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CORRELATION IN SOLID SOLUTIONS

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A method is proposed for describing the non-equilibrium states of solid solutions which is based on the furnishing of a system of correlation functions for the dissolved atoms. A method of determining the free energy of solid solutions in states of total or partial equilibrium is also proposed. In the general case, the free energy is expressed in terms of a double, triple, etc., "interaction" of impurity atoms, which are assumed known. For isotopic mixtures, the "vibrational interaction" energy is determined in closed form and the entire problem can be carried through to its conclusion. The correlation functions obtained for the dissolved atoms are determined with the aid of the expressions thus constructed. The effect of correlation on the scattering of neutrons by isotope solutions is ascertained

INTRODUCTION

THE thermodynamic properties of solid solutions can be investigated by means of methods which are to a certain degree similar to the methods developed in the theory of non-ideal gases. In such a case, use is made of the concept of the "interaction" of impurity atoms. By the "interaction" of n atoms of an impurity we mean the difference between the free energy of a system with n impurity atoms, located at some distance from one another, and the same quantity for impurity atoms that are infinitely far apart. It is obvious that these interactions are rapidly decreasing functions of the distances between the atoms.

The determination of such a type of interaction is separate problem. In the case of solutions of atoms which differ markedly from one another, the principal part of the energy of interaction is its static part. (In this case, usually, only the interaction of nearest neighbors is taken into account.) If the potential energy of the interaction does not depend on the type of atoms (isotope solutions), the vibrational part of the interaction plays the chief role. Its determination can be brought about by means of the method developed earlier.[1]

Considering the interaction as given, we have succeeded in obtaining a general expression for the equilibrium free energy of the solution.

Prescription of the non-equilibrium states is obtained through the use of a system of correlation functions which determine the probabilities relative to the location of the dissolved atoms. To date, so far as we know, there exists no such method for the description of the non-equilibrium states. The method developed here permits us to compute the free energy of the solution in a state of partial equilibrium.

As an example, we have obtained an explicit expression for the non-equilibrium free energy for the case in which the lack of equilibrium arises as the result of the quenching of the solution from the temperature Θ' to the temperature Θ.

The correlation functions of the impurity atoms are obtained with the help of expressions computed for the free energy. For isotope solutions, the energy for the vibrational interaction of which is computed in closed form, the determination of the correlation can be carried through to its conclusion.

We begin with the calculation of the equilibrium values of the free energy of the solution.

1. EQUILIBRIUM FREE ENERGY

The equilibrium free energy is given, as is well known, by the expression

$$F - = -\Theta \ln Z; \quad Z = \sum_{\mathfrak{M}} \sum_{E_\alpha(\mathfrak{M})} \exp\left\{-\frac{E_\alpha(\mathfrak{M})}{\Theta}\right\} = \sum_{\mathfrak{M}} \exp\left\{-\frac{F(\mathfrak{M})}{\Theta}\right\}. \qquad (1)$$

Here $\Theta = kT$, k = Boltzmann's constant, T = temperature $\mathfrak{M}$ = configuration of the impurity atoms, $E_\alpha(\mathfrak{M})$ is the energy level of the system for a given configuration, $F(\mathfrak{M})$ is the free energy of the solution for the given configuration. For n impurity atoms, the function $F(\mathfrak{M})$ can be expressed in the form

$$F(\mathfrak{M}) = F_0 + n\psi_1 + U_n(\mathfrak{M}), \quad U_n(\mathfrak{M}) = \psi_n(\mathfrak{M}) - n\psi_1. \tag{2}$$

F_0 is the free energy of the pure solvent ψ_1 is the change in the free energy upon the substitution of a single atom of impurity for an atom of solvent, $\psi_n(\mathfrak{M})$ is the change in the free energy upon replacing n atoms, $U_n(\mathfrak{M}) = U_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ is the free energy of interaction of n impurity atoms located at the sites $\mathbf{r}_1, \ldots, \mathbf{r}_n$. In the case of a simple lattice, where the interaction of the particles depends only on the mutual distance between them, U_n is completely determined by the position of $n-1$ particles relative to a single individual $[U_2 = U_2(\mathbf{r}_2 - \mathbf{r}_1)$, $U_3 = U_3(\mathbf{r}_2 - \mathbf{r}_1, \mathbf{r}_3 - \mathbf{r}_1)$ etc.]. It is evident that only the last term depends on the configuration in (2). According to (1) and (2), we have for the free energy of the solution in the case of dissolved atoms:

$$F = F_0 + n\psi_1 + N\Theta\,[c\ln c + (1-c)\ln(1-c)] - N\Theta\Phi_n, \quad \Phi_n = \Phi(c) = \frac{1}{N}\ln\overline{e^{-U_n/\Theta}}, \tag{3}$$

$$\overline{e^{-U_n/\Theta}} = 1 + \Delta_n, \quad \Delta_n = \frac{1}{\mathfrak{N}}\sum_{\mathfrak{M}}\left(\exp\left\{-\frac{U_n(\mathfrak{M})}{\Theta}\right\} - 1\right). \tag{4}$$

