ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE
University of Brussels, Brussels, Belgium

VOLUME XI

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EDITORIAL BOARD

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INTRODUCTION

In the last decades, chemical physics has attracted an ever-increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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PART I

EQUILIBRIUM STATISTICAL MECHANICS

STATISTICAL MECHANICS OF POINT-DEFECT INTERACTIONS IN SOLIDS

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I. INTRODUCTION

This article is concerned with the statistical mechanics of interactions between point defects in solids at thermodynamic equilibrium. The review is made entirely from the point of view of the cluster formalism recently presented.[3,4] Although cluster methods are very familiar in the theory of classical gases and dense fluids they have had hardly any impact on the statistical mechanics of defects. This seems a pity because the formalism allows a very concise development and also allows one to take full advantage of certain developments in the theory of fluids.

The remainder of Section I is devoted to a rather brief review of earlier work in the field in order to gain a little perspective. In Sections II to IV the basic results of the cluster method are derived. In Section V a very brief account of the application of the formal equations to some systems with short-range forces is given. Section VI is devoted to a review of the application to systems with Coulomb forces between defects, where the cluster formalism is particularly advantageous for bringing the discussion to the level of modern ionic-solution theory.[25] Finally, in Section VII a brief account is given of Mayer's formalism for lattice defects[59] since it is in certain respects complementary to that principally discussed here. We would like to emphasize that the material in Sections V and VI is illustrative of the method. This is not meant to be an exhaustive review of results obtainable.

The notion of point defects in an otherwise perfect crystal dates from the classical papers by Frenkel[22] and by Schottky and Wagner.[75,85] The perfect lattice is thermodynamically unstable with respect to a lattice in which a certain number of atoms are removed from normal lattice sites to the surface (vacancy disorder) or in which a certain number of atoms are transferred from the surface to interstitial positions inside the crystal (interstitial disorder). These forms of disorder can occur in many elemental solids and compounds. The formation of equal numbers of vacant lattice sites in both M and X sublattices of a compound M_aX_b is called Schottky disorder. In compounds in which M and X occupy different sublattices in the perfect crystal there is also the possibility of antistructure disorder in which small numbers of M and X atoms are interchanged. These three sorts of disorder can be combined to give three hybrid types of disorder in crystalline compounds. The most important of these is Frenkel disorder, in which equal numbers of vacancies and interstitials of the same kind of atom are formed in a compound. The possibility of Schottky–antistructure disorder (in which a vacancy is formed by transferring an atom from its own sublattice to an additional site on a "wrong" sublattice) and of interstitial–antistructure disorder (involving interstitial atoms of one sort and misplaced atoms of the other sort) was pointed out much later by Kröger,[42] but so far only the former has been observed.[41] In actual systems the types of disorder described may occur simultaneously. For example, it has been suggested that both Schottky and cationic Frenkel disorder occur in silver bromide.[41] The units which make up the various types of disorder, namely interstitial atoms, misplaced atoms, vacant lattice sites, are referred to as point defects. It is also convenient to include impurity atoms under this term.

The papers of Wagner and Schottky contained the first statistical treatment of defect-containing crystals. The point defects were assumed to form an "ideal solution" in the sense that they are supposed not to interact with each other. The equilibrium number of intrinsic point defects was found by minimizing the Gibbs free energy with respect to the numbers of defects at constant pressure, temperature, and chemical composition. The equilibrium between the crystal of a binary compound and its components was recognized to be a statistical one instead of being uniquely fixed.

