

Qualitatively analogous results are obtained in tests with water under the same conditions but with a lower initial temperature (13.8°C); however, the effect here appears more definitely, the temperature drops by 5.5°C maximum, and the pressure to -2 MPA. This fact is in agreement with the Briggs results which established that the limit bulk strength gradually diminished for water in the 5-50°C range as the temperature rose [1].

Recording the pressure and temperature at the point D2 at a 5-m distance from the cutoff yielded qualitatively analogous results.

Tests were also conducted with water with a surfactant added. The pressure reduction here is somewhat smaller and there is no negative pressure effect. This result agrees with the Frenkel theory about the role of surface tension in the appearance of a negative pressure. Tests also showed the significant attenuation of the effect as the percentage gas content increased in the flow.

Analogous results were obtained in tests with oil. A considerable temperature drop, up to 10°C, was here observed during the existence of the negative pressure.

The nonstationary effect pinpointed permits utilization of real fluid systems to obtain and investigate negative pressures, while great strictness relative to the fluid purity must be maintained in the static approach. This circumstance affords the possibility of producing and using brief negative pressures in many engineering processes.

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STATISTICAL THERMODYNAMICS OF SCHOTTKY DEFECTS IN MOLECULAR AND IONIC CRYSTALS

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UDC 548.4:536.75

A statistical thermodynamics of point defects is constructed that permits taking account of the influence of vacancies on both the thermodynamical and structural properties without involving any experimental information.

The study of the thermodynamics of point defects, and particularly of vacancies, is an important problem in connection with the influence they exert on the macroscopic properties of a substance [1].

A sequential description of the properties of defects should rely on the microscopic theory whose problem is to describe the local structure of the material in the neighborhood of the defect, on the one hand, and to give a description on this basis of the thermodynamical properties of a crystal with defects, on the other hand.

An approach of such a kind, based on the statistical method of conditional distributions [2], was developed earlier [3] and applied to an analysis of the equilibrium concentration of vacancies [4] in a molecular crystal. In this paper results are presented of systematic computations of the energy of vacancy formation for a molecular crystal, and in addition, the theory is extended to ionic crystals.

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Let us consider a multicomponent system containing N_α particles of the species α ($\alpha = 1, \dots, K$), where $\sum_{\alpha=1}^K N_\alpha = M$. We take the potential energy of such a system in the form

$$U = \frac{1}{2} \sum_{\alpha, \beta=1}^K \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \xi_\alpha \xi_\beta \Phi(i_\alpha, j_\beta).$$

Here ξ_α are configuration variables taking on the values 0 and 1 and being introduced as an equally likely "component" for inclusion in the vacancy scheme.

Let us divide the volume V occupied by the system into M equal cells $w_i = V/M$, and let us limit ourselves to taking account of only those states in which not more than one particle is in each cell.

On the basis of the Gibbs distribution, one-, two-, etc. particle distribution functions $F_i(i_\alpha)$, $F_{ij}(i_\alpha, j_\beta)$, ... can be introduced that govern the probability density that a particle of the species α will be near the point $i_\alpha \in w_i$ or two particles of the species α and β will be near the points $i_\alpha \in w_i$ and $j_\beta \in w_j$, etc. [2]. These functions can be represented in the form [5]

$$F_i(i_\alpha) = c_i^\alpha \exp\{-\beta\varphi_i(i_\alpha)\}, \quad (2)$$

$$F_{ij}(i_\alpha, j_\beta) = c_i^\alpha c_j^\beta \exp\{-\beta[\xi_\alpha \xi_\beta \Phi(i_\alpha, j_\beta) + \varphi_{ij}(i_\alpha, j_\beta)]\}. \quad (3)$$

Here

$$c_i^\alpha = n_\alpha / \int d(i_\alpha) \exp\{-\beta\varphi_i(i_\alpha)\}, \quad n_\alpha = N_\alpha/M; \quad (4)$$

$$\varphi_i(i_\alpha) = \sum_{l \neq i}^M \varphi_{i,l}(i_\alpha); \quad (5)$$

$$\varphi_{ij}(i_\alpha, j_\beta) = \sum_{l \neq i,j}^M \varphi_{ij,l}(i_\alpha, j_\beta). \quad (6)$$

