

Kinetics of Vacancy-Interstitial Annihilation. II. Di-Interstitial Formation*

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The equations for the kinetics of vacancy-interstitial annihilation with diinterstitial formation have been solved on an analog computer. At low temperature, or for high diinterstitial binding energy, the decomposition reaction can be neglected. Analytic approximations have been found and shown to be valid in this case. Conventional methods of activation energy determination are valid in this region for evaluating the interstitial migration energy. At high temperature, or for low binding energy, the diinterstitial concentration may be neglected and the resulting kinetics is the simple quadratic interstitial-vacancy annihilation governed by the interstitial migration energy. In the intermediate region no analytic approximations have been found and the rate constants, therefore, cannot be evaluated.

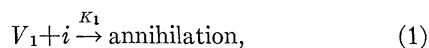
I. INTRODUCTION

IN the preceding paper¹ vacancy-interstitial annihilation with interstitial impurity trapping was discussed. In this paper the annihilation process is examined without impurities but with di-interstitial formation. In the impurity case a complete analytic solution was obtained, but this was not possible in the present case. The kinetics will be described, therefore, on the basis of selected analog computer calculations and some approximations.

II. GENERAL FORMULATION

As in the previous case, the solid is assumed to contain equal numbers of vacancies and interstitials randomly distributed. Also the study is restricted to the condition that the vacancies and interstitials can decay only by vacancy interstitial annihilation. The interstitials are assumed to be much more mobile than the vacancies.

Let the following notation be used: V_1 =mono-vacancy concentration (atomic fraction), i =free interstitial atom concentration (atomic fraction), i_2 =di-interstitial concentration (atomic fraction), and N =total defect concentration (atomic fraction). The above physical picture is described by the simple kinetic scheme:



and the corresponding differential equations are

$$dV_1/dt = -K_1 V_1 i, \quad (3)$$

$$di/dt = -K_1 V_1 i - K_2 i^2 + K_3 i_2, \quad (4)$$

$$di_2/dt = \frac{1}{2} K_2 i^2 - \frac{1}{2} K_3 i_2, \quad (5)$$

$$dN/dt = -2K_1 V_1 i, \quad (6)$$

with $N = V_1 + i + 2i_2$; $V_1 = i + 2i_2$; $V_1^0 = i^0$.

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¹ A. C. Damask and G. J. Dienes, preceding paper Phys. Rev. 125, 444 (1961).

An analytic solution of these equations has not been found. Valid approximations can be made at very high ($i_2 \cong 0$) and at very low ($K_3 \cong 0$) temperatures. No suitable approximations have been found in any region where none of the constants and none of the variables is negligible. This complex region was explored by analog computer calculations.

The rate constants are given by the relations

$$K_1 = 30\nu e^{-E_i/RT},$$

$$K_2 = 84\nu e^{-E_i/RT},$$

$$K_3 = 14\nu e^{-(E_i+B)/RT},$$

where $\nu = 10^{13}$, E_i =activation energy for interstitial migration, and B =binding energy of two interstitials.

Some assumptions are involved in selecting the numerical constants, i.e., the combinatory factors. The interstitial is taken to be in the "split" configuration.^{2,3} Further calculations by Vineyard⁴ indicate that the most stable configuration of the di-interstitial is that in which the two split interstitials are parallel to each other. The number of independent orientations of this parallel arrangement is 6, and therefore $K_2/K_3=6$. The coefficient for K_1 is the same as in the impurity case discussed in the previous paper since the number of ways an interstitial can arrive at a vacancy is the same as for combination with an impurity.

In all of the calculations it was assumed that the interstitial migrates much faster than the vacancy, and, therefore, the vacancy is taken to be stationary. Calculations were made for the following range of the variable parameters: $E_i=0.1, 0.4$ ev; $B=0.1, 0.2, 0.24, 0.3, 0.4$ ev, and twelve temperatures in the range of 50°K to 310°K. This range of temperatures was selected to illustrate the low- and high-temperature approximations and the complex intermediate behavior.

III. RESULTS AND DISCUSSION

1. General Case

As stated above, no analytic solutions or approximations have been found for the case when all the

² H. B. Huntington, Phys. Rev. 91, 1092 (1953).

³ J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. 120, 1229 (1960). (These calculations and the present one are for fcc metals.)

