects are distributed homogeneously throughout the sample volume V and that interstitials and vacancies belonging to the same pair are spatially correlated. Moreover, for low temperature studies, only the interstitial is thought to be able to migrate. This assumption will be made throughout the following discussion. Due to the initial correlation of interstitials and vacancies, it is necessary to introduce pairwise probability distributions for these defects such that

$$\{\rho_{10}\ (\vec{r}_i,\ \vec{r}_j;\ t)\}_{ij}\ \frac{d\,V_i\ d\,V_j}{V^2} \tag{5.1}$$

is the probability that i^{th} interstitial is in dV_i at $\vec{r}_i$ at time t, and the j^{th} vacancy is in dV_j at $\vec{r}_j$ at time t. Less detailed distribution functions are required for the other defect densities since these defects (dimers= diinterstitials, trimers, etc.) are always uniformly distributed throughout the volume and are formed as composites of defects which are uniformly distributed with respect to each other (interstitials). For this case, we define the density

$$\rho_{1n}\ (\vec{r}_i,\ \vec{r}_j;\ t)\ dV_i\ dV_j \tag{5.2}$$

to be the density of interstitials in dV_i at r_i and of n^{th} type defects in dV_j at r_j at t. We restrict the index n as follows:

$$\left.\begin{array}{ll} n = 0 & \text{vacancy} \\ n = 1 & \text{interstitial} \\ n = 2 & \text{dimer} \\ \vdots & \\ n = I & \text{interstitials trapped at impurities} \\ n = T & \text{impurity trap} \end{array}\right\} \tag{5.3}$$

Probability densities given by Equation (5.1) are related to Equation (5.2) by, for example,

$$\rho_{10}(t) = \sum_{i=1}^{N_1^o} \sum_{j=1}^{N_o^o} \{\rho_{10}\ (r_i,\ r_j;\ t)\}_{ij} \tag{5.4}$$

where $N_1^{\,o}$ and $N_o^{\,o}$ are the initial number of interstitials and vacancies, respectively. We also let ρ_n be the macroscopic density for the n^{th} type defect and take $\rho_n^{\,o}$ to be the initial concentration. For $n=T$, $\rho_T \equiv \rho_T^{\,o}$, i.e., unsaturable traps. In particular, note that for interstitials and vacancies

$$\rho_o(t)/\rho_o^{\,o} = \{\rho_o\,(r_i,\,t)\}_i \tag{5.5}$$

and

$$\rho_1(t)/\rho_1^{\,o} = \{\rho_1\,(r_i,\,t)\}_i \tag{5.6}$$

with $(\rho_1)_i \dfrac{dV_i}{V}$ = the probability that the i^{th} interstitial is in dV_i at r_i, t and similarly for $(\rho_o)_i$.

The above probability densities can change directly due to the i^{th} interstitial diffusing throughout V and reacting with any of the $n(n=0,1,---)$ type defects. Following Waite, we obtain a set of generalized diffusion equations for the pairwise densities.

$$\frac{\partial(\rho_{10})_{ij}}{\partial t} = D\,\nabla^2\,(\rho_{10})_{ij} + (f_{10})_{ij}\,(\rho_{10})_{ij} \tag{5.7}$$

$$i = 1, \ldots, N_1^{\,o} \qquad j = 1, \ldots N_o^{\,o}$$

With

$$(f_{10})_{ij} = \frac{1}{\rho_1} \sum_{k\neq j} \{[\frac{d(\rho_1)_i}{dt}]_o\}_k + \frac{1}{\rho_o} \sum_{m\neq i} \{[\frac{d(\rho_o)_j}{dt}]_1\}_m$$
$$+ \frac{1}{\rho_1} \sum_{n} [\frac{d\rho_1}{dt}]_n \qquad n \neq 0 \tag{5.8}$$

The first term on the right side of Equation (5.8) reflects the depletion of the interstitial concentration at random vacancies; the second term arises from the depletion of vacancies by random interstitials; and the third term arises from the loss of free interstitials due to all other reactions:

interstitial-interstitial, interstitial-dislocation, etc. Then $(f_{10})_{ij}(\rho_{10})_{ij}$ gives the rate at which $(\rho_{10})_{ij}$ changes due to the interstitial interacting with all the other n-type defects. For the other macroscopic densities, we likewise obtain

$$\frac{\partial \rho_{1n}}{\partial t} = (1 + \delta_{1,n})\, D\, \nabla^2 \rho_{1n} + \rho_{1n} \left[\frac{1}{\rho_1} \frac{d\rho_1}{dt} + \frac{1}{\rho_n} \frac{d\rho_n}{dt}\right] \qquad n \neq 0 \tag{5.9}$$

The $(1+\delta_{1,n})$ term takes account of the case of two interstitials diffusing each with a diffusion constant D, to react; then $\delta_{1,n}=1$. Otherwise, $\delta_{1,n}=0$. This assumes that only interstitial diffusion is significant.

Equations (5.7), (5.8), & (5.9) are coupled through the $(f_{10})_{ij}$ terms and $\rho_{1,n} \left[\frac{1}{\rho_1} \frac{d\rho_1}{dt} + \frac{1}{\rho_o} \frac{d\rho_o}{dt}\right]$; however, closed-form expressions can be obtained for the pairwise probabilities. We assume that vacancies, impurities, interstitials, etc. behave as capture volumes describable by a capture radius r_n. For i≠j Equation (5.8) essentially reduces to $\frac{1}{\rho_1} \frac{d\rho_1}{dt} + \frac{1}{\rho_o} \frac{d\rho_o}{dt}$. By making the substitution

$$\eta_o \equiv \frac{(\rho_{10})_{ij}}{\rho_1\, \rho_o} \tag{5.10}$$

with

$$\eta_o\ (t = 0) = \frac{1}{\rho_1^o\, \rho_o^o} \tag{5.11}$$

Equation (5.7) reduces to

$$\frac{\partial \eta_o}{\partial t} = D\, \nabla^2\, \eta_o \tag{5.12}$$

which is immediately integrable to give

$$(\rho_{10})_{ij} = \frac{\rho_1\, \rho_o}{\rho_1^o\, \rho_o^o} \left[1 + \frac{r_o}{r} \operatorname{erfc}\left(\frac{r - r_o}{\sqrt{4Dt}}\right)\right] \qquad i \neq j \tag{5.13}$$

Note that for large r

$$\{\rho_{10}(r \to \infty)\}_{ij} = \frac{\rho_1 \rho_o}{\rho_1^o \rho_o^o} \qquad i \neq j \tag{5.14}$$

i.e., the pair distribution becomes independent of r for large r. For the case i=j and the initial correlation conditions

$$\{\rho_{10}\ (t=0)\}_{ii} = g(r) \tag{5.15}$$

Equations(5.7) & (5.8) can be solved by the method of Waite. Let

$$F = \int_o^t (f_{10})_{ii}\, dt \tag{5.16}$$

F is associated with the probability that an interstitial is captured by a distant defect other than its own vacancy and is obviously not identically unity as has been suggested by Yurkov.(33) Further, let

$$\rho_{ii} = \frac{w_{ii}}{r} \quad e^F \tag{5.17}$$

define w_{ii}. Then Equation (5.7) reduces to

$$\frac{\partial w_{ii}}{\partial t} = D\, \nabla^2\, w_{ii} \tag{5.18}$$

The above solution for the $(\rho_{10})_{ij}$ are formally complete, but they still contain the (ρ_n)'s and their time derivatives. Thus, it is also necessary to solve the set of equations represented by Equation (5.9).

To solve Equation (5.9) we follow Schroder and let

$$\eta_n = \frac{\rho_{1n}}{\rho_1 \rho_n} \qquad n \neq 0 \tag{5.19}$$

and require

$$\eta_n \ (t = 0) \ = 1 \qquad n \neq 0 \tag{5.20}$$

Equations similar to Equation (5.13) are obtained for the macroscopic pair densities,

$$\rho_{1n} = \rho_1 \, \rho_n \left[1 + \frac{r_n}{r} \, \mathrm{erfc} \left(\frac{r - r_n}{\sqrt{(1+\delta_{1,n}) \, 4Dt}}\right)\right] \quad n \neq 0 \tag{5.21}$$

The rate equations for the densities ρ_n are obtained by considering the flux of interstitials into the capture surfaces $4\pi r_n^2$. Restricting cluster formation to dimers and trimers only, we obtain the following set of general rate equations for the

$$\frac{d\rho_o}{dt} = - e^{F_r} \rho_1^{\,o} \frac{d\phi_r}{dt} - \alpha_o \, \rho_o \, \rho_1 \tag{5.22 a}$$

$$\frac{d\rho_1}{dt} = \frac{d\rho_o}{dt} - 2 \, \rho_1^2 \, \alpha_1 - \rho_1 \, \rho_2 \, \alpha_2 - \rho_1 \, \rho_T^{\,o} \, \alpha_T \tag{5.22 b}$$

$$\frac{d\rho_2}{dt} = + \rho_1^2 \, \alpha_1 - \rho_1 \, \rho_2 \, \alpha_2 \tag{5.22 c}$$

$$\frac{d\rho_3}{dt} = \rho_1 \, \rho_2 \, \alpha_2 \tag{5.22 d}$$

$$\frac{d\rho_I}{dt} = \rho_1 \, \rho_T^{\,o} \, \alpha_T \tag{5.22 e}$$

$$\frac{dF_r}{dt} = - (\rho_1 + \rho_o) \alpha_o - 2\rho_1 \, \alpha_1 - \rho_2 \, \alpha_2 - \rho_T^{\,o} \, \alpha_T \tag{5.22 f}$$

with

$$\alpha_i \equiv 4\pi r_i D\{1 + r_i[(1 + \delta_{1,i})\pi Dt]^{-1/2}\}$$

(5.23)

If the impurities behave as nucleation traps,(34,35,36) then ρ_T^{o} becomes

$$\rho_T^{o} \rightarrow \rho_T^{o}\left[1 + \frac{\gamma(\rho_o - \rho_1 - 2\rho_2 - 3\rho_3)}{\rho_T^{o}}\right] \tag{5.24}$$

with γ the fractional increase in ρ_T^{o} when each impurity has trapped, on the average, one interstitial.

The extension of the above equations to include higher clusters, etc., is obvious.

The treatment for diffusion in one dimension proceeds similarly, of course. To conform to current thought, we refer to an interstital restrained to migrated along a line as a crowdion. Then the processes which we include in our consideration are (1) crowdion-vacancy annihilation, with the pair either spatially correlated or uncorrelated, (2) crowdion-crowdion encounter, leading to "double conversion," the formation of immobile ("Stage III") interstitials, and (3) crowdion-impurity encounters, leading also to conversion of crowdions to immobile interstitials. We do not include thermal conversion here--the possibility that the crowdion is sufficiently metastable to convert with thermal activation in addition to migrating diffusively. Thermal conversion is considered in Section VI.

Under these assumptions, a corresponding set of rate equations is derived which bears a formal resemblance to the set of equations for three-dimensional diffusion. These equations are listed below. In the discussion of this section, we shall emphasize the important differences between one and three dimensional formulations.

$$\frac{d\rho_o}{dt} = - e^{F_x} \rho_1^o \frac{d\phi_x}{dt} - 2 x_o^2 (\pi D t^{-1})^{-1/2} \rho_o \rho_1 \tag{5.25 a}$$

$$\frac{d\rho_1}{dt} = \frac{d\rho_o}{dt} - 4 x_1^2 (2\pi D t^{-1})^{1/2} \rho_1^2 - 2 x_T^2 (\pi D t^{-1})^{1/2} \rho_T^o \rho_1 \tag{5.25 b}$$

$$\frac{d\rho_2}{dt} = 2 x_1^2 (2\pi D t^{-1})^{1/2} \rho_1^2 \tag{5.25 c}$$

$$\frac{dF_x}{dt} = - (\rho_1 + \rho_o) 2 x_o^2 (\pi D t^{-1})^{1/2} - 4 x_1^2 (2 \pi D t^{-1})^{1/2} \rho_1 - 2 x_T^2 (\pi D t^{-1})^{1/2} \rho_T^o \tag{5.25 d}$$

B. Discussion

The solution of the above set of coupled differential equations appears to be formidable since eight parameters must be specified directly (in the three-dimensional case). In addition, if results are compared with resistivity data, the specific resistivities of the five types of defects must also be treated as parameters. At present, data are simply not available which are sufficiently accurate and extensive enough to obtain all of these parameters. Fortunately, few experiments require so detailed a treatment as presented in Equation (5.22). For example, substage I_d usually accounts for about 50-70% of the I_d-I_e recovery. This case has been adequately accounted for in the treatments of Section III. Moreover, for high purity materials and moderate defect densities, impurity trapping should not be of great importance. Also, trimer formation should be small when compared to direct interstitial-vacancy annihilation and dimer formation (or double conversion). Thus, with a choice of experiments providing varying concentrations of reactants, an unraveling of parameters becomes meaningful.

