
Statistical Thermodynamics of Binary Systems With Variable Valent States of One of the Components

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ABSTRACT: This report contains a generalization of the usual lattice model of multicomponent systems. The generalization allows us to take into account the following factors: (i) the short-range parts of interatomic repulsions; which are not identical for different pairs of atoms (therefore, it is impossible to take into account the repulsions by means of usual ideal lattice introduction); (ii) the long-range interatomic potentials are taken into account by means of effective fields approximation; (iii) the existence of the vacancies as one of the components in the system; (iv) the existence of comparatively stable multi-atomic complexes; and (v) some other factors due to specifics of constituents and their interactions, such as variable valence states and chemical reactions. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 104: 133–142, 2005

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Introduction

The ab initio quantitative theory of multicomponent condensed systems remains an almost hopeless problem. Moreover, a much more modest problem—computing the thermodynamic properties of systems with arbitrary interatomic potentials in classical approximation—has not yet been solved. The extremely simplified models, such as one- and two-dimensional Ising models, the Kac model, and the Baxter model, allow precise mathematical investigation. We do not have any three-dimensional exactly solved model.

The phenomenological approach to quantitative condensed matter theory is probably the only possible way. This approach can be based on various principles, but there are some common requirements to phenomenological models.

One of the most popular models of condensed matter is the lattice model (see, e.g., Refs. [1–5]) based on the assumption that atoms are distributed over the sites of some lattice. There are many variants of use of the lattice model and its development for equilibrium and nonequilibrium properties of condensed systems (mainly for solid or liquid states).

The most essential disadvantages of the lattice models are well known. First, we consider the assumption of some lattice existing independent of the difference of atomic sizes of its components. This assumption is comparatively plausible if the difference of component atomic sizes is small. As a rule, this condition does not take place. The introduction of lattice permits to take into account the short-range part of interatomic potentials. Difference of short-range parts of components interatomic potentials leads to lattice distortions and the notion of the lattice, strictly speaking, in this case becomes invalid.

Second, the postulate of the Fermi-like functional form of distribution function for average occupations numbers has no theoretical justification, as there are infinitely many functions with a range of values [0; 1].

Finally, the interatomic potentials in lattice-like models of condensed systems, as a rule, cannot be described with small number of parameters, such as interaction energy of nearest-neighbor interactions. The unavoidable lattice distortions lead to changes in interatomic distances, and short-range parts of interatomic potentials are not slowly changing functions.

In contrast, the phenomenological model of multicomponent condensed systems should take into account the following essential factors:

1. *Short-range interatomic repulsions:* These repulsions are not identical for different pairs of atoms; therefore, it is impossible to take into account the repulsions by means of lattice introduction (at best, the lattice model can be considered as a method of short-range interactions in the case of a one-component system and that with some essential restriction, related in particular neglect of thermal defects).
2. *Presence of local fields due to long-range parts of interatomic potentials:* These fields have an essential influence on both equilibrium properties and non-equilibrium processes on the corresponding scales.
3. *Existence of comparatively stable multi-atomic complexes:* This is manifested both in thermodynamics and in kinetics as one indivisible particle.

Moreover, in real systems, some other factors can be essential due to the specifics of constituents and their interactions, such as variable valent states, chemical reactions, and external field influences (e.g., irradiation).

This article presents a generalization of a lattice model. The method takes into account the following: (i) the short-range parts of interatomic potentials by means of geometrical restrictions method; (ii) the presence of internal fields due to long-range parts of interatomic potentials by means of effective field approximation; (iii) the existence of proper defects such as vacancies in condensed systems; and (iv) the existence of multi-atomic complexes in condensed matter (in particular, with variable valent states of components).

All the results are formulated on the basis of the unified mathematical approach and the common physical ideas. All the assumptions have clear physical sense, good foundations, and strictly based conditions of applicability.