⁴ G. H. Vineyard (to be published).

TABLE I. Parameters for the curves of Fig. 2.

Curve	Run No.	V_1^0	T ($^{\circ}\text{K}$)	B	K_1	K_2	K_3	K_3/K_1
1	12a	5×10^{-6}	290	0.4	3.48×10^7	9.74×10^7	1.88	5.4×10^{-8}
2	7	5×10^{-5}	210	0.2	7.92×10^4	2.22×10^5	6.02×10^{-1}	7.60×10^{-6}
3	3a	5×10^{-6}	190	0.2	7.78×10^3	2.18×10^4	1.86×10^{-2}	2.39×10^{-6}
4	6a	5×10^{-6}	200	0.2	2.36×10^4	7.36×10^4	1.15×10^{-1}	4.37×10^{-6}
5	7a	5×10^{-6}	210	0.2	7.92×10^4	2.22×10^5	6.02×10^{-1}	7.60×10^{-6}
6	5	5×10^{-5}	200	0.1	2.63×10^4	7.36×10^4	3.76×10^1	1.43×10^{-3}
7	5a	5×10^{-6}	200	0.1	2.63×10^4	7.36×10^4	3.76×10^1	1.43×10^{-3}
8	See text							

constants and variables are important. A typical analog computer solution is shown in Fig. 1. It is evident that vacancy-interstitial annihilation and di-interstitial formation are of about equal importance. Although V_1 and i_2 decay in a very similar way, steady-state approximation on i (a procedure which gave the correct long-time solution in the preceding paper) does not lead to a valid long-time solution even when i is much smaller than the case illustrated in Fig. 1.⁵ Other possible approximations, for example $V_1/i_2 = \text{constant}$, were also found to be invalid. In comparison with the equations of the previous paper, it is probably the i^2 term which accounts for the fact that these approximations do not apply.

A way of systematizing the analog computer solutions is shown in Fig. 2 where i/i_0 vs V_1/V_1^0 is plotted for a series of solutions (i is determined as a function of V_1 by eliminating the time t , graphically). The parameters for the various curves are given in Table I. The system of curves is bounded by two lines, a straight line for $i_2=0$, which corresponds to very high temperatures, and the line $K_3=0$, valid at very low temperatures. The solid curves show a systematic progression with

increasing K_3/K_1 . The dashed curves show the same features for a higher initial concentration. The importance of initial concentration is evident from a comparison of curves 2 and 5, and 6 and 7; the only change between these two pairs being the initial concentration. A characteristic of these curves is the inflection point near $V_1/V_1^0 = 0.5$. For comparison, a similar plot, curve 8, is shown for a case from the preceding paper ($I_0 = 10^{-5}$, $i_0 = V_1^0 = 5 \times 10^{-6}$, $K_1 = 2.562 \times 10^2$, $K_3 = 3.958 \times 10^{-3}$). It should be noted that there is no inflection point in curve 8 or in the other curves (not plotted) for the impurity case. It appears, therefore, that the i^2 term gives rise to this inflection point which prevents the use of approximations in the present case.

2. High-Temperature Approximations

At sufficiently high temperature, or for a small value of B , the decomposition reaction of i_2 is fast enough to render its concentration small, particularly past an initial transient. Under these conditions the annihilation reaction dominates giving quadratic decay for V_1 and i governed by rate constant K_1 . An example of

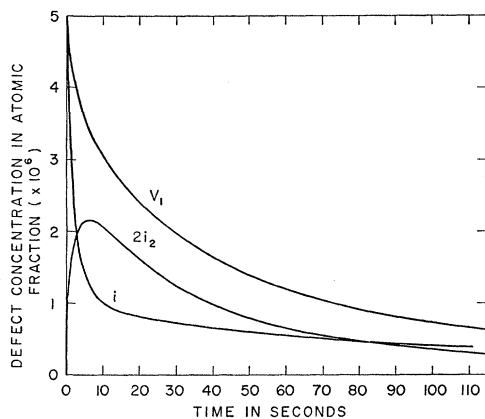


FIG. 1. Analog computer solution for the general case. (Run no. 6a of Table I.) $V_1^0 = i_0 = 5 \times 10^{-6}$, $T = 200^{\circ}\text{K}$, $E_i = 0.4$ ev, $B = 0.2$ ev.