One of the first detailed applications of these ideas was to the interpretation of ionic conductivity in simple ionic crystals. The vacancies in strongly ionic solids (e.g. alkali halides, silver halides, alkaline earth oxides) are ionic vacancies, i.e. they carry effective electrical charges equal and opposite to those of the missing ions. Similarly, an interstitial ion has an effective charge equal to the charge on the ion. Since the bulk of the crystal is electrically neutral it follows that in a pure uni-univalent stoichiometric crystal the numbers of oppositely charged defects must be equal. Since antistructure disorder is clearly unlikely, either Schottky or Frenkel disorder, or both, are the most probable forms of disorder in an ionic crystal, and ionic conduction can occur through the migration of the defects. An important method of distinguishing between the two possibilities and also of finding the number and mobility of the defects was devised by Koch and Wagner[39] and makes use of conductivity measurements on both the pure crystal and crystals containing small, controlled amounts of divalent cations. Provided these impurities are incorporated substitutionally in the crystal a vacancy must be added for every impurity ion to maintain electrical neutrality, and hence the number of additional vacancies is known. In this way alkali halide crystals have been shown to contain Schottky defects and AgBr and AgCl predominantly cationic Frenkel defects. More recently, the dynamics of the defects has been studied by a wide variety of techniques including dielectric loss,[50] nuclear magnetic resonance,[72] and paramagnetic resonance.[86] Recent work, principally diffusion and conductivity studies, has been reviewed by Lidiard.[53] The defects also make contributions to the equilibrium thermodynamic properties, but for ionic crystals these contributions are so small that it is only in relatively recent years that these contributions have been measured in favourable cases (e.g. the specific heat,[15] thermal expansion,[88] and adiabatic compressibility[82] of silver bromide. In this substance the site fraction of cation vacancies may be as high as 10^{-2} at the melting point. The degree of disorder appears to be smaller than this for most simple ionic solids, e.g. approximately 10^{-4} for sodium chloride at the melting point).

Since ionic vacancies are electrically charged they may trap electrons or holes into localized states. For example, KCl which has been heated in potassium vapour contains an excess of anion vacancies and these trap the electrons from the potassium ions to give *F*-centres. In the period following the Schottky–Wagner papers extensive studies of the formation and properties of such colour centres were commenced (see e.g. Mott and Gurney[66]). The Schottky–Wagner ideas also gave a background for the consideration of nonstoichiometry in a wide range of other solids. For example, $Fe_{1-x}O$ and $Fe_{1-x}S$ were found to contain cation vacancies but apparently perfect anion sublattices.[38] Studies were also made of titanium oxides and chalcogenides, the palladium hydride system, and various transition metal oxides and sulphides and selenides. More recently, extensive studies of point defects have been made in other materials, particularly metals[46] and semiconductors,[74] by diffusion studies and many other techniques.

The observations on defect-containing crystals show that they fall broadly into two groups. In the first group the deviations from the perfect crystal structure are detectable but very small. Examples are the intrinsic lattice disorder occurring in metals, in simple ionic conducting solids such as NaCl, AgBr noted above, and in ionic semiconductors such as PbS_{1-x}, ZnO_{1-x}, and F-centres in alkali halides. The second group comprises compounds which show gross deviations from stoichiometry, e.g. $Fe_{0.84}O$, the palladium hydride system, and very many other hydrides, oxides, and chalcogenides of transition metals. Anderson[7] has recently reviewed some of the characteristics of this group (see also the other papers in this book), in which a high proportion of the defects must be adjacent to each other or in small clusters of defects. The systems we have in mind in the present discussion belong primarily to the first group. However in Section VII we review briefly a method which should prove valuable for systems with larger deviations from stoichiometry, although detailed calculations are so far lacking.

Results of the "ideal solution" approach were found to be identical with those arrived at on the basis of a simple quasi-chemical method. Each defect and the various species occupying normal lattice positions may be considered as a separate species to which is assigned a "chemical potential", $\bar{\mu}$, and at equilibrium these are related through a set of stoichiometric equations corresponding to the "chemical reactions" which form the defects. For example, for Frenkel disorder the equation will be

$$\bar{\mu}_i + \bar{\mu}_v = \bar{\mu}_l \qquad (1)$$

corresponding to the reaction:

$$\begin{matrix}\text{Interstitial} \\ \text{atom}\end{matrix} + \begin{matrix}\text{Vacant lattice} \\ \text{site}\end{matrix} = \begin{matrix}\text{Atom in normal} \\ \text{lattice site}\end{matrix}$$