An example of the use of the rate equations in three dimensions is given in Figure (7). The Runge-Kutta technique was used in the computer-assisted evaluation of these equations. The correlated term was taken from $d\phi_4/dt$ in Equation (3.19d). Furthermore, trimer formation and nucleation traps were neglected. The parameters used in the fit to experimental data--the recovery of aluminum irradiated with 0.40 MeV electrons--are given in the figure caption.

The quantity which has been plotted in Figure (7) is

$$\Phi_I = \frac{\rho_o^o - \rho_o}{\rho_o^o} \qquad (5.26)$$

It is apparent that a most satisfactory fit to experiment is effected in this way. It should be noted that the analysis is framed to include dimer formation in the encounter of two interstitials; however, the mathematics is identical if we consider such encounters to lead to formation of any type of immobile species. In particular, the possibility that conversion of one type of mobile interstitial to another effectively immobile one (at least at the temperature under discussion), both three dimensional in diffusion character, remains.

Figure (7) also contains calculated results in which a varying amount of impurity concentrations were assumed. The effective capture (or conversion) radius of the impurity atom is arbitrarily taken as $r_T = r_o$. These calculations clearly show that an effective traps concentration of 10 ppm is sufficient to suppress the I_e recovery when the defect density is only a few ppm. This has been observed experimentally.$^{(2)}$ Interestingly, trap concentrations as high as 100 and 1000 ppm still do not suppress substage I_d. However, it should be appreciated that these calculations are largely representative and depend on the product $\rho_T r_T$. Clearly, the capture radius of an impurity atom will depend on impurity type, suggesting that controlled experiments with a variety of impurity atoms in Stage I should give valuable information concerning such radii.

We conclude that full diffusional fits, based on three-dimensional migration aided by computer techniques, can be most valuable and provide a basis for full comparison with experiment; the corresponding situation with regard to one-dimensional diffusion will be discussed shortly. However, before turning to this, we would like to consider a procedure which has been adopted by some investigators to avoid the need for involvement with a full treatment. In these cases, there has been an attempt to analyze separately the I_d (correlated) and I_e (uncorrelated) recovery processes.

We have attempted to determine to what extent such a separation procedure is valid. To test the validity of this method, we have compared the quantity

$$\Phi_I' = \Phi_d + [1 - \Phi_d(\infty)] \left\{ \frac{\rho_o^{o'} - \rho_o'}{\rho_o^{o'}} \right\} \qquad (5.27)$$

with the quantity, in Equation (5.26), calculated in full detail. The term in the curly brackets is the solution to Equation (5.22) without the correlated term. Figure (8) gives the results of this comparison with curve (a) referring to Φ_I and curve (b) referring to Φ_I'. As expected, the correlated portion of the recovery is quite identical in both cases; differences are manifested in the uncorrelated region, I_e. For the defect range presented here, several ppm, the separation of I_e appears to be largely justified for qualitative purposes in that the shapes of the two curves are quite similar. With adjustment in the normalization procedure, even better agreement should be possible.

Still another procedure was used by Corbett et al.$^{(2)}$ in comparing diffusion theory with their post-irradiation recovery data. Their analysis was less than rigorous in that it included dimer formation in a rather ad hoc manner. Figure (9) presents the analysis of these data based on the full diffusional treatment. The agreement is good, confirming the position of Corbett et al. that their procedure was generally valid.

With the apparent success of diffusion theory, in three dimensions, we turn to one-dimensional analyses. Several general observations can be made, based on the rate equations of Equation (5.25).

1. Even if all random terms are suppressed, leaving merely the correlated term, complete recovery is effected at infinite time. This is an inevitable feature of one-dimensional motion which could have been noted in Section III and will be referred to again in Section VI. This feature is in essential distinction to the case of three-dimensional migration where ultimate escape is possible.(37) As a result, the influence of competing processes is substantially less feasible in the one-dimensional case unless the interaction radii are adjusted appropriately. The adjustment is a large one.

This inability of a crowdion to escape its own vacancy is a feature of one-dimensional diffusion which is related to the fact that the crowdion must sample every site along the line until reaching its final destination. As a result, most sites are revisited many times. One-dimensional diffusion is, therefore, intrinsically slower than three-dimensional diffusion.

2. Whereas the above features of one-dimensional diffusion relate most directly to correlated recovery, there is also a significant difference between one- and three-dimensional diffusion in the non-correlated processes. In both cases, there exists a $t^{-\frac{1}{2}}$ term. This term dies out at long times in its significance in the three-dimensional case on comparison with the unity term, but persists in one dimension. Thus, the one-dimensional uncorrelated diffusion proceeds slowly while the correlated recovery is proceeding toward full completion. In addition, the one-dimensional case implies a sensitive dependence on all parameters affecting uncorrelated recovery, in particular, on the dose. This sharp dose-dependence is not observed experimentally.

Note also that the objections stated by Granato and Nilan(5) are borne out by the rate equations. Granato and Nilan pointed out that random one-dimensional diffusion leads to the prediction of third order kinetics at long times. This is demonstrated again in Section VII, but may be noted here on considering only the random phase of recovery, in one dimension:

$$\frac{d\rho}{dt} = -2x_o^2 (\pi D t^{-1})^{1/2} \rho^2 \qquad (5.28)$$

This equation can be integrated for the specific time dependence and, for long times, substituted back in for the $t^{-\frac{1}{2}}$ term to give

$$\frac{d\rho}{dt} = -8\pi x_o^4 D \rho^3 \qquad (5.29)$$

a third order reaction. Since high orders imply slow recovery, this is consistent with the slow random one-dimensional recovery cited just above.

3. The difficulties with a one-dimensional model in fitting post-irradiation recovery data is best demonstrated upon transforming the isothermal rate equations, Equation (5.25), to equations in which temperature is the independent variable, simulating experiments in which the temperature is increased continually (usually at a constant rate) or, effectively, in isochronal experiments. Using the variable $z = \left[4tD_o \exp(-Em/kT)\right]^{1/2}$, the "diffusion length," we have

$$\left(\frac{d\rho_o}{dT}\right)_x = \left\{-\rho_1^o e^{F_x} \left(\frac{d\phi}{dz}\right)_x - 2\pi^{1/2} x_o^2 \rho_o \rho_1\right\} \frac{dz}{dT} \qquad (5.30)$$

$$\left(\frac{d\rho_o}{dT}\right)_r = \left\{-\rho_1^o e^{F_r} \left(\frac{d\phi}{dz}\right)_r - 2\pi r_o z \left(1 + \frac{2 r_o}{\pi^{1/2} z}\right) \rho_o \rho_1\right\} \frac{dz}{dT} \qquad (5.31)$$

The first term in both cases are essentially the same; but the presence of the diffusion length in the second term in the three-dimensional case--and its absence in the one-dimensional case--is of key importance. In one dimension, the rate of correlated recovery decreases continually; in the three-dimensional case, the exponential dependence of z on temperature, allows for an increase in rate even though both ρ_o and ρ_1 are decreasing. As a result, the I_e peak can appear in three dimensions; there appears to be no way to produce I_e in one dimension. As an example, see Figure (10) and the absence of a I_e peak. In fact, we have been unable to fabricate any I_e peak in one-dimensional recovery.

These remarks, and ones to follow, are in disagreement with the work of Frank, Seeger, and Schottky(38) and the more recent work of Frank and Seeger. The discrepancy is, we submit, due to errors in these formulations. For example, Frank et al. state that "each crowdion moves with the probability ½ to 'its' vacancy, or in the opposite direction away from it," which is certainly not the case.(37) In this way, a division between I_d and I_e made its entrance into their work.

We conclude that models based on one-dimensional diffusion in Stage I cannot account for observation, implying that crowdion models are inappropriate to the analysis of Stage I recovery in metals. However, models which speak of two types of interstitials, one which migrates in Stage I but may be converted to another variety which migrates in Stage III, are not ruled out by these considerations. The requirement is simply that the interstitial which migrates in Stage I migrates in three dimensions.

VI. SPECIAL CASE OF DIFFUSION PROCESSES

A. Formulation

In Section V we have developed in detail the formalism for a full-diffusional treatment. The use of this formalism must almost inevitably rely on computer techniques. Here we would like to develop certain aspects of such treatments which admit to closed form solutions and which bear significantly and currently on the analysis of defect diffusion in metals.

1. Diffusion in the Presence of Generalized Traps or Sinks. The problems we wish to consider here concern the interaction of interstitials with traps or sinks which compete with vacancies. The problem is restricted further to the case in which the number of vacancies is appreciably less than the number of traps or sinks so the competition for interstitials takes place between such traps or sinks (we shall, henceforth, refer to both as traps) and the vacancy which is spatially correlated initially with the interstitial, the partner in a Frenkel defect. As a further limitation, we impose the less important assumption that the traps are unsaturable (may capture any number of interstitals without change in efficiency) or, nearly equivalently, that the number of traps is appreciably greater than the number of interstitials--essentially the same assumption made with regard to vacancies. In our consideration, we will assume complete randomness between interstitials and traps, thereby ignoring any correlation which might result from a preference of interstitial creation (i.e., atomic displacement) near interstitials.

Under these assumptions, the problem in three dimensions is formulated by considering $4\pi r^2\ P(r,t)\ dr$, the probability that an interstitial is in a shell of width dr at r from the position from its correlated vacancy at a time t. Then

$$\frac{\partial P(r,t)}{\partial t} = D \nabla^2 P(r,t) - B_s P(r,t) \tag{6.1}$$

where

$$B_s = 4\pi r_T DI_o \tag{6.2a}$$

or

$$B_s = DN_o \tag{6.2b}$$

B_s is a generalize sink "efficiency." The first of the expressions for B_s in Equation (6.2) holds for the case of impurities of capture radius r_T and fractional concentration I_o; the second, for dislocations (line traps) of concentration N_o (in units of cm^{-2}, for example). B_s could also consist of a sum of terms represented by Equation (6.2).

Our diffusion expression, Equation (6.1), is put into standard form with the substitution

$$U \equiv P \exp(-B_s t) \tag{6.3}$$

so that

$$\frac{\partial U}{\partial t} = D \nabla^2 U \tag{6.4}$$

The solution to Equation (6.4) can be written, with reference to Equation (3.13), for a delta function distribution with the initial i-v separation equal to r_i. Solutions for more arbitrary distributions can be synthesized from this solution subsequently, if desired, by averaging over the continuous initial distribution.

For the delta function distribution, the number of interstitials

$$n_r(r,t) = n_o P(r,t) \tag{6.5}$$

is given by

$$n_r(r,t) = \frac{n_o}{4\pi r_i r} (4\pi Dt)^{-1/2} \exp(-B_s t) \{\exp[-\frac{(r_i - r)^2}{4Dt}] - \exp[-\frac{(r_i + r - 2 r_o)^2}{4Dt}]\} \tag{6.6}$$

where n_o is the initial concentration of interstitials.