⁵ Steady state approximation on i gives an exponential solution for V_1 and i_2 [G. J. Dienes and A. C. Damask, Bull. Am. Phys. Soc. 6, 157 (1961)]. Even though parts of some of the decay curves obtained by machine solutions are exponential, the corresponding decay constant does not match the one in the equation.

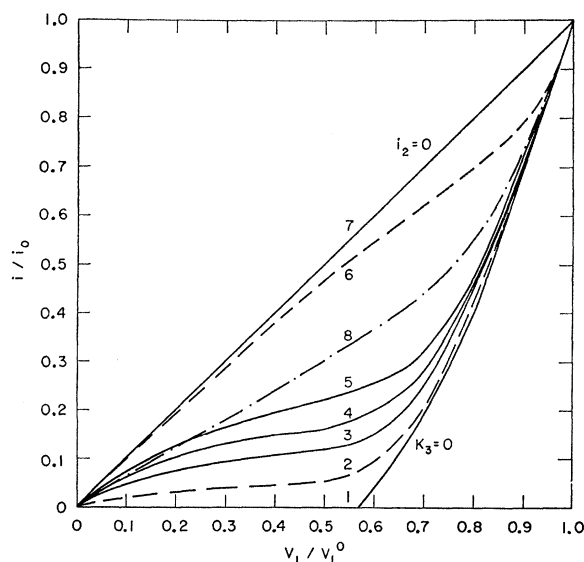


FIG. 2. Plot of i/i_0 vs V_1/V_1^0 for selected runs. The curves are identified in Table I of the text (curve 8 from previous paper).

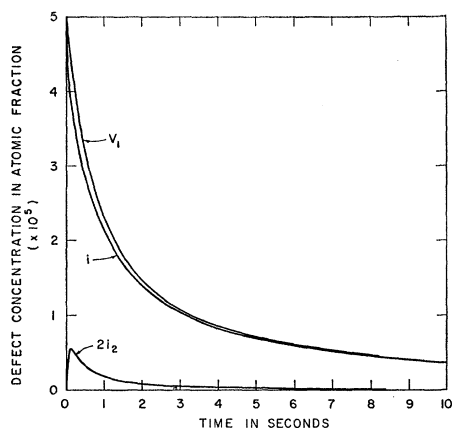


FIG. 3. Analog computer solution illustrating quadratic decay. (Run no. 5 of Table I.) $V_1^0 = i_0 = 5 \times 10^{-5}$, $T = 200^\circ\text{K}$, $E_i = 0.4$ ev, $B = 0.1$ ev.

this case is shown in Fig. 3, where V_1 and i obey a quadratic decay with the correct decay constant over the complete range in spite of the presence of the initial transient in i_2 .

3. Low-Temperature Approximations

At sufficiently low temperature, or for large values of B , the decomposition reaction for i_2 is extremely slow and one may let $K_3 = 0$. Thus, the interstitials decay to zero, a fraction forming i_2 and the remainder annihilating an equal number of V_1 's. V_1 and i_2 , therefore, will approach a constant. This behavior is illustrated in Fig. 4 for a run with a large B .

If $K_3 = 0$, then division of Eq. (4) by Eq. (3) gives

$$di/dV_1 = 1 + (K_2/K_1)(i/V_1). \quad (7)$$

Equation (7), and by substitution Eq. (3), can be integrated when K_2/K_1 is an integer or a simple fraction. For the choice of rate constants used in this

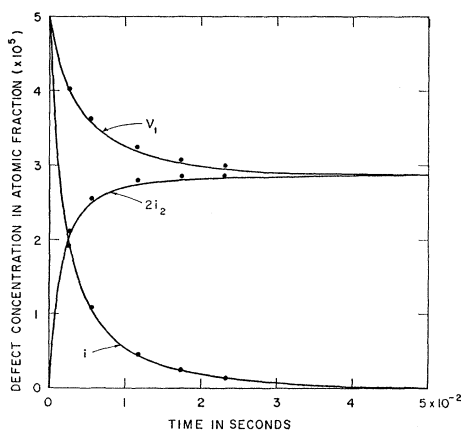


FIG. 4. Analog computer solution illustrating di-interstitial formation for small value of K_3/K_1 . $V_1^0 = i_0 = 5 \times 10^{-5}$, $T = 250^\circ\text{K}$, $E_i = 0.4$ ev, $B = 0.3$ ev. The circles represent calculated values from the equation of Table AI for $K_2/K_1 = 3$.

