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Quenching of Metals Containing Impurity.*
I. Face-Centered-Cubic Metals

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General kinetic equations between vacancies, divacancies, and impurity atoms are presented. Some applications of these equations to the reactions during quenching are treated. The critical temperatures or freezing temperatures which determine the status after the quench are also given. The treatment shows that the cooling rate near the critical temperature is important, and these temperatures are rather low in usual cases. The treatment is in good agreement with the results of the actual change during quenching calculated by a digital computer. A relation between the binding energy B_{Vi} of an impurity atom and a vacancy and the solubility limit C_L of the impurity is presented. A relation between the binding energy and the heat of solution H is also discussed. The tentative relation is $B_{Vi}=0.52H=(-0.088\log C_L+0.088)$ eV.

I. INTRODUCTION

In recent years a number of quenching, equilibrium, and diffusion experiments have been done on pure metals and dilute alloys. It has been shown that the point defects in pure metals and dilute alloys play an important role in these experiments. Two major factors for the interactions between vacancies and impurity atoms and between impurity atoms themselves are the distortion of lattice around the impurity atoms[1] and the electrostatic interaction between vacancies and impurity atoms.[2]

The total fractional concentration of single vacancies and single-vacancy impurity complexes in a dilute alloy at a thermal equilibrium is given by[2a]

$$c=c_{1V}+c_{Vi}$$
$$=A_1(1-12c_i)\exp(-E_V{}^F/kT)+12c_iA_2\exp\{-(E_V{}^F-B_{Vi})/kT\}\,,\quad(1)$$

where c_i is the fractional concentration of impurity atoms. The first term represents the fractional concentration of free vacancies c_{1V}, and the second term represents the fractional concentration of impurity-atom–vacancy complexes c_{Vi}. A_1 and A_2 are constants, and $E_V{}^F$ is the energy required to form a vacancy far from an impurity atom. B_{Vi} is the binding energy of impurity-vacancy complexes.

A quenching experiment is one of the ideal experiments to study the point defects in metals because the major defects present at high temperatures are vacancies. However, in a practical quench the quench speed is finite; and because of this the reactions between vacancies and other defects progress even during a high-speed quench. The quenched status, therefore, is not the same as that of quenching temperature. Koehler *et al.*[3] first investigated this problem. They realized that there exists a critical temperature T^*, above which the reaction is fast enough to maintain a thermal equilibrium and that below T^* the reaction is too slow to maintain the thermal equilibrium. Kimura *et al.*[4] also discussed this problem. Koehler, de Jong, and Seitz[5] extended this treatment. Fujiwara[6] analyzed the reaction between vacancies during quenching by means of a digital computer. Recently, Cotterill[7] also analyzed the reactions by use of an analog computer. Mori,[8] Meshii,[8,9] and Kauffman[8,9] studied experimentally the process occurring during quenching. This treatment was extended by Flynn, Bass, and Lazarus.[10] This paper treats general kinetic equations between point defects with impurity atoms. Simple applications of the equations to the process during quenching are also given.

II. KINETIC EQUATIONS OF POINT DEFECTS

The kinetic equations for vacancy motion in a dilute alloy can be treated in analogy to the paper by Koehler, de Jong, and Seitz,[5] who considered the case of pure metals. The four configurations of divacancy-impurity complexes and the three configurations of complexes containing two single vacancies with an impurity atom are shown in Fig. 1. The kinetic equations with geometrical coefficients in a face-centered-cubic metal are as follows:

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[1] For example, R. Swalin, Acta Met. **5**, 443 (1957).

[2] For example, D. Lazarus, Phys. Rev. **93**, 973 (1954).

[2a] More correctly the first term of Eq. (1) is $A_1(1-13c_i)\times\exp(-E_V{}^F/kT)$. The author is indebted to R. M. J. Cotterill for pointing out this correction.

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

[4] H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, Acta Met. **7**, 145, 154 (1959).

[5] J. S. Koehler, M. de Jong, and F. Seitz, *Proceedings of the International Conference of Crystal Lattice Defects* (1962); J. Phys. Soc. Japan **18**, Suppl. III, 1 (1963); M. de Jong and J. S. Koehler, Phys. Rev. **129**, 40 (1963); **129**, 49 (1963).

[6] H. Fujiwara, Technical Report, University of Illinois, 1960 (unpublished).

[7] R. M. J. Cotterill, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic Press, Inc., New York, 1965), p. 97.

[8] T. Mori, M. Meshii, and J. W. Kauffman, J. Appl. Phys. **33**, 2776 (1962).

[9] J. W. Kauffman and M. Meshii in Ref. 7, p. 77.

[10] C. P. Flynn, J. Bass, and D. Lazarus in Ref. 7, p. 639.

$$\begin{aligned}
dc_{1V}/dt= & -2\alpha_1(V,\ V\rightarrow V-V;\ a)c_{1V}^2+2\alpha_1(V-V\rightarrow V,\ V;\ a)c_{2V}-\alpha_1(i,\ V\rightarrow V-i,\ V;\ a)c_ic_{1V}\\
& +\alpha_1(V-i\rightarrow i,\ V;\ a)c_{Vi}+\alpha_1(D^{90}\rightarrow V-i,\ V;\ a_i)c_D^{90}+\alpha_1(D^{60}\rightarrow V-i,\ V;\ a)c_D^{60}\\
& +\alpha_1(D^{90}\rightarrow V-i,\ V;\ a)c_D^{90}+2\alpha_1(D^{90}\rightarrow i,\ V,\ V;\ a)c_D^{90}+\alpha_1(D^{120}\rightarrow V-i,\ V;\ a_i)c_D^{120}\\
& +\alpha_1(D^{120}\rightarrow V-i,\ V;\ a)c_D^{120}+2\alpha_1(D^{120}\rightarrow i,\ V,\ V;\ a)c_D^{120}+\alpha_1(D^{180}\rightarrow V-i,\ V;\ a_i)c^{120}\\
& +\alpha_1(D^{180}\rightarrow V-i,\ V;\ a)c_D^{180}+2\alpha_1(D^{180}\rightarrow i,\ V,\ V;\ a)c_D^{180}+\alpha_1(T^{90}\rightarrow V-i,\ V;\ a)c_T^{90}\\
& +\alpha_1(T^{120}\rightarrow V-i,\ V;\ a)c_T^{120}+\alpha_1(T^{180}\rightarrow V-i,\ V;\ a)c_T^{180}-\alpha_1(V-i,\ V\rightarrow D^{60};\ a)c_{Vi}c_{1V}\\
& -\alpha_1(V-i,\ V\rightarrow D^{90};\ a)c_{Vi}-\alpha_1(V-i,\ V\rightarrow D^{120};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow D^{180};\ a)c_{Vi}c_{1V}\\
& -\alpha_1(V-i,\ V\rightarrow T^{90};\ a)c_{Vi}c_{1V}+\alpha_1(V-i,\ V\rightarrow T^{120};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow T^{180};\ a)c_{Vi}c_{1V}\\
& -2\alpha_1(i,\ V,\ V\rightarrow D^{90};\ a)c_ic_{1V}^2-2\alpha_1(i,\ V,\ V\rightarrow D^{120};\ a)c_ic_{1V}^2-2\alpha_1(i,\ V,\ V\rightarrow D^{180};\ a)c_ic_{1V}^2\\
& \qquad -\alpha_1(V-i,\ V\rightarrow i,\ V-V;\ a)c_{Vi}c_{1V}+\alpha_1(i,\ V-V\rightarrow V-i,\ V;\ a)c_ic_{2V}+D_{1V}\nabla^2c_{1V};
\end{aligned}\tag{2a}$$

$$\begin{aligned}
dc_{2V}/dt= & \alpha_1(V,\ V\rightarrow V-V;\ a)c_{1V}^2-\alpha_1(V-V\rightarrow V,\ V;\ a)c_{2V}+\alpha_1(D^{90}\rightarrow i,\ V-V;\ a)c_D^{90}\\
& +\alpha_1(D^{120}\rightarrow i,\ V-V;\ a)c_D^{120}+\alpha_1(D^{180}\rightarrow i,\ V-V;\ a_2)c_D^{180}-\alpha_1(i,\ V-V\rightarrow D^{90};\ a_2)c_ic_{2V}\\
& -\alpha_1(i,\ V-V;\ D^{120};\ a_2)c_ic_{2V}-\alpha_1(i,\ V-V\rightarrow D^{180};\ a_2)c_ic_{2V}+\alpha_1(V-i,\ V\rightarrow i,\ V-V;\ a)c_{Vi}c_{1V}\\
& \qquad -\alpha_1(i,\ V-V\rightarrow V-i,\ V;\ a)c_ic_{2V}+D_{2V}\nabla^2c_{2V};
\end{aligned}\tag{2b}$$

$$\begin{aligned}
dc_i/dt= & -\alpha_1(i,\ V\rightarrow V-i;\ a)c_ic_{1V}+\alpha_1(V-i\rightarrow i,\ V;\ a)c_{Vi}+\alpha_1(D^{90}\rightarrow i,\ V-V;\ a)c_D^{90}\\
& +\alpha_1(D^{90}\rightarrow i,\ V,\ V;\ a)c_D^{90}+\alpha_1(D^{120}\rightarrow i,\ V-V;\ a)c_D^{120}+\alpha_1(D^{120}\rightarrow i,\ V,\ V;\ a)c_D^{120}\\
& +\alpha_1(D^{180}\rightarrow i,\ V-V;\ a_2)c_D^{180}+\alpha_1(D^{180}\rightarrow i,\ V,\ V;\ a)c_D^{180}-\alpha_1(i,\ V-V\rightarrow D^{90};\ a_2)c_ic_{2V}\\
& -\alpha_1(i,\ V-V\rightarrow D^{120};\ a_2)c_ic_{2V}-\alpha_1(i,\ V-V\rightarrow D^{180};\ a_2)c_ic_{2V}-\alpha_1(i,\ V,\ V\rightarrow D^{90};\ a)c_ic_{1V}^2\\
& -\alpha_1(i,\ V,\ V\rightarrow D^{120};\ a)c_ic_{1V}^2-\alpha_1(i,\ V,\ V\rightarrow D^{180};\ a)c_ic_{1V}^2+\alpha_1(V-i,\ V\rightarrow i,\ V-V;\ a)c_{Vi}c_{1V}\\
& \qquad -\alpha_1(i,\ V-V\rightarrow V-i,\ V;\ a_2)c_ic_{2V};
\end{aligned}\tag{2c}$$

$$\begin{aligned}
dc_{Vi}/dt= & -\alpha_1(V-i\rightarrow i,\ V;\ a)c_{Vi}+\alpha_1(D^{60}\rightarrow V-i,\ V;\ a)c_D^{60}+\alpha_1(D^{90}\rightarrow V-i,\ V;\ a_i)c_D^{90}\\
& +\alpha_1(D^{90}\rightarrow V-i,\ V;\ a)c_D^{90}+\alpha_1(D^{120}\rightarrow V-i,\ V;\ a_i)c_D^{120}+\alpha_1(D^{120}\rightarrow V-i,\ V;\ a)c_D^{120}\\
& +\alpha_1(D^{180}\rightarrow V-i,\ V;\ a_i)c_D^{180}+\alpha_1(D^{180}\rightarrow V-i,\ V;\ a)c_D^{180}+\alpha_1(T^{90}\rightarrow V-i,\ V;\ a)c_T^{90}\\
& +\alpha_1(T^{120}\rightarrow V-i,\ V;\ a)c_T^{120}+\alpha_1(T^{180}\rightarrow V-i,\ V;\ a)c_T^{180}-\alpha_1(V-i,\ V\rightarrow D^{60};\ a)c_{Vi}c_{1V}\\
& -\alpha_1(V-i,\ V\rightarrow D^{90};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow D^{120};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow D^{180};\ a)c_{Vi}c_{1V}\\
& -\alpha_1(V-i,\ V\rightarrow T^{90};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow T^{120};\ a)c_{Vi}c_{1V}-\alpha_1(V-i,\ V\rightarrow T^{180};\ a)c_{Vi}c_{1V}\\
& \qquad -\alpha_1(V-i,\ V\rightarrow i,\ V-V;\ a)c_{Vi}c_{1V}+\alpha_1(i,\ V-V\rightarrow V-i,\ V;\ a)c_ic_{2V}+D_{Vi}\nabla^2c_{Vi};
\end{aligned}\tag{2d}$$

