PHYSICAL REVIEW VOLUME 102, NUMBER 4 MAY 15, 1956

# Theory of Order-Disorder Kinetics*

GEORGE H. VINEYARD
*Brookhaven National Laboratory, Upton, New York*

(Received December 7, 1955)

The problem of relating fundamental atom movements to the change of the state of order of an alloy is attacked in a basic manner by introducing an infinite array of distribution functions for the occupation of all possible sets of lattice sites. These distribution functions determine all the kinds of order in the lattice, including the usual long- and short-range order. They are shown to obey general equations of motion which are linear and in which the kinetic parameters of atom movements occur as coefficients.

Solutions of the equations of motion must be found by approximations, and a variety of possible procedures are suggested. These depend on expressing higher order distribution functions by combinations of those of lower order. The simplest of these procedures is explored in detail for two mechanisms of atom movement, direct interchange and vacancy interchange, and for two common lattice types, $AB$ b.c.c. and $AB_3$ f.c.c. The result is a calculation of the time dependence of long-range order in homogeneous systems, and is expected to be reliable whenever the long-range order is reasonably high. The simple theory leads to the Bragg-Williams result at equilibrium, and gives a fundamental derivation and limitation of the conception that ordering is a "chemical reaction" of the type $A^\alpha+B^\beta \rightleftarrows A^\beta+B^\alpha$. The vacancy and direct interchange models lead to qualitatively similar, but not identical results. Present evidence suggests predominance of the vacancy mechanism, at least in close-packed systems.

The simple vacancy model is applied to experiments of Burns and Quimby on electrical resistivity in $Cu_3Au$. The observed relaxation times, over a range of temperatures below the critical temperature, are in reasonably good accord with theory when parameters derived from diffusion measurements in Cu and Au are employed.

## 1. INTRODUCTION

PREVIOUS treatments of the kinetics of order-disorder transformations can be classified as either atomic[1] or chemical[2–4] in nature. The chemical treatments, in which ordering is likened to a chemical reaction, are able to proceed with a small number of assumptions and with mathematical simplicity. The assumptions, however, are rather sweeping, and their validity is not clearly evident. Also, the parameters which enter are phenomenological rather than fundamental. Recently Dienes[2] and Rothstein[3] have each presented calculations of this sort which proceed from somewhat different assumptions and arrive at different results. The atomic theories with which the writer is acquainted are devoted to rather special models and approximational schemes. In the present paper it is shown how a more general approach from the atomic point of view can be formulated, and it is shown that this approach can lead to actual calculations at a variety of levels of approximation. A further result is the demonstration of the degree of validity of the chemical formulation given by Dienes, which is shown to rest on certain specific approximations, and it is shown how the phenomenological parameters of Dienes' theory are related to fundamental parameters of atom movements.

The theory of ordering kinetics involves two distinct problems. The first is to find the rate at which an atom of given species will move from one lattice site to another at a given temperature and with any given population on the lattice sites in its environment. This involves assuming one (or several) particular mechanisms for atom movement, and applying the concepts first developed in the theory of absolute reaction rates.[5] The second problem is essentially a combinatorial matter; it is to count the total number of movements of each type occurring in unit time at a given state of order and to relate this to the time rate of change of that state of order. We suggest in this paper that the convenient way to handle this is by means of a set of multiparticle distribution functions and their first time derivatives, and show how all likely mechanisms of ordering can be fitted into this scheme. The general equations cannot be solved rigorously by any known methods, as was to have been anticipated in view of the enormous complexity of the problem, but one is readily led to approximations by which solutions can be found.

These ideas are illustrated in the present paper by working out the simplest approximation, that in which the system is homogeneous and describable solely by means of a long-range order parameter. Both vacancy and direct interchange mechanisms are considered. It is intended in a future paper to extend the solutions to the case of short-range order, both with and without long-range order, and to consider the special problems connected with nucleation, growth, and coalescence of domains of order. It is felt that the very simple approximation worked out in detail here, which, in one form, is equivalent to the earlier Bragg and Williams

---

* Work done under the auspices of the U. S. Atomic Energy Commission.

[1] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) **A145**, 699 (1934); W. S. Gorsky, Physik. Z. Sowjetunion **8**, 443 (1935); G. Borelius, J. Inst. Metals **74**, 17 (1947); S. Iida, J. Phys. Soc. Japan **10**, 769 (1955). The last paper gives an approach much like the present one in considering the simultaneous development of short- and long-range order. Attention is restricted to the vacancy mechanism and the body-centered cubic lattice, however.

[2] G. J. Dienes, Acta Metallurgica **3**, 549 (1955).

[3] J. Rothstein, Phys. Rev. **94**, 1429 (1954); **98**, 1554 (1955); **99**, 614 (1955).

[4] Y. Takagi and T. Oguchi, Bull. Tokyo Inst. Technol. **B3**, 211 (1950); Takagi, Oguchi, and Shirane, Bull. Tokyo Inst. Technol. **B3**, 220 (1950).

[5] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941); C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley *et al.* (John Wiley and Sons, Inc., New York, 1952), pp. 289–314.

theory, is adequate to bring out most of the broad features of ordering kinetics in homogeneous systems, and that it is advisable to investigate these features before becoming deeply embroiled in higher approximations to the combinatorial problem. The formulation presented here is also capable of extension to problems of diffusion in multicomponent systems and of stress-induced ordering, to which we hope to devote attention in future publications.

## 2. MULTIPARTICLE DISTRIBUTION FUNCTIONS

The ordering process can be conveniently described in terms of a set of multiparticle distribution functions.[6] Consider atoms of several types, $A$, $B$, $C$, etc., (in general, $T_j$) which are to be distributed over the sites of a crystal lattice. Let $\mathbf{r}_1$, $\mathbf{r}_2 \cdots \mathbf{r}_n$ be an arbitrary set of $n$ lattice sites. Define $P_{T_1T_2\ldots T_n}(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_n)$ as the probability that the $n$ lattice sites be simultaneously occupied by $n$ atoms of specified types, type $T_1$ on site $\mathbf{r}_1$, type $T_2$ on site $\mathbf{r}_2$, etc.[7] These distribution functions characterize the ordering system, and are in general time dependent. The occurrence of lattice vacancies can be fitted into the formalism by regarding vacancies as a species of atom. Interstitials could likewise be allowed for if the lattice were enlarged to include all interstitial positions, some of which would be occupied by ordinary atoms, others by vacancies, but this complication will not be taken up here. Dislocations and linear compressions of the sort proposed by Paneth,[8] since they involve alterations in the lattice topology, cannot be incorporated without modifying basic ideas; it will be assumed that they are not of importance in the ordering process.

These multiparticle distribution functions obey certain identities. Summation of an $n$-site distribution function over all types of atoms present in the crystal gives an $(n-1)$-site distribution function. Thus

$$\begin{aligned}
&\sum_A P_A(\mathbf{r})=1,\\
&\sum_{A'} P_{AA'}(\mathbf{r}_1,\mathbf{r}_2)=P_A(\mathbf{r}_1),\\
&\sum_{A'} P_{A'A}(\mathbf{r}_1,\mathbf{r}_2)=P_A(\mathbf{r}_2),\\
&\sum_{A''} P_{AA'A''}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=P_{AA'}(\mathbf{r}_1,\mathbf{r}_2),\quad \text{etc.}
\end{aligned}\tag{1}$$

Summation over all sites in the crystal gives a simple result only with one-site distribution functions:

$$\textstyle\sum_{\mathbf{r}} P_A(\mathbf{r})=N_A,\tag{2}$$

where $N_A$ is the total number of $A$-type atoms in the crystal.

In addition there are the same symmetries (including periodicities) in the distribution functions as in the crystalline superlattice. Indeed, the symmetry of these distribution functions defines the superlattice.

In what we shall call a homogeneous system the distribution functions are invariant to translation by any vector of the super-lattice, that is, a family of relations such as $P_A(\mathbf{r}+\mathbf{R})=P_A(\mathbf{r})$ are valid, where $\mathbf{r}$ is any lattice vector and $\mathbf{R}$ is any superlattice vector. In an inhomogeneous system the distribution functions vary as one moves down the lattice, and domains of anti-phase order, for example, would be reflected in the values taken by the distribution functions.

On physical grounds one would expect that the occupation of lattice sites sufficiently far away from one another would be uncorrelated, so hereafter it will always be assumed that relations such as the following are valid:

$$P_{AA'}(\mathbf{r}_1,\mathbf{r}_2)\xrightarrow[|\mathbf{r}_2-\mathbf{r}_1|\to\infty]{}P_A(\mathbf{r}_1)P_{A'}(\mathbf{r}_2),\tag{3a}$$

$$P_{AA'A''}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\xrightarrow[|\mathbf{r}_3-\mathbf{r}_1|\to\infty]{}P_{AA'}(\mathbf{r}_1,\mathbf{r}_2)P_{A''}(\mathbf{r}_3),\tag{3b}$$

etc.