Short-Range Parts of Interatomic Potentials

This section presents the general approach that allows us to take into account the short-range interaction in the system, namely, intensive repulsion

between atoms at small distances. Note that the short-range repulsion in the system restricts the densities of components, and it can be taken into account as an appropriate geometrical condition. It should be noted that similar geometrical conditions (constraint equations) are widely used in classical mechanics instead of explicit forces.

Suppose that each atom of the i th component of the system has some proper volume ω_i . The introduction of proper volumes leads to the condition (restriction) on the local density $n_i(\mathbf{r})$ of the i th component at an arbitrary point \mathbf{r} in the system, i.e.,

$$n_i(\mathbf{r}) \leq \frac{1}{\omega_i}. \quad (1)$$

The above condition means that short-range parts of interatomic potentials approximated via the hard-core potential and the quantity ω_i^{-1} is the maximal value of the density of the i th component. The quantity $\omega_i n_i(\mathbf{r})$ is a simply volume local fraction of the i th component (the local fraction of volume occupied by the i th component). If each point of space is occupied, then the condition can be written in the following form

$$\sum_{i=1}^m \omega_i n_i(\mathbf{r}) - 1 = 0, \quad (2)$$

which, hereafter, will be termed the close packing condition.

It should be noted that condition Eq. (2) is excessively strict. In the general case, it should be replaced by more weak condition, namely,

$$\sum_{i=1}^m \omega_i n_i(\mathbf{r}) - 1 \leq 0, \quad (3)$$

because the short-range parts of interatomic potentials are not the bilateral constraints. The natural means of getting over this difficulty is introduction of vacancies, i.e., "empty" portions of space (holes). However, the hole does not take into account in implicit form in Eq. (2), because the corresponding generalization will be fulfilled in the following sections. In contrast, if we neglect vacancies in the condensed system considered, then total energy minimization should be carry out under the additional close-packing condition in Eq. (2).

Further, the next step of our description is fixation of particle numbers for each component. The law of conservation can be written as

$$\int_{(V)} n_i(\mathbf{r}) d\mathbf{r} - N_i = 0, \quad (4)$$

where N_i is the total number of particles of the i th component in the system.

Thus, in the absence of both chemical reactions and thermal defects (like vacancies), any model expressions for thermodynamic functions should be analyzed under the additional conditions shown in Eqs. (2) and (4).

Helmholtz Free Energy Functional and the Long-Range Parts of Interatomic Potentials

Consider a solution of m components whose spatial distributions are given by the local particle number densities $n_1(\mathbf{r}), n_2(\mathbf{r}), \dots, n_m(\mathbf{r})$. The Helmholtz free energy functional F for a given thermodynamic system can be written in the self-consistent field (SCF) approximation, taking account of only pair interactions, as

$$F = \frac{1}{2} \sum_{i,j=1}^m \iint_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + T \sum_{i=1}^m \int n_i(\mathbf{r}) \ln \left(\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) d\mathbf{r}, \quad (5)$$

where the first term is the configurational part of the free energy in the self-consistent field approximation, $K_{ij}(\mathbf{r} - \mathbf{r}')$ is the pair interaction potential of the i th and j th components located at points \mathbf{r} and \mathbf{r}' , respectively; the second term is the entropy term of the free energy in the regular-solutions approximations; T is temperature in energy units; the integration extends over the entire volume V of the system; and

$$n(\mathbf{r}) = \sum_{i=1}^m n_i(\mathbf{r}) \quad (6)$$

is the total particle number density.