$$\begin{aligned}
dc_D^{60}/dt= & -\alpha_1(D^{60}\rightarrow D^{90};\ a_2)c_D^{60}-\alpha_1(D^{60}\rightarrow D^{120};\ a_2)c_D^{60}-\alpha_1(D^{60}\rightarrow T^{90};\ a_i)c_D^{60}\\
& \qquad -\alpha_1(D^{60}\rightarrow T^{120};\ a_i)c_D^{60}-\alpha_1(D^{60}\rightarrow V-i,\ V;\ a)c_D^{60}+\alpha_1(D^{90}\rightarrow D^{60};\ a_{i2})c_D^{90}\\
& \qquad +\alpha_1(D^{120}\rightarrow D^{60};\ a_i)c_D^{120}+\alpha_1(V-i,\ V\rightarrow D^{60};\ a)c_{Vi}c_{1V};
\end{aligned}\tag{2e}$$

$$\begin{aligned}
dc_D^{90}/dt= & \alpha_1(D^{60}\rightarrow D^{90};\ a_2)c_D^{60}-\alpha_1(D^{90}\rightarrow D^{60};\ a_{i2})c_D^{90}-\alpha_1(D^{90}\rightarrow D^{120};\ a_2)c_D^{90}-\alpha_1(D^{90}\rightarrow V-i,\ V;\ a_i)c_D^{90}\\
& -\alpha_1(D^{90}\rightarrow V-i,\ V;\ a)c_D^{90}-\alpha_1(D^{90}\rightarrow i,\ V-V;\ a)c_D^{90}-\alpha_1(D^{90}\rightarrow i,\ V,\ V;\ a)c_D^{90}\\
& +\alpha_1(D^{120}\rightarrow D^{90};\ a_2)c_D^{120}+\alpha_1(T^{90}\rightarrow D^{90};\ i)c_T^{90}+\alpha_1(T^{90}\rightarrow D^{90};\ a)c_T^{90}+\alpha_1(V-i,\ V\rightarrow D^{90};\ a)c_{Vi}c_{1V}\\
& \qquad +\alpha_1(i,\ V-V\rightarrow D^{90};\ a_2)c_ic_{2V};
\end{aligned}\tag{2f}$$

$$\begin{aligned}
dc_D^{120}/dt= & \alpha_1(D^{60}\rightarrow D^{120};\ a_2)c_D^{60}+\alpha_1(D^{90}\rightarrow D^{120};\ a_2)c_D^{90}-\alpha_1(D^{120}\rightarrow T^{120};\ i)c_D^{120}-\alpha_1(D^{120}\rightarrow D^{60};\ a_i)c_D^{120}\\
& -\alpha_1(D^{120}\rightarrow D^{90};\ a_2)c_D^{120}-\alpha_1(D^{120}\rightarrow D^{180};\ a)c_D^{120}-\alpha_1(D^{120}\rightarrow V-i,\ V;\ a_i)c_D^{120}\\
& -\alpha_1(D^{120}\rightarrow V-i,\ V;\ a)c_D^{120}-\alpha_1(D^{120}\rightarrow i,\ V-V;\ a)c_D^{120}-\alpha_1(D^{120}\rightarrow i,\ V,\ V;\ a)c_D^{120}\\
& +\alpha_1(D^{180}\rightarrow D^{120};\ a_2)c_D^{180}+\alpha_1(T^{120}\rightarrow D^{120};\ i)c_T^{120}+\alpha_1(V-i,\ V\rightarrow D^{120};\ a)c_{Vi}c_{1V}\\
& \qquad +\alpha_1(i,\ V-V\rightarrow D^{120};\ a_2)c_ic_{2V}+\alpha_1(i,\ V,\ V\rightarrow D^{120};\ a)c_ic_{1V}^2+D_D^{120}\nabla^2c_D^{120};
\end{aligned}\tag{2g}$$

$$\begin{aligned}
dc_D^{180}/dt= & \alpha_1(D^{120}\rightarrow D^{180};\ a)c_D^{120}-\alpha_1(D^{180}\rightarrow T^{180};\ i)c_D^{180}-\alpha_1(D^{180}\rightarrow D^{120};\ a_2)c_D^{180}\\
& -\alpha_1(D^{180}\rightarrow V-i,\ V;\ a)c_D^{180}-\alpha_1(D^{180}\rightarrow V-i,\ V;\ a)c_D^{180}-\alpha_1(D^{180}\rightarrow i,\ V-V;\ a_2)c_D^{180}\\
& -\alpha_1(D^{180}\rightarrow i,\ V,\ V;\ a)c_D^{180}+\alpha_1(T^{180}\rightarrow D^{180};\ i)c_T^{180}+\alpha_1(V-i,\ V\rightarrow D^{180};\ a)c_{Vi}c_{1V}\\
& \qquad +\alpha_1(i,\ V-V\rightarrow D^{180};\ a_2)c_ic_{2V}+\alpha_1(i,\ V,\ V\rightarrow D^{180};\ a)c_ic_{1V}^2;
\end{aligned}\tag{2h}$$

$$\begin{aligned}
dc_T^{90}/dt= & \alpha_1(D^{60}\rightarrow T^{60};\ a_i)c_D^{60}+\alpha_1(D^{90}\rightarrow T^{90};\ i)c_D^{90}+\alpha_1(D^{90}\rightarrow T^{90};\ a_i)c_D^{90}-\alpha_1(T^{90}\rightarrow D^{90};\ i)c_T^{90}\\
& \qquad -\alpha_1(T^{90}\rightarrow D^{90};\ a)c_T^{90}-\alpha_1(T^{90}\rightarrow D^{60};\ a_i)c_T^{90}-\alpha_1(T^{90}\rightarrow T^{120};\ a_i)c_T^{90}\\
& \qquad -\alpha_1(T^{90}\rightarrow V-i,\ V;\ a)c_T^{90}+\alpha_1(T^{120}\rightarrow T^{90};\ a_i)c_T^{120}+\alpha_1(V{-}{-}i,\ V;\ T^{90};\ a)c_{Vi}c_{1V};
\end{aligned}\tag{2i}$$

$$dc_{T}{}^{120}/dt=\alpha_1(D^{60}\rightarrow T^{120};\,a_i)c_D{}^{60}+\alpha_1(D^{120}\rightarrow T^{120};\,i)c_D{}^{120}+\alpha_1(T^{90}\rightarrow T^{120};\,a_i)c_T{}^{90}-\alpha_1(T^{120}\rightarrow T^{180};\,a_i)c_T{}^{120}$$
$$-\alpha_1(T^{120}\rightarrow V-i,\,V;\,a)c_T{}^{120}+\alpha_1(V-i,\,V\rightarrow T^{120};\,a)c_{Vi}c_{1V}+D_T{}^{120}\nabla^2c_T{}^{120};\qquad(2\text{j})$$

$$dc_{T}{}^{180}/dt=\alpha_1(D^{180}\rightarrow T^{180};\,i)c_D{}^{180}+\alpha_1(T^{120}\rightarrow T^{180};\,a_i)c_T{}^{120}-\alpha_1(T^{180}\rightarrow D^{180};\,i)c_T{}^{180}$$
$$-\alpha_1(T^{180}\rightarrow T^{120};\,a_i)c_T{}^{180}-\alpha_1(T^{180}\rightarrow V-i,\,V;\,a)c_T{}^{180}+\alpha_1(V-i,\,V;\,T^{180};\,a)c_{Vi}c_{1V}.\qquad(2\text{k})$$

In these equations c_{1V} is the fractional concentration of single vacancies, c_{2V} is the fractional concentration of divacancies, c_i is the fractional concentration of free impurity atoms, c_{Vi} is the fractional concentration of single-vacancy–impurity-atom complexes, $c_D{}^{60}$ is the fractional concentration of divacancy–impurity-atom complexes [Fig. 1], $c_D{}^{90}$ is the fractional concentration of divacancy–impurity-atom complexes D^{90} having nearest-neighbor bonds at 90° [Fig. 1], $c_D{}^{120}$ is the fractional concentration of divacancy–impurity-atom complexes D^{120} having nearest-neighbor bonds at 120° [Fig. 1], and $c_D{}^{180}$ is the fractional concentration of divacancy–impurity-atom complexes D^{180} having the divacancy and impurity atom in a straight line [Fig. 1]. $c_T{}^{90}$ is the fractional concentration of two single-vacancy–impurity complexes T^{90} having two single vacancies at 90° [Fig. 1], $c_T{}^{120}$ is the fractional concentration of two single-vacancy–impurity-atom complexes T^{120} having two single vacancies at 120° [Fig. 1], and $c_T{}^{180}$ is the fractional concentration of two single-vacancy–impurity-atom complexes T^{180} in a straight line [Fig. 1]. Larger vacancy clusters are not considered here. D_{1V} is the diffusion constant associated with the motion of single vacancies. D_{2V} is the diffusion constant associated with the motion of divacancies. D_{Vi} is the diffusion constant associated with the motion of single-vacancy–impurity complexes. $D_D{}^{90}$, $D_D{}^{120}$, and $D_T{}^{120}$ are the diffusion constants associated with D^{90}, D^{120}, and T^{120}, respectively. The coefficients which appear in the differential equations are given in Table I. These coefficients are very useful for numerical calculations. ${}_1\nu_a$ is the frequency of vibration of the solvent atoms which are the nearest neighbors of a vacancy in a pure matrix [Fig. 2(a)]. ${}_2\nu_a$ is the frequency of vibration of the four solvent atoms which are the nearest neighbor of both of the vacancies in a divacancy [Fig. 2(b)]. The frequency of vibration of the other fourteen nearest neighbors of a divacancy is taken to be ${}_1\nu_a$, the same as in a pure matrix [Fig. 2(c)]. ${}_1\nu_i$ is the frequency of vibration of the impurity atom which is next to a vacancy [Fig. 2(d)]. ${}_{1i}\nu_a$ is the frequency of vibration of the four solvent atoms which are the common nearest neighbors of an impurity-atom–vacancy complex [Fig. 2(e)]. The frequency of vibration of the other seven nearest neighbors of the vacant site of an impurity-atom–vacancy complex is taken to be ${}_1\nu_a$ [Fig. 2(f)]. ${}_2\nu_i$ is the frequency of vibration of the impurity atom in a D^{60} configuration [Fig. 2(g)]. ${}_{2i}\nu_a$ is the frequency of vibration of the solvent atom at the top of a D^{60} configuration [Fig. 2(h)]. The frequency of vibration is taken to be ${}_2\nu_a$ for the two solvent atoms

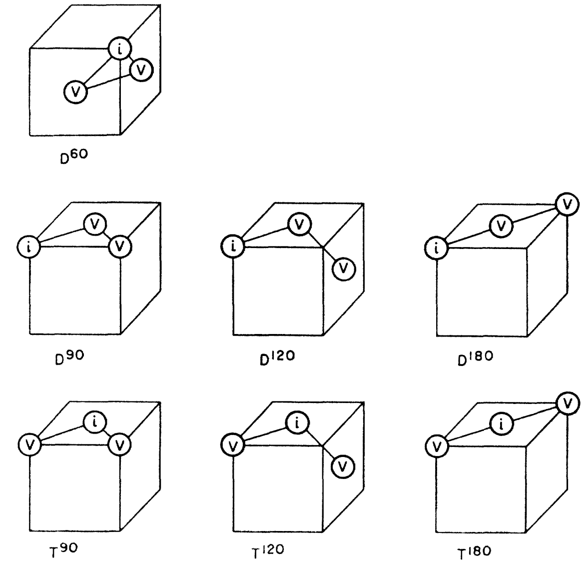

FIG. 1. The configurations of divacancy-impurity complexes (D^{60}, D^{90}, D^{120}, and D^{180}) and complexes containing two single vacancies and an impurity atom (T^{90}, T^{120}, and T^{180}).