The one-site distribution functions are related to the usual long-range order parameter, $S$, and the two-site distribution functions for neighboring sites are related to Bethe's short-range order parameter,[9] $\sigma$. For the case of a two-component alloy with stoichiometric composition, one finds

$$S=[P_A(\mathbf{r}_\alpha)-f_A]/(1-f_A),\tag{4}$$

where $f_A$ is the fraction of atoms of $A$-type, and $\mathbf{r}_\alpha$ denotes any $\alpha$-type site. The case of $\sigma$ is somewhat more complicated. For the body-centered cubic alloy of composition $AB$, one can show that

$$\sigma=4\langle P_{AB}(\mathbf{r},\,\mathbf{r}+\boldsymbol{\delta})\rangle-1,\tag{5}$$

and for the face-centered cubic alloy of composition $AB_3$ one finds

$$\sigma=16\langle P_{AB}(\mathbf{r},\,\mathbf{r}+\boldsymbol{\delta})\rangle-3.\tag{6}$$

Here $\boldsymbol{\delta}$ denotes any nearest neighbor distance and the angular brackets indicate averaging over $\mathbf{r}$ (which may be omitted if long range order is absent).

In order to carry the calculations to useful conclusion it will be necessary to make approximations. The general scheme which will prove useful is to express the distribution functions of higher order in terms of those of lowest order. One form of this is a superposition approximation,[6] analogous to that employed in the theory of fluids. The most drastic approximation which

---

[6] Such distribution functions were apparently first introduced into order-disorder problems (in the equilibrium case) by T. Murakami and S. Ono, Mem. Fac. Eng., Kyushu Imp. Univ. 12, 309 (1951).

[7] Notice that these are probabilities for certain types of atoms to be on particular sites, not probabilities for particular atoms to be on certain types of sites. For convenience in later work we admit redundant distribution functions by obvious definitions of the type $P_{AA}(\mathbf{r},\mathbf{r})=P_A(\mathbf{r})$, etc., and self-contradictory distribution functions such as $P_{AB}(\mathbf{r},\mathbf{r})$ (where $A\neq B$), all of which are defined to be zero.

[8] H. R. Paneth, Phys. Rev. **80**, 708 (1950).

[9] F. C. Nix and W. Shockley, Revs. Modern Phys. **10**, 1 (1938).

will sometimes be necessary will be called the *composition approximation*, and consists of using relations similar to Eqs. (3) but for lattice points which are not widely separated. In its most extreme form this approximation gives

$$P_{T_1T_2\cdots T_n}(\mathbf{r}_1,\mathbf{r}_2,\cdots \mathbf{r}_n)\cong P_{T_1}(\mathbf{r}_1)P_{T_2}(\mathbf{r}_2)\cdots P_{T_n}(\mathbf{r}_n). \quad (7)$$

This reduces the short-range order to an amount dependent entirely on the long-range order, giving for both the simple lattices cited above ($AB$ b.c.c. and $AB_3$ f.c.c.) $\sigma=S^2$. Above the critical temperature this approximation would be much too drastic, but for $S$ near 1 it is reasonably good, as is shown by x-ray data.[10] A rough lower limit of $S$ for the use of this approximation is $S=0.5$.

### 3. EQUATIONS OF MOTION

Away from equilibrium all of the distribution functions will be changing with time as the atoms exchange places on the lattice. Many different mechanisms of atom movements can be imagined, but the following work will take up just two in detail, namely, direct interchange and interchange with vacancies. Present evidence, mainly from diffusion data, but also from direct calculation, favors the vacancy mechanism of atom movement in many common systems. Because it is theoretically simpler, however, and because it is useful to contrast the behavior to be expected from several different models, calculations will also be made on the assumption that direct interchange is the predominant mechanism.

Consider a pair consisting of an $A$ atom on site $\mathbf{r}$ and a $B$ atom on a neighboring site $\mathbf{r}+\boldsymbol{\delta}$. At a given temperature and with any given set of atoms in the sites around this pair, there exists a certain rate at which the $AB$ pair will reverse itself so that the $B$ atom moves to $\mathbf{r}$ and simultaneously the $A$ atom moves to $\mathbf{r}+\boldsymbol{\delta}$. The influence of the environmental population must be taken into account, else no tendency toward ordering will be found. Suppose, for simplicity, that only those atoms which are nearest neighbors to the pair exert an influence (more distant neighbors could be taken into account in an obvious way), and let $\{X\}$ denote the particular set of atoms in these neighboring sites. Then by $R_{AB}(\{X\})$ we will denote the rate at which the $AB$ pair interchanges under these circumstances. Likewise let the rate of interchange of a $BA$ pair, similarly situated and with environmental set $\{X\}$, be denoted $R_{BA}(\{X\})$. $\{X\}$ is an ordered set of atoms occupying sites with definite positions around $\mathbf{r}$ and $\mathbf{r}+\boldsymbol{\delta}$; this set of sites will subsequently be denoted $\{\mathbf{x}\}$. From the context it will always be clear which pair of (ordered) neighbors determines $\{\mathbf{x}\}$. Since consideration will be limited to lattices in which all sites are geometrically similar, $R_{AB}(\{X\})$ and $R_{BA}(\{X\})$ do not depend on $\mathbf{r}$ and $\boldsymbol{\delta}$. Related to each $\{X\}$ is a set giving the same occupation of sites about $-\boldsymbol{\delta}$ as $\{X\}$ gives of sites about $\boldsymbol{\delta}$. Call this conjugate set $\{X\}_c$. Then, clearly,

$$R_{BA}(\{X\}_c)=R_{AB}(\{X\}). \quad (8)$$

Consider now a binary system, in which direct interchange is the predominant mechanism. The probability of finding an $A$ atom on $\mathbf{r}$, a $B$ atom on $\mathbf{r}+\boldsymbol{\delta}$, and the set $\{X\}$ on the neighboring sites $\{\mathbf{x}\}$, is $P_{AB\{X\}}(\mathbf{r},\ \mathbf{r}+\boldsymbol{\delta},\ \{\mathbf{x}\})$. In the case of the b.c.c. lattice this is a 16-particle distribution function; in the f.c.c. case it is a 20-particle function. The rate, on the average, at which $A$ atoms are disappearing from site $\mathbf{r}$ by interchange with a neighbor at $\mathbf{r}+\boldsymbol{\delta}$, when the surrounding atoms comprise the set $\{X\}$, is

$$P_{AB\{X\}}(\mathbf{r},\ \mathbf{r}+\boldsymbol{\delta},\ \{\mathbf{x}\})R_{AB}(\{X\}).$$

The total rate, on the average, at which $A$ atoms are disappearing from site $\mathbf{r}$ is the summation of this over all possible sets of neighbors $\{X\}$ and over all sites which are nearest neighbors to $\mathbf{r}$,

$$\sum_{\boldsymbol{\delta}}\sum_{\{X\}} P_{AB\{X\}}(\mathbf{r},\ \mathbf{r}+\boldsymbol{\delta},\ \{\mathbf{x}\})R_{AB}(\{X\}).$$

A quite similar expression gives the average rate at which $A$-type atoms are appearing on site $\mathbf{r}$, and the difference of these equals the net rate of increase of probability that site $\mathbf{r}$ be occupied by an atom of type $A$. Thus, one finds the basic equation

$$\frac{d}{dt}P_A(\mathbf{r})=\sum_{\boldsymbol{\delta}}\sum_{\{X\}} P_{BA\{X\}}(\mathbf{r},\ \mathbf{r}+\boldsymbol{\delta},\ \{\mathbf{x}\})R_{BA}\{X\} -\sum_{\boldsymbol{\delta}}\sum_{\{X\}} P_{AB}(\mathbf{r},\ \mathbf{r}+\boldsymbol{\delta},\ \{\mathbf{x}\})R_{AB}(\{X\}). \quad (9)$$

Interchanging $A$ and $B$ gives an equation for $dP_B(\mathbf{r})/dt$. This is seen to be the negative of $dP_A(\mathbf{r})/dt$, as is already demanded by the identity $P_A(\mathbf{r})+P_B(\mathbf{r})=1$.

In a binary system with two types of lattice sites, and with homogeneous order, the identities (1) and (2) show that $P_A(\mathbf{r})$ for a single value of $\mathbf{r}$ determines all other single site distribution functions. Thus, letting $\mathbf{r}_\alpha$ be an $\alpha$ site and $\mathbf{r}_\beta$ a $\beta$ site, one finds

$$P_A(\mathbf{r}_\beta)=(f_A/f_\beta)-(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha), \quad (10)$$

$$P_B(\mathbf{r}_\alpha)=1-P_A(\mathbf{r}_\alpha), \quad (11)$$

and

$$P_B(\mathbf{r}_\beta)=1-f_A/f_\beta+(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha), \quad (12)$$

where $f_A$ and $f_B$ are the fractions of the atoms which are of types $A$ and $B$, respectively, and $f_\alpha$ and $f_\beta$ are the fractions of the sites which are of types $\alpha$ and $\beta$, respectively ($f_A+f_B=f_\alpha+f_\beta=1$, but it is not necessary that $f_A=f_\alpha$). Thus, Eq. (9) with $\mathbf{r}$ taken equal to $\mathbf{r}_\alpha$, say, exhausts the possible equations of motion for one body probabilities in the homogeneous binary case.