The rate at which interstitials combine with their correlated vacancies is

$$q_r = - 4\pi r_o^2 D \frac{\partial n}{\partial r}\bigg|_{r=r_o} \tag{6.7}$$

or, evaluated,

$$q_r = - n_o (4\pi Dt^3)^{-1/2} \frac{r_o}{r_i} \Delta r \exp[-B_s t - \frac{\Delta r^2}{4Dt}] \tag{6.8}$$

where $\Delta r \equiv r_i - r_o$.

The rate of decay of interstitials, in all manners, is given by the Langevin's equation:

$$\frac{dn_r}{dt} = q_r(t) - B_s n_r \tag{6.9}$$

with solution

$$n_r(t) = \exp(-B_s t) \{n_o + \int_o^t \exp(B_s \xi) q(\xi) d\xi\} \tag{6.10}$$

so that, finally,

$$n_r(t) = n_o \exp(-B_s t) \{1 - \frac{r_o}{r_i} \operatorname{erfc} \frac{\Delta r}{\sqrt{4Dt}} \} \qquad (6.11)$$

We now find the number of interstitials which are lost (or trapped) at generalized sinks, τ_r. This is clearly given by

$$\frac{d\tau_r}{dt} = B_s n_r(t) \qquad (6.12)$$

with $n_r(t)$ from Equation (6.11). The integration of Equation (6.12) is tedious, yielding

$$\begin{aligned}\tau_r/n_o = {} & [1 - \exp(-B_s t)] + \frac{r_o}{r_i} \{\exp(-B_s t) \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}}] \\ & - 1/2 \exp [\Delta r(B_s/D)^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} + (B_s t)^{1/2}] \\ & - 1/2 \exp [-\Delta r (B_s/D)^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} - (B_s t)^{1/2}] \}\end{aligned} \qquad (6.13)$$

Finally, the fractional recovery, ϕ_r, (interstitials which return to their vacancies) at time t may be found from Equations (6.11) and (6.13):

$$\begin{aligned}\phi_r(t) = 1 - \frac{n_r + \tau_r}{n_o} = {} & \frac{1}{2} \frac{r_o}{r_i} \{\exp [\Delta r(\frac{B_s}{D})^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} + (B_s t)^{1/2}] \\ & + \exp [-\Delta r (\frac{B_s}{D})^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} - (B_s t)^{1/2}]\}\end{aligned} \qquad (6.14)$$

The expressions developed above give the proper expressions or values in the various limits: $t=0$, $t=\infty$, $B_s=0$, etc. Of particular interest for later discussion is the limiting case

$$\tau_r = n_o \{1 - \frac{r_o}{r_i} \exp [-\Delta r (\frac{B_s}{D})^{1/2}]\} \quad \text{at } t = \infty \tag{6.15}$$

which becomes, for the cases of impurity traps and dislocations, respectively,

$$\tau_r = n_o \{1 - \frac{r_o}{r_i} \exp [-\Delta r (4\pi r_T I_o)^{1/2}]\} \tag{6.16a}$$

and

$$\tau_r = n_o \{1 - \frac{r_o}{r_i} \exp [-\Delta r \, N_o^{1/2}]\} \tag{6.16b}$$

Both of these expressions, for infinite time, are independent of temperature, since only the geometry of the situation plays a role in this limit.

The analysis of the one-dimensional problem, with diffusion restricted to a line, proceeds in a parallel fashion, with the following significant results:

$$n_x = n_o \exp (-B_s t) \operatorname{erf} \frac{\Delta x}{(4Dt)^{1/2}} \tag{6.17}$$

$$
\begin{aligned}
\tau_x \;=\; n_o \{1 &- \exp\,(-B_s t)^{1/2}\ \mathrm{erf}\left[\frac{\Delta x}{(4Dt)^{1/2}}\right] \\
&- 1/2\ \exp\left[\Delta x \left(\frac{B_s}{D}\right)^{1/2}\right] \mathrm{erfc}\left[\frac{\Delta x}{(4Dt)^{1/2}} + (B_s t)^{1/2}\right] \\
&- 1/2\ \exp\left[-\Delta x \left(\frac{B_s}{D}\right)^{1/2}\right] \mathrm{erfc}\left[\frac{\Delta x}{(4Dt)^{1/2}} - (B_s t)^{1/2}\right]
\end{aligned}
\qquad (6.18)
$$

$$
\begin{aligned}
\phi_x(t) \;=\; 1/2\ \{&\exp\left[\Delta x \left(\frac{B_s}{D}\right)^{1/2}\right] \mathrm{erfc}\left[\frac{\Delta x}{(4Dt)^{1/2}} + (B_s t)^{1/2}\right] \\
&+ \exp\left[-\Delta x \left(\frac{B_s}{D}\right)^{1/2}\right] \mathrm{erfc}\left[\frac{\Delta x}{(4Dt)^{1/2}} - (B_s t)^{1/2}\right]\}
\end{aligned}
\qquad (6.19)
$$

$$
\tau_x \;=\; n_o \{1 - \exp\left[-\Delta x \left(\frac{B_s}{D}\right)^{1/2}\right]\} \qquad \text{at } t = \infty \qquad (6.20)
$$

In one dimension,

$$B_s = 8\pi r_T^4 DI_o^2 \tag{6.21}$$

2. Diffusion with Concurrent Thermal Conversion. The mathematics of this problem is identical with that of Subsection 1. Here, however,

$$B_s = \nu \exp [-E_c/kT] \ , \tag{6.22}$$

still merely a constant (we are assuming isothermal processes).

In Equation (6.22), ν is the atomic attempt frequency and E_c is the activation energy for thermal conversion. Since the diffusion coefficient, in three-dimensional diffusion, is given by

$$D = \frac{1}{6} \nu a_o^2 \exp [-E_m/kT] \tag{6.23}$$

the number of interstitials which are converted is given, with reference to Equation (6.15), as

$$C_r = n_o \{1 - \frac{r_o}{r_i} \exp [- \frac{\sqrt{6}\Delta r}{a_o} \exp (\frac{E_c - E_m}{kT})]\} \tag{6.24}$$

where a_o is the simple atomic jump distance, E_m is the defect migration energy, and we have assumed the same jump frequency, ν, as in Equation (6.22).

Note that the number of converted interstitials does depend on temperature even at infinite time, contrary to the cases involving impurity or dislocation trapping.

The remarks made just above carry over in an obvious manner to the case of diffusion restricted to one dimension, so that the number of converted interstitials here is

$$C_x = n_o \{1 - \exp [- \frac{\sqrt{2}\Delta x}{a_o} \exp (\frac{E_c - E_m}{kT})]\}. \tag{6.25}$$

3. *Diffusion in the Presence of Generalized Traps or Sinks with Simultaneous Defect Creation.* The problem treated here is the same as that of Subsection 1, except that we assume here that interstitials are created at a constant rate per unit time, ϕ'; in Subsection 1, we had assumed an initial concentration, n_o, of interstitials, with no further creation. To take creation into account, Equation (6.6) is modified to become

$$n_r(r,t) = \frac{\phi' (4\pi D)^{-1/2}}{4\pi r\, r_i} \int_o^t \{\frac{\exp [\frac{-(r_i - r)^2}{4D(t-\tau)}]}{(t - \tau)^{1/2}} - \frac{\exp [- \frac{(r_i + r - 2r_o)^2}{4D(t - \tau)}]}{(t - \tau)^{1/2}}\} \exp (-B_s t)\, d\tau \tag{6.26}$$

where τ is the time measured from the creation of a particular set of interstitials and t is the total time since the initiation of the creation and other processes.

Proceeding as in Subsection 1, the rate at which interstitials recombine with their correlated vacancies (we are again assuming a delta function distribution with characteristic separation, r_i) is

$$q_r = -1/2\ \phi' \frac{r_o}{r_i} \{ \exp [\Delta r (\frac{B_s}{D})^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} + (B_s t)^{1/2}]$$

$$+ \exp [-\Delta r (\frac{B_s}{D})^{1/2}] \operatorname{erfc} [\frac{\Delta r}{(4Dt)^{1/2}} - (B_s t)^{1/2}] \} \tag{6.27}$$

After an initial transient period, t_i, a steady state is reached; i.e., the number of free interstitials in the lattice remains constant. Then the i-v recombination rate is

$$q_r(t > t_i) = - \phi' \frac{r_o}{r_i} \exp [- \Delta r (\frac{B_s}{D})^{1/2}] \tag{6.28}$$

so that the fraction of interstitials which escape correlated recombination is

$$\frac{r_o}{r_i} \exp [- \Delta r (\frac{B_s}{D})^{1/2}] \equiv f_r \tag{6.29}$$

Once the steady state condition has been achieved, we may legitimately consider a rate equation approach:

$$\frac{dn_r}{dt} = + \phi' - f_r \phi' - B_s n_r = (1 - f_r)\phi' - B_s n_r \tag{6.30}$$

with the solution

$$n_r = (1 - f_r)\phi' B_s^{-1} [1 - \exp (-B_s t)] \tag{6.31}$$

Only the steady state limit of Equation (6.31) is truly valid

$$n_r = (1 - f_r)\, \phi'\, B_s^{-1} \tag{6.32}$$

And, in steady state, the concentration of trapped interstitials is given by the equation

$$\frac{d\tau_r}{dt} = B_s\, n \tag{6.33}$$

with the solution

$$\tau_r = (1 - f_r)\, \phi' t = \phi' t \{1 - \frac{r_o}{r_i} \exp [-\Delta r(\frac{B_s}{D})^{1/2}]\} \tag{6.34}$$

Since $\phi' t$ is the concentration of interstitials which have been created, it is apparent that Equation (6.33) expresses the same situation as does Equation (6.15).

Once again, the treatment in one dimension is parallel to the above three-dimensional treatment and yields similar results. We merely write down the concentration of interstitials which are trapped, similar, of course, to Equation (6.20).

$$\tau_x = \phi' t \{1 - \exp [-\Delta x\, (\frac{B_s}{D})^{1/2}]\} \tag{6.35}$$

B. Discussion

In formulating the mathematics in the previous section, we have included the case of dislocations; see Equation (6.2b). In fact, the conditions that dislocations traps outweigh competing traps is rarely met since the effective fractional dislocations trap desnity, for typical dislocation densities (10^8 cm^{-2}, for example) is probably less than 10^{-6}. Generally, both impurity and vacancy concentrations exceed this value. For the moment we shall concentrate on impurities, therefore, but we shall return to dislocations later to indicate how the calculations still apply to appropriate experimental situation there as well.

It is clear that the entire time dependences developed above are important in a detailed comparison of experiment with theory. In the absence of suitable data, we will be concerned solely with the infinite time expressions: Equations (6.15), (6.20), (6.24), and (6.25). An important feature to be noted is the presence of the factor r_o/r_i, in the three-dimensional expressions and the absence of any corresponding factor in expressions for one-dimensional diffusion (more correctly, the presence of a unity factor in the one-dimensional case). The presence of r_o/r_i or unity can, of course, be traced back to the probability of escape of an interstitial from its vacancy in the absence of competing traps, in the two cases. Still another major difference between one and three dimensions lies in the character of B_s in Equations (6.2) and (6.21). As a result of this difference, the exponential argument is proportional to $I_o^{1/2}$ in the three-dimensional case and I_o in the one-dimensional case.

At the moment it would not be judicious to insert values for the various parameters in the expressions for trapped interstitials with any large degree of confidence. However, such an exercise does give results which, when compared to experiments in which interstitial trapping is a significant factor, favor a three-dimensional formulation. Perhaps it is even more significant to note that the predicted dependence on impurity concentration in the one-dimensional case appears to be much stronger than observed. But a final test awaits more investigation with experiments in which the impurity level is varied carefully over an appropriate concentration range.