Here N is the total number of particles in the system, $c = n/N$, $\mathfrak{N} = N!/(N-n)!\,n!$ is the total number of configurations: Φ_n, as a function of the concentration c, does not have any singularities and can be represented in the form of a series in powers of c. In this case, we make use of the asymptotic relation (valid for $N \to \infty$)

$$\Phi_n = e^{c\hat{Q}}\,\Phi_k\,|_{k=0}, \tag{5}$$

where $\hat{Q}$ is the difference operator, analogous to the operator of differentiation with respect to the concentration. If $\hat{T}$ is the operator which changes the number of impurity atoms by unity, then

$$\hat{Q} = N(\hat{T} - 1). \tag{6}$$

(The change in the concentration upon the addition of one particle is equal to 1/N.) Equation (5) represents the discrete analogue of the formula for a function of continuous parameters

$$f(x + c) = e^{c\partial/\partial x} f(x)$$

and is obtained from it by replacing the operator $\partial/\partial x$ by the operator $\hat{Q}$. With accuracy up to terms proportional to c^3, the expression takes the form

$$\Phi_n = \left[N^2\frac{c^2}{2}\hat{T}^2 + N^3\frac{c^3}{3!}(\hat{T}^3 - 3\hat{T}^2)\right]\Phi_k\,|_{k=0}. \tag{7}$$

(Application of the unity operator and the operator $\hat{T}$ to $\Phi_k|_{k=0}$ yields zero, since $\Phi_0 = \Phi_1 = 0$.) Thus, we get*

$$\Phi_n = N^2\frac{c^2}{2}\ln(1+\Delta_2) + N^3\frac{c^3}{3!}[\ln(1+\Delta_3) - 3\ln(1+\Delta_2)], \tag{8}$$

$$\Delta_2 = \frac{1}{N}\sum_{\mathbf{r}}\left(\exp\left\{-\frac{U_2(\mathbf{r})}{\Theta}\right\} - 1\right), \quad \Delta_3 = \frac{1}{N(N-1)}\sum_{\mathbf{r},\mathbf{r}'}\left(\exp\left\{-\frac{U_3(\mathbf{r},\mathbf{r}')}{\Theta}\right\} - 1\right). \tag{9}$$

Here and below, the terms with $\mathbf{r} = 0$, $\mathbf{r}' = 0$, $\mathbf{r} = \mathbf{r}'$, etc. are excluded from the summation over $\mathbf{r}$ and $\mathbf{r}'$. Inasmuch as Δ_2 and Δ_3 are quantities of the order of 1/N, we can carry out a logarithmic expansion in (8). We note that in each successive term of (8) the expansion ought to be carried out with greater accuracy. For example, in the component $\sim c^2$ in the logarithmic expansion, it suffices to limit ourselves to the term of first order of smallness; in the component $\sim c^3$, the expansion ought to be carried out up to terms of order $1/N^2$. This circumstance is determined by the fact that in the expression

$$\ln(1+\Delta_3) - 3\ln(1+\Delta_2)$$

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*For simplicity here and in what follows (with the exception of Sec. 3) it is assumed that the lattice is simple. Generalization to the case of a complicated lattice presents no special difficulties.

the terms of first order of smallness vanish. Carrying through the expansion, we get

$$\Phi_n = \Phi(c) = \frac{c^2}{2} f_2 + \frac{c^3}{3!}(f_3 - 3f_2^2), \tag{10}$$

where

$$f_2 = \sum_{\mathbf{r}} \left(\exp\left\{ -\frac{U_2(\mathbf{r})}{\Theta} \right\} - 1 \right), \quad f_3 = \sum_{\mathbf{r},\mathbf{r}'} \left(\exp\left\{ -\frac{U_3(\mathbf{r},\mathbf{r}')}{\Theta} \right\} - 3\exp\left\{ -\frac{U_2(\mathbf{r})}{\Theta} \right\} + 2 \right). \tag{11}$$

The equilibrium free energy of the solution is equal to

$$F = F_0 + Nc\psi_1 + N\Theta\,[c\ln c + (1-c)\ln(1-c)] - N\Theta\left[\frac{c^2}{2} f_2 + \frac{c^3}{3!}(f_3 - 3f_2^2) \right]. \tag{12}$$

with the same accuracy. Thus the free energy of a solution is a functional of the interaction of two, three, etc., impurity atoms. Here the terms proportional to c^k are determined only by interactions of no more than k particles.