In this same case, all two-particle distribution func-

---

[10] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950); Phys. Rev. **72**, 669 (1950); B. W. Roberts and G. H. Vineyard, J. Appl. Phys. **27**, 203 (1956).

tions referring to two sites of given separation $\boldsymbol{\gamma}$ may be shown to depend on a two-particle distribution function of this type, say $P_{AA}(\mathbf{r}_\alpha, \mathbf{r}_\alpha+\boldsymbol{\gamma})$, and a one-one-particle distribution function, say $P_A(\mathbf{r}_\alpha)$. Two-particle distribution functions with a different $|\boldsymbol{\gamma}|$ are independent. There are, then, an infinite number of independent two-body equations of motion. They may be seen to have the form

$$
\begin{aligned}
\frac{d}{dt}&P_{AA}(\mathbf{r}, \mathbf{r}+\boldsymbol{\gamma})\\
&=\sum_{\boldsymbol{\delta}}^{\boldsymbol{\delta}\neq-\boldsymbol{\gamma}}\sum_{\{X\}} P_{ABA\{x\}}(\mathbf{r}, \mathbf{r}+\boldsymbol{\gamma}, \mathbf{r}+\boldsymbol{\gamma}+\boldsymbol{\delta}, \{\mathbf{x}\})R_{BA}(\{X\})\\
&\quad+\sum_{\boldsymbol{\delta}}^{\boldsymbol{\delta}\neq\boldsymbol{\gamma}}\sum_{\{X\}} P_{BAA\{x\}}(\mathbf{r}, \mathbf{r}+\boldsymbol{\gamma}, \mathbf{r}+\boldsymbol{\delta}, \{\mathbf{x}\})R_{BA}(\{X\})\\
&\quad-\sum_{\boldsymbol{\delta}}^{\boldsymbol{\delta}\neq-\boldsymbol{\gamma}}\sum_{\{X\}} P_{AAB\{x\}}(\mathbf{r}, \mathbf{r}+\boldsymbol{\gamma}, \mathbf{r}+\boldsymbol{\gamma}+\boldsymbol{\delta}, \{\mathbf{x}\})R_{AB}(\{X\})\\
&\quad-\sum_{\boldsymbol{\delta}}^{\boldsymbol{\delta}\neq\boldsymbol{\gamma}}\sum_{\{X\}} P_{AAB\{x\}}(\mathbf{r}, \mathbf{r}+\boldsymbol{\gamma}, \mathbf{r}+\boldsymbol{\delta}, \{\mathbf{x}\})R_{AB}(\{X\}).
\end{aligned}
\tag{13}
$$

Here, in the summations, $\boldsymbol{\delta}$ again ranges over all nearest neighbor displacements, except that when $\boldsymbol{\gamma}$ is a nearest neighbor displacement one value of $\boldsymbol{\delta}$ must always be excluded, as indicated; $\{X\}$ is the set of environmental sites around $\boldsymbol{\delta}$. The meaning of the terms in (13) is straightforward. The first evaluates ways of creating the $AA$ pair by starting with an $AB$ pair, the second term evaluates ways starting with a $BA$ pair; the third term evaluates ways of destroying the $AA$ pair by producing an $AB$ pair, the fourth term, by producing a $BA$ pair.

In a similar fashion, equations of motion for the distribution functions of all orders may be readily written down. The left-hand side is the time derivative of a distribution function, the right-hand side is always a linear combination of distribution functions of higher order, with the basic rate constants $R_{AB}(\{X\})$ as coefficients. Except for the assumption of the direct interchange process for atom movements and the assumption that each interchange occurs in a time short compared to the time between interchanges, the equations are rigorous. They are somewhat analogous to the basic equations of modern kinetic theories of fluids.[11]

Presumably the entire set of equations of the type of (9) and (13) and their higher order analogs uniquely determines the development of the system in time, given an initial set of distribution functions. Rigorous solutions are hardly to be expected, but the system offers an excellent starting point for finding approximate solutions by writing higher order distribution functions in terms of those of lower order, thus making the system finite.

The approximations can be made in a variety of ways, depending mainly upon the degree of complication one is willing to cope with. For systems with long-range order, a reasonably good approximation is to reduce everything to a one-site distribution function, as will be demonstrated in the next section, and then to work with only one equation of motion. A better approximation is to reduce many-site distribution functions to combinations of one-site distribution functions with two-site distribution functions for all pairs of sites which are nearest neighbors. The rates of change of several simultaneous variables must now be followed (two in the simplest systems). Iida[1] has shown how this may be done in one case and shows that the Bethe-Peierls approximation[9] emerges for the equilibrium state. Still higher forms of superposition or composition approximations may also be used, the number of independent variables rising rapidly as this is done. For most purposes it would not seem profitable to go beyond some form of two-site approximation.

## 4. APPROXIMATIONS TO THE EQUATIONS OF MOTION—DIRECT INTERCHANGE CASE

This section will be devoted to the simplest approximational scheme following from the preceding formalism. Attention will be restricted to homogeneous binary systems of stoichiometric composition, with a superlattice containing only two types of sites. The direct interchange mechanism will be considered to operate exclusively. Complete working out of the ordering kinetics will be done only for two systems, the $AB$ b.c.c. type of lattice and the $AB_3$ f.c.c. type.

Suppose that an $\alpha$ site is surrounded by $c$ nearest neighbors, all of them $\beta$ sites and geometrically equivalent. It is convenient to apply Eq. (9) by taking[12] $\mathbf{r}=\mathbf{r}_\alpha$; then $\mathbf{r}+\boldsymbol{\delta}$ always refers to a $\beta$ site. The composition approximation can now be applied to the right-hand side of (9) by writing

$$P_{BA\{x\}}(\mathbf{r}, \mathbf{r}+\boldsymbol{\delta}, \{\mathbf{x}\})\cong P_B(\mathbf{r})P_A(\mathbf{r}+\boldsymbol{\delta})P_{\{x\}}(\{\mathbf{x}\})$$

in the first term, with a similar replacement in the second term. On account of the similarity of the different neighbors, summing over $\boldsymbol{\delta}$ is equivalent to multiplying by $c$. One then finds

$$\frac{d}{dt}P_A(\mathbf{r}_\alpha)\cong K_O P_B(\mathbf{r}_\alpha)P_A(\mathbf{r}_\beta)-K_D P_A(\mathbf{r}_\alpha)P_B(\mathbf{r}_\beta), \tag{14}$$

where

$$K_O=c\sum_{\{X\}} P_{\{x\}}(\{\mathbf{x}\})R_{BA}(\{X\}), \tag{15a}$$

and

$$K_D=c\sum_{\{X\}} P_{\{x\}}(\{\mathbf{x}\})R_{AB}(\{X\}). \tag{15b}$$

Equation (14) may be conveniently rewritten in terms of a single variable, the long-range order param-

---

[11] H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, Inc., New York, 1952).

[12] As long as rigorous calculations are being made, it does not matter whether one starts with $\mathbf{r}=\mathbf{r}_\alpha$ or $\mathbf{r}=\mathbf{r}_\beta$. In nonsymmetric systems, such as the $AB_3$ f.c.c. type, differences can arise when approximations are introduced.

eter $S$, by means of Eq. (4) together with Eqs. (10), (11), and (12). Assuming stoichiometric proportions, one gets

$$dS/dt=(1/f_B)[K_0f_Af_B(1-S)^2 - K_D(f_A+f_BS)(f_B+f_AS)]. \quad (16)$$

This kinetic relation is precisely of the type postulated by Dienes[2] [see his Eq. (10)] on the assumption that ordering is a bimolecular reaction corresponding to the "chemical" equation $A^\alpha+B^\beta \rightleftarrows A^\beta+B^\alpha$, where $A^\alpha$ signifies an $A$ atom on an $\alpha$ site, etc. The present formulation goes further, however, in showing the makeup of the two rate constants of the reaction, Eqs. (15).

The rate constants themselves are seen to depend on the order through many-site distribution functions. They may be reduced to functions of the long range order only by further use of the composition approximation in the form

$$P_{\{X\}}(\{\mathbf{x}\}) \cong P_{X_1}(\mathbf{x}_1)P_{X_2}(\mathbf{x}_2)\cdots P_{X_n}(\mathbf{x}_n), \quad (17)$$

where $\mathbf{x}_1\cdots\mathbf{x}_n$ are the individual sites comprising the set $\{\mathbf{x}\}$, and $X_1\cdots X_n$ are the types of atoms comprising the set $\{X\}$.