The quantities $\bar{\mu}$ are not Gibbs chemical potentials since their definition involves the defect composition of the crystal. We shall call them defect chemical potentials and they are defined by the relation

$$\bar{\mu}_s = \left(\frac{\partial G}{\partial N_s}\right)_{T,P,N_r \neq N_s} \qquad (2)$$

where G is the Gibbs free energy of the crystal. From the "ideal solution" expression for G the chemical potentials are quickly found; for a small degree of Frenkel disorder we have

$$\begin{aligned} \bar{\mu}_i &= g_i + kT \log c_i + \mu_l^0 \\ \bar{\mu}_v &= g_v + kT \log c_v \\ \bar{\mu}_l &\simeq \mu_l^0 \end{aligned} \tag{3}$$

and Eq. (1) yields at once

$$c_i c_v = K = \exp\left[-(g_i + g_v)/kT\right] \tag{4}$$

In these equations g_v is the change in Gibbs free energy on taking one atom from a normal lattice site to the surface of the crystal and $(g_i + g_v)$ the change when an atom is taken from a normal lattice site to an interstitial site, both at constant temperature and pressure. c_r denotes a site fraction of species r on its sublattice, and μ_l^0 is the chemical potential of a normal lattice ion in the defect-free crystal.

The quasi-chemical method, namely the use of a set of reaction equations and corresponding equilibrium constants analogous to Eqs. (1) and (4), is the most widely used approach to defect properties and is presented in detail in the book by Kröger.[41] (We should note that there is a degree of arbitrariness in writing the reaction equations and defining a set of defect chemical potentials. This point is fully discussed by Kröger, sections 7.8 and 22.13. The definition above corresponds to assigning chemical potentials to what he calls "structure elements".) The corresponding defect chemical potentials are of value in discussions of matter transport via defects using the methods of irreversible thermodynamics.[6,37]

In the interpretation of many experiments, both equilibrium and non-equilibrium, it becomes necessary to recognize that defects interact so that their relative distribution is no longer random. For example, in the interpretation of thermal expansion measurements on aluminium[79] it is necessary to recognize the possibility of divacancies (two vacancies on adjacent lattice sites). The quasi-chemical method is then extended, the equilibrium between the species divacancy and vacancy being described by an additional mass-action equation and a certain binding energy, and the divacancy can be assigned a defect chemical potential as a separate species. Trivacancies or higher aggregates each characterized by further equilibria may exist. The quasi-chemical method is thus quite simply extended to compound defects such as nearest-neighbour aggregates or vacancies trapped as neighbours to solute atoms. In ionic crystals where the defect interactions are Coulombic except at small separations, the interactions are of long range and relatively important in their effect on defect-controlled properties. The interactions of divalent cations and cation vacancies in a sodium-chloride-like crystal are of particular interest in connection with the Koch and Wagner type of experiment described above. The extension of the quasi-chemical method is somewhat less straightforward in this case. Lidiard[61] has treated the thermodynamics of such a system by distinguishing between neutral "complexes", composed of a vacancy and an impurity ion on adjacent sites and characterized by a binding energy, and the interactions among defects not involved in complexes. The contribution of the latter interactions to the total free energy of the system was calculated by applying the results of the Debye–Hückel theory of electrolyte solutions. The effect of these interactions on the equilibrium could then be found. The use of this sort of theory, which is essentially a modification of the Bjerrum[11] theory of electrolyte solutions, and its assumptions will be reviewed in detail in a later section (VI-A). We may note here however that the Debye–Hückel law is only a limiting one and is derived for the case of a continuum rather than for discrete lattice sites. Furthermore it is recognized that the concept of a "complex" appears to be slightly arbitrary when considered in detail. Although the method is presumably quite adequate at low enough concentrations it is difficult to pin down the conditions under which deviations become important or to develop within the same framework a theory valid at high concentrations. (This particular problem provided one of the strongest motivations for setting up the cluster formalism.)