Equilibrium distribution of components minimizes the Helmholtz free energy in Eq. (5) under the additional conditions in Eqs. (2) and (4). The simplest way of extremum search is the Lagrange method. The corresponding Lagrange functional has the form

$$\begin{aligned} \mathcal{L}(\{n_i(\mathbf{r})\}, \{\Psi(\mathbf{r})\}, \mu_i) = & \frac{1}{2} \sum_{i,j=1}^m \iint_{(V)} K_{ij}(\mathbf{r}-\mathbf{r}') \\ & \times n_i(\mathbf{r})n_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + T \sum_{i=1}^m \int n_i(\mathbf{r}) \ln \left[\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right] d\mathbf{r} \\ & - \sum_{i=1}^m \mu_i \left[\int_{(V)} n_i(\mathbf{r})d\mathbf{r} - N_i \right] - \int_{(V)} \Psi(\mathbf{r}) \left[\sum_{i=1}^m \omega_i n_i(\mathbf{r}) \right. \\ & \left. - 1 \right] d\mathbf{r}, \quad (7) \end{aligned}$$

which depends on the functions $n_i(\mathbf{r})$, $\Psi(\mathbf{r})$ and parameters μ_i .

Extreme conditions have the usual form

$$\begin{cases} \frac{\delta \mathcal{L}}{\delta n_i(\mathbf{r})} = 0, \\ \frac{\delta \mathcal{L}}{\delta \Psi(\mathbf{r})} = 0, \\ \frac{\partial \mathcal{L}}{\partial \mu_i} = 0, \end{cases} \quad (8)$$

where $i = 1, 2, \dots, m$.

Hence we find

$$\begin{cases} T \ln \left(\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) + \sum_{j=1}^m \int_{(V)} K_{ij}(\mathbf{r}-\mathbf{r}')n_j(\mathbf{r}')d\mathbf{r}' \\ \quad - \omega_i \Psi(\mathbf{r}) - \mu_i = 0, \\ \sum_{i=1}^m \omega_i n_i(\mathbf{r}) - 1 = 0, \\ \int_{(V)} n_i(\mathbf{r})d\mathbf{r} - N_i = 0. \end{cases} \quad (9)$$

Equilibrium distributions of the components obey this set of equations. The total number of equations is equal to the number of unknown functions and parameters and equals $(2m + 1)$: $n_i(\mathbf{r})$ are

the local densities of the components, μ_i are the chemical potentials of the components, and $\Psi(\mathbf{r})$ is a function with dimensionality of pressure. At that, all the components are contained in the set of Eqs. (9) in rather symmetric forms.

It should be noted that the functions $K_{ij}(\mathbf{r})$ in the Helmholtz free energy are not "true" interatomic potentials, as the introduction of the proper atomic volume does not permit rapprochement of atoms at distances of less than

$$a_{ij} \approx [(\omega_i)^{1/3} + (\omega_j)^{1/3}]. \quad (10)$$

This condition leads to restriction of local densities in Eq. (2). Therefore, the functions $K_{ij}(\mathbf{r})$ are the result of some cutting of "true" interatomic potentials, i.e., the long-range parts of these potentials are:

$$K_{ij}(\mathbf{r}) = \begin{cases} W_{ij}(\mathbf{r}), & \text{if } |\mathbf{r}| \geq a_{ij}, \\ 0, & \text{otherwise,} \end{cases} \quad (11)$$

where $W_{ij}(\mathbf{r})$ is the "true" potential of interacting between atoms of the i th and j th components.

Thus, in the generalized lattice model, the singular short-range parts of the interatomic potentials do not give direct contribution into thermodynamic properties of system, but they appear via proper atomic volumes.

Vacancies in Condensed Matter

Suppose that a system contains the vacancies with the proper volume ω_0 and the local density $n_0(\mathbf{r})$. Then, instead of Eq. (2), the close-packing condition has the form

$$\sum_{i=0}^m \omega_i n_i(\mathbf{r}) - 1 = 0. \quad (12)$$

In contrast, the Helmholtz free energy functional Eq. (5) can be transformed into the following expression:

$$\begin{aligned} F = & \frac{1}{2} \sum_{i,j=1}^m \iint_{(V)} K_{ij}(\mathbf{r}-\mathbf{r}')n_i(\mathbf{r})n_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\ & + T \sum_{i=0}^m \int n_i(\mathbf{r}) \ln \left(\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) d\mathbf{r}. \quad (13) \end{aligned}$$