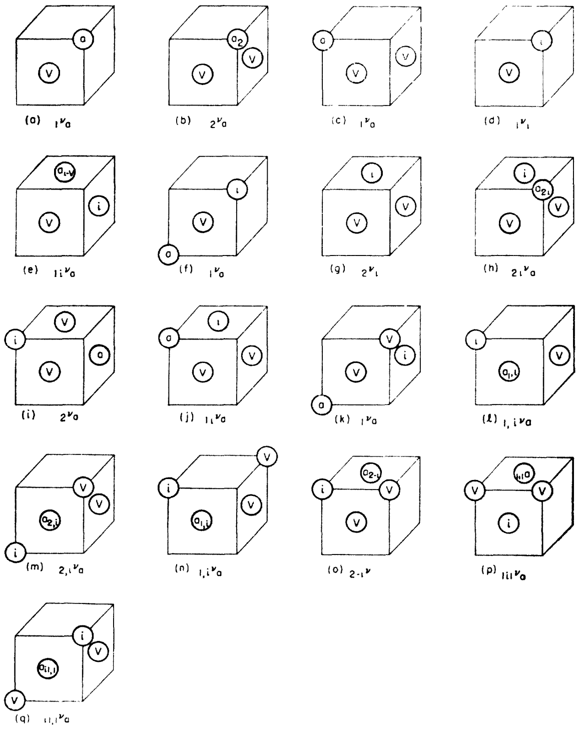

FIG. 2. The frequencies of vibration of atoms next to imperfections.

TABLE I. Coefficients of differential equations.

		Migrating atom	Reaction	Coefficients
I		a	$V \to V$	$\alpha_1(V \to V; a) = 12\,{}_1\nu_a \exp(-E_V{}^M/kT)$
II	1	a_2	$V-V \to V-V$	$\alpha_1(V-V \to V-V; a_2) = 8\,{}_2\nu_a \exp(-E_{2V}{}^M/kT)$
	2	a	$V-V \to V+V$	$\alpha_1(V-V \to V, V; a) = 14\,{}_1\nu_a \exp\{-[E_V{}^M + B_{2V} f(V-V \to V, V; a)]/kT\}$
III	1	i	$V-i \to V-i$	$\alpha_1(V-i \to V-i; i) = {}_1\nu_i \exp(-{}_1E_i{}^M/kT)$
	2	a_i	$V-i \to V-i$	$\alpha_1(V-i \to V-i; a_i) = 4\,{}_{1i}\nu_a \exp(-{}_{1i}E_a{}^M/kT)$
	3	a	$V-i \to i+V$	$\alpha_1(V-i \to i, V; a) = 7\,{}_1\nu_a \exp\{-[E_V{}^M + {}_1B_i f(V-i \to i, V; a)]/kT\}$
IV	1	i	$D^{60} \to D^{60}$	$\alpha_1(D^{60} \to D^{60}; i) = 2\,{}_2\nu_i \exp(-{}_2E_i{}^M/kT)$
	2	a_{2i}	$D^{60} \to D^{60}$	$\alpha_1(D^{60} \to D^{60}; a_{2i}) = 2\,{}_{2i}\nu_a \exp(-{}_{2i}E_a{}^M/kT)$
	3	a_2	$D^{60} \to D^{90}$	$\alpha_1(D^{60} \to D^{90}; a_2) = 2\,{}_2\nu_a \exp\{-[{}_2E_a{}^M + (B_{D^{60}} - B_{D^{90}}) f(D^{60} \to D^{90}; a_2)]/kT\}$
	4	a_2	$D^{60} \to D^{120}$	$\alpha_1(D^{60} \to D^{120}; a_2) = 2\,{}_2\nu_a \exp\{-[{}_2E_a{}^M + (B_{D^{60}} - B_{D^{120}}) f(D^{60} \to D^{120}; a_2)]/kT\}$
	5	a_i	$D^{60} \to T^{90}$	$\alpha_1(D^{60} \to T^{60}; a_i) = 2\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{D^{60}} - B_{T^{90}}) f(D^{60} \to T^{60}; a_i)]/kT\}$
	6	a_i	$D^{60} \to T^{120}$	$\alpha_1(D^{60} \to T^{120}; a_i) = 2\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{D^{60}} - B_{T^{90}}) f(D^{60} \to T^{120}; a_i)]/kT\}$
	7	a	$D^{60} \to V-i+V$	$\alpha_1(D^{60} \to V-i, V; a) = 10\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{D^{60}} - B_{V-i}) f(D^{60} \to V-i, V; a)]/kT\}$
V	1	i	$D^{90} \to T^{90}$	$\alpha_1(D^{90} \to T^{90}; i) = {}_1\nu_i \exp\{-[E_V{}^M + (B_{D^{90}} - B_{T^{90}}) f(D^{90} \to T^{90}; i)]/kT\}$
	2	$a_{1,i}$	$D^{90} \to T^{90}$	$\alpha_1(D^{90} \to T^{90}; a_{1,i}) = {}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M + (B_{D^{90}} - B_{T^{90}}) f(D^{90} \to T^{\ 0}; i)]/kT\}$
	3	a_{2i}	$D^{90} \to D^{90}$	$\alpha_1(D^{90} \to D^{90}; a_{2i}) = 2\,{}_{2-i}\nu_a \exp(-{}_{2-i}E_a{}^M/kT)$
	4	a_{2-i}	$D^{90} \to D^{60}$	$\alpha_1(D^{90} \to D^{60}; a_{2-i}) = 2\,{}_{2-i}\nu_a \exp\{-[{}_{2-i}E_a{}^M + (B_{D^{90}} - B_{D^{60}}) f(D^{90} \to D^{60}; a_{2i})]/kT\}$
	5	a_2	$D^{90} \to D^{120}$	$\alpha_1(D^{90} \to D^{120}; a_2) = 2\,{}_2\nu_a \exp\{-[E_{2V}{}^M + (B_{D^{90}} - B_{D^{120}}) f(D^{90} \to D^{120}; a_2)]/kT\}$
	6	a_{1i}	$D^{90} \to V-i+V$	$\alpha_1(D^{90} \to V-i, V; a_{1i}) = 2\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{D^{90}} - B_{V-i}) f(D^{90} \to V-i, V; a_i)]/kT\}$
	7	a	$D^{90} \to V-i+V$	$\alpha_1(D^{90} \to V-i, V; a) = 6\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{D^{90}} - B_{V-i}) f(D^{90} \to V-i, V; a)]/kT\}$
	8	a_2	$D^{90} \to V-V+i$	$\alpha_1(D^{90} \to V-V, i; a_2) = 2\,{}_2\nu_a \exp\{-[E_{2V}{}^M + (B_{D^{90}} - B_{2V}) f(D^{90} \to i, V-V; a_2)]/kT\}$
	9	a	$D^{90} \to i+V+V$	$\alpha_1(D^{90} \to i, V, V; a) = 4\,{}_1\nu_a \exp\{-[E_V{}^M + B_{D^{90}} f(D^{90} \to i, V, V; a)]/kT\}$
VI	1	i	$D^{120} \to T^{120}$	$\alpha_1(D^{120} \to T^{120}; i) = {}_1\nu_i \exp\{-[E_{V-i}{}^M + (B_{D^{120}} - B_{T^{120}}) f(D^{120} \to T^{120}; i)]/kT\}$
	2	a_{2-i}	$D^{120} \to D^{120}$	$\alpha_1(D^{120} \to D^{120}; a_{2-i}) = {}_{2-i}\nu_a \exp(-{}_{2-i}E_a{}^M/kT)$
	3	a_2	$D^{120} \to D^{120}$	$\alpha_1(D^{120} \to D^{120}; a_2) = {}_2\nu_a \exp(-E_{V-V}{}^M/kT)$
	4	a_{2-i}	$D^{120} \to D^{60}$	$\alpha_1(D^{120} \to D^{60}; a_{2-i}) = {}_{2-i}\nu_a \exp\{-[{}_{2-i}E_a{}^M + (B_{D^{120}} - B_{D^{60}}) f(D^{120} \to D^{60}; a_{2-i})]/kT\}$
	5	a_2	$D^{120} \to D^{90}$	$\alpha_1(D^{120} \to D^{90}; a_2) = {}_2\nu_a \exp\{-[E_{V-V}{}^M + (B_{D^{120}} - B_{D^{90}}) f(D^{120} \to D^{90}; a_2)]/kT\}$
	6	a_2	$D^{120} \to D^{180}$	$\alpha_1(D^{120} \to D^{180}; a_2) = {}_2\nu_a \exp\{-[E_{V-V}{}^M + (B_{D^{120}} - B_{D^{180}}) f(D^{120} \to D^{180}; a_2)]/kT\}$
	7	a_{1i}	$D^{120} \to V-i+V$	$\alpha_1(D^{120} \to V-i+V; a_{1i}) = 3\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{D^{120}} - B_{V-i}) f(D^{120} \to V-i, V; a_i)]/kT\}$
	8	a	$D^{120} \to V-i+V$	$\alpha_1(D^{120} \to V-i+V; a) = 7\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{D^{120}} - B_{V-i}) f(D^{120} \to V-i, V; a)]/kT\}$
	9	a_2	$D^{120} \to i+V-V$	$\alpha_1(D^{120} \to i+V-V; a_2) = 3\,{}_2\nu_a \exp\{-[E_{V-V}{}^M + (B_{D^{120}} - B_{V-V}) f(D^{120} \to i, V-V; a_2)]/kT\}$
	10	a	$D^{120} \to i+V+V$	$\alpha_1(D^{120} \to i+V+V; a) = 3\,{}_1\nu_a \exp\{-[E_V{}^M + B_{D^{120}} + (D^{120} \to i, V, V; a)]/kT\}$
VII	1	a	$D^{180} \to T^{180}$	$\alpha_1(D^{180} \to T^{180}; a) = {}_1\nu_i \exp\{-[E_V{}^M + (B_{D^{180}} - B_{T^{180}}) f(D^{180} \to T^{180}; a)]/kT\}$
	2	a_2	$D^{180} \to D^{120}$	$\alpha_1(D^{180} \to D^{120}; a_2) = 4\,{}_2\nu_a \exp\{-[E_{V-V}{}^M + (B_{D^{120}}) f(D^{180} \to D^{120}; a_2)]/kT\}$
	3	a_{1i}	$D^{180} \to V-i+V$	$\alpha_1(D^{180} \to V-i, V; a_{1i}) = 4\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{D^{180}} - B_{V-i}) f(D^{180} \to V-i, V; a_i)]/kT\}$
	4	a	$D^{180} \to V-i+V$	$\alpha_1(D^{180} \to V-i, V; a) = 7\,{}_1\nu_a \exp\{-[E_V{}^M + (B^{180} - B_{V-i}) f(D^{180} \to V-i, V; a)]/kT\}$
	5	a_2	$D^{180} \to i+V-V$	$\alpha_1(D^{180} \to i, V-V; a_2) = 4\,{}_2\nu_a \exp\{-[E_{V-V}{}^M + (B^{180} - B_{V-V}) f(D^{180} \to i, V-V; a_2)]/kT\}$
	6	a	$D^{180} \to i+V+V$	$\alpha_1(D^{180} \to i, V, V; a) = 4\,{}_1\nu_a \exp\{-[E_V{}^M + B_{D^{180}} f(D^{180} \to i, V, V; a)]/kT\}$
VIII	1	i	$T^{90} \to D^{90}$	$\alpha_1(T^{90} \to D^{90}; i) = 2\,{}_1\nu_i \exp\{-[E_{V-i}{}^M + (B_{T^{90}} - B_{D^{90}}) f(T^{90} \to D^{90}; i)]/kT\}$
	2	a	$T^{90} \to D^{90}$	$\alpha_1(T^{90} \to D^{90}; a) = 2\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{T^{90}} - B_{D^{90}}) f(T^{90} \to D^{90}; a)]/kT\}$
	3	$a_{\vert i\vert}$	$T^{90} \to D^{60}$	$\alpha_1(T^{90} \to D^{60}; a_{\vert i\vert}) = 4\,{}_{\vert i\vert}\nu_a \exp\{-[{}_{\vert i\vert}E_a{}^M + (B_{T^{90}} - B_{D^{60}}) f(T^{90} \to D^{60}; a_{\vert i\vert})]/kT\}$
	4	a_{1i}	$T^{90} \to T^{120}$	$\alpha_1(T^{90} \to T^{120}; a_{1i}) = 4\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{T^{90}} - B_{T^{120}}) f(T^{90} \to T^{120}; a_{1i})]/kT\}$
	5	a	$T^{90} \to V-i+V$	$\alpha_1(T^{90} \to V-i, V; a) = 12\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{T^{90}} - B_{V-i}) f(T^{90} \to V-i, V; a)]/kT\}$
IX	1	i	$T^{120} \to D^{120}$	$\alpha_1(T^{120} \to D^{120}; i) = 2\,{}_1\nu_i \exp\{-[{}_1E_i{}^M + (B_{T^{120}} - B_{D^{120}}) f(T^{120} \to D^{120}; i)]/kT\}$
	2	$a_{\vert i\vert}$	$T^{120} \to D^{60}$	$\alpha_1(T^{120} \to D^{60}; a_{\vert i\vert}) = 2\,{}_{\vert i\vert}\nu_a \exp\{-[{}_{\vert i\vert}E_a{}^M + (B_{T^{120}} - B_{D^{60}}) f(T^{120} \to D^{60}; a_{\vert i\vert})]/kT\}$
	3	a_{1i}	$T^{120} \to T^{90}$	$\alpha_1(T^{120} \to T^{90}; a_{1i}) = 2\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{T^{120}} - B_{T^{90}}) f(T^{120} \to T^{90}; a_{1i})]/kT\}$
	4	a_{1i}	$T^{120} \to T^{120}$	$\alpha_1(T^{120} \to T^{120}; a_{1i}) = 2\,{}_{1i}\nu_a \exp(-{}_{1i}E_a{}^M/kT)$
	5	a_{1i}	$T^{120} \to T^{180}$	$\alpha_1(T^{120} \to T^{180}; a_{1i}) = 2\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{T^{120}} - B_{T^{180}}) f(T^{120} \to T^{180}; a_{1i})]/kT\}$
	6	a	$T^{120} \to V-i+V$	$\alpha_1(T^{120} \to V-i, V; a) = 14\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{T^{120}} - B_{V-i}) f(T^{120} \to V-i, V; a)]/kT\}$
X	1	i	$T^{180} \to D^{180}$	$\alpha_1(T^{180} \to D^{180}; i) = 2\,{}_1\nu_i \exp\{-[{}_1E_i{}^M + (B_{T^{180}} - B_{D^{180}}) f(T^{180} \to D^{180}; i)]/kT\}$
	2	a_{1i}	$T^{180} \to T^{120}$	$\alpha_1(T^{180} \to T^{120}; a_{1i}) = 8\,{}_{1i}\nu_a \exp\{-[{}_{1i}E_a{}^M + (B_{T^{180}} - B_{T^{120}}) f(T^{180} \to T^{120}; a_{1i})]/kT\}$
	3	a	$T^{180} \to V-i+V$	$\alpha_1(T^{180} \to V-i, V; a) = 14\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{T^{180}} - B_{V-i}) f(T^{180} \to V-i, V; a)]/kT\}$
XI	1	a	$V-i+V \to D^{60}$	$\alpha_1(V-i, V \to D^{60}; a) = 20\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{V-i} - B_{D^{60}}) f(V-i, V \to D^{60}; a)]/kT\}$
	2	$a_{i1,1}$	$V-i+V \to D^{90}$	$\alpha_1(V-i, V \to D^{90}; a_{i1,1}) = 4\,{}_{i1,1}\nu_a \exp\{-[{}_{i1,1}E_a{}^M + (B_{V-i} - B_{D^{90}}) f(V-i, V \to D^{90}; a_{i1,1})]/kT\}$
	3	a	$V-i+V \to D^{90}$	$\alpha_1(V-i, V \to D^{90}; a) = 12\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{V-i} - B_{D^{90}}) f(V-i, V \to D^{90}; a)]/kT\}$
	4	$a_{i1,1}$	$V-i+V \to D^{120}$	$\alpha_1(V-i, V \to D^{120}; a_{i1,1}) = 12\,{}_{i1,1}\nu_a \exp\{-[{}_{i1,1}E_a{}^M + (B_{V-i} - B_{D^{120}}) f(V-i, V \to D^{120}; a_{i1,1})]/kT\}$
	5	a	$V-i+V \to D^{120}$	$\alpha_1(V-i, V \to D^{120}; a) = 28\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{V-i} - B_{D^{120}}) f(V-i, V \to D^{120}; a)]/kT\}$
	6	$a_{i1,1}$	$V-i+V \to D^{180}$	$\alpha_1(V-i, V \to D^{180}; a_{i1,1}) = 4\,{}_{i1,1}\nu_a \exp\{-[{}_{i1,1}E_a{}^M + (B_{V-i} - D^{180}) f(V-i, V \to D^{180}; a_{i1,1})]/kT\}$
	7	a	$V-i+V \to D^{180}$	$\alpha_1(V-i, V \to D^{180}; a) = 7\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{V-i} - B_{D^{180}}) f(V-i, V \to D^{180}; a)]/kT\}$
XII	1	$a_{i,1}$	$V-i+V \to T^{90}$	$\alpha_1(V-i, V \to T^{90}; a_{1,i}) = 12\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M + (B_{V-i} - B_{T^{90}}) f(V-i, V \to T^{90}; a_{1,i})]/kT\}$
	2	$a_{1,i}$	$V-i+V \to T^{120}$	$\alpha_1(V-i, V \to T^{120}; a_{1,i}) = 28\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M + (B_{V-i} - B_{T^{120}}) f(V-i, V \to T^{120}; a_{1,i})]/kT\}$
	3	$a_{1,i}$	$V-i+V \to T^{180}$	$\alpha_1(V-i, V \to T^{180}; a_{1,i}) = 7\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M + (B_{V-i} - B_{T^{180}}) f(V-i, V \to T^{180}; a_{1,i})]/kT\}$
XIII	1	$a_{2,i}$	$i+V-V \to D^{90}$	$\alpha_1(i, V-V \to D^{90}; a_{2,i}) = 48\,{}_{2,i}\nu_a \exp\{-[{}_{2,i}E_a{}^M + (B_{V-V} - B_{D^{90}}) f(i, V-V \to D^{90}; a_{2,i})]/kT\}$
	2	$a_{2,i}$	$i+V-V \to D^{120}$	$\alpha_1(i, V-V \to D^{120}; a_{2,i}) = 144\,{}_{2,i}\nu_a \exp\{-[{}_{2,i}E_a{}^M + (B_{V-V} - B_{D^{120}}) f(i, V-V \to D^{120}; a_{2,i})]/kT\}$
	3	$a_{2,i}$	$i+V-V \to D^{180}$	$\alpha_1(i, V-V \to D^{180}; a_{2,i}) = 48\,{}_{2,i}\nu_a \exp\{-[{}_{2,i}E_a{}^M + (B_{V-V} - B_{D^{180}}) f(i, V-V \to D^{180}; a_{2,i})]/kT\}$
XIV	1	$a_{1,i}$	$i+V+V \to D^{90}$	$\alpha_1(i, V, V \to D^{90}; a_{1,i}) = 96\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M - B_{D^{90}} f(i, V, V \to D^{90}; a_{1,i})]/kT\}$
	2	$a_{1,i}$	$i+V+V \to D^{120}$	$\alpha_1(i, V, V \to D^{120}; a_{1,i}) = 144\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M - B_{D^{120}} f(i, V, V \to D^{120}; a_{1,i})]/kT\}$
	3	$a_{1,i}$	$i+V+V \to D^{180}$	$\alpha_1(i, V, V \to D^{180}; a_{1,i}) = 24\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M - B_{D^{180}} f(i, V, V \to D^{180}; a_{1,i})]/kT\}$
XV	1	a	$V-i+V \to i+V-V$	$\alpha_1(V-i, V \to i, V-V; a) = 49\,{}_1\nu_a \exp\{-[E_V{}^M + (B_{V-i} - B_{V-V}) f(V-i, V \to i, V-V; a)]/kT\}$
	2	$a_{1,i}$	$i+V-V \to V-i+V$	$\alpha_1(i, V-V \to V-i, V; a_{1,i}) = 168\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M + (B_{V-V} - B_{V-i}) f(i, V-V \to V-i, V; a_{1,i})]/kT\}$
XVI		a	$V+V \to V-V$	$\alpha_1(V, V \to V-V; a) = 84\,{}_{1,1}\nu_a \exp\{-[{}_{1,1}E_a{}^M - B_{V-V} f(V, V \to V-V; a)]/kT\}$
XVII		a	$i+V \to V-i$	$\alpha_1(i, V \to V-i; a) = 84\,{}_{1,i}\nu_a \exp\{-[{}_{1,i}E_a{}^M - B_{V-i} f(i, V \to V-i; a)]/kT\}$