We can also represent the free energy in the form of a functional of pair interactions φ_2 and "polarization corrections" of third, fourth, etc., orders φ_k. It suffices here to make use of the relation

$$U_n(\mathbf{r}_1, \ldots, \mathbf{r}\ ) = \frac{1}{2}\sum_{i \neq k} \varphi_2(\mathbf{r}_i - \mathbf{r}_k) + \frac{1}{3!}\sum_{i \neq k \neq l} \varphi_3(\mathbf{r}_i - \mathbf{r}_l, \mathbf{r}_k - \mathbf{r}_l) + \ldots + \varphi_n(\mathbf{r}_2 - \mathbf{r}_1, \ldots, \mathbf{r}_n - \mathbf{r}_1). \tag{13}$$

Each of the $\mathbf{r}$ in the sums here run over all values of the radius vectors of the impurity atoms $(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ which are present for the given configuration. In particular, we have the relation

$$U_2(\mathbf{r}) = \varphi_2(\mathbf{r}), \; U_3(\mathbf{r}, \mathbf{r}') = \varphi_2(\mathbf{r}) + \varphi_2(\mathbf{r}') + \varphi_2(\mathbf{r} - \mathbf{r}') + \varphi_3(\mathbf{r}, \mathbf{r}'),$$

and conversely,

$$\varphi_2(\mathbf{r}) = U_2(\mathbf{r}), \; \varphi_3(\mathbf{r}, \mathbf{r}') = U_3(\mathbf{r}, \mathbf{r}') - U_2(\mathbf{r}) - U_2(\mathbf{r}') - U_2(\mathbf{r} - \mathbf{r}').$$

From the expression we have obtained for the free energy of solution, it is easy to determine the chemical potentials μ of the solvent and μ' of the dissolved material:

$$\begin{aligned} \mu &= \mu_0 + \Theta\ln(1-c) + \Theta\left[\frac{c^2}{2} f_2 + \frac{c^3}{3}(f_3 - 3f_2^2) \right], \\ \mu' &= \mu_0 + \psi_1 + \Theta\ln c - \Theta\left[cf_2 + \frac{c^2}{2}(f_3 - 3f_2^2 - f_2) - \frac{c^3}{3}(f_3 - 3f_2^2) \right]. \end{aligned} \tag{14}$$

Here μ_0 is the chemical potential of the pure solvent.

2. NON-EQUILIBRIUM STATES OF SOLID SOLUTIONS. CALCULATION OF THE FREE ENERGY, ENTROPY, AND CORRELATION FUNCTIONS

Keeping in mind the determination of the correlation functions, we compute the free energy of the solution in a state of particle equilibrium. The computation of such a quantity is of independent interest, inasmuch as the configuration of solid solutions is usually not an equilibrium one (because of the slowness of processes of rearrangement of the atoms).

First, it is necessary to establish the method of description of the macroscopic non-equilibrium states of solid solutions. As is shown, the most complete description of such a state can be obtained by giving the collection of correlation functions W_k connected with the probabilities $P(\mathbf{r}_1, \ldots, \mathbf{r}_k)$ of locating k foreign atoms at the sites $\mathbf{r}_1, \ldots, \mathbf{r}_k$ by the relations

$$P(\mathbf{r}_1, \ldots, \mathbf{r}_k) = c^k W_k(\mathbf{r}_2 - \mathbf{r}_1, \ldots, \mathbf{r}_k - \mathbf{r}_1). \tag{15}$$

In practice, it suffices to give the first few W_k (i.e., k = 2, 3, 4). This follows from the fact that the functions $\varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})$ in (18) rapidly fall off with the distances $\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}$ as well as with the number k.

The free energy of a non-equilibrium solution is determined in this case by the expression

$$F\{W\} = -\Theta \sum_{\mathfrak{M}\{W\}} \exp\left\{-\frac{F(\mathfrak{M})}{\Theta}\right\}, \tag{16}$$

where the summation runs only over the configurations which correspond to the given values of W. If $M_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})$ denotes the number of groups of k impurity atoms with distances $\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}$ between them, then, by Eq. (15), we have

$$M_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}) = Nc^k W_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}). \tag{17}$$

On the other hand, for an arbitrary configuration, the free energy is equal to

$$\begin{aligned} F(\mathfrak{M}) &= F_0 + Nc\psi_1 + \sum_k \frac{1}{k!} \sum_{\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}} M_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})\, \varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}) \\ &= F_0 + Nc\psi_1 + N\sum_k \frac{c^k}{k!} \sum_{\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}} W_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})\, \varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}). \end{aligned} \tag{18}$$

Here $\varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})$ is the pair interaction (k = 2) and the polarization correction (k = 2) determined above. This signifies that the F ($\mathfrak{M}$) are the same for all configurations corresponding to the same values of W. Therefore, we have

$$F(W) = F_0 + Nc\psi_1 + N\sum_k \frac{c^k}{k!} \sum_{\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}} W_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})\, \varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}) - \Theta\sigma\{W\}. \tag{19}$$

Here $\sigma\{W\} = -\ln \mathfrak{N}\{W\}$ is the configurational part of the entropy as a functional of the correlation functions, and $\mathfrak{N}\{W\}$ is the number of admissible configurations.