It should be noted that vacancies give the contributions into the close-packing condition in Eq. (12) and into the entropy term of the free energy functional in Eq. (13), but not into the potential energy term of the free energy (direct interaction of vacancies with any components absences). Total particle number density in Eq. (6) should be defined as

$$n(\mathbf{r}) = \sum_{i=0}^m n_i(\mathbf{r}). \quad (14)$$

Equilibrium distributions of the system are described by Eqs. (9) with obvious changes due to the indicated redefinitions in Eqs. (12)–(14):

$$\begin{cases} T \ln \left(\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) + \sum_{j=1}^m \int_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_j(\mathbf{r}') d\mathbf{r}' - \omega_i \Psi(\mathbf{r}) - \mu_i = 0, & (i = 0 \div m), \\ \sum_{i=0}^m \omega_i n_i(\mathbf{r}) - 1 = 0, \\ \int_{(V)} n_i(\mathbf{r}) d\mathbf{r} - N_i = 0, \end{cases} \quad (15)$$

(i = 0 ÷ m).

This system of equations contains all the components (including the vacancies) in symmetric form, but the vacancies are not the quite substantial particles. Indeed, when we calculate the chemical potential of *i*th component (*i* ≠ 0) by the formula

$$\mu_i = \left(\frac{\delta \mathcal{F}}{\delta n_i(\mathbf{r})} \right)_{T,V,n_j(\mathbf{r})}, \quad (j \neq i),$$

at a fixed volume of the system, we should replace *i*th particles by the corresponding quantity of vacancies. It means that chemical potentials, defined by Eq. (15), should be renormalized as follows:

$$\tilde{\mu}_i = \left[\frac{\delta \mathcal{F}}{\delta n_i(\mathbf{r})} \right]_{T,V,n_j(\mathbf{r})} + \int \left[\frac{\delta \mathcal{F}}{\delta n_0(\mathbf{r}') } \right]_{T,V,n_j(\mathbf{r}')} \left[\frac{\delta n_0(\mathbf{r}')}{\delta n_i(\mathbf{r})} \right] d\mathbf{r}'.$$

Using identity

$$\begin{cases} \tilde{\mu}_i = T \left\{ \ln \left[\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right] - \frac{\omega_i}{\omega_0} \ln \left[\frac{n_0(\mathbf{r})}{n(\mathbf{r})} \right] \right\} + \sum_{j=1}^m \int_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_j(\mathbf{r}') d\mathbf{r}', & (i = 0 \div m), \\ \sum_{i=0}^m \omega_i n_i(\mathbf{r}) - 1 = 0, \\ \int_{(V)} n_i(\mathbf{r}) d\mathbf{r} - N_i = 0, \end{cases} \quad (17)$$

(i = 0 ÷ m).

The set of nonlinear integral Eqs. (17) is closed and describes the equilibrium distributions of com-

$$\left[\frac{\delta n_0(\mathbf{r}')}{\delta n_i(\mathbf{r})} \right] = - \frac{\omega_i}{\omega_0} \delta(\mathbf{r} - \mathbf{r}'),$$

we have

$$\begin{aligned} \tilde{\mu}_i = \mu_i - \frac{\omega_i}{\omega_0} \mu_0 = T \left\{ \ln \left[\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right] - \frac{\omega_i}{\omega_0} \ln \left[\frac{n_0(\mathbf{r})}{n(\mathbf{r})} \right] \right\} \\ + \sum_{j=1}^m \int_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_j(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (16)$$

This renormalization of chemical potentials permits to eliminate the function $\Psi(\mathbf{r})$, which has not clear physical sense yet. Equations (16) under the conditions in Eq. (12) and fixations of particles and vacancies numbers determine the thermodynamic equilibrium in the system

ponents in the system taking into account vacancies.