which are the common nearest neighbors of the two vacant sites of a D^{60} configuration, but these atoms are not the nearest neighbor of the impurity atom of the D^{60} configuration [Fig. 2(i)]. The frequency of vibration is taken to be ${}_{1i}\nu_a$ for the four atoms which are common nearest neighbors of the impurity atom and one of the two vacant sites of a D^{60} configuration, but not for the atom which is the common nearest neighbor of the impurity atom and the divacancy of the D^{60} configuration [Fig. 2(j)]. The frequency of vibration is taken to be ${}_{1}\nu_a$ for the other six nearest-neighbor solvent atoms of the divacancy of the D^{60} configuration [Fig. 2(k)]. ${}_{1,i}\nu_a$ is the frequency of vibration of a solvent atom which is between an impurity atom and a vacancy [Fig. 2(l)]. ${}_{2,i}\nu_a$ is the frequency of vibration of a solvent atom which is a common nearest neighbor of an impurity atom and a divacancy. The frequency of vibration is taken to be ${}_{1,i}\nu_a$ for an atom which is a common nearest neighbor of an impurity atom and one site of a divacancy.

$E_V{}^M$, $E_{2V}{}^M$, and ${}_1E_i$ are the activation energies for the migration of a single vacancy, a divacancy, and an impurity atom, respectively. ${}_{1i}E_a{}^M$ is the activation energy for the migration of one of the four solvent atoms which are the common nearest neighbors of an impurity-atom–vacancy complex, namely, the motion of the atom a_{1-V} in Fig. 2(e) into the vacant site. ${}_2E_i{}^M$ is the activation energy for the migration of the impurity atom in a D^{60} configuration, which is moving into one of the two vacant sites [Fig. 2(g)]. ${}_{2i}E_a{}^M$ is the activation energy for the migration of the common nearest-neighbor atom of a D^{60} configuration which is moving into one of the two vacant sites [Fig. 2(h)]. ${}_{1-i}E_a{}^M$ is the activation energy for the migration of a solvent atom which is between an impurity atom and a vacancy moving into the vacant site. ${}_{2-i}E_a{}^M$ is the activation energy for the migration of a solvent atom which is between an impurity atom and a divacancy and is moving into one of the two vacant sites. B_{2V}, B_{Vi}, $B_D{}^{60}$, $B_D{}^{90}$, $B_D{}^{120}$, and $B_D{}^{180}$ are the total binding energies of a divacancy, an impurity-atom–vacancy complex, and the D^{60}, D^{90}, D^{120}, and D^{180} configurations, respectively. $B_T{}^{90}$, $B_T{}^{120}$, and $B_T{}^{180}$ are the binding energies of the T^{90}, T^{120}, and T^{180} configurations, respectively. The f's are constants between unity and zero. The relation between $f(A\rightarrow B;C)$ and $f(B\rightarrow A;C)$ is

$$f(A\rightarrow B;C)+f(B\rightarrow A;C)=1\,, \tag{3}$$

$f(A\rightarrow B;C)$ is often taken to be zero for an exothermic reaction and unity for an endothermic reaction.

Some of the applications of the kinetic equations will be considered in the following sections.

III. REACTIONS DURING QUENCHING

When a specimen is quenched from a high temperature to a low temperature, imperfections in thermal equilibrium at the high temperature can be frozen in. However, the vacancies can migrate and reactions between the defects could progress even during quenching because the cooling rate is finite in the practical experiments. It can be considered that above a critical temperature T^* the reactions between the defects are in thermal equilibrium during quenching because the reactions between the defects are fast enough to maintain the thermal equilibrium between the defects. Below T^*, however, the reactions are too slow to maintain the thermal equilibrium and the situation at T^* is frozen in. It is assumed in this section that the total number of imperfections do not change during quenching; i.e., the imperfections are not absorbed during quenching. This assumption is not very serious because the loss of vacancies above T^* does not affect the argument. At T^* the vacancies are in thermal equilibrium with impurity atoms. Therefore, the loss above T^* just lowers the apparent quench temperature. The cooling rate above T^* determines the loss of vacancies during quenching and the cooling rate at T^* determines the relative concentrations between the quenched-in defects. It is important to emphasize that T^* is fairly low as shown in the latter part of this section.