Thermal conversion, the subject of Section VI-B, is of particular current interest. The presence of a Boltzman-type factor, exp $(E_c-E_m)/kT$, leads to the prediction of a sharp temperature range in which conversion progresses from insignificance to the dominant effect. There are no experiments available which would test Equations (6.24) or (6.25) and it may be unfeasible to perform such an experiment. Typically, one would wish to irradiate at low temperature to avoid both diffusion and thermal conversion, then rise rapidly to different temperatures in the range in which thermal conversion becomes important. The minimal information available indicates that the time to reach such temperatures, through the temperature range in which diffusion dominates, is necessarily too long. However, irradiations performed <u>in</u> the critical temperature range should be able to provide information needed to fit the appropriate expressions and to make a choice between one- and three-dimensional diffusion models.

There have been some early experiments performed to test thermal conversion models. Bauer and Sosin(39) compared annelaing above 80°K or bombardment at 10°K and annealing to 80°K. No significant difference in annealing pattern above 90°K was observed. This null result indicates that thermal conversion does not take place or that the temperature range is above 90°K. Keefer,(40) using dislocation pinning effects as a basis of observation, noted small differences in pinning which pointed to the possible importance of conversion in the range about 100-125°K. The most sensitive measurements which relate to this question have been reported very recently by Thompson,(41) again using dislocation pinning, here by gamma irradiation. However, until the full details of this experiment and others certain to follow are available, the question of thermal conversion remains unresolved. Nevertheless, on the basis particularly of the results of Section V and some of the previous comments made in the discussion, we believe that thermal conversion, if confirmed, will involve conversion of an interstitial from one capable of performing three-dimensional migration to another form presumably also capable of three-dimensional migration.

VII. ORDER OF REACTION

The literature in the area of defect annealing is dominated by chemical rate theory, a point made in the Introduction. A parameter of central importance in these analyses is the order of the reaction, γ. In this section we shall investigate the utility of such references to orders of reaction when the analysis is carried through from a more rigorous base of diffusion theory.

For a rate theory analysis, it is assumed that the rate of decay of a species with concentration C is given by an expresssion of the form

$$\frac{dC}{dt} = - K\ f\ (C) = - K(C - C_{\infty})^{\gamma} \qquad (7.1)$$

where K is a temperature-dependent, concentration-independent constant and γ is the quantity upon which we fix our attention. By algebraic manipulation, we have

$$\gamma = \frac{C - C_{\infty}}{f} \frac{df}{dC} \qquad (7.2)$$

where we have explicitly indicated that the concentration may not go to zero at infinite times. This is a harbinger of the difficulties that the oversimplified statement of Equation (7.1) bears. We now apply this to a particular case of contemporary interest.

We consider the case, first in three dimensions, of migration of interstitials to either vacancies or to other interstitials encountered in random manner. No i-v correlations are assumed. Then the governing rate equations, as generally written, are

$$\frac{dC_i}{dt} = - K\, C_i\, C_v - 2\, K\, C_i^2 \qquad (7.3a)$$

$$\frac{dC_v}{dt} = - K\, C_i\, C_v \qquad (7.3b)$$

where the factor of two arises since the net diffusion rate of interstitials is the sum of the individual rates. To correspond to a typical irradiation experiment, we assume that the initial concentrations of interstitials and vacancies are equal: $(C_i)_o = (C_v)_o$. Only a single reaction constant, K, is written; introduction of separate "cross-sections" for each of the two reactions would alter the final result only slightly for any sensible values. Carrying through the operations of Equation (7.2) with the solution to Equation (7.3) yields the results:

$$\gamma = 3 - \frac{(C_v)_o}{C_v} \qquad (7.4)$$

and

$$C_v = 1/2(C_v)_o \quad \text{at} \quad t=\infty \qquad (7.5)$$

The last equation results from the use of a single reaction constant; this is consistent with Corbett, Smith, and Walker's observation that about one-half of the vacancies participating in I_e remain after the completion of Stage I for copper. A factor other than ½ would follow from the use of two reactions constant. The order of reaction in Equation (7.4), therefore, varies from an initial value of two to a final value of one, a well-known result. On identifying Stage I_e as the long range process in copper, we find that $C_v \sim 3/4\ C_o$ at the peak of the stage, Equation (7.5) predicts $\gamma \sim 1.7$, (at this point) consistent with the results of Granato and Nilan$^{(5)}$ and of Snead et al.$^{(11)}$

Viewed from diffusional considerations, Equation (7.3) is incorrect. The more correct expressions have been presented by Nihoul and Stals$^{(42)}$ and are apparent from Equation (5.22); these are

$$\frac{dC_i}{dt} = -K\,(1+\alpha t^{-1/2})\ C_i\ C_v - 2K\,(1+\alpha t^{-1/2})\ C_i^{\,2} \qquad (7.6a)$$

$$\frac{dC_v}{dt} = -K\,(1+\alpha t^{-1/2})\ C_i\ C_v \qquad (7.6b)$$

where $K=4\pi r_o D$ and $\alpha=r_o(\pi D)^{-\frac{1}{2}}$. We have also assumed that $r_1=r_o$ and we made the negligible approximation that $\alpha=\alpha/\sqrt{2}$ in the coefficient of the dimer term.

Carrying through the necessary operations,

$$\gamma = 3 - \frac{(C_v)_o}{C_v} +$$

$$\frac{1}{4}\left[\frac{(C_v)_o}{C_v}\right]^2 \frac{[4(C_v)_o\, r_o^{\,3}]^{-1}\left\{1-[4(C_v)_o\, r_o^{\,3}]^{-1}\left[\frac{(C_v)_o}{C_v} - 1 + 2\,\ell n\left(2-\frac{(C_v)_o}{C_v}\right)\right]\right\}^{-1}}{\left\{1-[4(C_v)_o\, r_o^{\,3}]^{-1}\left[\frac{(C_v)_o}{C_v} - 1 + 2\,\ell n\left(2-\frac{(C_v)_o}{C_v}\right)\right]\right\}^{1/2} \quad -1}$$

$$(7.7)$$

and it remains true that $C_v = \frac{1}{2}(C_v)_o$ at infinite time. The limits of γ as given by Equation (7.7) are $\gamma = \infty$ at $t=0$ and $\gamma = 1$ at $t = \infty$. To appreciate the intervening behavior, it is necessary to adopt values of r_o and $(C_v)_o$. Taking r_o to be about four lattice constants and an initial fractional vacancy concentration of 10^{-6} gives $\beta \equiv 4r_o(C_v)_o \approx 10^{-3}$. The behavior of γ for this choice of parameters and for others as well is given in Figure (11). It will be seen that, for any of the choices of β, γ decreases rapidly from high values toward 2, the initial value predicted in the simple rate theory approach. The agreement is best for the smallest value of β, corresponding to the smallest choice of r_o. Since our choice of r_o, four lattice constants is rather large already (about 1,000 lattice sites would be included in this region), this result is comforting.

For one-dimensional diffusion, the correct kinetic expressions for the same problem, based on diffusion theory, are

$$\frac{dC_i}{dt} = -K\,C_i\,C_v\,t^{-1/2} - 2K\,C_i^{\,2}\,t^{-1/2} \tag{7.8a}$$

$$\frac{dC_v}{dt} = -K\,C_i\,C_v\,t^{-1/2} \tag{7.8b}$$

with the resulting expression for γ given by

$$\gamma = \left[3 - \frac{(C_v)_o}{C_v}\right] - 1/2\left[\frac{(C_v)_o}{C_v}\right]^2 \left[\frac{(C_v)_o}{C_v} - 1 + 2\,\ell n\left(2 - \frac{(C_v)_o}{C_v}\right)\right]^{-1} \tag{7.9}$$

Here, $K=2r_o^{2}(\pi D)^{\frac{1}{2}}$ and it is still true that $C_v=\frac{1}{2}(C_v)_o$ at $t=\infty$.

The limits on γ in Equation (7.9) are the same predicted for the three-dimensional case. However, the actual behavior with time is considerably different. Note that there are no explicit adjustable factors in Equation (7.9); there is an implicit presence of such factors, by virtue of our use of a single rate constant, K, but this is small.

Figure (11) shows that γ retains high values--values well in excess of 2--throughout almost the entirety of the annealing process. Once again this prediction is at variance with observation of Stage I_e, suggesting again that one-dimensional diffusion is not the basis of this annealing stage. Of course, other models should be examined but it seems inevitable that the objections to one-dimensional diffusion found here and in previous sections will remain in any case.

APPENDIX

In this appendix, we indicate the mathematics for the difference in temperature in a linear heating experiment for two i-v separations. We define

$$\xi \equiv \frac{r_i - r_o}{(4Dt)^{1/2}} \tag{A.1}$$

so that (see Equation [3.19a])

$$\phi_1 = \frac{r_o}{r_i} \operatorname{erfc} \xi \tag{A.2}$$

The compensated time to temperature is given through the expression:(42)

$$Dt = \frac{D_o \, kT^2}{\beta \, E_m} \exp\left(-E_m/kT\right) \tag{A.3}$$

On evaluating, for a "peak temperature,"

$$\left.\frac{d^2\phi_1}{dT^2}\right|_{T=T_c} = 0 \tag{A.4}$$

we have

$$\xi^2 = 1/2 \left[1 - \frac{4T\left(\frac{E_m}{k} + T\right)}{\left(\frac{E_m}{k} + 2T\right)^2}\right] \tag{A.5}$$

Combining this last expression with Equation (A.1) gives, to a good approximation,

$$\left(\frac{r_i}{r_o} - 1\right)^2 \exp\left(\frac{E_m}{kT}\right) = \text{constant} \tag{A.6}$$

Using Equation (A.6) let $r_1 \rightarrow r_2$ and $r_2 \rightarrow r_1$, two i-v separations of approximately equal magnitude, we have, again to a good approximation,

$$\ell n \left[\frac{r_2 - r_o}{r_1 - r_o}\right] = \frac{E_m}{2kT} \frac{\Delta T}{T} \tag{A.7}$$

where T in Equation (A.7) is the center temperature of either process and ΔT is the difference between the two center temperatures.

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FIGURE CAPTIONS

Figure 1a. A schematic diagram of potential energy vs. distance for the migration of an interstitial atom in the region near a vacancy. Potential wells A, B, and C refer to bound close-pairs whereas D and E refer to sites for "free" diffusion. U_1 and U_2 refer to unstable interstitial sites.

Figure 1b. A, B, C, D_1, D_2, ... refer to a series of close-pair defect configurations, gradually leading to the series limit of free migration.

Figure 2. The radial distribution of interstitials about their vacancies for various values of the parameter z. The modified exponential initial distribution function was used for this calculation.

Figure 3. A comparison of experimental data on 0.40 MeV electron irradiated aluminum with theoretical results that are given by the solid lines. The appropriate parameters are $E_m/k = 1320°K$, $D_o/r_o^2 = 2.5 \times 10^{12}/\mathrm{sec}$, $\lambda_3 = 0.335$, $\lambda_4 = 0.417$, $\lambda_5 = 1.05$.

Figure 4. The radial distribution functions describing the initial interstitial-vacancy separation distances corresponding to the curves of Figure 3.

Figure 5. A theoretical curve showing the numerical derivative of correlated recovery resulting from a discrete initial distribution of interstitials about their vacancies. The heating rate corresponds to ½°K temperature increments with 10 minute holding times. The appropriate parameters are $E_m/k = 1320°K$: $D_o/r_o^2 = 2.5 \times 10^{12}/\mathrm{sec}$; $r_1/r_o = 1.05$, $r_2/r_o = 1.21$, $r_3/r_o = 1.75$, $r_4/r_o = 2.00$, $r_5/r_o = 2.20$; $\frac{n_1^o}{n_o} = 0.10$, $\frac{n_2^o}{n_o} = 0.16$, $\frac{n_3^o}{n_o} = 0.30$, $\frac{n_4^o}{n_o} = 0.22$, $\frac{n_5^o}{n_o} = 0.22$.