For equilibrium values of the correlation functions $\tilde{W}_k$, the free energy acquires the value

$$F = F_0 + Nc\psi_1 + N\sum_k \frac{c^k}{k!} \sum_{\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}} \tilde{W}_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1})\, \varphi_k(\mathbf{r}_1, \ldots, \mathbf{r}_{k-1}) - \Theta\sigma\{\tilde{W}\}, \tag{20}$$

which, on the other hand, is determined by Eqs. (11) and (12). Inasmuch as the free energy is a minimum for the equilibrium values of $\tilde{W}$, the relation

$$N\frac{c^k}{k!}\varphi_k - \Theta\delta\sigma\{\tilde{W}\}/\delta\tilde{W}_k = 0, \tag{21}$$

holds, where the functional derivative appears in the second term. Taking (21) into account, it is easy to see that $\tilde{W}_k$ and $\sigma\{\tilde{W}\}$ are determined from the equilibrium energy by means of the relations

$$N\frac{c^k}{k!}\tilde{W}_k = \delta F/\delta\varphi_k|_\Theta, \tag{22}$$

$$\sigma\{W\} = -\partial F/\partial\Theta|_{F_0,\, \psi_1,\, \varphi_k}. \tag{23}$$

Equations (22) and (23) determine the equilibrium correlations and the configurational part of the entropy of solution in terms of the function φ_k.

If we use Eq. (12) for F, then we get

$$\tilde{W}_2(\mathbf{r}) = e^{-\varphi_2(\mathbf{r})/\Theta} + c\sum_{\mathbf{r}'}\left(e^{-U_3(\mathbf{r}, \mathbf{r}')/\Theta} - 2e^{-[\varphi_2(\mathbf{r}) + \varphi_2(\mathbf{r}')]/\Theta} + e^{-\varphi_2(\mathbf{r})/\Theta}\right). \tag{22a}$$

$$\tilde{W}_3(\mathbf{r}, \mathbf{r}') = e^{-U_3(\mathbf{r}, \mathbf{r}')/\Theta} \quad (U_3(\mathbf{r}, \mathbf{r}') = \varphi_2(\mathbf{r}) + \varphi_2(\mathbf{r}') + \varphi_2(\mathbf{r} - \mathbf{r}') + \varphi_3(\mathbf{r}, \mathbf{r}')),$$

$$\begin{aligned} \sigma = -N\Big\{&c\ln c + (1-c)\ln(1-c) + \frac{c^2}{2}\sum_{\mathbf{r}}\left[1 - e^{-\varphi_2(\mathbf{r})/\Theta}\left(1 + \frac{\varphi_2(\mathbf{r})}{\Theta}\right)\right] \\ &+ \frac{c^3}{3!}\sum_{\mathbf{r}, \mathbf{r}'}\left[1 - e^{-U_3(\mathbf{r}, \mathbf{r}')/\Theta}\left(1 + \frac{U_3(\mathbf{r}, \mathbf{r}')}{\Theta}\right) - 3e^{-\varphi_2(\mathbf{r})/\Theta}\left(1 + \frac{\varphi_2(\mathbf{r})}{\Theta}\right) + 3e^{-[\varphi_2(\mathbf{r}) + \varphi_2(\mathbf{r}')]/\Theta}\left(1 + \frac{2\varphi_2(\mathbf{r})}{\Theta}\right)\right] + \ldots\Big\}. \end{aligned} \tag{23a}$$

We can consider Eqs. (22a) and (23a) as parametric expressions for the entropy. The expression for the entropy in terms of the correlation functions is obtained by solving (22a) for φ_2 and φ_3, and substituting the resultant values in (23a):

$$\varphi_2(\mathbf{r}) = -\Theta\left\{\ln\tilde{W}_2(\mathbf{r}) - \frac{c}{\tilde{W}_2(\mathbf{r})}\sum_{\mathbf{r}'}[\tilde{W}_3(\mathbf{r}, \mathbf{r}') - 2\tilde{W}_2(\mathbf{r})\tilde{W}_2(\mathbf{r}') + \tilde{W}_2(\mathbf{r})], \quad U_3(\mathbf{r}, \mathbf{r}') = -\Theta\ln\tilde{W}_3(\mathbf{r}, \mathbf{r}'),\right.$$

$$\sigma\{W\} = -N\left\{c\ln c + (1-c)\ln(1-c) + \frac{c^2}{2}\sum_{\mathbf{r}}[W_2(\mathbf{r})\ln W_2(\mathbf{r}) - W_2(\mathbf{r}) + 1] + \right.$$

$$+\frac{c^3}{3!}\sum_{\mathbf{r},\mathbf{r}'}[W_3(\mathbf{r},\mathbf{r}')\ln W_3(\mathbf{r},\mathbf{r}')-W_3(\mathbf{r},\mathbf{r}')+1-3(W_3(\mathbf{r},\mathbf{r}')\ln W_2(\mathbf{r})-W_2(\mathbf{r})W_2(\mathbf{r}')+W_2(\mathbf{r}'))]+\dots\Big\}. \tag{23b}$$

[The sign of the equilibrium of the correlation functions is omitted in (23b), inasmuch as the resultant expression for the entropy is valid (as is easy to show) for arbitrary values of W_k.]