A. $c_i \ll c_t$

In the case in which the fractional concentration of impurity atoms is much smaller than the fractional concentration of total defects, the treatment is the same as that of pure metals. Since this case has been treated in detail,[3,5,6,8–10] we will not discuss it here.

B. $c_i \gg c_t$

1. $c_i \gg c_t$ and $B_{2V} < B_{vi}$

We will next consider the case in which the fractional concentration of impurity atoms is much higher than the fractional concentration of vacancies and in which the binding energy B_{2V} of a divacancy is smaller than the binding energy B_{Vi} of a single vacancy and an impurity atom. In this case the formation of divacancies can be ignored because a single vacancy has more chance to encounter an impurity atom than another vacancy. The reaction between single vacancies and impurity atoms is important in this case. Since it is assumed that the vacancies do not anneal out to sinks during quenching, the number of total voids is constant, i.e.,

$$c_{1V}+c_{Vi}=c_t\,. \tag{4}$$

The differential equations governing the process are

$$\begin{aligned} dc_{1V}/dt&=-\beta_1c_{1V}c_i+\beta_2c_{Vi}\,,\\ dc_{Vi}/dt&=\beta_1c_{1V}c_i-\beta_2c_{Vi}\,,\\ dc_i/dt&=-\beta_1c_{1V}c_i+\beta_2c_{Vi}\,,\end{aligned} \tag{5}$$

and

$$dc_{1V}/dt=-dc_{Vi}/dt=dc_i/dt\,,$$

where

$$\beta_1=84\nu_1\exp(-E_V{}^M/kT)\,,$$
$$\beta_2=7\nu_1\exp\{-(E_V{}^M+B_{Vi})/kT\}\,. \tag{6}$$

If there is thermal equilibrium between single vacancies and impurity atoms, the fractional concentration of single-vacancy–impurity-atom complexes is given by

$$c_{Vi}=12c_{1V}c_i\exp(B_{Vi}/kT)\,. \tag{7}$$

To obtain the rate of formation of vacancy–impurity-atom complexes we differentiate Eq. (7) with respect to time t. Combining this with Eq. (5), the rate of formation of vacancy–impurity-atom complexes in thermal equilibrium is

$$\left(\frac{dc_{Vi}}{dt}\right)_e=-\frac{12c_{1V}c_iB_{Vi}\exp(B_{Vi}/kT)}{kT^2\{1+12(c_i+c_{1V})\exp(B_{Vi}/kT)\}}\left(\frac{dT}{dt}\right). \tag{8}$$

As the temperature goes down during a quench, the motion of vacancies becomes too slow to maintain the equilibrium concentration of vacancy–impurity-atom complexes. It is assumed that above the critical temperature T^* the formation of vacancy–impurity-atom complexes maintains a thermal equilibrium but below T^* no vacancy–impurity-atom complexes are formed. One obtains the following equation:

$$\left(\frac{dT}{dt}\right)_{\text{at }T^*}=-\frac{7kT^{*2}\nu_1}{B_{Vi}}\exp\left(-\frac{E_V{}^M}{kT^*}\right)\left\{12(c_i+c_{1V})+\exp\left(-\frac{B_{Vi}}{kT^*}\right)\right\}, \tag{9}$$

where

$$c_i=c_{it}-c_t+\frac{1}{24}\left[-\left\{\exp\left(-\frac{B_{Vi}}{kT}\right)+12(c_{it}-c_t)\right\}+\left[\left\{\exp\left(-\frac{B_{Vi}}{kT}\right)+12(c_{it}-c_t)\right\}^2+48c_t\exp\left(-\frac{B_{Vi}}{kT}\right)\right]^{1/2}\right],$$

$$c_{1V}=\frac{1}{24}\left[-\left\{\exp\left(-\frac{B_{Vi}}{kT}\right)+12(c_{it}-c_t)\right\}+\left[\left\{\exp\left(-\frac{B_{Vi}}{kT}\right)+12(c_{it}-c_t)\right\}^2+48c_t\exp\left(-\frac{B_{Vi}}{kT}\right)\right]^{1/2}\right].$$

These equations can be derived from Eqs. (4), (7), and $c_{it}=c_i+c_{Vi}$. Here c_{it} is the fractional concentration of impurity (the sum of fractional concentration of free impurity c_i and that of associated impurity c_{Vi}).

The right side of Eq. (9) will be called the critical cooling rate hereafter. The values of the critical cooling rate for aluminum are plotted in Fig. 3. ν_1, $E_V{}^M$, c_{it}, and c_t are taken to be 10^{13} sec^{-1}, 0.68 eV, 10^{-3} and 10^{-5}, respectively. Knowing the cooling rate during the quench, one can calculate the critical temperature T^*. If one plots the cooling rate during the quench on Fig. 3, while the cooling curve is below the critical-cooling-rate curve the reaction between vacancies and impurity atoms is in thermal equilibrium. The intersection of the cooling curve and the critical-cooling-rate curve gives the critical temperature T^*. This characteristic temperature depends upon the cooling rate only at the critical temperature, the binding energy of an impurity-atom–vacancy complex, the fractional concentration of impurity atoms, and the activation energy for the migration of a vacancy. The shape of a quenching curve is not important for this treatment if the cooling rate at T^* is the same. In Fig. 4 the values of the critical cooling rate for aluminum are plotted. ν, $E_V{}^M$, c_i, and c_t are taken to be 10^{13} sec^{-1}, 0.68 eV, 10^{-4} and 10^{-5}, respectively. Some of the values of the critical temperature T^* in aluminum are given in Table II. As shown in Figs. 3 and 4, the critical temperatue is lower as the quenching rate becomes lower. The critical

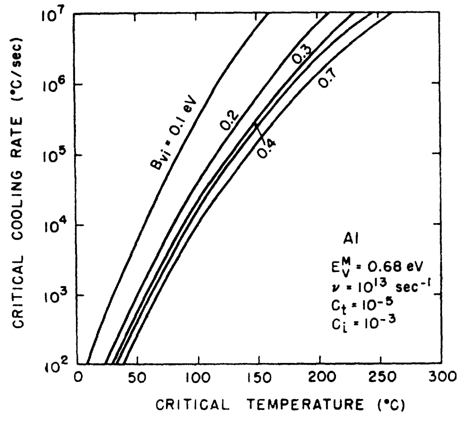

FIG. 3. The values of the critical cooling rate versus temperature in aluminum. The figure is equivalent to the plot of quenching rate versus critical temperature.

TABLE II. The values of critical temperature in aluminum ($c_i=10^{-3}$, $c_t=10^{-5}$) (in °C).

$E_{Vi}{}^B$ (eV)	Quenching rate (deg/sec) 10^3	10^4	2×10^4	5×10^4	10^5	10^6
0.1	31	56	64	76	84	118
0.2	50	80	90	104	115.5	158
0.3	55.5	88	99	113.5	125	173
0.4	59	93	103	118	131	179
0.5	63	96	107	123	135.5	185
0.6	65	99	111	126	139	189
0.7	67	102	113	129	142	193

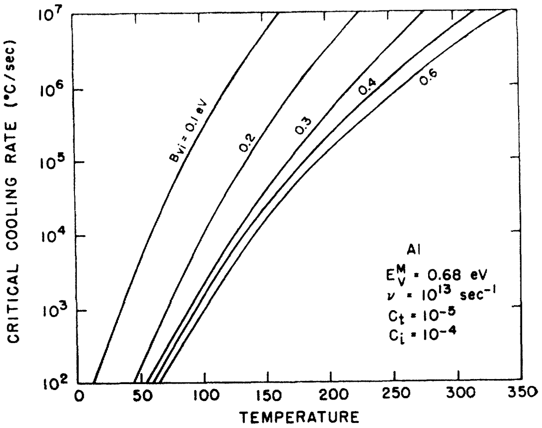

FIG. 4. The values of the critical cooling rate versus temperature in aluminum.

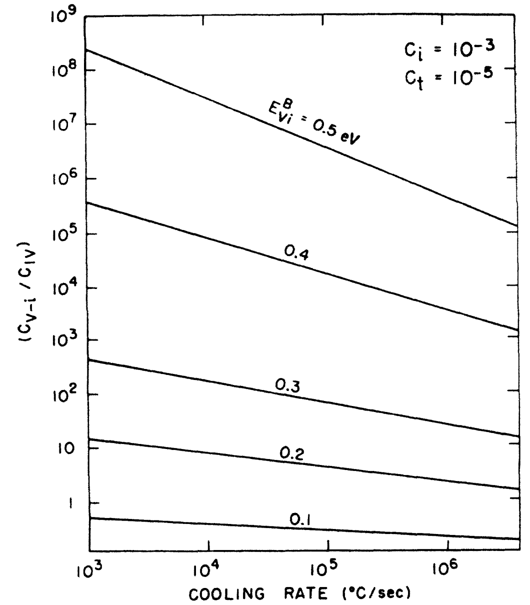

FIG. 5. The logarithm of the ratio of the fractional concentration of vacancy–impurity-atom complexes to that of free vacancies after quenching versus cooling rate.

temperature is lower as the binding energy between a vacancy and an impurity atom becomes lower. This is shown in Fig. 5. It was also found that the critical temperature is not so sensitive to the concentration of vacancies in the range near $c_i = 10^{-4}$. The lower the critical temperature is, the higher the quenching temperature is. The critical temperature is practically independent of the quenching temperature in aluminum containing $c_i = 10^{-3}$. The fractional concentration of vacancy–impurity-atom complexes after the quench is given by

$$(c_{Vi})_0 = 12(c_{1V})_0 c_i \exp(B_{Vi}/kT^*),$$

or

$$\left(\frac{c_{Vi}}{c_{1V}}\right)_0 = 12c_i \exp\left(\frac{B_{Vi}}{kT^*}\right). \qquad (10)$$

This ratio is plotted in Fig. 6 as a function of cooling rate.

The kinetic Eqs. (5) were numerically integrated by means of a CDC-3600 digital computer for the case of dilute aluminum alloys. The values of the binding energy between a vacancy and an impurity atom are taken to be 0.1, 0.2, and 0.3 eV. The quench temperature, the quenching rate, the concentration of impurity, and the vibrational frequency were taken to be 400°C, 3×10^4 deg/sec, and 1×10^{13} sec^{-1}, respectively. The change of the fractional concentration of free vacancies and the change of the fractional concentration of vacancy-impurity complexes during quenching are plotted in Figs. 7 and 8, respectively. The dotted lines are the fractional concentrations at the equilibrium state. As discussed previously, the actual concentrations of free vacancies and complexes deviate fairly sharply from the equilibrium curve near the critical temperature. The concentrations of free vacancies or complexes do not change below the critical temperature. The reactions between free vacancies and impurity atoms are frozen. The values of the critical temperature calculated by the integration of kinetic equations are in good agreement with the values given in Table II, which were calculated by means of Eq. (9). The general tendency is in good agreement with the results obtained by an analog computer.[7] The ratio of the concentration of free vacancies to that of complexes is not compared here because Cotterill used all of the geometrical factors the same for simplicity. The concentrations of free vacancies and vacancy impurity atom complexes cal-

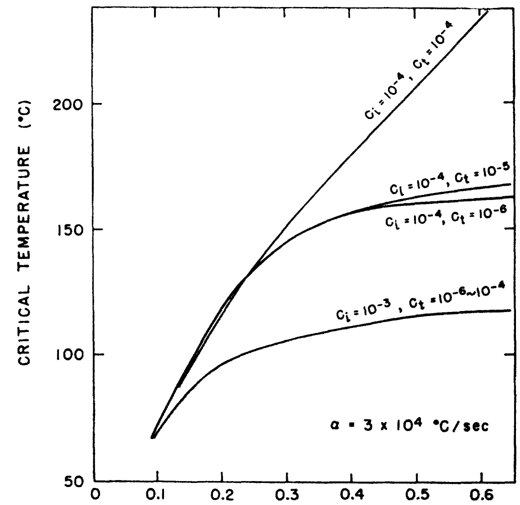

FIG. 6. Relation between critical temperature and the binding energy between a vacancy and an impurity atom in aluminum as a function of the fractional concentration of total vacancies and of impurity. The cooling rate is taken to be 3×10^4 deg/sec.

culated from Eq. (9) are also in good agreement with those calculated by the elaborate integration of Eqs. (5).