The preceding paragraphs illustrate that analogies between point defects in a crystal and solute molecules in a solution have been used previously but in a fairly elementary way. However, the implications of the existence of such analogies in the formulation of the statistical mechanics of interacting defects has not been considered in detail apart from an early paper by Mayer,[59] who was interested primarily in the relation of defect interactions to the solid–liquid phase transition in crystals with short-range forces. The formalism described here is analogous in intent to the McMillan–Mayer[64,33] theory of solutions and is suitable for crystals containing small concentrations of defects, up to say one per cent. The contribution of the defect interactions to each thermodynamic function can be expressed as a "cluster expansion", i.e. a power series in the concentration of the defects. The coefficients of the power series are defined in terms of the summations over coordinates of functions analogous to the "f" functions of imperfect gas and solution theory.[33] In particular, the expressions for the defect chemical potentials and the expressions for defect concentrations derived from them are merely changed by the inclusion of activity coefficients for which cluster expansions are available. The use of the law of mass action is thus avoided. Within such a formalism the spatial distribution of defects, previously described in terms of "complexes", divacancies, or higher aggregates using the law of mass action, must be reformulated as the study of the relative distribution functions of the defects. Cluster expansions are derived for these quantities. These quantities prove essential for a systematic development of the phenomenological coefficients in diffusion,[26] although we shall not discuss this here.

II. CONFIGURATIONAL SPECIFICATION OF DEFECT-CONTAINING CRYSTALS

To state clearly the problem at hand it is necessary to introduce initially a detailed notation for the composition of a crystal. For much of the later manipulations it is possible to use a very much simpler, abbreviated version of the notation. From the point of view of thermodynamics, the composition of an imperfect crystal is specified when the number of atoms of each of the different chemical species present is given. Let atoms which appear in a perfect crystal be denoted by a subscript 0, and let $\mathbf{N}_0$ denote the N_0 atoms of σ different species ($N_{01}, N_{02}, \ldots, N_{0\sigma}$), all of which species appear in the perfect crystal, i.e.

$$\mathbf{N}_0 = \sum_{s=1}^{\sigma} N_{0s} \tag{5}$$

Let $\mathbf{N}_a$ denote the set of N_a atoms of ν species ($N_{a1}, N_{a2}, \ldots, N_{a\nu}$), none of which species occurs in a perfect crystal of the material, so that

$$\mathbf{N}_a = \sum_{s=1}^{\nu} N_{as} \tag{6}$$

Then the composition of an imperfect crystal is given thermodynamically by the set of numbers $\mathbf{N} = \mathbf{N}_0 + \mathbf{N}_a$. For each species there is a chemical potential; thus μ_{0s} is the chemical potential for an atom of species $0s$, $\boldsymbol{\mu}_0$ denotes the set of σ such quantities, and similarly for $\boldsymbol{\mu}_a$.

We turn now to the microscopic description of an imperfect crystal. The various defects in any imperfect crystal can be imagined to be formed from a corresponding perfect crystal by one or more of the following processes: (a) remove an atom of species $0s$ from the crystal leaving a vacant lattice site, (b) remove an atom of species $0s$ from the crystal and replace it by an atom of a different species (either $0t$ or at), (c) add to the crystal an atom of any species to a site on a sublattice unoccupied in the perfect crystal. We refer to the latter as atoms in interstitial positions. Let $\mathbf{B}$ be a set of numbers such that B^r is the number of sites on sublattice number r in the perfect crystal, and let ϕ be the number of sublattices in the crystal (including interstitial sublattices not occupied in the perfect crystal). The total number of sites of all kinds in the perfect crystal is then

$$B = \sum_{r=1}^{\phi} B^r \tag{7}$$

Thus atoms of species $0s$ may be found in an imperfect crystal in their normal lattice positions, occupying sites on the "wrong" sublattice (that is a sublattice occupied by an atom of a different species in the perfect crystal), or in interstitial positions. Let the numbers of such atoms be N_{0s}^R, N_{0s}^W, N_{0s}^I, respectively, so that

$$N_{0s} = N_{0s}^R + N_{0s}^W + N_{0s}^I \tag{8}$$

An atom on a wrong sublattice may be classified according to the number of the sublattice it is on (and hence the species of atom it has replaced). Thus, we have