Thermodynamic Functions of Homogeneous Multicomponent Phases

The Helmholtz free energy (5) for a homogeneous system ($n_i(\mathbf{r}) = \text{const}$) takes the following form:

$$F = \frac{1}{2} \sum_{i,j=1}^m K_{ij}^{(0)} \frac{N_j N_i}{V} + T \left[N_0 \ln \left(\frac{N_0}{N} \right) + \sum_{i=1}^m N_i \ln \left(\frac{N_i}{N} \right) \right], \quad (18)$$

where $K_{ij}^{(0)} = \int_{(V)} K_{ij}(\mathbf{r}) d\mathbf{r}$, $N_i = V n_i$ is the total number of the particles of the i th kind in the system, $N = \sum_{i=0}^m N_i$ is the total number of the particles and vacancies, and V is the volume of the system.

Arbitrary change in the volume of the system at fixed numbers of the particles N_1, N_2, \dots, N_m leads to change in the number of vacancies. Therefore, pressure should be determined by the formula

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N_1, \dots, N_m} = - \left(\frac{\partial F}{\partial V} \right)_{T, N_0, N_1, \dots, N_m} - \left(\frac{\partial F}{\partial N_0} \right)_{V, T, N_1, \dots, N_m} \cdot \left(\frac{\partial N_0}{\partial V} \right)_{T, N_1, \dots, N_m}. \quad (19)$$

In contrast, change in the volume of the system can be written as

$$dV = \omega_0 dN_0. \quad (20)$$

The use of relations (18)–(20) yields

$$P = \frac{1}{2} \sum_{i,j=1}^m K_{ij}^{(0)} n_i n_j + \frac{T}{\omega_0} \ln \left(\frac{n}{n_0} \right). \quad (21)$$

Finally, the chemical potentials of components of the homogeneous system can be obtained in a similar way. Then,

$$\mu_i = \sum_{j=1}^m K_{ij}^{(0)} n_j + T \left[\ln \left(\frac{n_i}{n} \right) - \frac{\omega_i}{\omega_0} \ln \left(\frac{n_0}{n} \right) \right]. \quad (22)$$

For further description, it is convenient to change over from densities n_i to the atomic concentrations x_i using the following relations:

$$x_i = \frac{n_i}{\sum_{j=1}^m n_j}. \quad (23)$$

By introducing the function (ω, x) as

$$(\omega, x) = \sum_{i=1}^m x_i \omega_i = \frac{1 - \omega_0 n_0}{\sum_{j=1}^m n_j}, \quad (24)$$

we have relations between old and new variables:

$$n_i = \frac{1 - \omega_0 n_0}{(\omega, x)} x_i. \quad (25)$$

Substituting Eq. (25) into Eq. (21) yields

$$P = \frac{(1 - n_0 \omega_0)^2}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j + \frac{T}{\omega_0} \ln \left[1 + \frac{1 - n_0 \omega_0}{n_0(\omega, x)} \right]. \quad (26)$$

Furthermore, the chemical potentials in terms of atomic concentrations take the form

$$\begin{aligned} \mu_i = & \frac{1 - n_0 \omega_0}{(\omega, x)} \sum_{j=1}^m K_{ij}^{(0)} x_j \\ & + T \left(\ln x_i + \ln \left[\frac{1 - n_0 \omega_0}{1 - n_0 [\omega_0 - (\omega, x)]} \right] \right) \\ & + \frac{\omega_i}{\omega_0} \ln \left[\frac{1 - n_0 [\omega_0 - (\omega, x)]}{n_0(\omega, x)} \right]. \quad (27) \end{aligned}$$

Equations (26) and (27) establish the relations between the chemical potentials μ_i and atomic concentrations x_i at given temperature and pressure. Unfortunately, it is impossible to eliminate the number of vacancies N_0 and represent the chemical potentials μ_i as explicit functions of P, T, x_j in the general case. However, this elimination is possible for two essential special cases, which are considered below.