Figure 6. A theoretical curve showing the numerical derivative of the recovery resulting from a series of bound close-pair defect configurations. The heating rate corresponds to ½°K temperature increments with 10 minute holding times. The appropriate parameters are $A = 10^{12}$; $\frac{n_1^o}{n_o} = 0.2$, $\frac{n_2^o}{n_o} = 0.25$, $\frac{n_3^o}{n_o} = 0.35$, $\frac{n_4^o}{n_o} = 0.12$, $\frac{n_5^o}{n_o} = .08$; $E_1/k = 1095°K$, $E_2/k = 1158°K$, $E_3/k = 1231°K$, $E_4/k = 1316°K$, $E_5/k = 1387°K$.

Figure 7. The fractional recovery obtained from the solutions of Equations 5.22 (using the modified exponential distribution, q_4) plotted as a function of annealing temperature and compared with data for 0.40 MeV electron irradiated aluminum. The appropriate parameters are $\rho_o^o = 2$ P.P.M., $D_o/r_o^2 = 2.5 \times 10^{12}$/sec, $\lambda_4 = 0.417$, $r_o = 3.5\ a_o$, $r_1 = 9.0\ a_o$, $r_T = 3.5\ a_o$. The impurity concentration, I_o, is given in the figure.

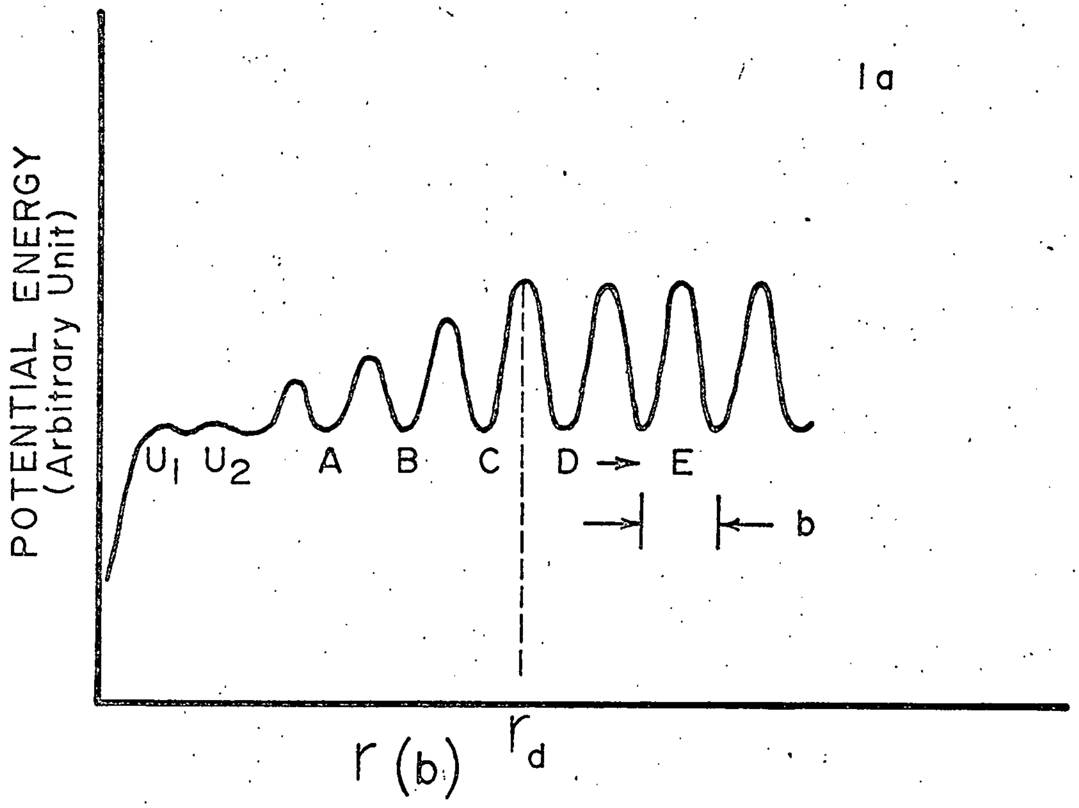
Figure 8. A comparison of the complete diffusional treatment (curve a) with one that treats correlated recovery separately from random recovery and dimer formation (curve b). The parameters for this calculation are the same as those listed in the caption to Figure 7.

Figure 9. The fractional recovery obtained from the solution of Equation 5.22 (using the Gaussian initial distribution, g_5) plotted as a function of equivalent time and compared with 1.4 MeV electron-irradiated copper. The appropriate parameters are $\rho_o^o = 1$ P.P.M., $D_o/r_o^2 = 5 \times 10^{11}$/sec, $E_m/k = 1360°K$, $\lambda_5 = 1.30$, $r_o = 3.6\ a_o$, $r_1 = 4.5\ a_o$, $r_2 = r_T = 0$.

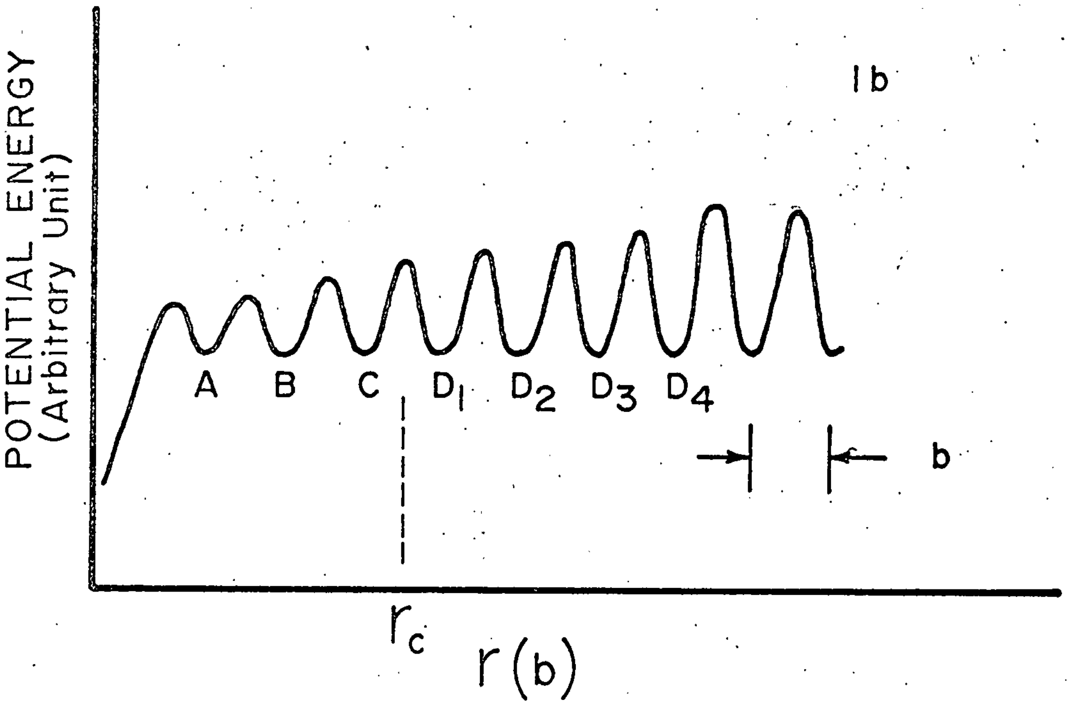
Figure 10. Representative solutions to Equation (using the modified exponential distribution, $_4$) corresponding to correlated and random recovery with impurity trapping and double conversion. The appropriate parameters are--for the curve with $\nu = 3 \times 10^{13}$/sec--$E_m/ = 1320°K$; $\lambda_4 = 0.417$, $r_o = r_1 = r_T = 25\ a_o$, $\rho_T^o = 1$ P.P.M.; for the curves with $\nu = 3 \times 10^{15}$/sec--$r_o = r_1 = r_T = 30\ a_o$.

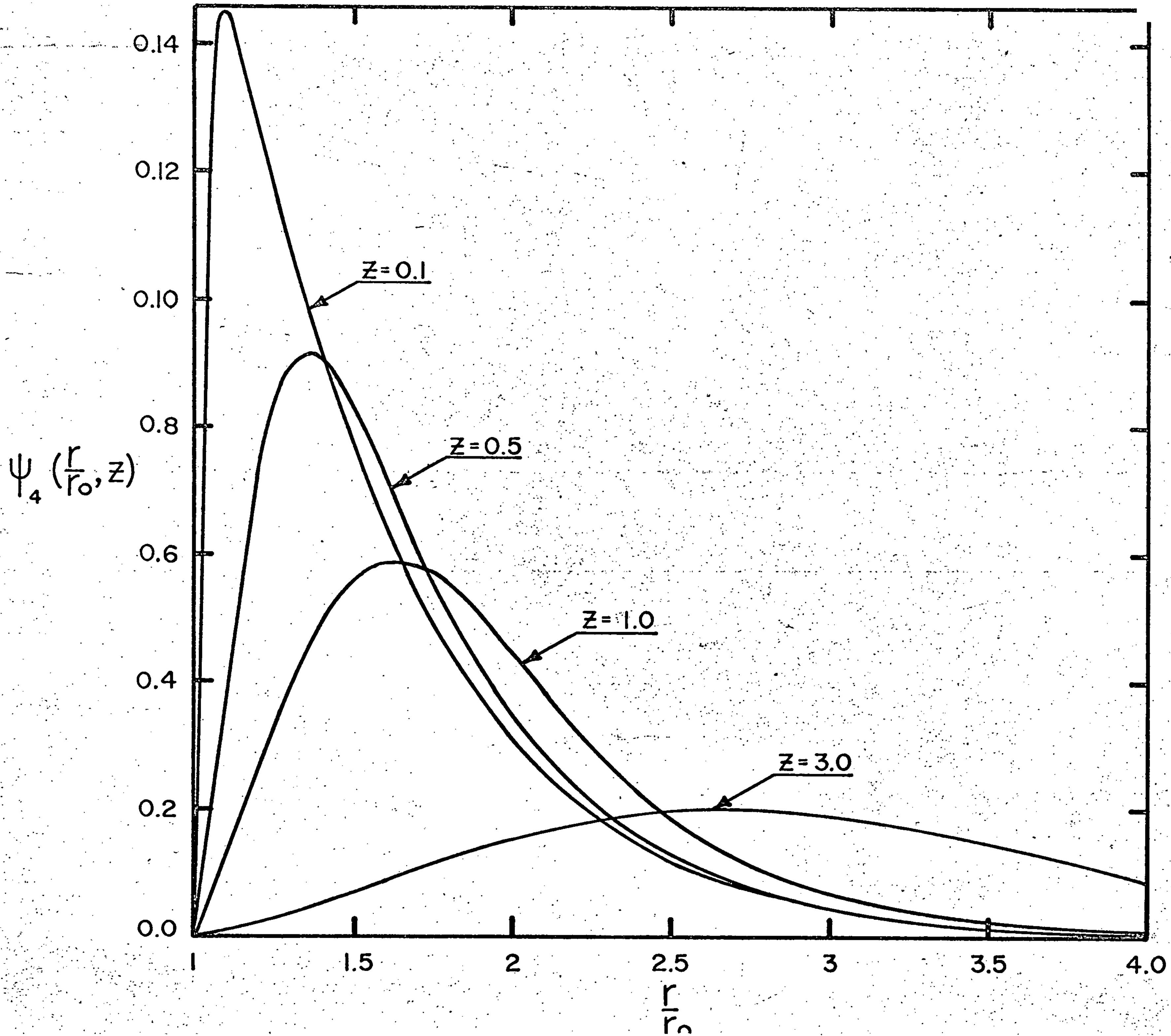
Figure 11. Reaction kinetics for one and three dimensional diffusional formulations involving random recovery and/or dimer formation and double conversion. Curve (a) presents γ as a function of the fractional vacancy concentration for the one dimensional case. Note the high order of the reaction throughout most of the annealing. Curves (b), (c), (d) represent γ for the three dimensional case with $(4cr_o^3)_b = 10^{-1}$, $(4cr_o^3)_c = 10^{-2}$, $(4cr_o^3)_d = 10^{-3}$.