$$N_{0s}^W = \sum_{r=1}^{\theta}{}' N_{0s}^{Wr} \tag{9}$$

where N_{0s}^{Wr} is the number of atoms of species 0*s* which occupy sites on sublattice number *r*, which would be occupied by some other species 0*t* in the perfect crystal. In Eq. (9), the limit of the summation, θ, is the number of occupied sublattices in the perfect crystal. The prime indicates the exclusion from the sum of sublattices occupied by atoms of species 0*s* in the perfect crystal. In a similar manner if N_{0s}^{Ir} is the number of interstitial atoms of species 0*s* which occupy interstitial sites of kind *r*, then

$$N_{0s}^{I} = \sum_{r=1}^{\tau} N_{0s}^{Ir} \tag{10}$$

where τ is the number of kinds of interstitial sites. Similarly we have

$$N_{0s}^{R} = \sum_{r=1}^{\theta}{}' \, N_{0s}^{Rr} \tag{11}$$

where N_{0s}^{Rr} is the number of species 0*s* on "right" lattice sites of type *r*. Here the prime indicates the exclusion of sublattices occupied by atoms of species $0t \neq 0s$ in the perfect crystal. The N_{as} solute atoms of species *as* may occupy interstitial or substitutional positions. If the numbers of such atoms are N_{as}^{I}, N_{as}^{S} respectively then

$$N_{as} = N_{as}^{I} + N_{as}^{S} \tag{12}$$

$$N_{as}^{I} = \sum_{r=1}^{\tau} N_{as}^{Ir} \tag{13}$$

$$N_{as}^{S} = \sum_{r=1}^{\theta} N_{as}^{Sr} \tag{14}$$

where N_{as}^{Ir} is the number of solute atoms of type *as* which occupy interstitial sites of type *r*, and N_{as}^{Sr} is the number of solute atoms of the same kind which are substitutionally incorporated into the crystal replacing an atom on sublattice number *r*. In addition to sites occupied in the various ways already described there may be vacant lattice sites. Let N_{0s}^{Vr} be the number of vacant lattice sites on sublattice number *r* which have been formed by removing an atom of type 0*s* from the perfect crystal.

A notation for the various sets of atoms defined in the last paragraph will now be introduced. Let $\mathbf{N}_0^W$ denote the set of numbers $(N_{01}^{W2}, N_{01}^{W3}, \ldots)$, a typical member of the set being N_{0s}^{Wr}. Similarly, let $\mathbf{N}_0^R$, $\mathbf{N}_0^I$, $\mathbf{N}_a^S$, $\mathbf{N}_a^I$, $\mathbf{N}_0^V$ denote the sets of numbers, typical members of which sets are N_{0s}^{Rr}, N_{0s}^{Ir}, N_{as}^{Sr}, N_{as}^{Ir}, N_{0s}^{Vr} respectively. The six sets of numbers just defined specify the microscopic composition of the lattice completely; their definitions and interrelations are summarized in Fig. 1. It should be noted that it is not necessary to specify the chemical potential of a species in such detail because for a system in equilibrium the chemical potential of a species is the same whatever the site it is occupying. The chemical potential of a vacancy is zero because it is a structural rather than a compositional entity; making a vacancy need not involve transfer of the atom to a reservoir.

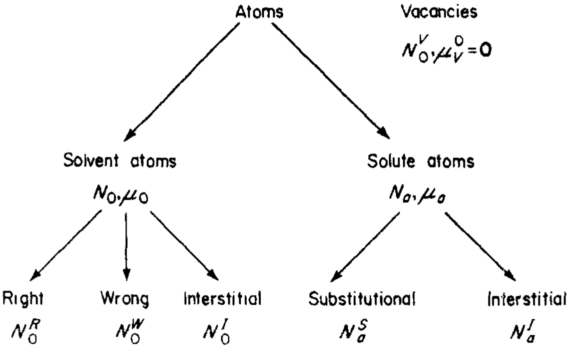

Fig. 1. Summary of the classification of atoms in an imperfect crystal.