In the case in which all the polarization corrections are equal to zero (the interaction of the particles is composed of their pair interactions) it suffices, for the determination of the non-equilibrium state, to give only the binary correlation functions W_2. The remaining functions are determined from the condition of a minimum for the free energy (21) and is given in terms of W_2.

In particular, for W_3, Eq. (21) yields in this case

$$W_3(\mathbf{r},\mathbf{r}')=W_2(\mathbf{r})W_2(\mathbf{r}')W_2(\mathbf{r}-\mathbf{r}').$$

[In using (21), it should be recalled that the expression under the sign of the double sum in (23b) should be symmetrized relative to a permutation of the particles.] The expression for the entropy in this case is materially simplified and has the form

$$\sigma=-N\Big\{c\ln c+(1-c)\ln(1-c)+\frac{c^2}{2}\sum_{\mathbf{r}}[(1+V_2(\mathbf{r}))\ln(1+V_2(\mathbf{r}))-V_2(\mathbf{r})]-\frac{c^3}{3!}\sum_{\mathbf{r},\mathbf{r}'}V_2(\mathbf{r})V_2(\mathbf{r}')V_2(\mathbf{r}-\mathbf{r}')+\cdots\Big\}. \tag{24}$$

Here

$$V_2(\mathbf{r})=W_2(\mathbf{r})-1.$$

We note that in this case the entropy is specified parametrically by means of only two relations. Actually, Eq. (23) determines the entropy as a functional only of the pair interaction $\varphi_2(\mathbf{r})$, which can be determined from the expression for the binary correlation function $W_2(\mathbf{r})$.

The free energy of a solid solution corresponding to a non-equilibrium configuration is determined from Eq. (19) by substitution in it of the expression for the entropy, found with the necessary accuracy.

Let us consider the special case in which the non-equilibrium comes about as the result of a quenching of the solution from the temperature Θ' to the temperature Θ. Obviously the configuration of the solution is not changed in the quenching, and the values of the correlation coefficients in the non-equilibrium state thus obtained are equal to their equilibrium values at the temperature Θ'. The free energy in this case is equal to

$$F(\Theta,\Theta',c)=F_0(\Theta)+Nc\psi_1(\Theta)+N\sum_k\frac{c^k}{k!}\sum_{\mathbf{r}_1,\dots,\mathbf{r}_{k-1}}\widetilde{W}_k(\mathbf{r}_1,\dots,\mathbf{r}_{k-1},\Theta')\varphi_k(\mathbf{r}_1,\dots,\mathbf{r}_{k-1},\Theta)-\Theta\sigma\{\widetilde{W}_k\}(\Theta')\Big\}. \tag{25}$$

If we substitute the explicit expressions for the correlation functions and the entropy, we then obtain (with accuracy up to terms $\sim c^2$)

$$F(\Theta,\Theta',c)=F(\Theta,c)+N\frac{c^2}{2}\sum_{\mathbf{r}}\Big\{e^{-\varphi_2(\mathbf{r},\Theta')/\Theta'}\Big[\varphi_2(\mathbf{r},\Theta)-\frac{\Theta}{\Theta'}\varphi_2(\mathbf{r},\Theta')\Big]-\Theta\,[e^{-\varphi_2(\mathbf{r},\Theta')/\Theta'}-e^{-\varphi_2(\mathbf{r},\Theta)/\Theta}]\Big\}.$$

Here $F(\Theta, c)$ is the equilibrium free energy of the solution.

3. SOLUTIONS OF ISOTOPES

The method just developed for the determination of the free energy is applicable for solutions of general form. In this case the interactions of the impurity atoms U_k or, what amounts to the same thing, the φ_k, ought to be given, and are the parameters of the system. Here we have a case in which all the calculations can be carried through to completion. The latter applies to a solution of isotopes, for which the functions U_n (and the φ_n) are the energy of vibrational interaction of the impurity isotope and can be expressed in terms of the spectrum of frequencies of an ideal crystal (i.e., the lattices of the pure isotope).*

The change in the vibrational part of the free energy in the case in which there are n atoms of the principal isotope with mass m, located at the lattice sites $\mathbf{r}_1,\dots,\mathbf{r}_n$, are replaced by impurity atoms with mass m′, is given by the expression[1]

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*Part of the results contained in Ref. 1 was later obtained independently by Montroll and Potts[2] who determined the energy of the vibrational interaction of the defects of the lattice.