GASEOUS PHASE

For the gaseous phase, the total fraction of volume that occupied by the particles is very small, i.e.,

$$\epsilon_1 = 1 - \omega_0 n_0, \quad \epsilon \ll 1. \quad (28)$$

Extracting from Eqs. (26) and (27) the main terms with respect to ϵ_1 gives

$$P = \epsilon_1 \frac{T}{(\omega, x)}, \quad (29)$$

and

$$\begin{aligned} \mu_i = T \ln \left[\epsilon_1 \frac{\omega_0 x_i}{(\omega, x)} \right] \\ + \frac{\epsilon_1}{(\omega, x)} \left\{ T[\omega_i - \omega_0 + (\omega, x)] + \sum_{j=1}^m K_{ij}^{(0)} x_j \right\}. \end{aligned} \quad (30)$$

By eliminating parameter ϵ_1 , we obtain the chemical potentials as functions of temperature, pressure, and composition of the gaseous phase, namely,

$$\begin{aligned} \mu_i = T \ln \left(\frac{\omega_0 x_i}{T} P \right) \\ + P \left\{ [\omega_i - \omega_0 + (\omega, x)] + \frac{1}{T} \sum_{j=1}^m K_{ij}^{(0)} x_j \right\}. \end{aligned} \quad (31)$$

CONDENSED PHASE

In contrast to the gaseous phase, in the condensed phase, the fraction of the volume occupied by vacancies $\omega_0 n_0$ is small, and it can be considered as a small parameter, i.e.,

$$\epsilon_2 = \omega_0 n_0 \ll 1. \quad (32)$$

Extracting from Eqs. (26) and (27) the main terms with respect to ϵ_2 yields

$$\begin{aligned} P = - \frac{T}{\omega_0} \ln(\epsilon_2) \\ + \left\{ \frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j - \frac{T}{\omega_0} \ln \left[\frac{(\omega, x)}{\omega_0} \right] \right\}, \end{aligned} \quad (33)$$

and

$$\begin{aligned} \mu_i = -T \left(\frac{\omega_i}{\omega_0} \right) \ln(\epsilon_2) + \left[T \ln(x_i) - T \left(\frac{\omega_i}{\omega_0} \right) \ln \left(\frac{(\omega, x)}{\omega_0} \right) \right. \\ \left. + \frac{1}{(\omega, x)} \sum_{j=1}^m K_{ij}^{(0)} x_j \right]. \end{aligned} \quad (34)$$

Hence we get the expression of chemical potentials via pressure, temperature, and composition of the condensed phase

$$\begin{aligned} \mu_i = \omega_i P + T \ln(x_i) + \left[\frac{1}{(\omega, x)} \sum_{j=1}^m K_{ij}^{(0)} x_j \right] \\ - \omega_i \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right]. \end{aligned} \quad (35)$$

Equations of Phase Equilibrium Without Chemical Reactions

As is well known, the conditions of equilibrium in system at fixed temperature and pressure are equalities of chemical potentials in coexisting phases. Using expressions (31) and (34) for chemical potentials in the gaseous and condensed phases, we have the following system of equations:

$$\begin{aligned} T \ln \left(\frac{\omega_0 y_i}{T} P \right) + P \left\{ [\omega_i - \omega_0 + (\omega, y)] + \frac{1}{T} \sum_{j=1}^m K_{ij}^{(0)} y_j \right\} \\ = \omega_i P + T \ln(x_i) + \left[\frac{1}{(\omega, x)} \sum_{j=1}^m K_{ij}^{(0)} x_j \right] \\ - \omega_i \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right], \quad (i = 1 \div m), \end{aligned} \quad (36)$$

where x_i and y_i are the atomic concentrations in condensed and gaseous phases, respectively.

This system of equations allows us (in principle) to find the composition of one of the phase via the composition of another phase.

Equations of Phase Equilibrium With Chemical Reactions

Phase transitions and related rearrangements in systems are an extreme form of interatomic poten-

tials manifestation. In the general case, the interatomic potential influence on equilibrium parameters of systems and apparent in kinetic processes.