Finally, it is necessary to estimate the basic rate constants $R_{BA}(\{X\})$. Here the common assumption will be invoked that there is a pairwise interaction energy effective between nearest neighbors only,[9] of amount $V_{AA}$, $V_{AB}$, and $V_{BB}$, between $AA$, $AB$, and $BB$ pairs, respectively, and a very simple treatment will be given. Let $v=\frac{1}{2}(V_{AA}+V_{BB}-2V_{AB})$, where the signs have been so chosen that for an ordering system $v>0$. Consider an $AB$ pair. Around the $A$ atom there is a shell of neighbors which are not neighbors to the $B$ atom, $c'$ in number, and around the $B$ atom there is a similar shell of $c'$ exclusive neighbors.[13] Call these the $A$ shell and the $B$ shell, respectively. Suppose that of the atoms in the $A$ shell $j$ are of $A$ type, $c'-j$ are of $B$ type, while of the atoms in the $B$ shell, $k$ are of $A$ type, $c'-k$ are of $B$ type. Then one finds that interchanging the members of the $AB$ pair increases the energy of the system by an amount

$$\Delta E_{jk}=2(k-j)v.$$

If one plots the potential energy of the system as a function of a coordinate measuring the fractional displacement of the pair from the $AB$ configuration toward the $BA$ configuration, it is reasonable to assume the curves are about as shown in Fig. 1. For a symmetric environment the two minima must lie at the same level, as shown by the solid line. For an excess of $A$ atoms in the $B$ shell the energy is increased on passing from the $AB$ to the $BA$ configuration, and about half of this energy increase has been acquired at the half-way point. The large extra energy of deformation, $U$, (see Fig. 1) should be substantially independent of the population of the $A$ and $B$ shells, so that the entire curve has the course of the dotted line in Fig. 1. A similar argument applies when there is an excess of $B$ atoms in the $B$ shell and gives the dashed curve of Fig. 1. As a result one predicts that the activation energy for passing from $AB$ to $BA$ is $U+(k-j)v$, for passing from $BA$ to $AB$ is $U-(k-j)v$. The environment, $\{X\}$, of the pair is thus characterized by the parameter $k-j$.

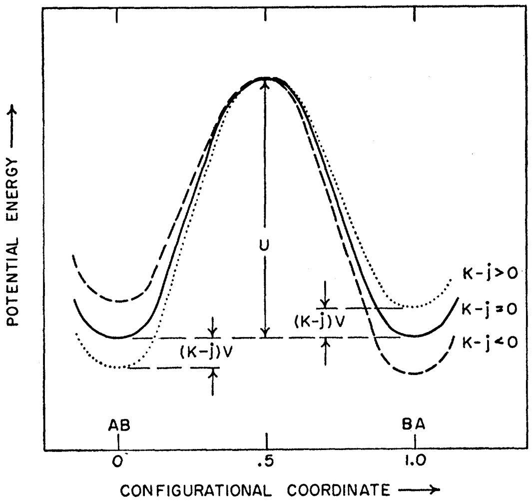

FIG. 1. Potential energy *vs* configurational coordinate during direct interchange of an $AB$ pair. The different curves show effects of different environments.

If $\nu$ is the frequency of the vibrational mode associated with interchange of the pair, one has, from absolute rate theory,

$$R_{AB}(\{X\})=\nu\exp\{-[U+(k-j)v]/RT\}, \quad (18)$$

where any activation entropy which occurs may be absorbed in the $\nu$, making this an effective frequency. From Eqs. (17) and (18) one may now evaluate the rate constants (15). This will first be done for the $AB$ b.c.c. case. Remembering that $\{\mathbf{x}\}$ must refer to the environment about a pair of sites of which the first is an $\alpha$, the second a $\beta$, one sees that the $A$ shell consists entirely of $\beta$ sites, the $B$ shell entirely of $\alpha$ sites. Any assignment of $j$ $A$ atoms to particular sites in the $A$ shell and $k$ $A$ atoms to particular sites in the $B$ shell has then the probability

$$P_{\{X\}}(\{\mathbf{x}\})=[P_A(\mathbf{r}_\beta)]^j[P_B(\mathbf{r}_\beta)]^{c'-j} \times[P_A(\mathbf{r}_\alpha)]^k[P_B(\mathbf{r}_\alpha)]^{c'-k}.$$

With Eqs. (10), (11), and (12), in which $f_\alpha=f_A=f_\beta=f_B=\frac{1}{2}$, this becomes

$$(1-p)^jp^{c'-j}p^k(1-p)^{c'-k},$$

where we have put $P_A(\mathbf{r}_\alpha)=p$. The number of sets $\{X\}$ characterized by the numbers $j$ and $k$ is $\binom{c'}{j}\binom{c'}{k}$

---

[13] In both b.c.c. and f.c.c. systems, $c'=7$.

(binomial coefficients), so one finds

$$\begin{aligned}K_D&=c\sum_{\{X\}}P_{\{X\}}(\{\mathbf{x}\})R_{AB}(\{X\})\\&=c\sum_{j=0}^{c'}\sum_{k=0}^{c'}\binom{c'}{j}\binom{c'}{k}(1-p)^jp^{c'-j}p^k(1-p)^{c'-k}\nu\\&\qquad\qquad\times\exp\{-[U+(k-j)v]/RT\}\\&=8\nu\exp[-U/RT]a^7[1+p(a^{-1}-1)]^{14},\end{aligned}\tag{19}$$

where $a=\exp[v/RT]$, and the summations on $j$ and $k$ have been carried out by the binomial theorem. From Eqs. (8) and (15a) one sees that $K_O$ is derived from $K_D$ by interchanging $k$ and $j$ in the term

$$\exp\{-[U+(k-j)v]/RT\}$$

at the start of the calculation, since $\{X\}_c$ is characterized by the parameter $j-k$ rather than $k-j$. This is equivalent to replacing $v$ by $-v$, so the formula for $K_O$ can be found by replacing $a$ by $a^{-1}$ on the right-hand side of (19).

The calculation for the $AB_3$ f.c.c. case proceeds similarly, though slightly complicated by the fact that the $A$ shell consists of 7 $\alpha$ sites, the $B$ shell of 3 $\alpha$ sites and 4 $\beta$ sites. One finds

$$\begin{aligned}K_D=12\nu\exp[-U/RT]a^{-7}[1+\tfrac{1}{3}(a-1)(1-p)]^7\\\times[1+(a-1)(1-p)]^3[1+\tfrac{1}{3}(a-1)(2+p)]^4,\end{aligned}\tag{20}$$

and again $K_O$ is found from this expression by replacing $a$ by $a^{-1}$ throughout.

Useful approximations to these formulas result when one replaces $\exp(v/RT)-1$ by $v/RT$ and uses further approximations of the type $(1+x)^n\cong e^{nx}$. By these methods one finds

$$\left.\begin{matrix}K_O\\K_D\end{matrix}\right\}\cong 8\nu\exp[(-U\pm 7vS)/RT],\tag{21}$$

for the $AB$ b.c.c. case, and

$$\left.\begin{matrix}K_O\\K_D\end{matrix}\right\}\cong 12\nu\exp[(-U\pm 3vS)/RT],\tag{22}$$

for the $AB_3$ f.c.c. case. Here $p$ has been replaced by $S$ by use of Eq. (4). The formulas are obviously good approximations to (19) and (20) when $T\gg v/R$. Furthermore, owing to the fact that they become exact for $S=1$ at all temperatures, they remain fairly accurate for $S$ near equilibrium at all temperatures, and for arbitrary $S$ at temperatures as low as half the critical temperature for ordering.

Equation (16) together with the approximations (21) and (22) to $K_O$ and $K_D$ gives the same kinetics as the theory of Dienes,[2] except that here $S$ enters $K_O$ and $K_D$ in a symmetric way, while Dienes has calculated under the assumption that $K_O$ is independent of $S$. The parameters of Dienes' theory can be so chosen that his ratio $K_O/K_D$ is the same as that given by Eqs. (21) and (22), and in this case there is rather little qualitative difference between the two formulations. The frequency employed by Dienes, which will here be written $\nu^D$, must be related to the more fundamental frequency of the present treatment by the formula $\nu^D=16\nu$ in both lattices. The parameter $V_0$ of Dienes is given by $V_0=14v$, in the $AB$ b.c.c. case, and by $V_0=6v$ in the $AB_3$ f.c.c. case.