The quantities defined by (5) and (6) have the meaning of potentials of the mean forces (MFP) and can, in turn, be expressed in terms of the distribution functions

$$\nabla_{i_\alpha} \varphi_{i,l}(i_\alpha) = \sum_{\gamma=1}^K \xi_\alpha \xi_\gamma \int d(l_\gamma) \nabla_{i_\alpha} \Phi(i_\alpha, l_\gamma) \frac{F_{il}(i_\alpha, l_\gamma)}{F_i(i_\alpha)}, \quad (7)$$

$$\nabla_{i_\alpha} \varphi_{ij,l}(i_\alpha, j_\beta) = \sum_{\gamma=1}^K \xi_\alpha \xi_\gamma \int d(l_\gamma) \nabla_{i_\alpha} \Phi(i_\alpha, l_\gamma) \frac{F_{ijl}(i_\alpha, j_\beta, l_\gamma)}{F_{ij}(i_\alpha, j_\beta)}. \quad (8)$$

This latter expression connects the two-particle function (3) with three-particle functions, while system (2)-(8) is the beginning of an infinite chain of equations. Functions (2) and (3) are interrelated by strict relationships:

$$F_i(i_\alpha) = \sum_{\beta=1}^K \int d(j_\beta) F_{ij}(i_\alpha, j_\beta). \quad (9)$$

The free energy and the configuration integral of the system have the forms

$$F = -\frac{1}{\beta} \ln Q_M, \quad (10)$$

$$Q_M = \prod_{\alpha=1}^K \prod_{i=1}^M \left\{ \left[\int d(i_\alpha) \exp\{-\beta\varphi_i(i_\alpha)\} \right] / n_\alpha \right\}^{n_\alpha},$$

and the MFP must be known for their computation. Seeking the MFP is associated with the closure procedure consisting in the expansion of the MFP into irreducible parts [6]

$$\varphi_{ij,l}(i_\alpha, j_\beta) = \varphi_{i,l}(i_\alpha) + \varphi_{j,l}(j_\beta) + \omega_{ij,l}(i_\alpha, j_\beta) \quad (11)$$

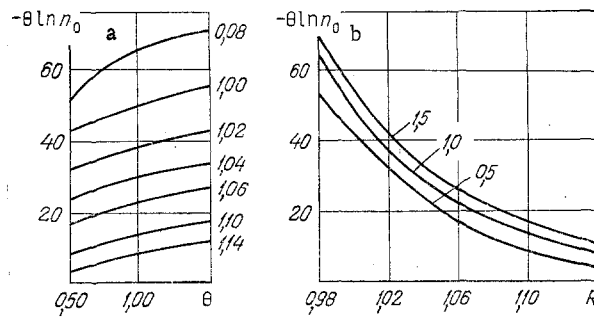


Fig. 1. Dependence of the vacancy concentration on: a) the temperature for different values (indicated on the right) of the distance between nearest neighbors; b) the distance between nearest neighbors for different values of the temperature.

with the subsequent discarding of the quantity ω .

Consequently, the binary functions (3) take the form

$$F_{ij}(i_\alpha, j_\beta) = \exp \{ \beta [\varphi_{i,j}(i_\alpha) + \varphi_{j,i}(j_\beta) - \xi_\alpha \xi_\beta \Phi(i_\alpha, j_\beta)] \} F_i(i_\alpha) F_j(j_\beta). \quad (12)$$

Substituting this expression into (9) results in a closed system of nonlinear integral equations for the MFP

$$\exp \{ -\beta \varphi_{i,j}(i_\alpha) \} = \sum_{\beta=1}^K \int_j d(j_\beta) \exp \{ \beta [\varphi_{j,i}(j_\beta) - \xi_\alpha \xi_\beta \Phi(i_\alpha, j_\beta)] \} F_j(j_\beta). \quad (13)$$

Let us now examine application of the general scheme to specific systems.