2. $c_i \gg c_0$ and $B_{2V} > B_{Vi}$

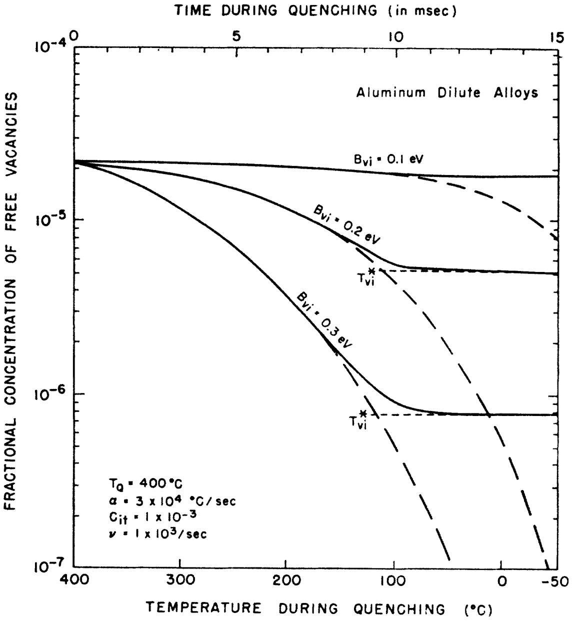

FIG. 7. The change of free vacancies during quenching in aluminum dilute alloys.

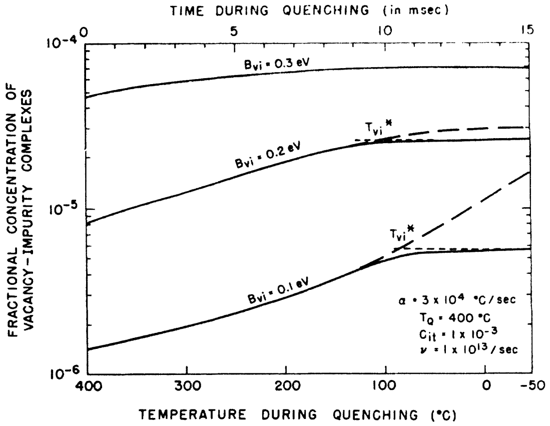

FIG. 8. The change of vacancy-impurity complexes during quenching in aluminum dilute alloys.

When the binding energy B_{Vi} between a vacancy and an impurity atom is small compared with the binding energy B_{2V} of a divacancy, not many impurity-atom–vacancy complexes are formed during quenching, even if a vacancy encounters an impurity atom. An impurity-atom–vacancy complex breaks up in a short time. If, in this case, the binding energy of a divacancy is large, the production of divacancies is more important than the production of vacancy–impurity-atom complexes. The reactions during quenching can be treated as follows: As the temperature goes down during the quench, the divacancy formation is first frozen, then, the impurity-atom–vacancy complex formation is frozen. Finally, the divacancies which are made during the quench form impurity-atom–divacancy complexes, and when the temperature is low enough the impurity-atom–divacancy complex formation is frozen. In this case three critical temperatures can be defined: T_{2V}^*, T_{Vi}^*, and T_{2V-i}^*. T_{2V}^* is the critical temperature above which the divacancy formation is fast enough to maintain thermal equilibrium. Below T_{2V}^* the divacancy formation is too slow to maintain the equilibrium divacancy concentration. T_{Vi}^* is the critical temperature above which the impurity-atom–vacancy complex formation is fast enough to maintain thermal equilibrium between the vacancy concentration and the complex concentration. Below T_{Vi}^* the complex formation is too slow to maintain the equilibrium complex concentration. T_{2V-i}^* is the critical temperature above which the impurity-atom–divacancy complexes formation is fast enough to maintain the thermal equilibrium between the complexes and the divacancies, but below T_{2V-i}^* the formation of impurity-atom–divacancy complexes is too slow to maintain the equilibrium complex concentration. It is again assumed that the annealing to sinks is negligible during quenching. However, this effect is not critical as was mentioned in the previous section. We first consider the reaction between single vacancies and divacancies as treated by Koehler *et al.*[5] The kinetic equation governing the process is

$$\frac{dc_{1V}}{dt} = -168\nu_1 c_{1V}^2 \exp\left(-\frac{E_V^M}{kT}\right) + 28\nu_1 c_{2V} \exp\left(-\frac{E_V^M + B_{2V}}{kT}\right),$$

where

$$c_{1V} + 2c_{2V} = c_t,$$
$$c_{2V} = 6c_{1V}^2 \exp(B_{2V}/kT). \qquad (11)$$

The following equation can be obtained[11]

$$\left(\frac{dT}{dt}\right)_{T=T_2^*} = -\frac{14kT_2^*\nu_1}{B_{2V}} \left\{24c_{1V} + \exp\left(-\frac{B_{2V}}{kT_2^*}\right)\right\} \times \exp\left(-\frac{E_V^M}{kT^*}\right). \qquad (12)$$

A specimen quenched from T_Q will therefore contain a fractional concentration of divacancies given by

$$c_{2V} = 6A \exp(-2E_V^F/kT_Q) \exp(B_{2V}/kT_2^*). \qquad (13)$$

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[11] M. Doyama, in Ref. 7, p. 185; Eq. (22) on p. 205 was misprinted.

Table III. The values of critical temperature in aluminum (in °C).

Binding energy (eV)	Quenching rate °C/sec ($c_i=10^{-3}$, $c_t=10^{-5}$) 1×10^4		2×10^4		5×10^4		10^5	
	T_{Vi}^*	T_{2V-i}^*	T_{Vi}^*	T_{2V-i}^*	T_{Vi}^*	T_{2V-i}^*	T_{Vi}^*	T_{2V-i}^*
0.01	2	−70	8	−65.5	17	−59	24	−55
0.02	11.5	−61	18	−57	27	−50	34	−45
0.03	19	−55.5	26	−50.5	35	−43	43	−38
0.05	32	−45	39.5	−40	49	−32	57	−26
0.07	42	−37	50	−31	60	−23	68	−17
0.10	56	−28	64	−21	76	−13	84	−5.5
T_{2V}^*	84.5		93.5		105.6		115	

T_{Vi}^* can be found in the same manner, i.e., solving the following equation

$$\left(\frac{dT}{dt}\right)_{T=T_{Vi}^*}=-\frac{7kT_{Vi}^{*2}\nu}{B_{Vi}}\exp\left(-\frac{E_V{}^M}{kT}\right)\times\left\{12(c_i+c_{1V})+\exp\left(-\frac{B_{Vi}}{kT}\right)\right\}. \quad (14)$$

We will next determine how many divacancy–impurity-atom complexes are present after a quench. Initially divacancies are formed during the quench. Their concentration is determined by T_{2V}^*. If $c_i \gg c_{1V}$, then the divacancies thus formed move about forming divacancy–impurity-atom complexes. The treatment is the same as before. In this section, however, D^{60}, D^{90}, D^{120}, and D^{180} are not distinct and, therefore, will be represented by D for simplicity. The equations are

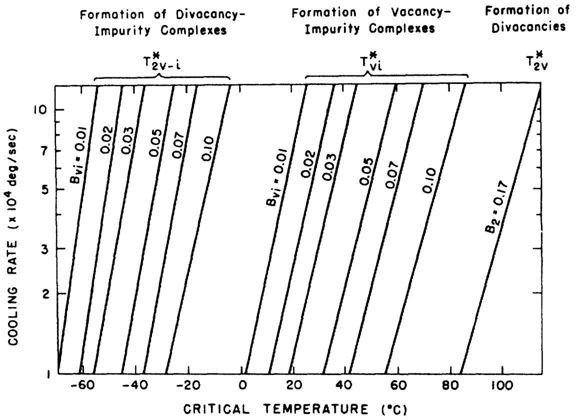

Fig. 9. Critical temperatures T_{2V-i}^*, T_{Vi}^*, and T_{2V}^* versus cooling rate.

$$c_{2V}+c_D=(c_{2V})_0, \quad (15)$$

$$c_D=18c_{2V}c_i\exp\{(B_D-B_{2V})/kT\}, \quad (16)$$

$$\frac{dc_D}{dt}=240\nu_2c_{2V}c_i\exp\left(-\frac{E_{2V}{}^M}{kT}\right)-9c_D\nu_2\exp\left(-\frac{E_V{}^M+B_D-B_{2V}}{kT}\right), \quad (17)$$

where $(c_{2V})_0$ is the fractional concentration of divacancies at the critical temperature T_{2V}^*; and c_{2V}, c_D and c_i are the fractional concentration of divacancies, divancy–impurity-atom complexes, and free-impurity atoms, respectively. $B_D(=B_{2V-i})$ and B_{2V} are the binding energies of an impurity divacancy complex and a divacancy, respectively. $E_V{}^M$ and $E_{2V}{}^M$ are the activation energies for the motion of a single vacancy and a divacancy, respectively. The critical temperature T_{2V-i}^* for the process of making divacancy–impurity-atom complexes can be treated in the same manner. The critical temperature T_{2V-i}^* can be evaluated by solving the following equation:

$$\left(\frac{dT}{dt}\right)_{\text{at } T_{2V-i}^*}=-\frac{40\nu_2kT_{2V-i}^{*2}}{3(B_{2V-i}-B_{2V})}\exp\left(-\frac{E_{2V}{}^M}{kT_{2V-i}^*}\right)\times\left\{18(c_i+c_{2V})+\exp\left(-\frac{B_{2V-i}-B_{2V}}{kT}\right)\right\}. \quad (18)$$

This temperature is also independent of the quench temperature. The value of the right side of Eq. (18) can be evaluated if ν_2, $E_{2V}{}^M$, $B_{2V-i}-B_{2V}$, and c_i are known. The critical temperature T_{2V-i}^* can be calculated if the cooling rate during the quench (dT/dt) at T_{2V-i}^* is known. Therefore, the fractional concentration of divacancy–impurity-atom complexes after the quench is

$$(c_D)_0=18c_ic_{2V}\exp\{(B_D-B_{2V})/kT^*\}$$
$$=108Ac_i\exp\left(-\frac{2E_V{}^F}{kT_Q}\right)\exp\left(\frac{B_{2V}}{kT_2^*}\right)\times\exp\left(\frac{B_{2V-i}-B_{2V}}{kT_{2V-i}^*}\right). \quad (19)$$

Some of the values of the critical temperatures T_{2V}^*, T_{Vi}^*, and T_{2V-i}^* are given in Table III for the case of aluminum. These critical temperatures are also plotted in Fig. 9.

IV. DISCUSSIONS

A. Apparent Activation Energy for Formation of Vacancies

The equilibrium fractional concentration of vacancies in a metal containing impurity atoms is higher than that in a pure matrix if the binding energy between a vacancy and an impurity atom is positive. The relation between the concentration of vacancies and the temperature can be written from Eq. (1) as follows:

$$\begin{aligned} c &= A_3 \exp\{-E_V{}^A(T)/kT\} \\ &= A_3 \exp\{-[E_V{}^F - f(T)]/kT\}. \end{aligned} \tag{20}$$

Here $E_V{}^A$ corresponds to the formation energy of a vacancy in a pure metal $E_V{}^F$. $E_V{}^A$ is called the apparent formation energy hereafter. $E_V{}^A(T)$ and $f(T)$ are not constants but functions of temperature. A_3 is a function of A_1 and A_2. At high temperatures Eqs. (1) and (20) can be compared. The following relation can be obtained:

$$A_3 = A_1[1-12c_i(1-\alpha)],$$

where

$$A_2 = \alpha A_1.$$

$f(T)$ and $E_V{}^A$ can be rewritten as

$$\begin{aligned} f(T) &= kT \ln\left[\frac{1-12c_i+12c_i\alpha\exp(B_{Vi}/kT)}{1-12c_i(1-\alpha)}\right], \\ E_V{}^A &= E_V{}^F - kT \ln\left[\frac{1-12c_i+12c_i\alpha\exp(B_{Vi}/kT)}{1-12c_i(1-\alpha)}\right]. \end{aligned} \tag{21}$$

The difference $f(T)$ between the formation energy of a vacancy in a pure matrix and the apparent formation energy is plotted in Fig. 10. It should be noted that $f(T)$ is independent of the formation energy of a vacancy in the pure matrix, but it is dependent upon the fractional concentration c_i of impurity atoms, the temperature, and the binding energy B_{Vi} between a vacancy and an impurity atom. The fractional change F from the number of vacancies in an alloy to the number of vacancies in the pure matrix is

$$F = \frac{c_{\text{alloy}} - c_{\text{pure}}}{c_{\text{pure}}} = 12c_i\{\alpha \exp(B_{Vi}/kT) - 1\}.$$

The value of the ratio of the fractional concentration of vacancies in the alloy and that in the pure matrix is plotted in Fig. 11, where α and c_i are taken to be unity and 1×10^{-3}. This value also is independent of the formation energy of vacancies in the pure matrix. As shown in Fig. 10, if the impurity atom concentration of the alloy is less than 0.1% and the binding energy B_{Vi} between an impurity atom and a vacancy is less than 0.15 eV, it is not easy to determine the binding energy from the apparent formation energy or measuring F.