Dienes has set up his equation so that the equilibrium degree of order is identical with that calculated from the theory of Bragg and Williams.[1] The parameter $V_0$ thus enters the Bragg and Williams theory, where it was defined as the energy change (per mole) upon interchanging an $A$ and $B$ pair at the state of perfect order. According to the discussion of Nix and Shockley,[9] the interchange considered should be between distant sites. In this manner one finds $V_0=16v$ and $8v$ in the $AB$ and $AB_3$ cases, respectively. One could argue with about equal force that the best definition of the Bragg and Williams parameter would involve an interchange between neighboring sites (because of the approximate character of the theory, neither definition is demanded). In this case one finds $V_0=14v$ and $6v$ in the $AB$ and $AB_3$ cases, respectively, in exact agreement with the kinetically derived results above.

In its most approximate form the foregoing theory thus reduces to the Bragg and Williams static theory at equilibrium and forms a natural extension of that theory away from equilibrium. In their original paper Bragg and Williams also derived a relaxation time for approach to equilibrium, assuming small departures and a direct interchange mechanism of atom movement. Their kinetics are likewise contained in the present theory. One can readily invent schemes for treating the foregoing equations of motion more accurately, but these will not be taken up in this paper.

## 5. EQUATIONS OF MOTION FOR THE VACANCY MECHANISM

When vacancies (symbolized $V$) are present in the lattice interchanges with them will occur, and four new types of basic rate constants arise: Given an $A$ atom on $\mathbf{r}$ and a vacancy on $\mathbf{r}+\boldsymbol{\delta}$, with a prescribed population $\{X\}$ on the sites around this pair, the rate of interchange between $A$ and vacancy will be denoted $R_{AV}(\{X\})$. The rate of the reverse interchange will be written $R_{VA}(\{X\})$, and the two similar processes, in which a $B$ atom occurs in place of the $A$ atom will be given the rate constants $R_{BV}(\{X\})$ and $R_{VB}(\{X\})$, respectively. Again, for simple lattices, one has the conjugate relations

$$R_{VA}(\{X\}_c)=R_{AV}(\{X\}),\tag{23a}$$

and

$$R_{VB}(\{X\}_c)=R_{BV}(\{X\}).\tag{23b}$$

As previously noted, the distribution functions must be generalized so that the vacancy is treated as a third species of atom. With two types of superlattice sites, six kinds of one-body distribution functions can be defined, and it can be shown that two of these are independent. [See Eqs. (26) to (29).] Thus, it is necessary to write two equations of motion to deal with the kinetics of long-range order, and for this purpose we choose to investigate $dP_A(\mathbf{r})/dt$ and $dP_V(\mathbf{r})/dt$, where $\mathbf{r}$ will shortly be taken to be $\mathbf{r}_\alpha$.

For simplicity, we assume that vacancy interchange occurs much more frequently than $AB$ interchange and neglect the latter. Arguments exactly like those which established Eq. (9), with $B$ replaced by $V$ everywhere, lead to the basic result

$$\begin{aligned}\frac{d}{dt}P_A(\mathbf{r})=&\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{VA\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{VA}(\{X\})\\&-\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{AV\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{AV}(\{X\}).\end{aligned}\tag{24}$$

Consider now the rate at which probability of occupation of site $\mathbf{r}$ by a vacancy must change. It increases in cases where $\mathbf{r}$ is first occupied by an $A$, the neighbor $\mathbf{r}+\boldsymbol{\delta}$ by a $V$, after which there is an interchange, and in cases where $\mathbf{r}$ is first occupied by a $B$, $\mathbf{r}+\boldsymbol{\delta}$ by a $V$, following which there is an interchange; it decreases in two ways which are the inverses of these. The corresponding equation of motion contains four terms, and is readily seen to be

$$\begin{aligned}\frac{d}{dt}P_V(\mathbf{r})=&\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{AV\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{AV}(\{X\})\\&+\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{BV\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{BV}(\{X\})\\&-\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{VA\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{VA}(\{X\})\\&-\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{VB\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})R_{VB}(\{X\}).\end{aligned}\tag{25}$$

The simplest useful approximations to these equations of motion can be found by much the same procedure as before. The multisite distribution functions are broken up by composition approximations in the form

$$P_{VA\{X\}}(\mathbf{r},\mathbf{r}+\boldsymbol{\delta},\{\mathbf{x}\})\cong P_V(\mathbf{r})P_A(\mathbf{r}+\boldsymbol{\delta})P_{\{X\}}(\{\mathbf{x}\}),\quad \text{etc.}$$

Effective rate constants are defined which will later be evaluated by further use of the composition approximation in the manner of (17). Finally, it will be assumed that the vacancy concentration, $f_V$, is always small, so that terms of higher than first order in $f_V$ may be discarded. Generalization of the relations (10) to (12) for the ternary case ($f_A+f_B+f_V=f_\alpha+f_\beta=1$, but it it is not necessary that $f_A=f_\alpha$) are

$$P_A(\mathbf{r}_\beta)=(f_A/f_\beta)-(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha),\tag{26}$$

$$P_B(\mathbf{r}_\alpha)=1-P_A(\mathbf{r}_\alpha)-P_V(\mathbf{r}_\alpha)\cong 1-P_A(\mathbf{r}_\alpha),\tag{27}$$

$$\begin{aligned}P_B(\mathbf{r}_\beta)=&1-(f_A/f_\beta)+(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha)\\&-(f_V/f_\beta)+(f_\alpha/f_\beta)P_V(\mathbf{r}_\alpha)\\\cong&1-(f_A/f_\beta)+(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha),\end{aligned}\tag{28}$$

$$P_V(\mathbf{r}_\beta)=(f_V/f_\beta)-(f_\alpha/f_\beta)P_V(\mathbf{r}_\alpha),\tag{29}$$

where the approximate forms depend on the condition $f_V\ll 1$, and will be employed in the following.

Using these results, with $\mathbf{r}=\mathbf{r}_\alpha$, $\mathbf{r}+\boldsymbol{\delta}=\mathbf{r}_\beta$, (24) and (25) now become

$$\begin{aligned}\frac{d}{dt}P_A(\mathbf{r}_\alpha)\cong&O_AP_V(\mathbf{r}_\alpha)[(f_A/f_\beta)-(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha)]\\&-D_AP_A(\mathbf{r}_\alpha)[(f_V/f_\beta)-(f_\alpha/f_\beta)P_V(\mathbf{r}_\alpha)],\end{aligned}\tag{30}$$

and

$$\begin{aligned}\frac{d}{dt}P_V(\mathbf{r}_\alpha)\cong&\{D_AP_A(\mathbf{r}_\alpha)+O_B[1-P_A(\mathbf{r}_\alpha)]\}\\&\times[(f_V/f_B)-(f_\alpha/f_\beta)P_V(\mathbf{r}_\alpha)]\\&-\{O_A[(f_A/f_\beta)-(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha)]\\&+D_B[1-(f_A/f_\beta)+(f_\alpha/f_\beta)P_A(\mathbf{r}_\alpha)]\}P_V(\mathbf{r}_\alpha),\end{aligned}\tag{31}$$

where

$$O_A=\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{\{X\}}(\{\mathbf{x}\})R_{VA}(\{X\}),\tag{32a}$$

$$D_A=\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{\{X\}}(\{\mathbf{x}\})R_{AV}(\{X\}),\tag{32b}$$

$$O_B=\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{\{X\}}(\{\mathbf{x}\})R_{BV}(\{X\}),\tag{32c}$$

$$D_B=\sum_{\boldsymbol{\delta}}\sum_{\{X\}}P_{\{X\}}(\{\mathbf{x}\})R_{VB}(\{X\}).\tag{32d}$$

An important feature of this ordering process is apparent from the form of Eqs. (30) and (31). The right-hand sides of both equations are of the order of $f_V$, but since $P_V(\mathbf{r}_\alpha)$ can never be larger than $f_V$ while $P_A(\mathbf{r}_\alpha)$ can be as large as 1, $P_V(\mathbf{r}_\alpha)$ is capable of changing at a very much larger rate, relative to its final value, than $P_A(\mathbf{r}_\alpha)$. As a result, $P_V(\mathbf{r}_\alpha)$ does most of its changing in the very beginning stages of the ordering process, after which it remains in quasi-stationary equilibrium while $P_A(\mathbf{r}_\alpha)$ varies to lits limiting value. This is to say that one can, with very good accuracy so far as $P_A(\mathbf{r}_\alpha)$ is concerned, set $(d/dt)P_V(\mathbf{r}_\alpha)$ equal to zero in (31), solve this for $P_V(\mathbf{r}_\alpha)$ in terms of $P_A(\mathbf{r}_\alpha)$, and use this to eliminate $P_V(\mathbf{r}_\alpha)$ from (30), thus reducing the problem to one with a single dependent variable. This same procedure is sometimes known as the stationary state approximation in chemical kinetics.[14] A rigorous discussion can be given, but will not be attempted here. It should also be noted that the equilibrium value reached by $P_A(\mathbf{r}_\alpha)$ is the same with and without use of the approximation. Following this procedure [and noting that the rate constants (32)

---

[14] S. Glasstone, *Text Book of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940), p. 1059.

will not depend appreciably on $P_V(\mathbf{r}_\alpha)$], one finds a simplified equation of motion:

$$\frac{dP_A}{dt}\cong\left(\frac{f_V}{f_\beta}\right)\left\{\frac{O_A[f_A-f_\alpha P_A][O_B+(D_A-O_B)P_A]-D_AP_A[f_AO_A+(f_\beta-f_A)D_B+f_\alpha(D_B-O_A)P_A]}{f_AO_A+f_\alpha O_B+(f_\beta-f_A)D_B+f_\alpha[D_A+D_B-O_A-O_B]P_A}\right\}, \tag{33}$$

where $P_A\equiv P_A(\mathbf{r}_\alpha)$.