$$\psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \int \xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n)\,\chi'(z)\,dz, \tag{26}$$

$$\xi_n = \frac{1}{\pi} \arg D\left(\delta_{pq}\delta_{xx'} + \varepsilon z \int I^{xx'}_{\mathbf{r}_p-\mathbf{r}_q}(\mu)\frac{d\mu}{\mu - z - i0}\right) (p, q = 1, 2, \ldots, n;\ x, x' = 1, 2, 3), \tag{27}$$

$$I^{xx'}_{\mathbf{r}}(\mu) = \sum_j \int\limits_{\omega_j^2(\mathbf{k})=\mu} \frac{d\Omega_j}{|\nabla\omega_j^2|} e^{2\pi i\mathbf{kr}} u_j^x(\mathbf{k})\,u_j^{x'*}(\mathbf{k}'),\quad \varepsilon = \frac{m - m'}{m},\ \chi(z) = \Theta \ln(1 - e^{-\hbar\sqrt{z}/\Theta}) + \frac{1}{2}\hbar\sqrt{z}. \tag{28}$$

Here **k** is the wave vector, $\omega_j(\mathbf{k})$ is the j-th member of the frequencies of the pure fundamental isotope, $\mathbf{u}_j(u_j^1, u_j^2, u_j^3)$ is the normalized polarization vector $d\Omega_j$ is the element of area of the surface $\omega_j^2(\mathbf{k}) = \mu$ over which the integration is carried out.* The interaction of n impurity atoms, as is easily seen, is equal to

$$U_n = \psi_n - n\psi_1 = \int (\xi_n - n\xi_1)\,\chi'(z)\,dz. \tag{29}$$

We find the expression for φ_k by means of Eq. (13). In particular, we have

$$\varphi_2(\mathbf{r}) = \psi_2(\mathbf{r}) - 2\psi_1,\quad \varphi_3(\mathbf{r}, \mathbf{r}') = \psi_3(\mathbf{r}, \mathbf{r}') - \psi_2(\mathbf{r}) - \psi_2(\mathbf{r}') - \psi_2(\mathbf{r} - \mathbf{r}') + 3\psi_1.$$

For small values of ϵ, these relations become materially simplified. With an accuracy up to terms $\sim \epsilon^2$ we have, for z lying in the region of the continuous spectrum of the pure solvent,

$$\begin{aligned} \xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n) = n\Big[\varepsilon z \sum_x I_0^{xx}(z) - \varepsilon^2 z^2 \operatorname{Re} \sum_{x,x'} I_0^{xx'}(z) {\int}' I_0^{x'x}(\mu)\frac{d\mu}{\mu - z}\Big] \\ - \varepsilon^2 z^2 \operatorname{Re} \sum_{p\neq q} \sum_{x,x'} I^{xx'}_{\mathbf{r}_p-\mathbf{r}_q}(z) {\int}' I^{x'x}_{\mathbf{r}_q-\mathbf{r}_p}(\mu)\frac{d\mu}{\mu - z}\quad (p, q = 1, 2, \ldots, n;\ x, x' = 1, 2, 3), \end{aligned} \tag{30}$$

Here $\int'$ is the principal value of the integral. For the given values of z,

$$\int I^{xx'}_{\mathbf{r}}(\mu)\frac{d\mu}{\mu - z - i0} = {\int}' I^{xx'}_{\mathbf{r}}(\mu)\frac{d\mu}{\mu - z} + i\pi I^{xx'}_{\mathbf{r}}(z).$$

Outside the region of the continuous spectrum, $\xi_n = 0$ in the case of sufficiently small ϵ. It is easy to be convinced that (30) can be written in the form

$$\xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n) = n\xi_1(z) + \frac{1}{2}\sum_{p\neq q}(\xi_2(z, \mathbf{r}_p - \mathbf{r}_q) - 2\xi_1(z)\ (p, q = 1, 2, \ldots, n). \tag{31}$$

Then, taking Eq. (29) into account, we obtain

$$U_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{1}{2}\sum_{p\neq q} U_2(\mathbf{r}_p - \mathbf{r}_q). \tag{32}$$

Thus the interaction of an arbitrary number of atoms of the impurity isotope, with accuracy up to terms $\sim \epsilon^2$, is composed of their pair interactions.† The interaction of two impurity atoms is equal (with the same accuracy) to

$$U_2(\mathbf{r}) = -2\varepsilon^2 \operatorname{Re}\int dz\left[z^2\chi'(z) \sum_{x,x'} I^{xx'}_{\mathbf{r}}(z) {\int}' I^{x'x}_{-\mathbf{r}}(\mu)\frac{d\mu}{\mu - z}\right. . \tag{33}$$

If we substitute the expression $\chi = h\sqrt{z}/2$ (which is valid for low temperatures) in Eq. (33) and change over to integration over the wave vector **k**, we get

$$U_2(\mathbf{r}) = \frac{1}{4}\varepsilon^2\hbar \operatorname{Re}\sum_{j,j'}\int d\mathbf{k}\,d\mathbf{k}'\,\frac{\omega_j^2(\mathbf{k}) + \omega_j(\mathbf{k})\,\omega_{j'}(\mathbf{k}') + \omega_{j'}^2(\mathbf{k})}{\omega_j(\mathbf{k}) + \omega_{j'}(\mathbf{k}')} e^{2\pi i(\mathbf{k}-\mathbf{k}')\mathbf{r}} |\mathbf{u}_j(\mathbf{k}),\ \mathbf{u}_{j'}(\mathbf{k}'))|^2. \tag{34}$$

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*In Ref. 1 the corresponding formulas were written for the idealized case of a simple lattice with a single direction of polarization, when only one frequency mode exists and the vector **u** is a unit vector in the direction of polarization. Formulas (42) and (43) correspond to the case of three directions of polarization in Ref. 1 for small ϵ.