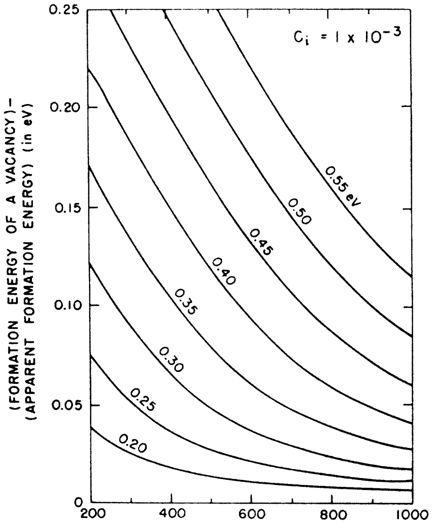

FIG. 10. The difference $f(T)$ between the formation energy of a vacancy in a pure matrix and the apparent formation energy versus temperature.

Hasiguti[12] has found an interesting empirical rule on the vacancy-impurity binding energy in aluminum. According to Hasiguti, the experimental rule is expressed by

$$B_{Vi} = E_0 + vE_v + [(d-d_0)/d_0]E_s,$$

where B_{Vi} is the binding energy, E_0, E_v, and E_s are the constants with the dimension of energy, v is the valence of a solute impurity atom, d is the atomic diameter of a solute impurity atom, and d_0 is a constant (or a critical diameter). The third term on the right-hand side is omitted if $d \lesseqgtr d_0$. Hasiguti determined the values of the constants for B-group impurity atoms in aluminum dilute alloys. The values are $E_0 = 0.20$ eV, $E_v = 0.02$ eV, $E_s = 0.54$ eV, and $d_0 = 2.55$ Å.

The binding energy B_{Vi} of a vacancy and a gold atom in aluminum was determined to be 0.38 eV.[13] The binding energy B_{Vi} of a vacancy and a silver atom in aluminum is reported to be 0.08±0.01 eV [14] and 0.25 eV.[15] It is difficult to explain the difference of these two cases only by Hasiguti's rule, because the atomic diameter of gold and silver are both 2.88 Å and the valence is one for both cases. In these cases a factor other than the valence effect and the size effect is important.

The solubility limit of impurity atoms in a matrix is considered here. The solubility limit has indeed a close relationship with the valence effect and the size

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[12] R. R. Hasiguiti, J. Phys. Soc. Japan **20**, 625 (1965).

[13] M. Doyama and J. S. Koehler, Bull. Am. Phys. Soc. **9**, 295 (1964).

[14] D. R. Beaman, R. W. Balluffi, and R. O. Simmons, Phys. Rev. **134**, A532 (1964).

[15] F. Hashimoto, J. Phys. Soc. Japan **20**, 366 (1956).

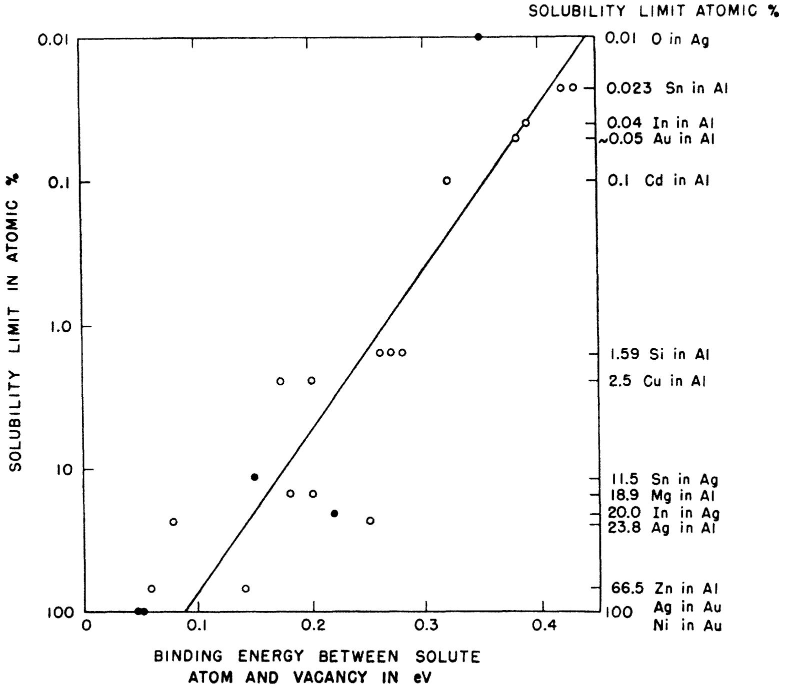

FIG. 11. A relation between the vacancy-impurity binding energy B_{Vi} and the solubility limit C_L of the impurity in aluminum, gold, and silver. The straight line is $B_{Vi}=-0.088 \log C_L+0.088$ where B_{Vi} is in eV and C_L is in the fractional concentration.

effect. Table IV[13–30] gives the values of the experimental binding energy and the solubility limit[31] of solutes. The relation between the vacancy-impurity binding energy B_{Vi} and the logarithm of the solubility limit of the impurity is shown in Fig. 11. It is still early to draw any definite quantitative relationship between the solubility limit and the binding energy B_{Vi} because the analysis of the experiments is based upon many assumptions. If one assumes the linear relationship between the logarithm of the solubility limit and the binding energy B_{Vi}, the following formula is obtained:

$$B_{Vi}=-0.088 \log C_L+0.088 \text{ (eV)}, \qquad (22a)$$

where B_{Vi} is the binding energy between a vacancy and an impurity atom in eV, and C_L is the fractional concentration at the solid solubility limit of the solute. The calculated values of the binding energy using the above equation are also given in Table IV. The values of the constants in Eq. (22a) should not be taken seriously for the case of gold- and silver-base alloys because the

TABLE IV. The relation between the solubility limit and the vacancy-impurity binding energy.

		Solubility limit	Binding energy B_{Vi}		
Solvent	Solute	(at. %)	Calculated (eV)	Observed (eV)	Reference
Al	Zn	66.5	0.10	0.06	16
				0.14	30
				0.19	18
	Ag	23.8	0.14	0.08	14
				0.25	15
	Mg	18.9	0.15	0.18	17
				0.20	20
	Cu	2.5	0.23	0.20	18
				0.16	30
				<0.23	19
	Si	1.59	0.25	0.26	17
				0.27	21
				0.28	22
	Cd	0.1	0.35	0.32	24
	Au	~0.05	0.38	0.38	13
	In	0.04	0.39	0.39	23
	Sn	0.023	0.41	0.42	24, 25
				0.43	22
Au	Ag	100	0.09	0.05	26
	Ni	100	0.09	0.05	27
Ag	In	20	0.15	0.24	28
	Sn	11.5	0.17	0.15	28
	O	0.01	(0.44)	0.35	29

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[16] C. Panseri and T. Federighi, Acta Met. **8**, 217 (1960).

[17] J. Takamura in Ref. 7, p. 521.

[18] H. Kimura, A. Kimura, and R. R. Hasiguti, Acta Met. **10**, 607 (1962).

[19] M. Ohta and F. Hashimoto, J. Phys. Soc. Japan **19**, 130 (1964).

[20] J. Takamura, K. Okazaki, and I. G. Greenfield, J. Phys. Soc. Japan **18**, Suppl. III, 78 (1963).

[21] K. Okazaki and J. Takamura, Suiyokaishi **15**, 89 (1963).

[22] M. Ohta and F. Hashimoto, J. Phys. Soc. Japan **19**, 1331 (1964).

[23] M. Ohta and F. Hashimoto, J. Phys. Soc. Japan **19**, 1987 (1964).

[24] H. Kimura and R. R. Hasiguti, Acta Met. **9**, 1076 (1961).

[25] H. Kimura and R. R. Hasiguti, J. Phys. Soc. Japan **18**, Suppl. III, 73 (1963).

[26] R. Kloske and J. W. Kauffman, Phys. Rev. **126**, 123 (1962).

[27] F. Cattaneo and E. Germagnoli, Nuovo Cimento **28**, 923 (1963).

[28] S. D. Gertsriken and B. P. Slyusan, Ukr. Fiz. Zh. **4**, 137 (1959).

[29] Y. Quéré, J. Phys. Soc. Japan **18**, Suppl. III, 91 (1963).

[30] T. Federighi, in Ref. 7, p. 217.

[31] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

data are not sufficient, particularly for the case of oxygen in silver. Pure oxygen is gaseous at the temperature when the experiment was performed, and the solubility limit is a function of the pressure of oxygen.

It is not difficult to understand the relationship between the solubility limit and the binding energy, B_{Vi}, of a vacancy and an impurity atom. If the energy required to replace a solute atom with an impurity atom, that is, the heat of solution, is high, the solubility limit is low; and also the distortion (lattice and electronic) near the impurity atom is high. When a vacancy is trapped next to the impurity atom, this distortion is relaxed. The relaxation energy, that is, the binding energy, is higher as the distortion is higher.

According to the above discussion the heat of solution and the binding energy B_{Vi} of a vacancy and an impurity atom must have some relationship. In the simplest case the solubility c can be written as[32]

$$\frac{c}{1-c}=A\exp\left\{\frac{-H(1-2c)}{kT}\right\}, \tag{22b}$$

where k is Boltzmann constant, T is the absolute temperature, A is a constant related to the vibrational entropy, and H is the heat of solution. The heat of solution H is given by[33]

$$H=zV=z\{V_{AA}-\tfrac{1}{2}(V_{AA}+V_{BB})\}.$$

Here z is the coordination number of the crystal structure, V_{AA} is the interaction energy between two solvent atoms, V_{BB} is the interaction energy between two solute atoms, and V_{AB} is the interaction energy between a solute atom and a solvent atom. One can determine H by fitting Eq. (22b) to the solubility curve.[34] H was determined from the tangent of $\ln c/(1-c)$ and $(1-2c)/T$. There may exist some complexity in relating directly H and the experimental heat of solution which is the heat absorbed by the system when 1 g mole of solute atoms enters into solution. Sometimes the precipitated phase does not have the same crystal structure as the pure solvent crystal or the pure crystal structure of solute.

In Fig. 12 are plotted the binding energy, B_{Vi}, between a vacancy and an impurity atom, and the heat of solution H determined by fitting Eq. (22b) to the solid solubility curve. It is quite surprising that it has indeed a proportional relationship:

$$B_{Vi}=aH,$$

where a was found to be 0.52. This means that about one-half of the distortion energy around an impurity atom is relaxed when a vacancy associates with it. Using this equation and Eq. (22b), Eq. (22a) can be derived in the case that the solid solubility is low. When the solid solubility is high Eq. (22b) has to be modified. In this respect, zinc, magnesium, and silver, which have high solid solubility in aluminum, may deviate from this rule. It is inadvisable to use the heat of solution measured by a calorimetric method here, because accurate measurements are difficult for the case of low solid solubility and Eq. (22b) is not valid for the case of high solubility.