VACANCIES IN MOLECULAR SYSTEMS

A molecular crystal with vacancies can be considered as a two-component system containing N particles and N_0 holes, $N + N_0 = M$. For the formal passage from the described multicomponent system to a system consisting of particles and vacancies, we should set $\xi_\alpha = 1$ for α , corresponding to the particles, and $\xi_\alpha = 0$ for the vacancies. In this case (10) goes over into

$$Q_M = \prod_{i=1}^M \left\{ \left[\int_i \exp \{ -\beta \varphi_i(i) \} \right] / n \right\}^n (1/n_0)^{n_0}, \quad (14)$$

where $n + n_0 = 1$, $n = N/M$, and the integral equation for the MFP takes on the form

$$\exp \{ -\beta \varphi_{i,j}(i) \} = n_0 + \int_j d(j) \exp \{ \beta [\varphi_{j,i}(j) - \Phi(i, j)] \} F_j(j). \quad (15)$$

The quantity n_0 is the vacancy concentration and is unknown, and can be sought from the condition of the minimum of the thermodynamic potential $G = F + PV$. We consequently have [4]

$$n_0 = \exp \{ -\beta [\langle \psi_i(i) \rangle + P\omega] \}, \quad (16)$$

where the angular brackets denote taking the average by using the one-particle function of an ideal crystal, and

$$\psi_i(i) = \left. \frac{\partial \varphi_i(i)}{\partial n_0} \right|_{n_0=0}. \quad (17)$$

We now turn to solving the integral equation (15). The smallness of the vacancy concentration permits seeking the solution in the form of a series in n_0 , limited here to linear terms

$$\varphi_{i,j}(i) = \varphi_{i,j}^*(i) + n_0 \psi_{i,j}(i). \quad (18)$$

Then (15) reduces to two systems of integral equations: nonlinear

$$\exp \{ -\beta \varphi_{i,j}^*(i) \} = \langle \exp \{ \beta [\varphi_{j,i}^*(j) - \Phi(i, j)] \} \rangle, \quad (19)$$

TABLE 1. Vacancy Concentration and Gibbs Potential for Vacancy Formation; $T/\epsilon = 0.668$, $R/r = 1.1344$

Source	$n_v \cdot 10^4$	$\Delta G/\epsilon = -\theta \ln n_v$	Source	$n_v \cdot 10^4$	$\Delta G/\epsilon = -\theta \ln n_v$
[9]	2,1	5,65	[12]	1,25	6,00
[10]	1,02	6,14	This paper	0,88	6,24
[11]	0,93	6,20	[19]	1,64	5,84

which agrees with the system of equations for an ideal (vacancy-free) crystal [7], and linear
$$\beta\psi_{i,j}(i) = 1 - \exp[\beta\varphi_{i,j}^*(i)] \{1 - \beta \langle [\psi_j(j) - \psi_{j,i}(j)] \exp\{\beta[\varphi_{j,i}^*(j) - \Phi(i,j)]\} \rangle - \beta \langle \psi_j(j) \rangle. \quad (20)$$

In the crystalline state the one-particle function has a sharp maximum at a lattice site, which permits evaluation of the integral in (19) and (20) by the Laplace method [8]. Taking account of the first two terms of the asymptotic, we have for (19) [7]

$$\varphi = [\Phi - \{\ln(1 - \Gamma)\}/\beta]/2, \quad g = (2\beta\Phi''g - \Phi_3)/2\beta\sigma(1 - \Gamma), \quad (21)$$

$$\Delta\varphi^* = \Delta\Phi + \beta g^2 + g[\Phi_4 - 2\beta(K + \Phi_3g)]/(2\beta\Phi'' - \Phi_3),$$

where Δ is the Laplace operator, $\Phi_3 = \Phi^{(3)} + 2(\Phi'' - \Phi'/R)/R$, $\Phi_4 = \Phi^{(4)} + 4\Phi^{(3)}/R$, $K = (\Phi'')^2 + 2(\Phi'/R)^2$, $\varphi \equiv \varphi_{i,j}^*(0)$, $g = \Phi' - k$, $\nabla\varphi^* = k\mathbf{R}/R$, R is the distance between nearest neighbors, whose number is z , $\Gamma = (\Delta\Phi - \Delta\varphi^* - \beta g^2)/2\sigma$, $\sigma = z\Delta\varphi^*/3$, the values of all the quantities are taken at the sites.