Having clearly stated in detail the microscopic composition, we now introduce a simpler, abbreviated notation which is convenient for the subsequent manipulations. The set of numbers $\mathbf{N}_0^R$ may be relabelled to give in their place a set of numbers $\mathbf{N}_1$, a typical member of the set being N_{1s}^r, which is the number of atoms of kind s on sublattice number r. The other five sets of numbers, $\mathbf{N}_0^W$, $\mathbf{N}_0^I$, $\mathbf{N}_a^S$, $\mathbf{N}_a^I$, $\mathbf{N}_0^V$, which specify completely the defect composition of the crystal, will be similarly relabelled to give a set of numbers $\mathbf{N}_2$, a typical member of the set being N_{2s}^r. The number N_{2s}^r is the number of defects of type s, and they are situated on the sublattice number r. (By the definitions employed, one kind of defect can only appear on one sublattice but one sublattice may contain more than one kind of defect. Although r is specified by s, the double labelling of r and s in N_{2s}^r is used because it is convenient to be able to distinguish whether two different kinds of defect occupy the same or different sublattices.) The total number of defects on sublattice r is

$$N_2^r = \sum_{s_r=1}^{\gamma(r)} N_{2s}^r \tag{15}$$

where $\gamma(r)$ is the number of different sorts of defect on sublattice number r. The sum is over the $\gamma(r)$ types of defect s_r on the r sublattice. The microscopic composition of the crystal is completely specified by the set of numbers $(\mathbf{N}_1 + \mathbf{N}_2)$, and $\mathbf{N}_2$ refers solely to the defect composition.

It is convenient to employ the set notation of Meeron[61] with minor modifications suited to the present problem. Thus for a set of defects $\mathbf{N}_2$ of ω kinds we define

$$\mathbf{N}_2! = \prod_{s=1}^{\omega} N_{2s}^r! \tag{16}$$

and for a set of quantities $\mathbf{x}_2$ pertaining to the same set of particles

$$\mathbf{x}_2^{\mathbf{N}_2} = \prod_{s=1}^{\omega} (x_{2s}^r)^{N_{2s}^r} \tag{17}$$

We shall also employ the convenient notation

$$\mathbf{N}_2 \cdot \mathbf{x}_2 = \sum_{s=1}^{\omega} N_{2s}^r x_{2s}^r \tag{18}$$

For a crystal of ϕ sublattices we define

$$(\mathbf{N}_2!)^* = \prod_{r=1}^{\phi} N_2^r! \tag{19}$$

where N_2^r is defined by Eq. (15). Similarly we use the notation

$$(\mathbf{B}^{\mathbf{N}_2})^* = \prod_{r=1}^{\phi} (B^r)^{N_2^r} \tag{20}$$

We use the symbol $\{\mathbf{N}_2\}$ to denote a configuration of $\mathbf{N}_2$ defects, that is a particular assignment of the set of $\mathbf{N}_2$ defects, all distinguishable, to the lattice sites of the crystal, the latter being all labelled and distinguishable. Although the notation above is rather different from that generally employed in discussions of defects it will be found to have great advantages in developing the statistical mechanics.

After these preliminaries we can now set up the partition function for a canonical ensemble of systems of composition $\mathbf{N} = \mathbf{N}_0 + \mathbf{N}_a$ in volume V at temperature T. It is

$$Q(\mathbf{N}, V, T, \mathbf{N}_2) = \sum_{\{\mathbf{N}_2\}} \sum_i \exp [- E_i(\mathbf{N}, V, \{\mathbf{N}_2\})/kT]/\mathbf{N}_2! \quad (21)$$

In the equation $E_i(\mathbf{N}, V, \{\mathbf{N}_2\})$ is one (number i) of a complete set of energy eigenvalues for a crystal of composition $\mathbf{N}$ and volume V in which $\mathbf{N}_2$ defects are in a specified configuration denoted by $\{\mathbf{N}_2\}$. (Implicit in this labelling of quantum states is the assumption that the kinetic energy associated with defect diffusion is negligible, as discussed below.) The summations are over all the eigenstates for a given configuration of defects and over all possible configurations of defects for the given composition and defect constitution $\mathbf{N}_2$. The factor $\mathbf{N}_2!$ arises because in specifying the configuration of defects we have treated defects of the same kind as distinguishable. The justification for the preceding equation may be found by considering briefly the application of the Born–Oppenheimer approximation to the crystal.