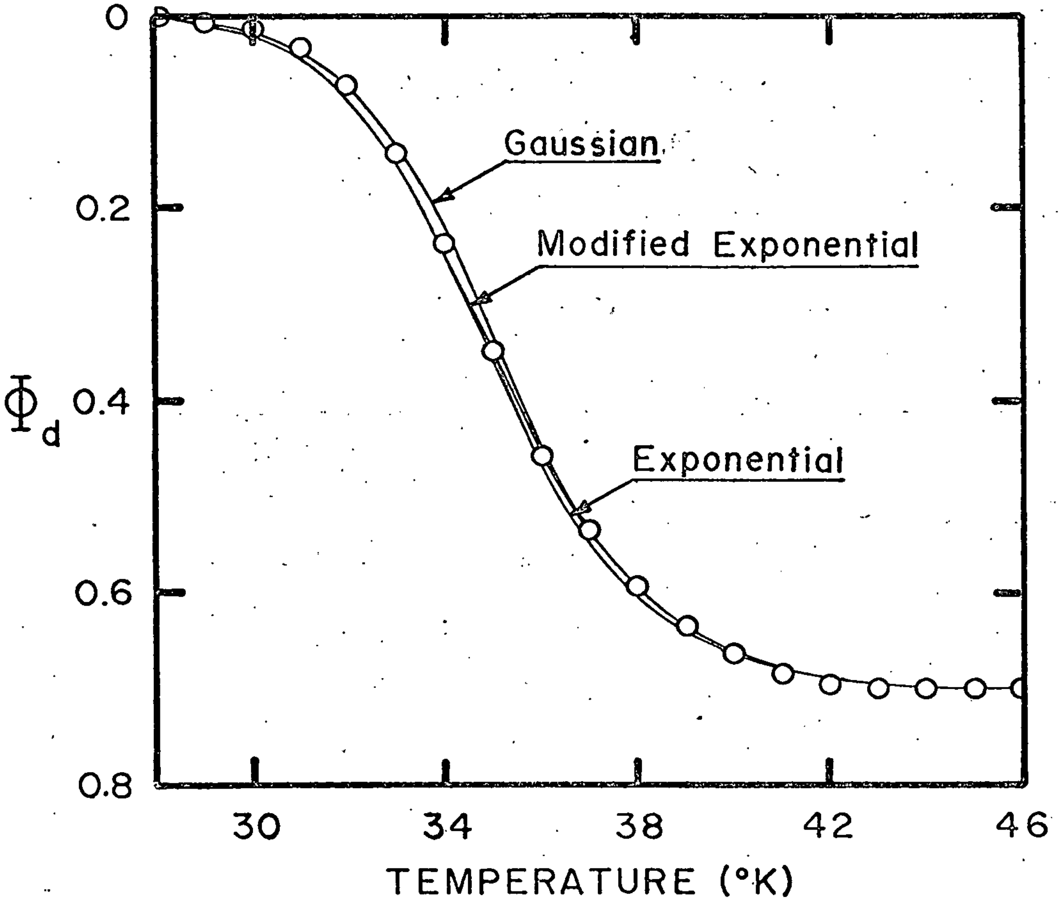
1a


POTENTIAL ENERGY
(Arbitrary Unit)
U1
U2
A
B
C
D
E
b
r (b)
rd

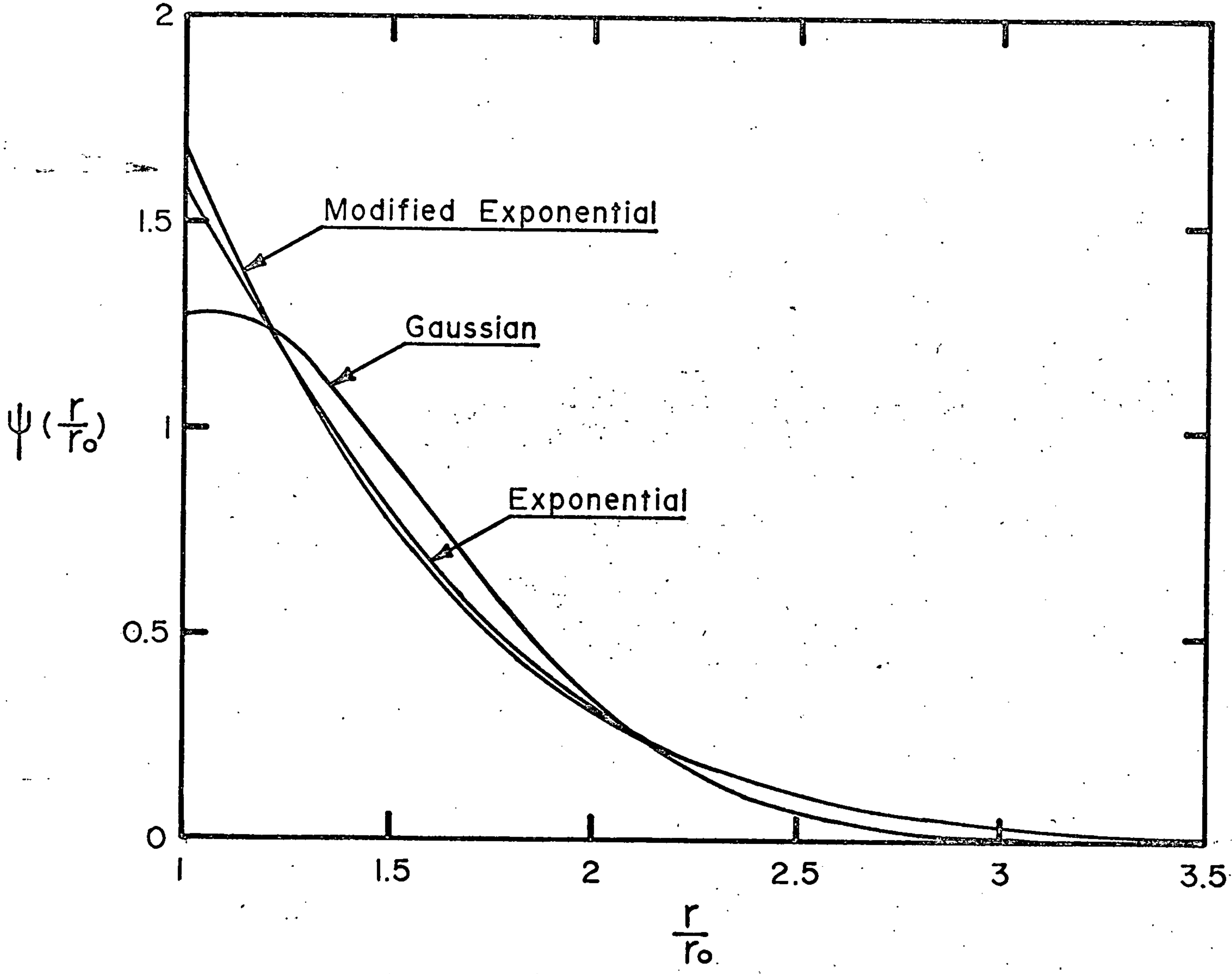
1b


POTENTIAL ENERGY
(Arbitrary Unit)
A
B
C
D1
D2
D3
D4
b
rc
r (b)

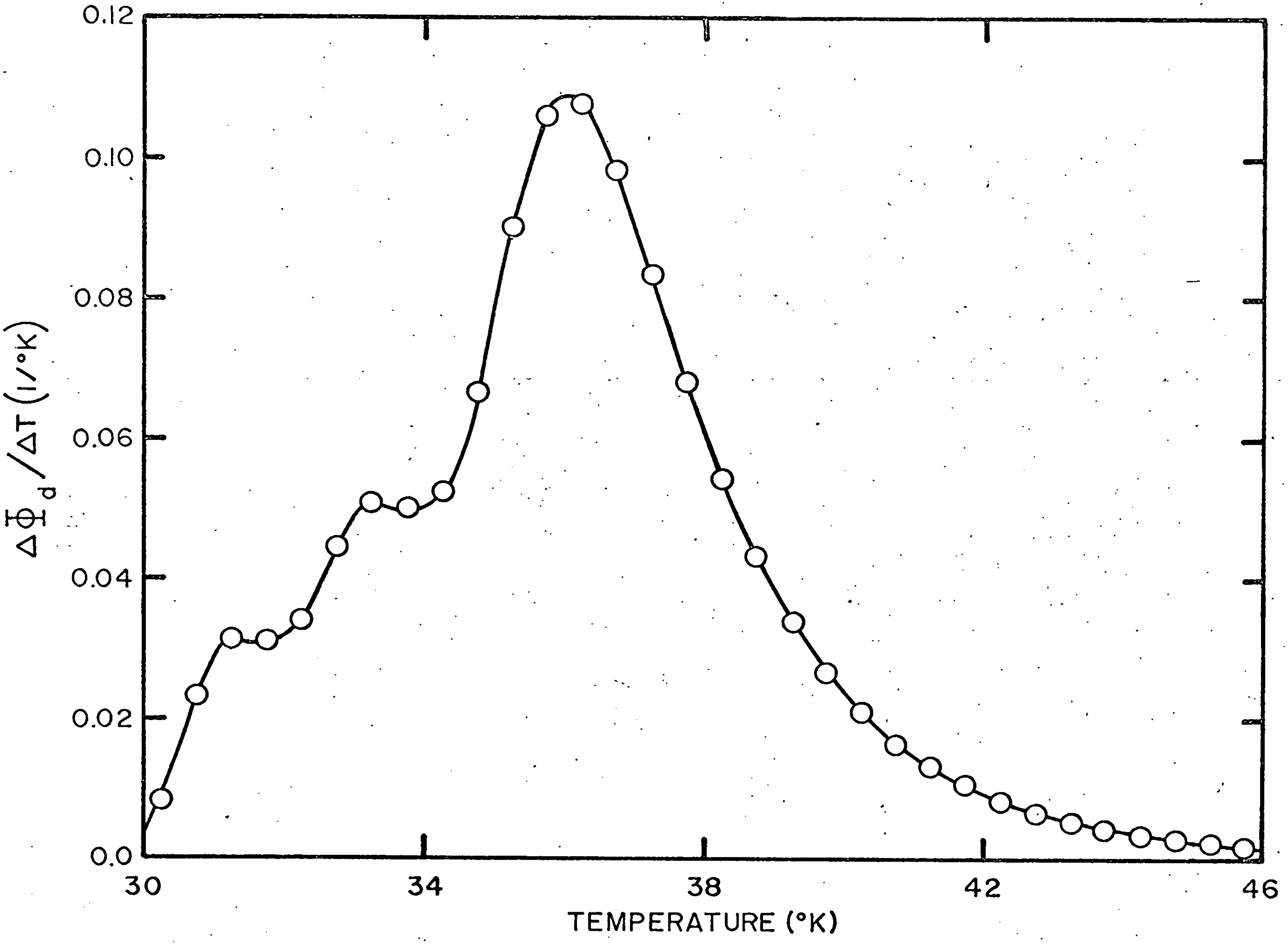

0.14
0.12
0.10
0.8
0.6
0.4
0.2
0.0
$\psi_4(\frac{r}{r_0}, z)$
Z = 0.1
Z = 0.5
Z = 1.0
Z = 3.0
1
1.5
2
2.5
3
3.5
4.0
$\frac{r}{r_0}$