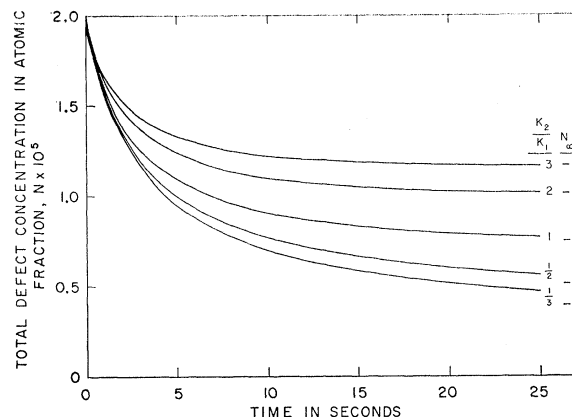


FIG. 5. N vs time curves for various values of K_2/K_1 plotted from equations of Table AI. $E_i = 0.1$ ev, $T = 50^\circ\text{K}$.

calculation $K_2/K_1 \cong 3$. The solution in this case is given in the Appendix and calculations from this solution yield the circles shown in Fig. 4. The results are obviously in good agreement with the analog computer solution.

Vineyard's calculation⁴ has shown that there are several configurations of i_2 of differing but close binding energies. It is, therefore, possible that the i_2 configuration chosen here is not the correct one, and furthermore, several configurations may occur simultaneously. For this reason, Eqs. (7) and (3) have been integrated in the Appendix for several other values of K_2/K_1 . The asymptotic value of N , N_∞ , as well as the shape of the N vs time curve, depends on this ratio. In Fig. 5 curves are shown for the cases that have been integrated.

It should be noted from Table AI of the Appendix that for all values of K_2/K_1 the reaction rate is governed by K_1 . The form of the equations is such that conventional methods of activation energy analysis, such as the cross-cut method, are applicable to V , i , i_2 , and N . Thus, the activation energy for interstitial migration is directly determinable from the low-temperature buildup curve. It should be recalled that the quadratic decay of the high-temperature approximation also yields only K_1 ; no method has been found for deriving the value of K_3 .

ACKNOWLEDGMENT

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APPENDIX

In the low-temperature region $K_3 = 0$, and division of Eq. (4) by Eq. (3) of the text gives

$$di/dV_1 = 1 + (K_2/K_1)(i/V_1). \quad (A1)$$

$K_1 = K_2$ is a special case which is solved first. Let

TABLE AI. Solutions for diinterstitial formation with $K_3=0$.

K_2/K_1	Solution for V_1	Formula for i	$(V_1/V_1^0)_{t=\infty}$
3	$\frac{1}{V_1^0} - \frac{1}{V_1} + \frac{\sqrt{3}}{2V_1^0} \left[\ln \frac{-(\sqrt{3}V_1/V_1^0)-1}{(\sqrt{3}V_1/V_1^0)-1} - \ln \frac{-\sqrt{3}-1}{\sqrt{3}-1} \right] = \frac{1}{2}K_1t$	$i = \frac{2}{3}V_1[(V_1/V_1^0)^2 - \frac{1}{3}]$	$1/\sqrt{3}=0.577$
2	$\frac{1}{V_1^0} - \frac{1}{V_1} - \frac{2}{V_1^0} \left\{ \ln \left[2V_1^0 \left(\frac{V_1}{V_1^0} - \frac{1}{2} \right) / V_1 \right] \right\} = K_1t$	$i = 2V_1[(V_1/V_1^0) - \frac{1}{2}]$	$\frac{1}{2}=0.50$
1	$-0.80 - \ln[1 + \ln(V_1/V_1^0)] + [1 + \ln(V_1/V_1^0)]/1! - [1 + \ln(V_1/V_1^0)]^2/2 \times 2! + \dots = (K_1V_1^0/e)t$	$i = V_1[1 + \ln(V_1/V_1^0)]$	$1/e=0.37$
$\frac{1}{2}$	$-\frac{2}{(V_1^0V_1)^{\frac{1}{2}}} + \frac{2}{V_1^0} + \frac{4}{V_1^0} \left[\ln \frac{V_1^{\frac{1}{2}}}{V_1^{\frac{1}{2}} - \frac{1}{2}(V_1^0)^{\frac{1}{2}}} - \ln 2 \right] = K_1t$	$i = -V_1[(V_1^0/V_1)^{\frac{1}{2}} - 2]$	$\frac{1}{4}=0.25$
$\frac{1}{3}$	$\frac{3}{V_1^0} - \frac{3}{(V_1^0)^{\frac{2}{3}}(V_1)^{\frac{1}{3}}} + \frac{3\sqrt{3}}{2V_1^0} \ln \left[\frac{(-1+\sqrt{3})}{(-1-\sqrt{3})} \left(\frac{-(V_1^0)^{\frac{1}{3}} - \sqrt{3}(V_1)^{\frac{1}{3}}}{-(V_1^0)^{\frac{1}{3}} + \sqrt{3}(V_1)^{\frac{1}{3}}} \right) \right] = \frac{1}{2}K_1t$	$i = -\frac{1}{2}V_1[(V_1^0/V_1)^{\frac{1}{3}} - 3]$	$(\frac{1}{3})^{\frac{1}{3}}=0.192$