The Schrödinger equation for the system is

$$[T_N + T_E + V(\mathbf{r}, \mathbf{R})]\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \quad (22)$$

Here T_N and T_E are the kinetic energy operators for the nuclei and electrons respectively, and $V(\mathbf{r}, \mathbf{R})$ is the total Coulombic energy of nuclei and electrons. $\mathbf{r}$ and $\mathbf{R}$ denote the sets of coordinates of the electrons and nuclei respectively. One seeks wave functions of the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi(\mathbf{R}, \mathbf{r})\chi(\mathbf{R}) \quad (23)$$

The function Φ is determined approximately for a fixed set of $\mathbf{R}$ from the equation

$$[T_E + V(\mathbf{r}, \mathbf{R})]\Phi = U(\mathbf{R})\Phi \quad (24)$$

The eigenvalues of this equation have local minima, each one for some particular value of the coordinates $\mathbf{R}_0$, and U may be expanded about its value at the local minimum

$$U(\mathbf{R}) = U_0 + (\mathbf{R} - \mathbf{R}_0) \cdot \nabla U_0 + \tfrac{1}{2}[(\mathbf{R} - \mathbf{R}_0) \cdot \nabla]^2 U_0 + \cdots \tag{25}$$

The value of U for each local minimum is used to set up an equation for the nuclear motion

$$[T_N + U]\chi = E\chi \tag{26}$$

which determines the function $\chi(\mathbf{R})$ and a set of eigenvalues E_i. Equation (26) can be deduced by substitution of Eq. (23) in Eq. (22) neglecting the terms

$$\chi T_N \Phi + \sum_a \mathbf{p}_a \chi \cdot \mathbf{p}_a \Phi / 2m_a \tag{27}$$

and then multiplying by Φ^* and integrating over the electron coordinates. In Eq. (27) $\mathbf{p}_a$ is the momentum operator for nucleus a whose mass is m_a. Under the conditions that the Born–Oppenheimer approximation converges, the neglected terms can be treated as a small perturbation. Even if the convergence is poor, the classifying of states by means of local minima in U plus index i remains. If we neglect the contribution of diffusive motion to the energy of the system then the eigenenergy E_i is accurately the total energy of the system and is indeed a function of the configuration of the defects $\{\mathbf{N}_2\}$ (which is equivalent to the set of minimal positions $\mathbf{R}_0$) in the crystal of given composition and volume in the manner indicated in Eq. (21). Furthermore, the sum over states is the sum over the complete set of eigenvalues for a given configuration $\{\mathbf{N}_2\}$ (that is, for a given local minimum in $U(\mathbf{R})$), followed by a sum over all configurations $\{\mathbf{N}_2\}$ (that is, a sum over all local minima $U(\mathbf{R})$ for a crystal of defect composition $\mathbf{N}_2$). The complete expression for the partition function would of course contain a summation over all defect compositions $\mathbf{N}_2$ consistent with the given $\mathbf{N}$, V, T. We have retained in Eq. (21) only the eigenstates corresponding to the value of $\mathbf{N}_2$ found by minimizing the Helmholtz free energy $-kT \log Q(\mathbf{N}, V, T)$ at constant $\mathbf{N}$, V, T with respect to the set $\mathbf{N}_2$. The summation over eigenstates for a given configuration appearing in Eq. (23) can be written as

$$\sum_i \exp[-E_i(\mathbf{N}, V, \{\mathbf{N}_2\})/kT] = \exp[-F(\mathbf{N}, V, T;\ \{\mathbf{N}_2\})/kT] \tag{28}$$

where $F(\mathbf{N}, V, T;\ \{\mathbf{N}_2\})$ is a Helmholtz free energy. The free energy may be written in the form

$$F(\mathbf{N}, V, T;\ \{\mathbf{N}_2\}) = F_0(\mathbf{N}) + F(\mathbf{N}_2\!:\!\mathbf{N}) + F(\{\mathbf{N}_2\}) \tag{29}$$