This equation is still more complex than that for the direct-interchange case. It can be readily shown, however, that the equilibrium degree of order is the same on both models providing the previous rate constants are related to the new ones by the formula

$$K_O/K_D=(O_AO_B)/(D_AD_B). \tag{34}$$

This result can also be understood in the terminology of chemical kinetics: With the composition approximation the vacancy model is equivalent to the two "chemical" reactions:

$$A^\alpha+V^\beta \underset{O_A}{\overset{D_A}{\rightleftarrows}} A^\beta+V^\alpha \quad\text{and}\quad B^\beta+V^\alpha \underset{O_B}{\overset{D_B}{\rightleftarrows}} B^\alpha+V^\beta,$$

and *at equilibrium* this reduces to the single reaction

$$A^\alpha+B^\beta \underset{O_AO_B}{\overset{D_AD_B}{\rightleftarrows}} A^\beta+B^\alpha.$$

The vacancy rate constants can easily be evaluated by the methods used previously. We assume analogously to (18) that

$$R_{AV}(\{X\})=\nu_A\exp\{-[U_A+(k-j)v_A]/RT\}, \tag{35}$$

where $\nu_A$ is approximately the Einstein vibrational frequency of an $A$-type atom, $U_A$ is the activation energy for $AV$ interchange in a symmetric environment, $j$ is the number of $A$-type atoms in the $A$ shell, $k$ is the number of $A$-type atoms in the shell of sites around the vacancy, and $v_A=\frac{1}{2}(V_{AA}-V_{AB})$. Likewise, replacing $A$ by $B$ throughout,

$$R_{BV}(\{X\})=\nu_B\exp\{-[U_B+(k-j)v_B]/RT\}. \tag{36}$$

Since the vacancy concentration is small, no account need be taken of possible vacancies in the environment of the pair. $D_A$ is now evaluated from (32b) and (35), with full use of the composition approximation in simplifying $P_{\{X\}}(\{\mathbf{x}\})$. The calculation is precisely similar to that made earlier for the direct interchange case, and the results (19) and (20) can be taken over by inserting suitable modified parameters. We assume stoichiometric proportions and express the results in terms of the long-range order parameter, $S$, instead of $P$. Letting $a_A\equiv\exp[v_A/RT]$, $a_B=\exp[v_B/RT]$, we find the following results.

$AB$ b.c.c. case:

$$\left.\begin{matrix}O_A\\D_A\end{matrix}\right\}=8\nu_A\exp[-U_A/RT]\times a_A^{\mp7}[1+\tfrac{1}{2}(a_A^{\pm1}-1)(1+S)]^{14} \tag{37a}$$

$$\cong8\nu_A\exp[(-U_A\pm7v_AS)/RT]. \tag{37b}$$

The formulas for $O_B$ and $D_B$ are obtained from these by replacing $A$ by $B$ throughout.

$AB_3$ f.c.c. case:

$$\left.\begin{matrix}O_A\\D_A\end{matrix}\right\}=12\nu_A\exp[-U_A/RT]\times a_A^{\pm7}[1+\tfrac{1}{4}(a_A^{\mp1}-1)(1-S)]^7\times[1+\tfrac{3}{4}(a_A^{\mp1}-1)(1-S)]^3\times[1+\tfrac{1}{4}(a_A^{\mp1}-1)(3+S)]^4 \tag{38a}$$

$$\cong12\nu_A\exp[(-U_A\pm3v_AS)/RT]. \tag{38b}$$

Again replacement of $A$ by $B$ everywhere converts these into expressions for $O_B$ and $D_B$.

The exponential approximations (37b) and (38b) have been derived in the same way as (21) and (22), and are accurate over the same regions.

With the relation $v_A+v_B=v$, one finds from the above formulas that (34) is satisfied if the exponential approximation is used for all the rate constants, but not otherwise. This means that the vacancy mechanism and direct interchange mechanism operating separately would produce only approximately the same order at equilibrium. According to the principle of detailed balancing, however, the two mechanisms should be in individual equilibrium simultaneously, and the discrepancy is symptomatic of the approximate nature of the calculation. This suggests, of course without proving it, that the exponential approximation to the rate constants may compensate some earlier approximations and give a better answer than the more elaborate formulas.

Finally, it should be recorded that the equation of motion by the vacancy mechanism, (33), takes the following forms when written in terms of the long range order parameter, with stoichiometric proportions, for the two systems of present interest:

$AB$ case,

$$\frac{dS}{dt}=2f_V\left[\frac{O_AO_B(1-S)^2-D_AD_B(1+S)^2}{(O_A+O_B)(1-S)+(D_A+D_B)(1+S)}\right]; \tag{39}$$

$AB_3$ case,

$$\frac{dS}{dt}=\frac{4}{3}f_V\left[\frac{3O_AO_B(1-S)^2-D_AD_B(1+3S)(3+S)}{3(O_A+O_B)(1-S)+D_A(1+3S)+3D_B(3+S)}\right]. \tag{40}$$

## 6. DISCUSSION OF LONG-RANGE ORDERING

Each of the foregoing equations of motion has the form

$$dS/dt=F(S), \tag{41}$$

where $F(S)$ depends on temperature, composition, type of lattice, and predominant mechanism of atom movement. In general it is not possible to integrate this equation analytically, but an adequate understanding of the theoretical predictions can be had from consideration of $F(S)$. States of equilibrium occur at zeros of $F(S)$, stable or metastable equilibrium occurring at zeros where $F(S)$ has negative slope, unstable equilibrium at zeros with positive slope.

In all cases $F(S)$ has a zero at the origin. The reason for this is that a completely disordered system has no reason for preferring to establish order by making any particular sublattice become the $\alpha$ lattice, and while one choice leads to increasing $S$, other choices lead to decreasing $S$. At temperatures above the critical temperature the equilibrium $S=0$ is also stable.

The $AB$ b.c.c. system has the following simple behavior: Below the critical temperature one additional zero of $F(S)$ occurs, the zero at the origin becoming unstable, the new zero being stable and corresponding to the equilibrium degree of long-range order. With the exponential approximation to the rate constants, as already noted, the equilibrium order agrees with the prediction of the Bragg-Williams theory, rising monotonically from zero to one as the temperature falls. Both the direct interchange and vacancy models give qualitatively similar results. The most important quantitative distinction is that the absolute value of $F(S)$ is proportional to $\exp(-U/RT)$ in the interchange case, and to $f_V \exp(-U_A/RT)$ in the vacancy case (we suppose now that $U_A \cong U_B$). Since the vacancy concentration, $f_V$, is proportional to the exponential of the energy of vacancy formation, the vacancy mechanism will dominate if the energy of formation plus activation energy of motion of a vacancy is appreciably less than the activation energy for pairwise interchange.

Dienes[15] has given illustrative curves of $dS/dt$ for the direct-interchange case, choosing the parameters (in the notation of this paper) $\nu=6.2\times10^{11}$ sec$^{-1}$, $U/R=5000$°K and $v/R=143$°K (so that $T_c$, the critical temperature, is 250°K). [In Dienes' plot, $K_D$ is proportional to $\exp(-14\,vS/RT)$ while $K_O$ is independent of $S$, but the quantitative difference between this and the case of rate constants given by (21) is not great.] In Fig. 2 we give a similar example of $dS/dt$ for the vacancy case, using the exponential approximations (37b) for rate constants. We have chosen

$$U_A/R=U_B/R=1540°\text{K},\quad v_A/R=v_B/R=35.7°\text{K}$$

(so again $T_c=250$°K), $\nu_A=\nu_B=6.2\times10^{11}$ sec$^{-1}$, and $f_V=5\times10^{-7}$. The figure shows a family of curves of $dS/dt$ plotted against $S$ for various temperatures. The minima at high $S$ found for the interchange case do not appear, but otherwise the curves are very similar. (With Dienes' formula these minima occur for $S$ less than 1, with the present formula, they occur at larger $S$.) The vertical scale is intended to be illustrative only, as very different values could be arrived at by choosing other equally plausible values for $v_A$ and $f_V$.