To the same accuracy the system (20) is reduced to a system of algebraic equations

$$A_{ij}\psi_j = B_i \quad (i, j = 1, 2, 3), \quad (22)$$

where

$$\begin{aligned} \psi_1 &= \psi_i(0) \equiv \psi; \quad \psi_2 = f; \quad \nabla_i\psi_i = f\mathbf{R}/R; \quad \psi_3 = \Delta\psi_i \equiv \Delta\psi; \\ B_1 &= z(1 - \exp\beta\varphi); \quad B_2 = -\beta k \exp\beta\varphi; \quad B_3 = -z\beta(\Delta\varphi^* + \beta k^2) \exp\beta\varphi; \\ A_{11} &= 2\beta; \quad A_{12} = -z\beta/\sigma(1 - \Gamma)^{1/2}; \quad A_{31} = (1 - z\Gamma)/2\sigma(1 - \Gamma)^{1/2}; \\ A_{21} &= (z - 1)[\beta g^2 + \beta(\Phi_3 - 2\beta g\Phi'')/2\sigma(1 - \Gamma)^{1/2}]/z; \quad A_{22} = \beta[1 + (\beta g^2 - \Phi'')/\sigma(1 - \Gamma)^{1/2}]; \quad A_{23} = (z - 1)\beta g/2z\sigma(1 - \Gamma)^{1/2}; \\ A_{31} &= (z - 1)\{\beta^2(\Delta\Phi - \Delta\varphi^* - \beta g^2) - \beta[\Phi_4 - 2\beta(K + \Phi_3g) + \\ &+ 2\beta^2 g^2\Phi'']/2\sigma(1 - \Gamma)^{1/2}\}; \quad A_{32} = z\beta(\beta g\Gamma/2\sigma - \Phi_3 + 2\beta g\Phi'')/\sigma(1 - \Gamma)^{1/2}; \\ A_{33} &= \beta[1 - (z - 1)\Gamma/(1 - \Gamma)^{1/2}]. \end{aligned}$$

Specific computations, whose results are represented in Fig. 1, were performed by using the Lennard-Jones potential (6)-(12) ($\epsilon/k = 119.8^\circ\text{K}$; $r = 3.405 \text{ \AA}$).

Unfortunately, a systematic comparison of the results obtained with the results of other authors is often made difficult either by the incompleteness of the initial parameters mentioned there (for instance, the temperature dependence of the vacancy concentration is given without indicating the density or pressure at which it is calculated) or by utilization of other potentials. The greatest quantity of data is available for argon at $T = 80^\circ\text{K}$ and $R/r = 1.1344$ (Table 1). The first three values have been obtained by the Monte Carlo method, the fourth by dynamical theory, the fifth is the result of this paper. The closest agreement is, as is seen, with the paper [12], where the method of "overlapping distributions" [13, 14] is used in the Monte Carlo computation, which has a number of advantages over the approaches in [9, 10]. Meanwhile, all the results are sufficiently close, indicating their adequate reliability.

SCHOTTKY DEFECTS IN IONIC SYSTEMS

The condition of complete electrical neutrality, according to which the strict equality between the quantities of positive and negative charges should be used, imposes specific constraints on Schottky defects in ionic crystals: they can be formed only by vapors. An ideal (vacancy-free) ionic crystal can be considered as a binary alloy consisting of ions of two species that remains completely ordered down to the melting point [15].

From the viewpoint of the statistical scheme described in the first section, an ionic crystal is a three-component system consisting of ions of two species and vacancies which are understood to be the unfilled sites of the crystalline lattice. The singularities induced by the condition of electrical neutrality and complete ordering appear in the fact

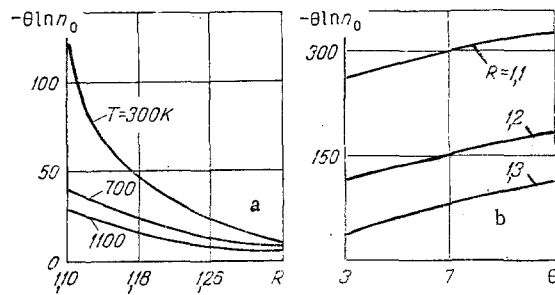


Fig. 2. Dependence of the energy of Schottky defect formation on a) the distance between nearest ions of different name for different temperatures; b) the temperature for different distances (in units of the sum of ionic radii).

that, just as an ideal crystal, a crystal with defects consists of two imbedded sublattices, each of which contains ions of just one sign, but part of the sites in the sublattices is not filled, where the number of empty sites in both sublattices is exactly equal.