†Similarly, it can be shown that with accuracy up to terms $\sim \epsilon^k$, the interaction of an arbitrary number of impurity atoms consists of their pair interactions and polarization corrections of order no higher than k.

To facilitate the estimate of the energy of interaction, we write its value in the idealized case of a simple lattice with a single direction of polarization:

$$U_2(\mathbf{r}) = -\varepsilon^2 \frac{\hbar}{4} \operatorname{Re} \int d\mathbf{k}\, d\mathbf{k}' \, \frac{\omega(\mathbf{k})\,\omega(\mathbf{k}')}{\omega(\mathbf{k}) + \omega(\mathbf{k}')} e^{2\pi i (\mathbf{k}-\mathbf{k}')\mathbf{r}}.$$

Substitution of the expressions obtained here for the interactions into the general formulas yields the thermodynamic functions and the equilibrium value of the correlation for solutions of isotopes.

In the general case of a complicated lattice, the expressions for the interactions of the impurity isotopes are somewhat more involved. Let the position of the p-th atom of the impurity be given by the radius vector $\mathbf{r}_p + \mathbf{r}(s_p)$, where $\mathbf{r}_p$ is determined by the fundamental cell of the lattice, while $\mathbf{r}(s_p)$ is the position of the impurity atom inside this cell. Then a change in the vibrational free energy upon the insertion of n atoms of impurity is determined by the expressions

$$\psi_n(\mathbf{r}_1, \ldots, \mathbf{r}_n, s_1, \ldots, s_n) = \int \xi_n(z, \mathbf{r}_1, \ldots, \mathbf{r}_n, s_1, \ldots, s_n)\, \chi'(z)\, dz; \tag{35}$$

$$\xi_n = \frac{1}{\pi} \arg D \left(\delta_{pq}\delta_{xx'} + \varepsilon z \int I_{\mathbf{r}_p - \mathbf{r}_q}^{s_p x,\, s_q x'}(\mu) \frac{d\mu}{\mu - z - i0} \right), \quad I_{\mathbf{r}}^{sx,\, s'x'}(\mu) = \sum_j \int_{\omega_j^2(\mathbf{k}) = \mu} \frac{d\Omega_j}{|\nabla \cdot \omega_j^2|} e^{2\pi i \mathbf{k}\mathbf{r}} v_j^{sx}(\mathbf{k})\, v_j^{s'x'}(\mathbf{k}),$$
$$v_j^{sx} = u_j^{sx}(\mathbf{k})\, e^{2\pi i \mathbf{k}\mathbf{r}(s)}, \tag{36}$$

where ϵ and $\chi(z)$ are determined by Eqs. (27) and (28). In the case under consideration, ψ_1 depends on which atom of the basic cell is replaced by the impurity. Therefore, the interaction of n impurity atoms is determined by the relation

$$U_n = \psi_n - \sum_s n_s \psi_1(s),$$

where n_s is the number of impurity particles which replace atoms of type s of the basic lattice. It is easy to show that, with accuracy up to terms $\sim \epsilon^2$ the following relations hold

$$U_n(\mathbf{r}_1, \ldots, \mathbf{r}_n, s_1, \ldots, s_n) = \frac{1}{2} \sum_{p \neq q} U_2(\mathbf{r}_p - \mathbf{r}_q, s_p, s_q) \tag{37}$$

$$U_2(\mathbf{r}, s, s') = -2\varepsilon^2 \operatorname{Re} \int dz \left[z^2 \chi'(z) \sum_{x,\, x'} I_{-\mathbf{r}}^{sx,\, s'x'}(z) \int' I_{-\mathbf{r}}^{s'x',\, s'x'}(\mu) \frac{d\mu}{\mu - z} \right]. \tag{38}$$

Transformation to integration over the wave vector puts Eq. (36) in the following form for the low temperature case:

$$U_2(\mathbf{r}, s, s') = \varepsilon^2 \frac{\hbar}{4} \operatorname{Re} \sum_{j,\, j'} \int d\mathbf{k}\, d\mathbf{k}' \, \frac{\omega_j^2(\mathbf{k}) + \omega_j(\mathbf{k})\, \omega_{j'}(\mathbf{k}') + \omega_{j'}^2(\mathbf{k}')}{\omega_j(\mathbf{k}) + \omega_{j'}(\mathbf{k}')} e^{2\pi i (\mathbf{k}-\mathbf{k})\mathbf{r}} |(\mathbf{v}_j^s(\mathbf{k}),\ \mathbf{v}_{j'}^{s'}(\mathbf{k}'))|^2. \tag{39}$$