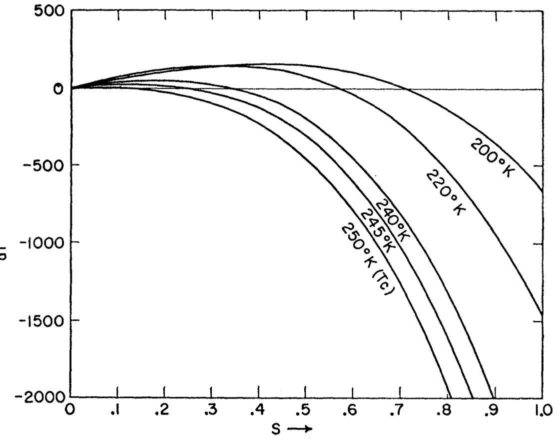

FIG. 2. Rate of change of long-range order *vs* long-range order, for several temperatures. $AB$ b.c.c. case, vacancy-interchange mechanism.

For small departures from equilibrium order the return to equilibrium will follow an exponential law with a relaxation time $\tau$ equal to the reciprocal of the slope of $F(S)$ at the equilibrium point. This argument has already been used by Bragg and Williams[1] in their early discussion of ordering kinetics. An analytic expression for $\tau$ can be derived from the foregoing formulas, but is too complex to be very informative. From Fig. 2 it can be seen that $\tau$ has a minimum at a temperature about 0.9 $T_c$, and approaches infinity as $T$ rises toward $T_c$ and also as $T$ approaches zero. The meaning of this is clear—at low temperatures relaxation slows as all motion freezes out, and in the vicinity of $T_c$ relaxation again slows as the driving force for ordering slackens. From Dienes' curves it is apparent that the interchange model gives a minimum relaxation time at a temperature much nearer $T_c$. Consideration shows that if one plots $\log\tau$ *vs* $1/T$ a curved line will result, with only its low-temperature end asymptotic to a straight line with a meaningful activation energy. In the direct interchange case, this energy is $U$, in the vacancy case it is the energy of vacancy formation plus either $U_A$ or $U_B$, whichever is the larger.

The $AB_3$ f.c.c. lattice shows a somewhat more complicated behavior, caused by its peculiarity in having many $B-B$ pairs even at perfect order. Dienes[16] gives $dS/dt$ curves for the direct interchange case (again with the unimportant difference that $K_O$ does not depend on $S$) using the same parameters as for the $AB$ case. In Fig. 3 of this paper are shown illustrative curves for the vacancy mechanism. In this the same parameters have been chosen as for Fig. 2. The vacancy and interchange mechanisms again give qualitatively,

---

[15] See reference 2, Figs. 1 and 2.

[16] See reference 2, Fig. 6.

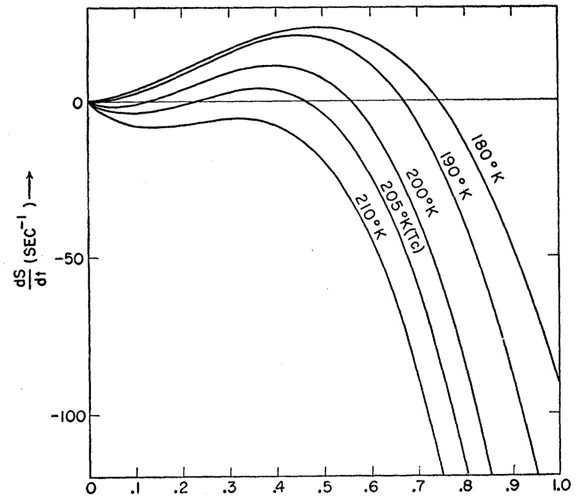

FIG. 3. Rate of change of long-range order *vs* long-range order, for several temperatures. $AB_3$ f.c.c. case, vacancy-interchange mechanism.

but not quantitatively similar results. At sufficiently low temperatures the curves are rather like the $AB$ curves, but for temperatures in the vicinity of $T_c$ the curves develop a re-entrant portion leading to a negative slope at $S=0$ and a third, unstable, equilibrium point at intermediate $S$. This peculiarity is, in the exponential approximation to the ordering rates, exactly correlated with the appearance of multiple roots in the Bragg-William equation for equilibrium order.[1] The critical temperature, deduced from equality of free energies, is 205°K, and the point $S=0$ is seen to be in metastable equilibrium down to temperatures appreciably below this. Likewise the state of equilibrium order becomes metastable as $T$ goes above $T_c$. Borelius[17] has already deduced the existence of a possible temperature hysteresis on the basis of the Bragg-Williams theory. A treatment of the nucleation processes by which the system escapes from metastable states requires going beyond the homogeneous and uncorrelated model which we have employed up to now. This question will be taken up in a subsequent paper. The relaxation time associated with small departures from equilibrium has a minimum at a temperature near the critical temperature, and does not approach infinity until the critical temperature has been exceeded by about one percent.

### 7. APPLICATION TO $Cu_3Au$

The recent measurements of Burns and Quimby[18] on resistivity changes in $Cu_3Au$ give an opportunity of applying the present theory. Unlike all earlier investigations, these involved changes of order under contions where nucleation and variations of domain size did not occur. In one series of measurements,[19] carefully annealed wires were brought to equilibrium at 388°C, a temperature about 5°C below the critical temperature, and then quenched to final temperatures in the range from 338°C to 385°C. Following quench the electrical resistivity was observed as a function of time at constant temperature. In a second series,[20] samples were equilibrated at 338°C, then rapidly heated to final temperatures in the range 348°C to 388°C, and electrical resistivity was again observed as a function of time at constant temperature. Under these conditions the domains of order presumably do not change appreciably in size, and the relaxation of resistivity observed is a measure of the relaxation of long-range order toward its equilibrium value.

Unfortunately there is no information available by which the order can be determined accurately from the resistivity. Theory[21] shows that for sufficiently small excursions the change in order is proportional to the change in resistivity, but is unable to place reliable limits on the region of linearity. Consequently we shall direct attention to the region of small departures from equilibrium, and only assume that resistivity and order are linearly related in this region. Under these conditions the ordering rate, $F(S)$, can also be approximated by a linear function, and, as discussed above, the relaxation of order toward equilibrium follows an exponential law:

$$S-S_e=A\exp[-t/\tau], \tag{42}$$

where $S_e$ is the equilibrium order, and

$$1/\tau=dF/dS \text{ evaluated at } S_e.$$

The relaxation curves of Burns and Quimby can be approximated by decaying exponentials of the form of (42). The fit is adjusted to be best near equilibrium. It

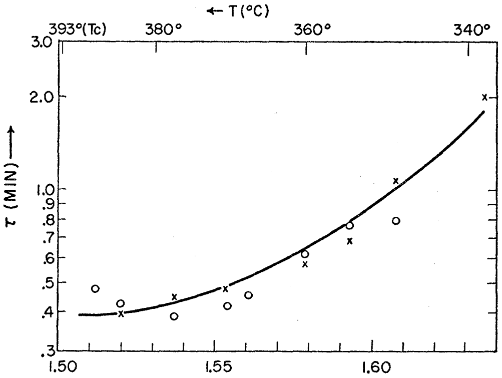

FIG. 4. Relaxation time for long-range ordering *vs* temperature in $Cu_3Au$. Crosses (order increasing) and circles (order decreasing) are from data of Burns and Quimby. Solid line is from present theory.

---

[17] G. Borelius, Ann. Physik **20**, 57 (1934).

[18] F. P. Burns and S. L. Quimby, Phys. Rev. **97**, 1567 (1955).

[19] See reference 18, Fig. 6.

[20] See reference 18, Fig. 7.

[21] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **30**, 99 (1936).

is then good to within about 5% everywhere except for four cases in which the misfit at small times ranges up to 25%. In view of the two approximations already discussed this would seem to be an adequate agreement. The relaxation times thus determined are plotted logarithmically against $1/T$ in Fig. 4. The points fall on a fairly well defined curve, which, as anticipated, is far from linear.