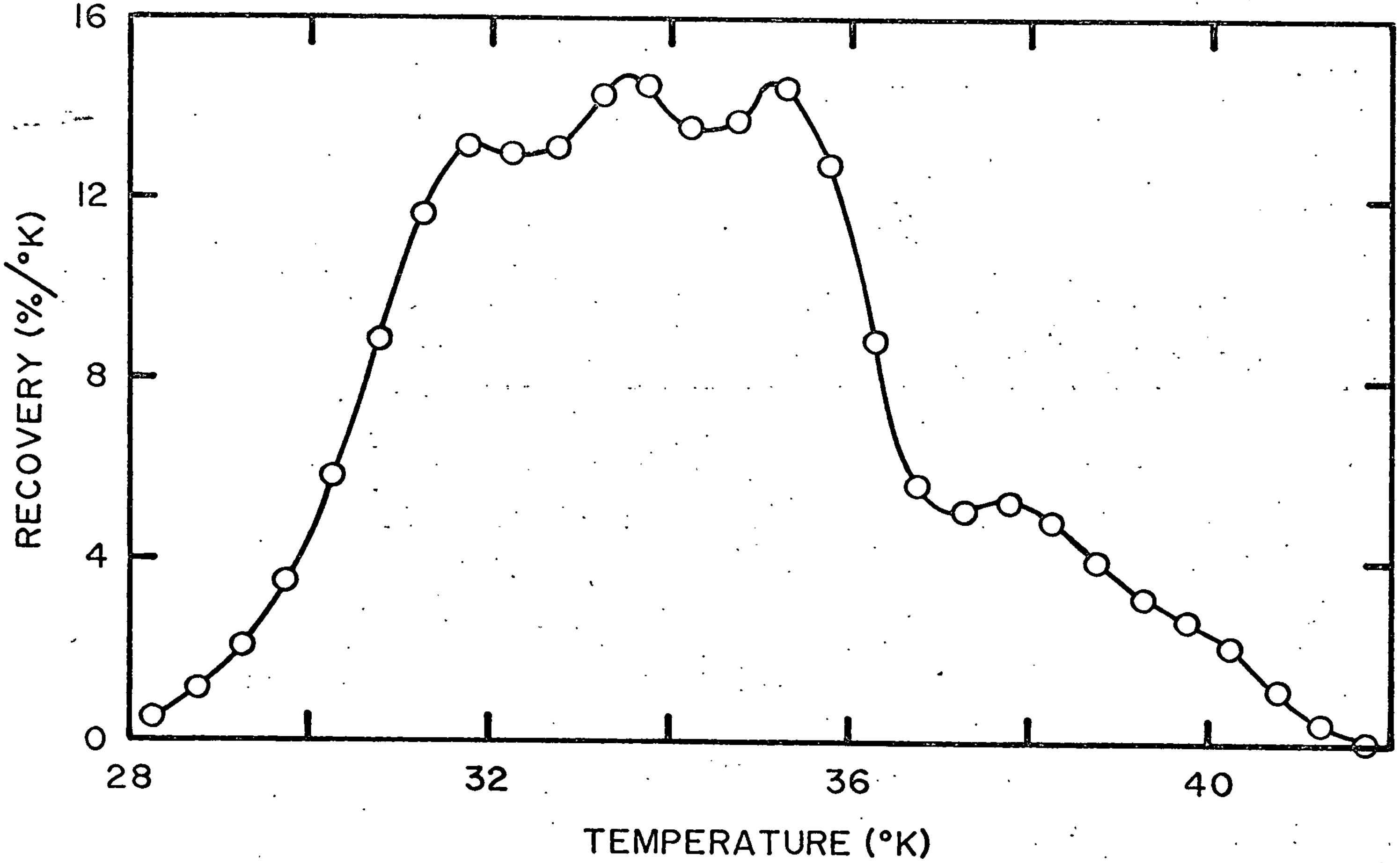


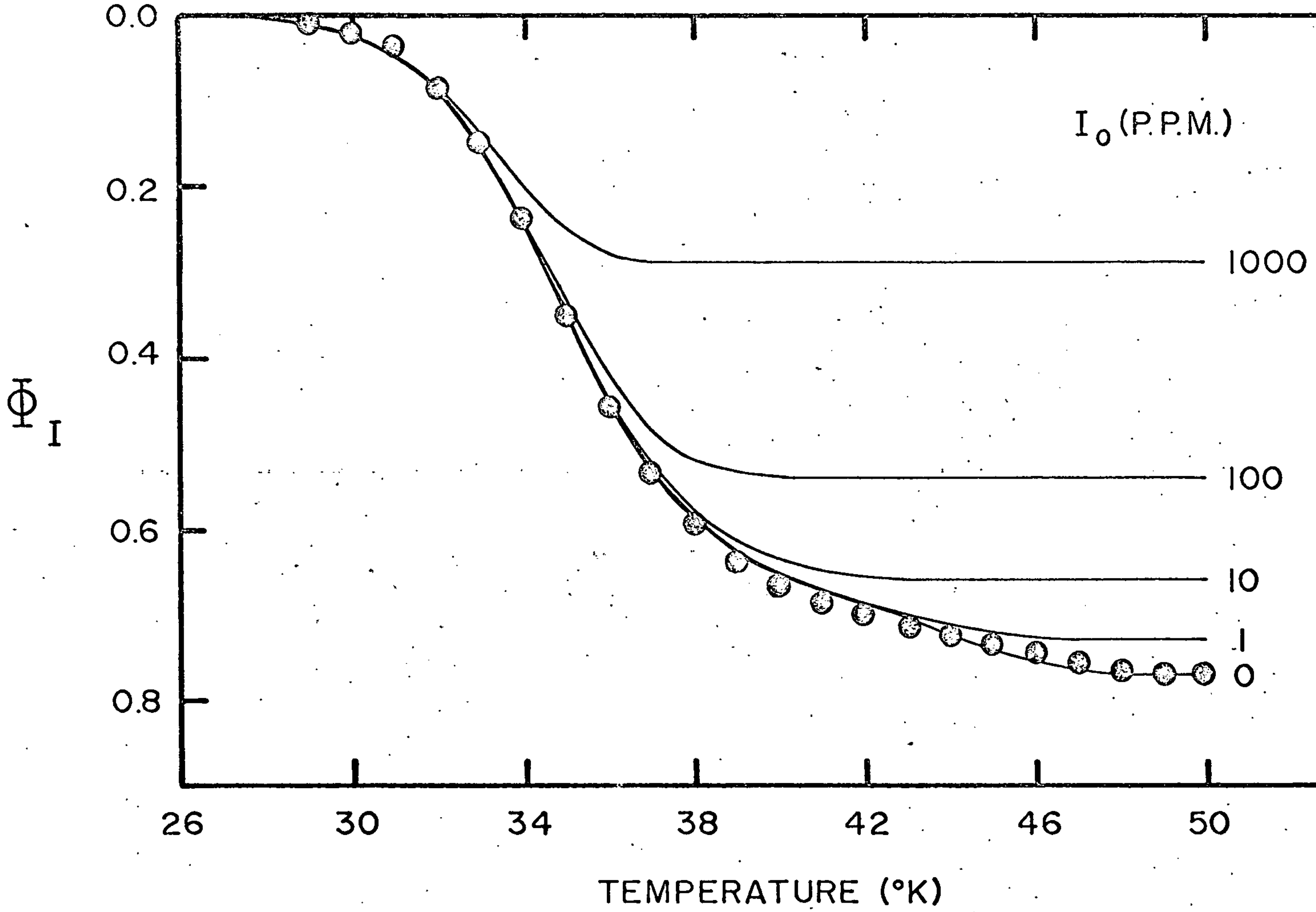
0
0.2
0.4
0.6
0.8
Φ_d
30
34
38
42
46
TEMPERATURE (°K)
Gaussian
Modified Exponential
Exponential



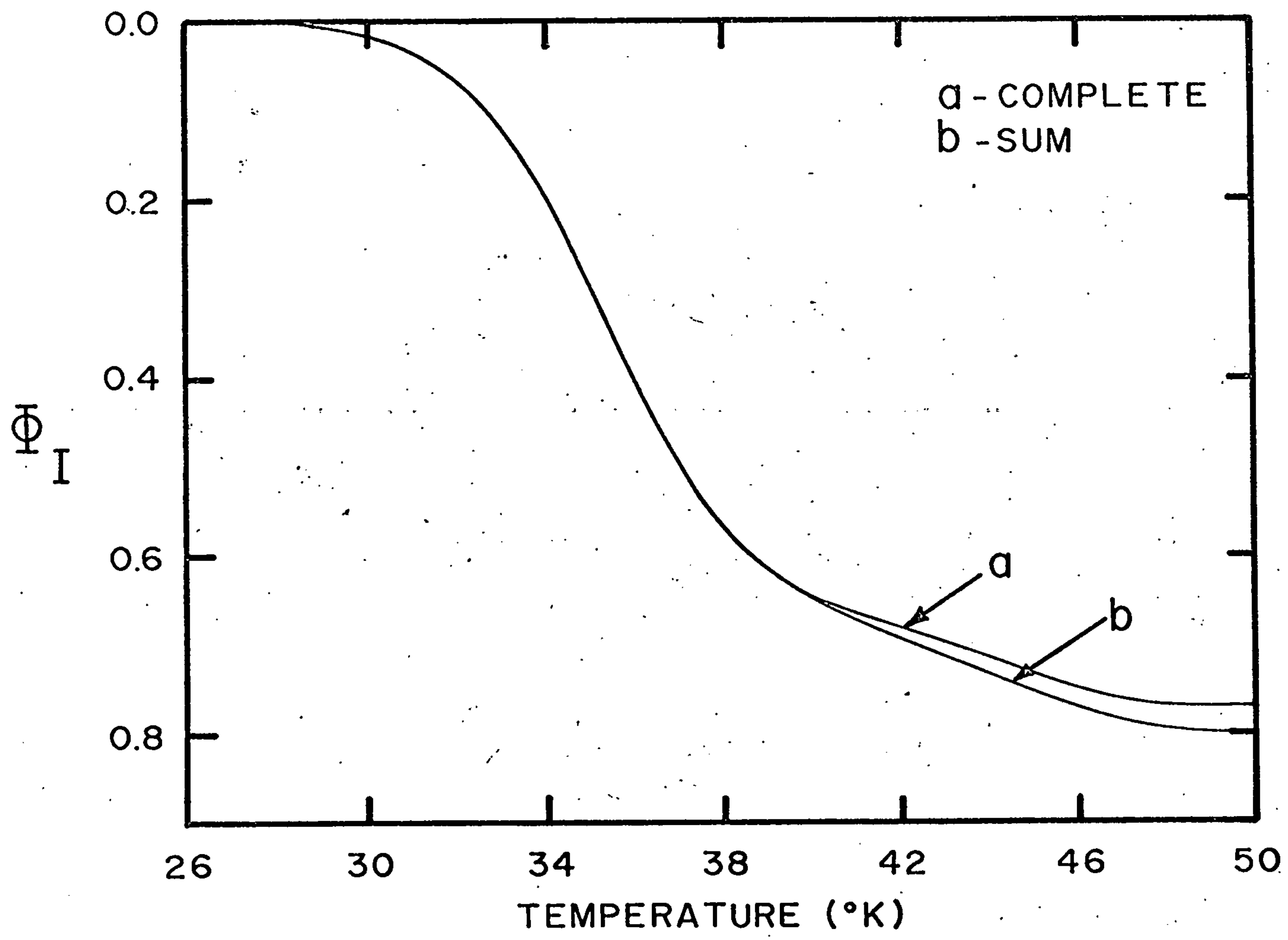
2
1.5
1
0.5
0
$\psi(\frac{r}{r_o})$
Modified Exponential
Gaussian
Exponential
1
1.5
2
2.5
3
3.5
$\frac{r}{r_o}$


0.12
0.10
0.08
0.06
0.04
0.02
0.0
30
34
38
42
46
TEMPERATURE (°K)
$\Delta\Phi_d/\Delta T$ (1/°K)