We assume that a chemical reaction takes place in the system considered. In addition, suppose that the chemical reaction can be written as follows

$$\sum_i \nu_i A_i = 0, \quad (37)$$

$$\begin{cases} K_g = \left(\frac{P\omega_0}{T}\right)^{-\sum_i \nu_i} \exp\left(-\frac{P}{T}\left\{\sum_i \nu_i[\omega_i - \omega_0 + (\omega, y)] + \frac{1}{T} \sum_{i,j} \nu_i K_{ij}^{(0)} y_j\right\}\right), \\ K_c = \exp\left\{-\left[\frac{1}{T(\omega, x)} \sum_{i,j} \nu_i K_{ij}^{(0)} x_j\right] + \frac{\sum_i \nu_i \omega_i}{T} \left[\frac{\sum_{i,j} K_{ij}^{(0)} x_i x_j}{2(\omega, x)^2} - P\right]\right\}, \end{cases} \quad (39)$$

where

$$K_g = \left[\prod_i (y_i)^{\nu_i}\right], \quad K_c = \left[\prod_i (x_i)^{\nu_i}\right] \quad (40)$$

are the constants of the equilibrium of chemical reaction (37) in gaseous and condensed phases, respectively. Note that, in the general case, constants K_g and K_c have different values.

We have m kinds of molecules and s independent chemical reactions in a two-phase system. Then, at fixed external conditions (i.e., fixed T and P), there are $2(m - 1)$ unknown concentrations [$(m - 1)$ independent concentrations in each phase]. Equalities of chemical potentials in coexisting phases give m equations, whereas conditions of chemical equilibrium for each of s reactions give m equations. Thus, for description of the m -component two-phase system, it is necessary to find $2(m - 1)$ unknowns that obey the set of $m + s$ equations.

URANIUM-OXYGEN SYSTEM

General Relations

Consider a multi-component system with chemical reaction of the kind

$$\sum_i \nu_i A_i = B, \quad (41)$$

where ν_i and A_i are the stoichiometric coefficients and chemical symbols of the reagents, respectively, B is the chemical symbol of the reaction product.

where ν_i are the stoichiometric coefficients, A_i are the chemical symbols of the components. Then, the condition of chemical equilibrium in the system has the form

$$\sum_i \nu_i \mu_i = 0. \quad (38)$$

Substituting expressions for chemical potentials in both gaseous and condensed phases yields

As an example of such a reaction, it can be considered the formation of the multi-particle complex $U_x O_y Vac_z$, where Vac denotes a vacancy. The chemical equilibrium condition has the form

$$\mu_B = \sum_i \nu_i \mu_i; \quad (42)$$

i.e., the chemical potential of the complex is the linear combination of the constituents' chemical potentials.

It should be noted that chemical potential of vacancies in the generalized lattice model is equal to zero; therefore, the chemical potential of the complex does not depend on presence vacancies.

In addition, it is known that most essential compounds between uranium U and oxygen O are UO_2 and UO_3 . Further, suppose the system contains the particles of the following kinds:



Then, the equation of chemical reaction with production of particles UO_2 and UO_3 has the form

$$2UO_2 + O_2 - 2UO_3 = 0. \quad (44)$$

Hence, the equation for chemical equilibrium for both gaseous and condensed phases is given by

$$2\mu_1 + \mu_3 - 2\mu_2 = 0, \quad (45)$$

where subscripts 1, 2, and 3 correspond to UO_2 , UO_3 , and O_2 , respectively.

At a given temperature T and pressure P , the total number of unknowns is four (two independent concentrations for each phase). In contrast, the number of independent equations is four too [equality of chemical potentials (36) with $m = 3$ and equation of chemical equilibrium (38)]. Thus, at fixed temperature and pressure, the number of

unknown concentrations is equal to number of equations. Therefore, compositions of both phases predetermined unambiguously by external conditions (if the system of equations has a unique solution). This system of equations for the equilibrium compositions of coexisting phases is written as follows:

