Thermodynamics of binary solutions of the eutectic type with several intermediate phases of constant composition

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Abstract. An universal method is proposed for calculating the phase diagrams of binary solutions with several intermediate phases of constant composition. The proposed method is based on the nonlinear transformations of the concentration axes and makes it possible to correctly reduce the calculation of the phase diagrams with several intermediate phases to a sequence of phase diagrams of individual subsystems. The thermodynamics of binary solutions of the eutectic type with several intermediate phases of constant composition is described using the proposed method within the framework of the generalized lattice model. The results of the calculations performed are compared with phase diagrams of real binary solutions.

1. Introduction
Calculation of phase diagrams is one of the most interesting problem of physics of multicomponent systems \cite{1, 2}. The present work is devoted to the development of a new direction in the theory of solutions with chemical bonding. The purpose of this study was to devise a consistent method for calculating the phase diagrams of binary solutions with several intermediate phases of constant composition. The proposed method is based on nonlinear transformations of concentration variables of solutions. These transformations allow one to correctly reduce the calculation of the aforementioned phase diagrams to a sequence of phase diagrams of individual subsystems. These transformations allow one to correctly reduce the calculation of the aforementioned phase diagrams to a sequence of phase diagrams of individual subsystems.

2. Method
Let us consider the phase diagram of an $A\text{--}B$ binary solution with a negligible solubility of the components in the solid state in the presence of two intermediate phases of constant composition (i.e., a congruently melting chemical compounds $A_{m_1}B_{n_1}$ and $A_{m_2}B_{n_2}$). Without a loss in the generality of the subsequent analysis, we examine a binary system of the eutectic type. The phase diagram of this system is schematically presented in Figure 1. It is easy to see that the left, central and right parts of the initial phase diagram are similar to a conventional phase diagram with a simple eutectic. The fundamental difference between all parts of the phase diagram in Figure 1 and the phase diagram with the simple eutectic is that the mole fractions $x$ of the $B$
component (reckoned along the concentration axis) vary in the range $0 \leq x \leq n_1/(m_1 + n_1)$ for the left subsystem $A-A_{m_1}B_{n_1}$, in the range $n_1/(m_1 + n_1) \leq x \leq n_2/(m_2 + n_2)$ for the central subsystem $A_{m_1}B_{n_1}-A_{m_2}B_{n_2}$ and in the range $n_2/(m_2 + n_2) \leq x \leq 1$ for the right subsystem $A_{m_2}B_{n_2}-B$. As a consequence, the lengths of the segments that correspond in the concentration axis to the left, central and right parts of the diagram are not equal to unity, whereas the length of the concentration axis in any phase diagram should be equal to unity. These differences do not permit one to directly use the well-developed methods for calculating phase diagrams in the case of simulation of the components of phase diagrams for systems with intermediate phases. Nevertheless, this problem can be solved with the corresponding change in the concentration variables according to the procedure described below.

At the beginning we shall consider the central part of Figure 1. Here, the chemical compound $A_{m_2}B_{n_2}$ considered an independent molecular component of a new binary system $A_{m_1}B_{n_1}-A_{m_2}B_{n_2}$. Then, the mole fractions of the molecular components can be written as follows:

$$y = \frac{N_{A_{m_2}B_{n_2}}}{N_{A_{m_1}B_{n_1}} + N_{A_{m_2}B_{n_2}}}, \quad 1 - y = \frac{N_{A_{m_1}B_{n_1}}}{N_{A_{m_1}B_{n_1}} + N_{A_{m_2}B_{n_2}}}$$

where $N_{A_{m_1}B_{n_1}}$ and $N_{A_{m_2}B_{n_2}}$ are the total numbers of particles of the molecular components of the $A_{m_1}B_{n_1}-A_{m_2}B_{n_2}$ binary system, $y$ and $1 - y$ are the mole fractions of the molecular components $A_{m_2}B_{n_2}$ and $A_{m_1}B_{n_1}$, respectively. From the above expression, we have

$$N_{A_{m_2}B_{n_2}} = \frac{y}{1-y} N_{A_{m_2}B_{n_2}}$$

On the other hand, the old independent concentration variable $x$ of the $A-B$ initial solution is defined as follows:

$$x = \frac{\bar{N}_A}{\bar{N}_A + \bar{N}_B}$$
where
\[ \bar{N}_A = m_1 N_{A_m_1 B_n_1} + m_2 N_{A_m_2 B_n_2}, \]
\[ \bar{N}_B = n_1 N_{A_m_1 B_n_1} + n_2 N_{A_m_2 B_n_2}. \] (4)

From equations (1)–(4), we obtain
\[
x(y) = \frac{n_1 + y(n_2 - n_1)}{m_1 + n_1 + y(m_2 + n_2 - m_1 - n_1)}, \quad y(x) = \frac{x(m_1 + n_1) - n_1}{n_2 - n_1 - x(m_2 + n_2 - m_1 - n_1)}. \] (5)

Expressions (5) describe a sought one-to-one correspondence between the old \((x)\) and new \((y)\) concentration variables for the central system \(A_m_1 B_n_1 – A_m_2 B_n_2\). In additional, we obtain the correct limiting values \(y(n_1/(m_1 + n_1)) = 0\) and \(y(n_2/(m_2 + n_2)) = 1\) and the desired range of the new variable \(0 \leq y \leq 1\).

The rest binary systems \((A – A_m_1 B_n_1\) and \(A_m_2 B_n_2 – B)\) are considered in a similar way. In particular these cases were studied in detail in paper [3]. For this reason, we do not write out the explicit expressions for the nonlinear transformations of the concentration axes, which can be found in the paper mentioned above.

It should be noted that transformations (5) were derived without recourse to any specific model of a solution, and, in this sense, they are universal. It is evident that relations (5) can be used for calculating not only eutectic phase diagrams but also any phase diagrams with several intermediate phases of constant composition. Below, we will illustrate how these relationships can be used to calculate the phase diagrams with several intermediate phases of constant composition in terms of the generalized lattice model [4, 5].

3. Phase diagram calculation
The thermodynamics of binary solutions of the eutectic type with several intermediate phases of constant composition was described using the proposed method within the framework of the generalized lattice mode [4, 5] (see also [6]).

![Figure 2. Phase diagrams of the Ag–Er and Ag–Ho systems. Dashed lines are the experimental data taken from [7–10]. Solid lines indicate the results obtained from theoretical calculations.](image)

The corresponding phase diagram are shown in Figure 2. It can be seen from Figure 2 that the phase diagrams are consistent with the experimental data available in the literature [7–10].

In conclusion, we briefly note the prospects for further development of the proposed theory. First, in the model, the possible dissociation of the compounds was ignored. However, it is
well known that the dissociation of chemical compounds has a substantial effect on the liquidus curves in the vicinity of the dystectic point. Second, it is interesting to investigate systems with intermediate phases of variable composition in the case when the components are mutually soluble in the solid state.

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