The present theory has also been used to calculate these relaxation times. The vacancy interchange mechanism was assumed [Eq. (40)] and the exponential approximations to the rate constants were employed. In the absence of clear indications to the contrary, it was assumed that $U_A=U_B$, $v_A=v_B$, and $\nu_A=\nu_B$. The concentration of vacancies, $f_V$, was assumed to be given by the usual formula

$$f_V=f_V{}^0\exp[-W/RT].$$

In this $T$ was always taken as the temperature after quenching, since the time for equilibration of the vacancy concentration can be calculated to be very much shorter than the times involved in these measurements. One then finds

$$\tau=(8\nu_A f_V{}^0)^{-1}\exp[(U_A+W)/RT]\left[\frac{(1+3S_e)(3+S_e)}{3(1-S_e)^2}\right]^{\frac{1}{4}}$$
$$\times\left\{\frac{[3(1+3S_e)(3+S_e)]^{\frac{1}{2}}+5+3S_e}{\dfrac{(1+3S_e)(3+S_e)}{(1-S_e)}\left[\dfrac{6v_A}{RT}(1-S_e)-2\right]-10-6S_e}\right\}. \quad (43)$$

To fit the known critical temperature for ordering of this alloy (393°C) it is necessary to take $v_A/R=541$°K. Since the present theory now predicts $S_e$ at each temperature, giving the Bragg-Williams result for this, there are only two remaining parameters, $\nu_A f_V{}^0$ and $U_A+W$. These can be related to a coefficient of diffusivity as follows: Within the assumption of $A-B$ symmetry being employed, the self-diffusivity of either $A$ or $B$ in the alloy can be shown to be given approximately by $D=D_0\exp(-Q/RT)$, where $D_0=b^2\nu_A f_V{}^0$, $Q=U_A+W$, and $b$ is the lattice constant. Careful measurements of $D_0$ and $Q$ in $Cu_3Au$ have apparently not been made, but it can be argued that these quantities should not differ widely from their values for pure copper or pure gold. Recent work gives, for Cu,[22] $D_0=0.20$ cm²/sec, $Q=47.1$ kcal/mole; for Au,[23] $D_0=0.028$ cm²/sec, $Q=39.2$ kcal/mole. Also the chemical diffusivity of Au in Cu at low concentrations gives $D_0=0.1$ cm²/sec, $Q=44.9$ kcal/mole.[24] We choose, arbitrarily, $U_A+W=44$ kcal/mole, which is intermediate between the values for the pure metals, and $\nu_A f_V{}^0=7\times10^{13}$ sec$^{-1}$, which, by the above relation, gives $D_0=0.1$ cm²/sec. Employing (43) a theoretical curve of $\tau$ is found which is shown as the solid line in Fig. 4. The agreement with the experimental points seems to be quite as satisfactory as the rough nature of the calculation would require.

Rothstein[8] has also fitted his quasi-chemical theory to the Burns and Quimby measurements. As yet a full account has not appeared in print, but it is apparent that the parameters which he deduces are quite different from those found here. In particular, the energy change on ordering is very much larger in his picture, and the equilibrium degree of long-range order is predicted to be exceedingly close to unity in the temperature range concerned. X-ray, thermal, and other evidence is not in accord with these conclusions.

By refining the present calculations, even closer fits to the curves of Burns and Quimby could be attained. In particular, the departure of $F(S)$ from linearity in the vicinity of $S_e$ could be allowed for, and this would change the time dependence of the relaxation from a single exponential to a more complicated form. Any improved experimental agreement at larger departures from equilibrium would, in our opinion, be without significance unless adequate linearity of the order-resistivity relation had been established.

## 8. SUMMARY AND CONCLUSIONS

(1) The set of multiparticle distribution functions introduced here, although seeming to comprise a rather elaborate formalism, gives a natural and powerful apparatus with which to discuss the ordering process. In terms of these functions, general kinetic relations (equations of motion) can be immediately written down, and various schemes of approximation for simplifying the equations suggest themselves.

(2) The simplest possible approximation is that in which all distribution functions are expressed as products of one-particle distribution functions. It is reasonably good for cases where long-range order is high (say, roughly, $S>0.5$), and allows the kinetics of ordering, for homogeneous systems, to be worked out in simple and plausible forms.

(3) The vacancy and the direct interchange mechanisms studied in the simplest approximation, give qualitatively, but not quantitatively, similar results. The vacancy mechanism, on present evidence, is likely to predominate.

(4) The $AB$ b.c.c. system and the $AB_3$ f.c.c. system have been treated. There are some characteristic differences, independently of the interchange mechanism assumed, the $AB_3$ system being susceptible to undercooling and superheating.

(5) The simplest approximation leads to the same equilibrium degree of long-range order as the Bragg-Williams calculations. It also admits an explanation in "chemical" terms, the direct interchange mechanism being equivalent to the "chemical reaction"

$$A^\alpha+B^\beta\rightleftarrows A^\beta+B^\alpha,$$

---

[22] A. Kuper *et al.*, Phys. Rev. **98**, 1870 (1955).

[23] B. Okkerse, Bull. Am. Phys. Soc. Ser. II, **1**, 149 (1956).

[24] A. B. Martin and F. Asaro, Phys. Rev. **80**, 123 (1950).

and the vacancy mechanism being equivalent to the two "chemical reactions" $A^{\alpha}+V^{\beta}\rightleftarrows A^{\beta}+V^{\alpha}$ and $B^{\alpha}+V^{\beta}\rightleftarrows B^{\beta}+V^{\alpha}$. The reaction rates in these models are derived in terms of the fundamental parameters of atom movements, and are themselves order-dependent.

(6) The vacancy-interchange model has been applied to the case of $Cu_3Au$, which has been studied experimentally by Burns and Quimby. $A-B$ symmetry was assumed, an activation energy and a pre-exponential factor were taken from the measurements of self-diffusion in pure copper and pure gold, and the remaining parameter of the theory was adjusted to produce agreement with the known critical temperature for ordering in this system. The theory then gives reasonably good agreement with relaxation times observed by Burns and Quimby over the temperature range of the experiments, 338°C to 388°C.

(7) The developments outlined above have been concerned with homogeneous systems. The basic apparatus of multiparticle distribution functions and their equations of motion is equally applicable to inhomogeneous systems, including cases of domains of order in a disordered matrix, domains of antiphase order, and diffusion in alloys.

## 9. ACKNOWLEDGMENTS

The writer is indebted to G. J. Dienes for numerous discussions and some important suggestions in the course of this work, and to S. L. Quimby for supplying information about his $Cu_3Au$ experiments.

---

PHYSICAL REVIEW VOLUME 102, NUMBER 4 MAY 15, 1956

# Ionization Interaction between Impurities in Semiconductors and Insulators

R. L. LONGINI AND R. F. GREENE
*Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania*

(Received October 26, 1955; revised manuscript received February 17, 1956)

It is known that the free energy of an imperfect semiconductor or insulator crystal contains terms which arise from the ionizability of these imperfections and which represent chemical interactions between imperfections of the same and different kinds. We show that these ionization terms, which involve the Fermi level and the parameters of the energy band model, explain the systematic differences between $n$- and $p$-type semiconductors in lattice vacancy concentration, in substitutional atom diffusion coefficients, and in amphoteric impurity behavior. The ionization terms also explain the variation of solid-liquid impurity distribution coefficients with the crystal growth rate of certain semiconductors, and also the well-known "charge balance" effect in insulators.

## 1. INTRODUCTION

It is well known[1–3] that the solubility of an ionizing impurity in a semiconductor is affected by the electron and hole concentrations. This happens because, roughly speaking, the free energy needed to insert, say, a donor atom in a semiconductor lattice is reduced by the energy liberated in the ionization of the donor, i.e. by an electron falling from the donor level to the Fermi level.

Reiss[2] has given a statistical treatment of this effect, showing that the chemical potentials of donor and acceptor impurities have the form

$$\mu_d=B_d(p,T)+kT\ln X_d+E_F-kT\ln\left(1+2\exp\frac{E_F-E_d}{kT}\right), \tag{1.1a}$$

$$\mu_a=B_a(p,T)+kT\ln X_a-E_F-kT\ln\left(1+2\exp\frac{E_a-E_F}{kT}\right), \tag{1.1b}$$

where $X_d$ and $X_a$ are the donor and acceptor concentrations, and $E_F$, $E_d$, and $E_a$ are the Fermi level, donor level, and acceptor level, respectively. The main assumptions behind (1.1) are as follows:

(a) The energy band model is adequate. (For definiteness the donor and acceptor levels are assigned statistical weight 2.)

(b) The ionization interaction provides the only departure from regularity[4] of the donor and acceptor solutions.

(c) The difference between Gibbs and Helmholtz free energy is negligible.

Using (1.1), Reiss calculated[3] the distribution coefficient for an ionizing impurity atom between two phases, in terms of the concentration of other ionizing impurities. The results agree with experiment.[3]

In Sec. 2 of this paper, we present an alternative

---

[1] C. Wagner and K. Grunewald, Z. Phys. Chem. **B40**, 455 (1938); C. Wagner, J. Chem. Phys. **18**, 62 (1950), J. Chem. Phys. **19**, 626 (1951), K. Hauffe, *Halbleiterprobleme*, edited by W. Schottky (Friedrick Vieweg und Sohn, Braunschweig, 1954), Chap. 5; C. Goldberg, Phys. Rev. **88**, 920 (1952); F. A. Kroger and H. J. Vink, Physica **20**, 950 (1954); C. S. Fuller and H. Reiss, Phys. Rev. **99**, 624(A) (1955).

[2] H. Reiss, J. Chem. Phys. **21**, 1209 (1953).

[3] H. Reiss and C. S. Fuller, J. Metals (to be published).

[4] E. A. Guggenheim, *Mixtures* (Oxford University Press, Oxford, 1952).