Here $F_0(\mathbf{N})$ is the Helmholtz free energy for the perfect crystal from which the imperfect crystal of composition $\mathbf{N}$ can be imagined formed in the manner described in the second paragraph of this section. $F(\mathbf{N}_2\!:\!\mathbf{N})$ is the part of the Helmholtz free energy of the crystal of composition $\mathbf{N}$ containing $\mathbf{N}_2$ defects which is independent of the configuration of the defects, but dependent on the defect composition. $F(\{\mathbf{N}_2\})$ is the configuration-dependent part of the free energy. (All three quantities on the right-hand side of Eq. (29) are of course functions of V and T.) The expression for the partition function can be written in the required form, using Eqs. (28) and (29), as the product

$$Q(\mathbf{N}, V, T;\ \{\mathbf{N}_2\}) = Q_0 Q_c \tag{30}$$

where Q_0 is independent of defect configuration, and Q_c depends on the configuration of the defects.

$$Q_0 = \exp\left[-\,(F_0(\mathbf{N}) + F(\mathbf{N}_2\!:\!\mathbf{N}))/kT\right] \tag{31}$$

$$Q_c = \sum_{\{\mathbf{N}_2\}}{}' (\exp\left[-F(\{\mathbf{N}_2\})/kT\right])/\mathbf{N}_2! \tag{32}$$

The summation is over all possible configurations of the defects, each defect being allowed to occupy any site on its particular sublattice subject to the restriction indicated by the prime that no two defects can occupy the same site. It is convenient to refer to this condition as the excluded site property.

It will be assumed that the free energy of interaction can be expanded as a sum of component potentials

$$\begin{aligned} F(\{\mathbf{N}_2\}) = \sum_{i,j \subset \mathbf{N}_2} F_{ij}^{(2)}(\{i, j\}) + \sum_{i,j,k \subset \mathbf{N}_2} F_{ijk}^{(3)}(\{i, j, k\}) \\ + \ldots F_{N_2}^{(N_2)}(\{\mathbf{N}_2\}) \end{aligned} \tag{33}$$

The first sum is over all pairs i, j of the set $\mathbf{N}_2$, and similar definitions apply to higher terms. The retention of higher order than pair interactions is essential for the problem at hand, but the cluster method is only of value if the terms decrease fairly rapidly in magnitude, $F^{(N_2)}$ being negligible for large N_2.

The defect interaction energies appearing in Eq. (33) are, for the purposes of the present article, assumed to be known either from theory or experiment. Certain other quantities appear in the final expressions for the thermodynamic functions and must therefore be known. The quantity defined by the relation

$$F_{0is}^{r} = \left(\frac{\partial F_0(\mathbf{N})}{\partial N_{is}^{r}}\right)_{T,V,N_{ju}^{t} \neq N_{is}^{r}} \quad (i = 1,\, 2) \tag{34}$$

is equal to the chemical potential (in the pure crystal) of the atom which would occupy in the perfect crystal the site occupied by species *is* on sublattice *r* in the imperfect crystal. (It is zero for interstitial defects since, by definition, these sites are unoccupied in the perfect crystal.) We also require the defect formation energies defined by the relation

$$F_{2s}^{r} = F_{02s}^{r} + \left(\frac{\partial F(\mathbf{N}_2 : \mathbf{N})}{\partial N_{2s}^{r}}\right)_{T,V,N_{2u}^{t} \neq N_{2s}^{r}} \tag{35}$$

The second term on the right hand of this equation has a simple meaning for each defect. For example, for a vacancy it is the change in Helmholtz free energy on forming the vacancy by transporting an atom from the site to infinite distance from the crystal at constant temperature and volume apart from the contribution from defect interactions. For other defects it is the change in free energy under the same conditions when the atom (if any) which occupies the site in the perfect crystal is removed from the crystal and replaced by the defect atom. It would be logical to review at this point the calculation of the defect formation energies for systems with small concentrations of point defects. However, the recent review by Howard and Lidiard includes just such an account.[37] We shall merely note here that adequate calculations of three-defect or higher-order interactions have not so far been made for even the simplest solids nor are they available with any certainty from experiment, although they may sometimes be important as will be noted in examples below. A comprehensive account of the defect interaction energies from both experiment and theory can be found in Kröger's book.[41]