$i/V_1=x$; then (A1) becomes

$$dV_1/V_1=dx, \quad (\text{A2})$$

and integration gives

$$i = V_1[1 + \ln(V_1/V_1^0)], \quad (\text{A3})$$

As

$$t \rightarrow \infty, \quad i \rightarrow 0 \quad \text{and} \quad (V_1/V_1^0) \rightarrow 1/e.$$

Substitution in Eq. (3) of the text gives

$$dV_1/dt = -K_1V_1^2[1 + \ln(V_1/V_1^0)]. \quad (\text{A4})$$

Let $\ln(V_1/V_1^0)=y$, then (A4) becomes

$$dy/dt = -K_1V_1^0e^y(1+y),$$

and the substitution $y=z-1$ gives

$$dz/dt = (-K_1V_1^0/e)ze^z, \quad (\text{A5})$$

which has a known series for an integral. The result is

$$\begin{aligned} & \ln[1 + \ln(V_1/V_1^0)] - [1 + \ln(V_1/V_1^0)]/1 \times 1! \\ & + [1 + \ln(V_1/V_1^0)]^2/2 \times 2! + \dots \\ & = (-K_1V_1^0/e)t + A, \end{aligned} \quad (\text{A6})$$

where A , to a high accuracy, is equal to -0.80 . The final equation is

$$\begin{aligned} & -0.80 - \ln[1 + \ln(V_1/V_1^0)] + [1 + \ln(V_1/V_1^0)]/1 \times 1! \\ & - [1 + \ln(V_1/V_1^0)]^2/2 \times 2! + \dots = (K_1V_1^0/e)t. \end{aligned} \quad (\text{A7})$$

If $K_2 \neq K_1$ Eq. (A1) becomes, again by letting $i/V_1=x$,

$$\frac{dV_1}{V_1} = \frac{dx}{1 + (K_2/K_1 - 1)x}, \quad (\text{A8})$$

which finally integrates to

$$i = \frac{K_2}{K_2 - K_1} V_1 \left[\left(\frac{V_1}{V_1^0} \right)^{(K_2/K_1) - 1} - \frac{K_1}{K_2} \right]. \quad (\text{A9})$$

As

$$t \rightarrow \infty; \quad i \rightarrow 0$$

and

$$(V_1/V_1^0) \rightarrow (K_1/K_2)^{1/(K_2/K_1) - 1}. \quad (\text{A10})$$

Substitution in Eq. (3) of the text gives

$$\frac{dV_1}{dt} = -\frac{K_1K_2}{K_2 - K_1} V_1^2 \left[\left(\frac{V_1}{V_1^0} \right)^{(K_2/K_1) - 1} - \frac{K_1}{K_2} \right], \quad (\text{A11})$$

which cannot be solved in closed form in general but can be integrated for given values of K_2/K_1 . The two extremes are clear. If $K_1=0$ a pure quadratic decay of i to i_2 occurs; if $K_2=0$ V_1 decays in a purely quadratic way by recombination [see Eqs. (3) and (4) of the text]. Equation (A11) has been integrated for various values of K_2/K_1 . The results are shown in Table AI, where the equations for V_1 , i , and $(V_1/V_1^0)_{t=\infty}$ are presented.