Let us use Greek letters for the positive ion, and Latin letters for the negative ion coordinates. The total number of sites is $M = N_+ + N_- + 2N_0$. The free energy has the form

$$F = -\frac{1}{\beta} \ln Q_M, \quad (24)$$

$$Q_M = (Q_\alpha/n_+)^{N_+} (Q_i/n_-)^{N_-} (1/2n_0)^{2N_0},$$

$$n_+ = N_+/M, \quad n_- = N_-/M, \quad n_0 = N_0/M,$$

and the system (12) reduces to four integral equations

$$\begin{aligned} \exp[-\beta\varphi_{\alpha,i}(\alpha)] &= n_0 + \int_i d(i) \exp\{\beta[\varphi_{i,\alpha}(i) - \Phi(\alpha, i)]\} F_i(i), \\ \exp[-\beta\varphi_{\alpha,\beta}(\alpha)] &= n_0 + \int_\beta d(\beta) \exp\{\beta[\varphi_{\beta,\alpha}(\beta) - \Phi(\alpha, \beta)]\} F_\beta(\beta), \\ \exp[-\beta\varphi_{i,\alpha}(i)] &= n_0 + \int_\alpha d(\alpha) \exp\{\beta[\varphi_{\alpha,i}(\alpha) - \Phi(i, \alpha)]\} F_\alpha(\alpha), \\ \exp[-\beta\varphi_{i,j}(i)] &= n_0 + \int_j d(j) \exp\{\beta[\varphi_{j,i}(j) - \Phi(i, j)]\} F_j(j). \end{aligned} \quad (25)$$

We again seek the solution in form (18). Then system (25) reduces to eight integral equations: four nonlinear of the type (19) and four linear of the type (20). The same reasoning relative to the maximum of the one-particle function permits utilization of the Laplace method here also, whereupon the integral equations reduce, respectively, to a system of transcendental equations of the type (21) and linear algebraic equations of the type (22).

As should have been expected, the main distinction of the system obtained is associated with the Coulomb energy [15] which it is impossible to take into account by restriction to the nearest-neighbor approximation. Although it enters in screened form in equations of the types (21) and (22) the large value of the Coulomb energy (as compared with the short-range repulsion) results in the need to take account of several coordination spheres; the contribution of the Coulomb interaction is actually taken into account until it is commensurate with the short-range contribution for the nearest neighbors.

The expression for the Schottky defect concentration in an ionic crystal has formally the same form as (16) for the molecular crystal with the difference, understandably, that the values in the exponential are determined by the solution of the system (25). It is also obtained from the condition of the minimum of the Gibbs free energy.

Specific computations are performed for the NaCl crystal. The interaction potential was selected in the Born-Mayer form [16] with the addition of Coulomb energy. Results of the computations are represented in Fig. 2.

TABLE 2. Vacancy Concentration and Gibbs Potential of Vacancy Formation in NaCl; T = 1100°K, P = 0

Source	N_v/M	ΔG (eV)
[17]	$7,9 \cdot 10^{-4} - 6,8 \cdot 10^{-5}$	0,225 - 0,3015
This paper	$8,13 \cdot 10^{-4}$	0,2237

A comparison with results obtained for a NaCl crystal at the melting point and zero external pressure in [17] is presented in Table 2. The agreement should be considered good.

In conclusion, we examine the influence of the vacancies on thermodynamics. From (14) and (16) an expression follows for the free energy of a crystal with vacancies

$$F = F_0 - N_0 [\langle \psi_i(i) \rangle + Pw - \Theta], \quad (26)$$

where F_0 is the free energy of a crystal without vacancies. Expanding this expression, the contribution of vacancies to all the thermodynamic characteristics of the crystal can be computed.

NOTATION

β , reciprocal temperature; F, Helmholtz free energy; G, Gibbs free energy; φ , potential of the mean forces; n_v , vacancy concentration; and $\phi(i, j)$, interparticle interaction potential.

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