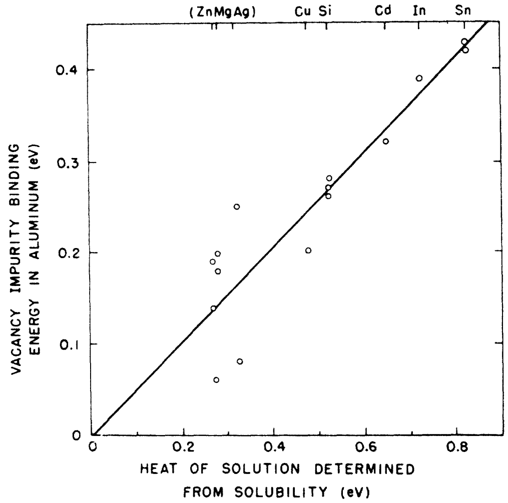

FIG. 12. A proportional relationship between the vacancy-impurity binding energy B_{Vi} and the heat of solution H determined from the solid solubility curve. The relation is $B_{Vi}=0.52H$.

B. Equations for Thermal Equilibrium and for Quasi-Equilibrium

In thermal equilibrium the fractional concentration of single vacancies $(c_{1V})_e$ is written as

$$(c_{1V})_e=A_1\exp(-E_V{}^F/kT), \tag{23a}$$

where $E_V{}^F$ is the formation energy of a single vacancy, and A_1 is a constant. Using Eqs. (2) and (23a) the fractional concentrations in thermal equilibrium are as follows:

$$(c_{2V})_e=6A_{2V}\exp\{-(2E_V{}^F-B_{2V})/kT\}, \tag{23b}$$

$$(c_{Vi})_e=12A_{Vi}c_i\exp\{-(E_V{}^F-B_{Vi})/kT\}, \tag{23c}$$

$$(c_{D^{60}})_e=24A_{D^{60}}c_i\exp\{-(2E_V{}^F-B_{D^{60}})/kT\}, \tag{23d}$$

$$(c_{D^{90}})_e=24A_{D^{90}}c_i\exp\{-(2E_V{}^F-B_{D^{90}})/kT\}, \tag{23e}$$

$$(c_{D^{190}})_e=48A_{D^{120}}c_i\exp\{-(2E_V{}^F-B_{D^{120}})/kT\}, \tag{23f}$$

$$(c_{D^{180}})_e=12A_{D^{180}}c_i\exp\{-(2E_V{}^F-B_{D^{180}})/kT\}, \tag{23g}$$

$$(c_{T^{90}})_e=12A_{T^{90}}c_i\exp\{-(2E_V{}^F-B_{T^{90}})/kT\}, \tag{23h}$$

$$(c_{T^{120}})_e=24A_{T^{120}}c_i\exp\{-(2E_V{}^F-B_{T^{120}})/kT\}, \tag{23i}$$

$$(c_{T^{180}})_e=6A_{T^{180}}c_i\exp\{-(E_V{}^F-B_{T^{180}})/kT\}. \tag{23j}$$

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[32] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Dover Publications, Inc., New York, 1964).

[33] For example, A. H. Cottrell, *Theoretical Structural Metallurgy* (St. Martin's Press, Inc., New York, 1955), p. 156.

[34] C. Zener, *Thermodynamics in Physical Metallurgy* (The American Society for Metals, Cleveland, 1950), p. 20.

[35] C. E. Birchnenall, *Thermodynamics in Physical Metallurgy* (The American Society for Metals, Cleveland, 1950), p. 158.

Here the A's are constants related to the vibrational frequencies. At a temperature T_A a quenched specimen has a fractional concentration of single vacancies much higher than the equilibrium concentration of a specimen that has been fully annealed at the temperature T_A. However, a quasithermal equilibrium can be obtained during aging at a suitable annealing temperature. This quasi-equilibrium state is defined as the equilibrium between two or more types of defects. For example, the quasi-equilibrium between single vacancies and divacancies does not require that the total concentration of vacancies be in thermal equilibrium with the lattice. In quasithermal equilibrium the fractional concentration of divacancies, vacancy impurity atom complexes, and the D^{60}, D^{90}, D^{120}, D^{180}, T^{90}, T^{120}, and T^{180} configurations are as follows:

$$c_{2V}=6c_{1V}^2F_{2V}\exp(B_{2V}/kT), \tag{24a}$$

$$c_{Vi}=12c_{1V}c_iF_{Vi}\exp(B_{Vi}/kT), \tag{24b}$$

$$c_{D^{60}}=2c_{1V}c_{Vi}F_{D^{60}}\exp\left(\frac{B_{D^{60}}-B_{Vi}}{kT}\right)=24c_ic_{1V}^2F_{D^{60'}}\exp\left(\frac{B_{D^{60}}}{kT}\right)=4c_ic_{2V}F_{D^{60''}}\exp\left(\frac{B_{D^{90}}-B_{2V}}{kT}\right), \tag{24c}$$

$$c_{D^{90}}=2c_{1V}c_{Vi}F_{D^{90}}\exp\left(\frac{B_{D^{90}}-B_{Vi}}{kT}\right)=24c_ic_{2V}^2F_{D^{90'}}\exp\left(\frac{B_{D^{90}}}{kT}\right)=4c_ic_{2V}F_{D^{90''}}\exp\left(\frac{B_{D^{90}}-B_{2V}}{kT}\right), \tag{24d}$$

$$c_{D^{120}}=4c_{1V}c_{Vi}F_{D^{120}}\exp\left(\frac{B_{D^{120}}-B_{Vi}}{kT}\right)=48c_ic_{1V}^2F_{D^{120'}}\exp\left(\frac{B_{D^{120}}}{kT}\right)=8c_ic_{2V}F_{D^{120''}}\exp\left(\frac{B_{V^{120}}-B_{2V}}{kT}\right), \tag{24e}$$

$$c_{D^{180}}=c_{1V}c_{Vi}F_{D^{180}}\exp\left(\frac{B_{D^{180}}-B_{Vi}}{kT}\right)=12c_ic_{1V}^2F_{D^{180'}}\exp\left(\frac{B_{D^{180}}}{kT}\right)=2c_ic_{2V}F_{D^{180''}}\exp\left(\frac{B_{D^{180}}-B_{2V}}{kT}\right), \tag{24f}$$

$$c_{T^{90}}=c_{1V}c_{Vi}F_{T^{90}}\exp\left(\frac{B_{T^{90}}-B_{Vi}}{kT}\right)=12c_ic_{1V}^2F_{T^{90'}}\exp\left(\frac{B_{T^{90}}}{kT}\right)=2c_ic_{2V}F_{T^{90''}}\exp\left(\frac{B_{T^{90}}-B_{2V}}{kT}\right), \tag{24g}$$

$$c_{T^{120}}=2c_{1V}c_{Vi}F_{T^{120}}\exp\left(\frac{B_{T^{120}}-B_{Vi}}{kT}\right)=24c_ic_{1V}^2F_{T^{120'}}\exp\left(\frac{B_{T^{120}}}{kT}\right)=4c_ic_{2V}F_{T^{120''}}\exp\left(\frac{B_{T^{120}}-B_{2V}}{kT}\right), \tag{24h}$$

$$c_{T^{180}}=\tfrac{1}{2}c_{1V}c_{Vi}F_{T^{180}}\exp\left(\frac{B_{T^{180}}-B_{Vi}}{kT}\right)=6c_ic_{1V}^2F_{T^{180'}}\exp\left(\frac{B_{T^{180}}}{kT}\right)=c_ic_{2V}F_{T^{180''}}\exp\left(\frac{B_{T^{180}}-B_{2V}}{kT}\right). \tag{24i}$$

The F's are constants related with the vibrational frequencies. The ratio of the fractional concentration of vacancy–impurity-atom complexes to that of single vacancies in a dilute alloy does not depend upon the formation energy of a vacancy.

C. Critical Temperature

The critical temperature, or the freezing temperature, was defined by the temperature at which the reaction freezes. As we calculated in the previous sections, these temperatures are rather low.

The critical temperatures shown in Table II are typical examples for the case in which the fractional concentration of impurity atoms is much higher than the fractional concentration of vacancies and in which the binding energy B_{2V} of a divacancy is smaller than the binding energy B_{Vi} of a single vacancy and an impurity atom. This case is for impurities in aluminum. As we see from Table II, the critical temperature is near 100°C in practical quench experiments. This shows that the quenched state is governed by the quench speed near 100°C and that the quench speed near 100°C is important. The critical temperature can be seen clearly in Figs. 7 and 8. The values of the critical temperature calculated by the numerical integration of kinetic Eqs. (5) are in good agreement with the values given in Table II which were calculated by means of Eq. (9). This indicates that a simple treatment such as Eq. (9) gives a good approximation during quenching. The critical temperature T^* is not sensitive to the total fractional concentration of defects. The plot of the logarithm of $(c_{Vi}/c_{1V})_0$ versus the logarithm of the cooling rate gives a straight line (Fig. 5). This can be shown as follows: Eq. (9) can be written as

$$-\left(\frac{dT}{dt}\right)_{\text{at }T^*}=\frac{84\nu c_ikT^{*2}}{B_{Vi}}\exp\left(-\frac{E_V{}^M}{kT^*}\right), \tag{25}$$

when $12c_i \gg \exp(-B_{Vi}/kT^*)$. ($T^*$ is near 100°C. Therefore, this condition occurs when $B_{Vi}>0.1$ eV in the case of aluminum.) Taking the logarithm of Eqs. (17) and

(18), one obtains the following equation:

$$\ln\frac{(c_{Vi})_0}{(c_{1V})_0}=-\frac{B_{Vi}}{E_M{}^V}\ln\left(-\frac{dT}{dt}\right)_{\text{at }T^*}+\ln 12c_i$$

$$+\frac{B_{Vi}}{E_M{}^V}\ln\frac{84\nu_1c_ikT^{*2}}{B_{Vi}}. \quad (26)$$

Since the last term is not very sensitive to (dT/dt), one can plot the logarithm of the quench speed against $\ln(c_{Vi})_0/(c_{1V})_0$. The resulting curve is a straight line as is shown in Fig. 4. The slope of the line is $-B_{Vi}/E_M{}^V$. When $12c_i \ll \exp(-B_{Vi}/kT^*)$ (this condition normally exists when $B_{Vi} \ll 0.1$ eV),

$$\left(\frac{dT}{dt}\right)\cong\frac{7\nu_1kT^{*2}}{B_{Vi}}\exp\left(-\frac{E_V{}^M+B_{Vi}}{kT}\right),$$

$$\ln\frac{(c_{Vi})_0}{(c_{1V})_0}=-\frac{B_{Vi}}{E_V{}^M+B_{Vi}}\ln\left(\frac{dT}{dt}\right)_{\text{at }T^*}+\ln c_i \quad (27)$$

$$+\frac{B_{Vi}}{E_V{}^M+B_{Vi}}\ln\frac{7\nu_1kT^{*2}}{B_{Vi}}.$$

The curve is again a straight line and the slope is $-B_{Vi}/(E_V{}^M+B_{Vi})$.

Table III is a typical example for the case that $c_i \gg c_0$ and $B_{2V} > B_{Vi}$. The constants are chosen for aluminum dilute alloys. As we expected, the highest temperature is $T_{2V}{}^*$ at which the divacancy formation freezes. The next highest temperature is $T_{Vi}{}^*$ at which the formation of vacancy and impurity freezes. Table III shows that the critical temperature $T_{2V-i}{}^*$ is below 0°C. This suggests that the reactions between divacancies and impurity atoms after a normal quench are in thermal equilibrium at the temperature of the quenching medium. Therefore, during a quench, most of the divacancies are bound with impurity atoms.

V. SUMMARY

(1) General kinetic equations between vacancies, divacancies, and impurity atoms are presented.

(2) As an application of these kinetic equations the reactions during quenching were discussed.

(3) The quenched state can be estimated by calculating the critical temperatures or freezing temperatures. These temperatures are rather low. The critical temperatures for the formation of vacancy-impurity atom complexes are near 100°C for the case of aluminum. The critical temperatures for the formation of divacancy-impurity atom complexes are below 0°C for aluminum dilute alloys. The simple analytical treatment gives results which are in good agreement with the actual numerical integration of the kinetic equations.

(4) A relation between the binding energy B_{Vi} of an impurity atom and a vacancy and the solubility limit C_L and the heat of solution H of the impurity is given. The tentative relation is

$$B_{Vi}=0.52H=(-0.088\ln C_L+0.088)\text{ eV}.$$

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