$$\left\{ \begin{array}{l}
 T \ln \left(\frac{\omega_0 y_1}{T} P \right) + P \left\{ [\omega_1 - \omega_0 + (\omega, y)] + \frac{1}{T} \sum_{j=1}^m K_{1j}^{(0)} y_j \right\} \\
 = \omega_1 P + T \ln(x_1) + \left[\frac{1}{(\omega, x)} \sum_{j=1}^m K_{1j}^{(0)} x_j \right] - \omega_1 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right]; \\
 T \ln \left(\frac{\omega_0 y_2}{T} P \right) + P \left\{ [\omega_2 - \omega_0 + (\omega, y)] + \frac{1}{T} \sum_{j=1}^m K_{2j}^{(0)} y_j \right\} \\
 = \omega_2 P + T \ln(x_2) + \left[\frac{1}{(\omega, x)} \sum_{j=1}^m K_{2j}^{(0)} x_j \right] - \omega_2 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right]; \\
 T \ln \left(\frac{\omega_0 y_3}{T} P \right) + P \left\{ [\omega_3 - \omega_0 + (\omega, y)] + \frac{1}{T} \sum_{j=1}^m K_{3j}^{(0)} y_j \right\} \\
 = \omega_3 P + T \ln(x_3) + \left[\frac{1}{(\omega, x)} \sum_{j=1}^m K_{3j}^{(0)} x_j \right] - \omega_3 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right]; \\
 2 \left\{ \omega_1 P + T \ln(x_1) + \frac{1}{(\omega, x)} \sum_{j=1}^m K_{1j}^{(0)} x_j - \omega_1 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right] \right\} \\
 - 2 \left\{ \omega_2 P + T \ln(x_2) + \frac{1}{(\omega, x)} \sum_{j=1}^m K_{2j}^{(0)} x_j - \omega_2 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right] \right\} \\
 + \left\{ \omega_3 P + T \ln(x_3) + \frac{1}{(\omega, x)} \sum_{j=1}^m K_{3j}^{(0)} x_j - \omega_3 \left[\frac{1}{2(\omega, x)^2} \sum_{i,j=1}^m K_{ij}^{(0)} x_i x_j \right] \right\} = 0; \\
 x_1 + x_2 + x_3 = 1; \\
 y_1 + y_2 + y_3 = 1.
 \end{array} \right. \quad (46)$$

Systems With Variable Valent States

Now, suppose that the condensed phase can be represented as a "compound" $\text{UO}_{2+\epsilon}$, $0 < \epsilon < 1$ with variable valence of uranium. Then, the problem is to evaluate ϵ as a function of the external thermodynamic conditions P , T and parameters of the atoms and their interactions in the system.

Using Eq. (43), we obtain the relation between unknowns x_k and ϵ in the form

$$\epsilon = \frac{2x_1 + 3x_2}{x_1 + x_2} - 2. \quad (47)$$

Thus, the nonstoichiometry function ϵ can be found, in principle, from the system of equations (46) at given values of parameters of components and their interactions. However, it is difficult to determine these parameters from independent measurements.

At the same time, it is possible to find some of these parameters from experimental data on phase equilibria of individual substances, such as the temperature dependence of saturated vapor pressure, but other parameters should be found from experimental data on related binary systems.

Conclusion

The most essential results of this study are the following: (1) the model expression for Helmholtz free energy of a multicomponent system, taking into account both short-range parts of interatomic potentials (including difference of atomic sizes) and long-range parts of interatomic potentials in mean field approximation; (2) interrelations between local thermodynamic variables (densities of components, temperature, and chemical potentials) for multicomponents in both gaseous and condensed systems with vacancies; (3) equations of equilibrium between condensed and gaseous phases with chemical reactions; and (4) the simple model for description of the system with variable valent states of one of the components.

The basic ideas related to the generalized lattice model were published in preliminary form in Refs. [6, 7]. More recent results on the model and its development were published in part in Refs. [8–10]. Most of the recent results related to mutual renormalizations of internal fields and interatomic potentials are presented in Refs. [11–13].

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