As must follow from the relations obtained, the interactions of the isotopes are very small. For the minimum separation of the atoms, in accordance with (33), the interaction has the value $\sim \epsilon^2 \Theta_D$ ($\Theta_D = kT_D$, T_D is the Debye temperature). Obviously, an appreciable correlation in the positions of the atoms will take place only at temperatures of the order or smaller than $\epsilon^2 T_D$. However, in a solid because of the slowness of the diffusion of the atoms at arbitrarily low temperatures, configurations actually exist which are in equilibrium at the temperature of solidification. Therefore, it is essential for the appearance of correlation in solutions of isotopes that the solidification itself take place at a temperature $T \sim \epsilon^2 T_D$. Hydrogen, for which $T_D \sim 100°$, $T_{so} \sim 20°$, $\epsilon \sim 1/2$ satisfies this condition. For other substances, sufficiently low temperatures of solidification can exist in the case of their solidification from the gaseous phase (in the sublimation region).

It should be pointed out that the lattice of hydrogen is molecular and the important role at energies $\varphi_2, \ldots$ is played not by vibrational but by rotational interactions, in which different statistics are essential. It should further be noted that in the general case still another circumstance can make a contribution to the energy of interaction of the isotopes. Because of the presence of anharmonics, the mean volume occupied by the atom (under consideration of the zero vibrations) depends on the amplitude, i.e., on the mass of the isotope. Therefore, upon substitution of an impurity atom at any lattice point, there arises an additional elastic energy. A semi-empirical estimate of this energy carried out for hydrogen by Prigogine et al.,[3] gives the value $U_2 \sim 10^{-15}$ erg, which corresponds to a temperature of $T \sim 10°$.

The presence of correlation measures the non-ideality of the solutions of isotopes. In particular, for sufficiently large values of the interaction, a separation of the solution takes place into phases; this was recently observed for impurities of hydrogen isotopes.[*][4]

In the case in which the interaction is insufficient for a separation of the solution, the presence of correlation can be found with the aid of a study of slow neutron scattering. As is known, the probability that in passage through the crystal the neutron possesses the momentum $\mathbf{p}'$ if its initial momentum was $\mathbf{p}$ is proportional to the quantity

$$\overline{\left|\sum_{\mathbf{r}} A_{\mathbf{r}} \exp\left\{\frac{2\pi i}{\hbar}(\mathbf{p}'-\mathbf{p})\mathbf{r}\right\}\right|^2 = \sum_{\mathbf{r},\mathbf{r}'}(A_{\mathbf{r}}-\bar{A})(A_{\mathbf{r}'}-\bar{A})\exp\left\{\frac{2\pi i}{\hbar}(\mathbf{p}'-\mathbf{p})(\mathbf{r}-\mathbf{r}')\right\}} + \bar{A}^2\left|\sum_{\mathbf{r}} \exp\left\{\frac{2\pi i}{\hbar}(\mathbf{p}'-\mathbf{p})\mathbf{r}\right\}\right|^2. \quad (40)$$

Here $\mathbf{r}$ denotes the equilibrium position of the atoms of the crystal, $A_{\mathbf{r}}$ characterizes the interaction between neutrons and the nucleus at site $\mathbf{r}$ (in the case under analysis, A depends only on the mass). Averaging is carried out over 11 possible configurations. The second component in (40) determines the coherent scattering of the neutron. It gives sharp maximum of intensity of scattered neutrons, determined by the relation $\mathbf{p}' - \mathbf{p} = \hbar\tau$, here τ is the vector of the reciprocal lattice. The first term in (40) in the case of absence of correlation, when all terms with $\mathbf{r} \neq \mathbf{r}'$ reduce to zero, is equal to

$$N(\overline{A^2} - \bar{A}^2)$$

and determines the background noise which does not depend on the scattering angle. If correlation exists, the noise is equal to

$$N(\overline{A^2} - \bar{A}^2) + Nc_2(A_1 - A_2)^2 \sum_{\mathbf{r}} (W_2(\mathbf{r}) - 1)\exp\left\{\frac{2\pi i}{\hbar}(\mathbf{p}'-\mathbf{p})\mathbf{r}\right\}. \quad (41)$$

Here the indices 1 and 2 refer to isotopes of the solvent and impurity, respectively. According to (41) the noise is inhomogeneous in the presence of correlation, and we can determine the value of the correlation functions from the structure of the noise.

It should be observed that Eqs. (40), (41) are approximate, inasmuch as they were obtained without account of the thermal vibrations of the crystal. Account of the latter obviously does not reduce to the addition of a thermal factor, since the amplitudes of the vibration depend on the kind of isotope and on the correlation of the atoms of the lattice.

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[*] This conclusion (which did not appear in the published paper of Ref. 4, and which was kindly communicated to us by the authors) can be made on the basis of an analysis of x-rays of the mixture $H_2 - D_2$ with high concentration of both isotopes, in this case, two systems of lines are quite clearly seen.