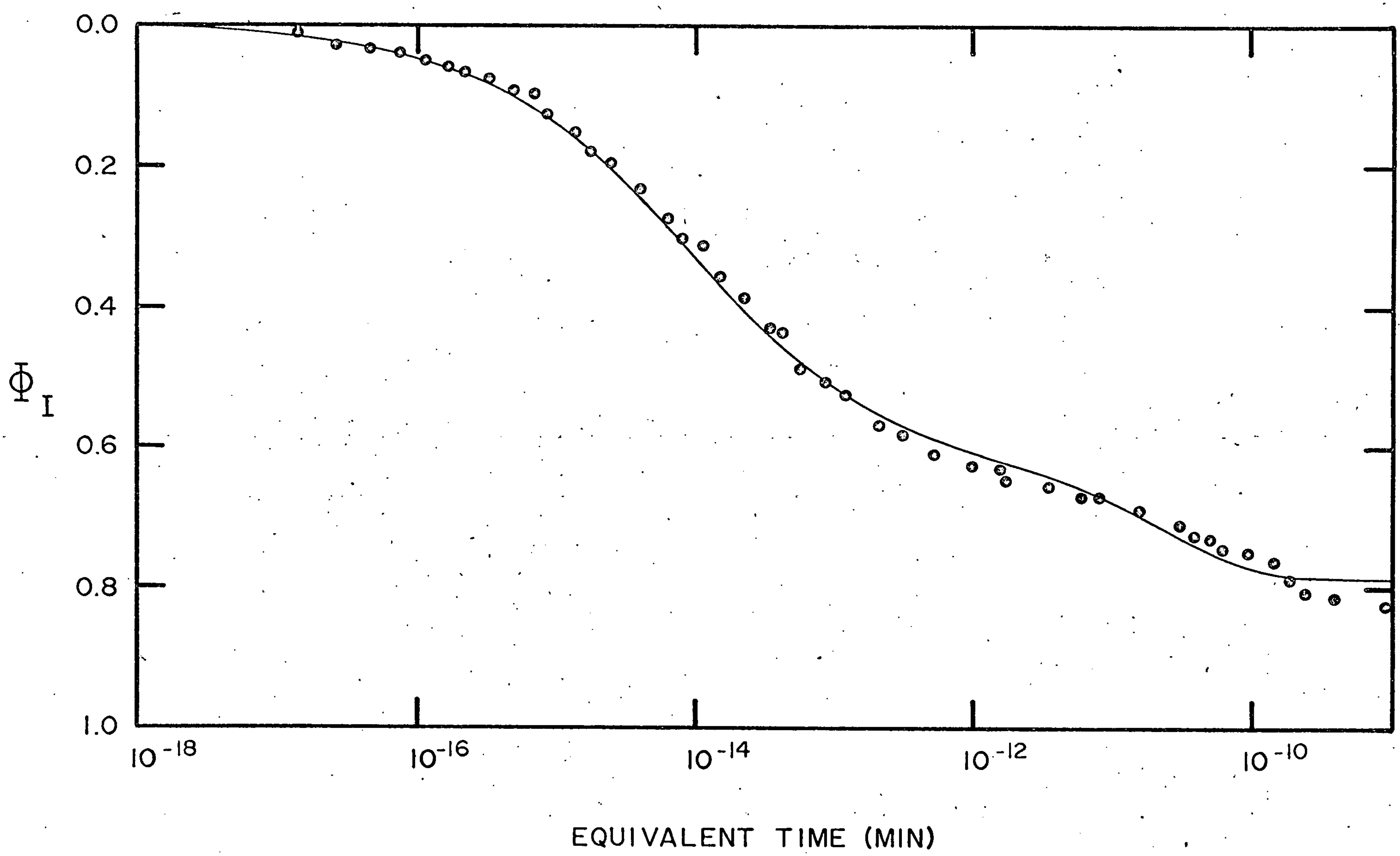

16
12
8
4
0
28
32
36
40
RECOVERY (%/°K)
TEMPERATURE (°K)



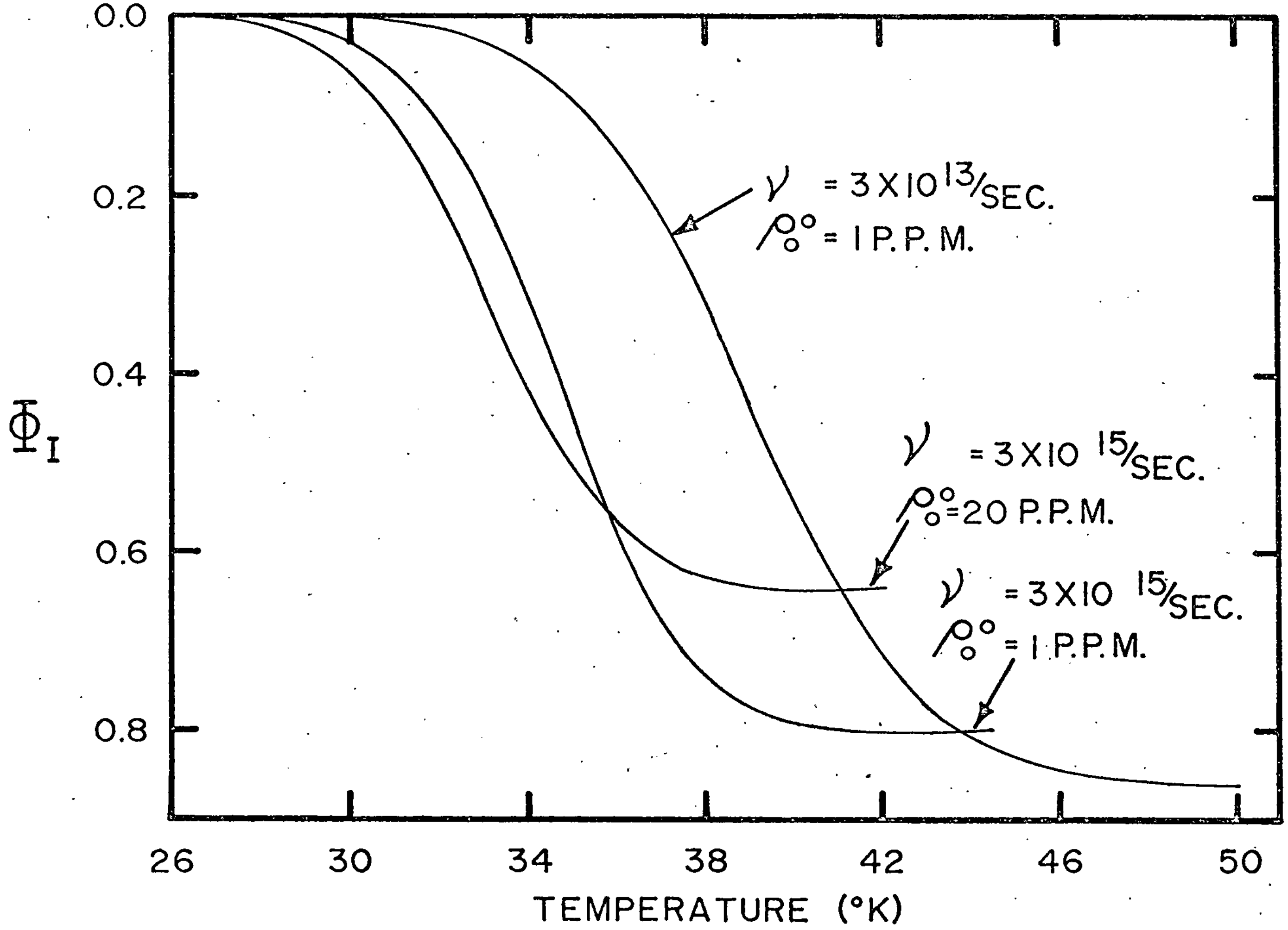
0.0
0.2
0.4
0.6
0.8
Φ_I
I_0 (P.P.M.)
1000
100
10
1
0
26
30
34
38
42
46
50
TEMPERATURE (°K)



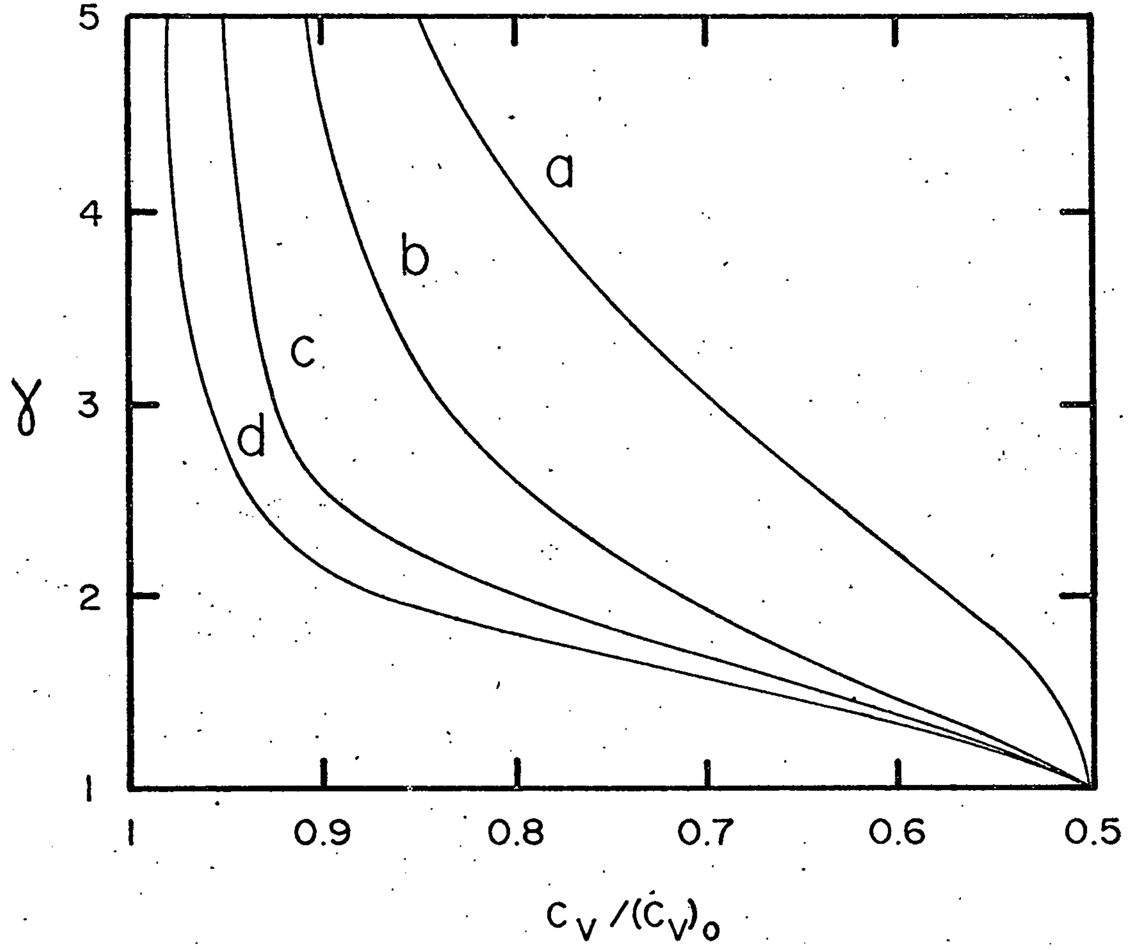
0.0
0.2
0.4
0.6
0.8
Φ_I
a - COMPLETE
b - SUM
a
b
26
30
34
38
42
46
50
TEMPERATURE (°K)



0.0
0.2
0.4
0.6
0.8
1.0
Φ_I
10^{-18}
10^{-16}
10^{-14}
10^{-12}
10^{-10}
EQUIVALENT TIME (MIN)



0.0
0.2
0.4
0.6
0.8
Φ_I
26
30
34
38
42
46
50
TEMPERATURE (°K)
$\nu = 3\times10^{13}$/SEC.
$\rho_o^o = 1$ P.P.M.
$\nu = 3\times10^{15}$/SEC.
$\rho_o^o = 20$ P.P.M.
$\nu = 3\times10^{15}$/SEC.
$\rho_o^o = 1$ P.P.M.


5
4
3
2
1
γ
a
b
c
d
1
0.9
0.8
0.7
0.6
0.5
$c_V/(c_V)_0$