Phase diagram calculation of binary solutions of the peritectic type in the generalized lattice model

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Abstract. Thermodynamics of the binary solutions of the peritectic type is studied within the framework of the generalized lattice model accounting for the specific volumes of components. The corresponding equations describing two- and three-phase chemical equilibria are derived on the base of proposed approach. Several of phase diagrams of the peritectic type are calculated. The theoretically calculated phase diagrams are compared with the corresponding experimental diagrams.

1. Introduction
One of the most important problems of thermodynamics of multicomponent systems is description of two-, three- and multi-phase equilibria in solutions and the construction of the corresponding phase diagrams [1, 2]. A lot of theoretical and experimental works are devoted to these problems (see, for example, [3–5]). Among the various types of phase diagrams of binary solutions, the description of peritectic equilibrium causes significant difficulties. At present there is no ab initio models describing the nature of peritectic solutions. As a consequence, the number of phase diagrams of the peritectic type is relatively small. In this study, we developed a thermodynamical approach for the calculation of phase diagrams of peritectic type that is based on the generalized lattice model (see, for example, [6, 7]).

2. Model
According to the basic principles of the generalized lattice model, the chemical potentials of a homogeneous binary solution (per mole of a material) can be represented in the form [8, 9]

\[ \mu_1 = \mu_{10} + RT \ln x + W \lambda \left( \frac{1-x}{x + \lambda(1-x)} \right)^2, \]
\[ \mu_2 = \mu_{20} + RT \ln(1-x) + W \left( \frac{x}{x + \lambda(1-x)} \right)^2, \]

(1)

where \( \mu_{i0} \) is the standard chemical potential of the \( i \)th component, \( R \) is the universal gas constant, \( T \) is the temperature of the system, \( x \) is the mole fraction of the first component, \( W \) is an analog of the energy of mixing in the generalized lattice model, \( \lambda = \omega_2/\omega_1 \), and \( \omega_i \) is the characteristic atomic volume of the \( i \)th component.

Further let us consider the phase diagram of an \( A-B \) binary solution of peritectic type. The corresponding phase diagram is schematically presented in Figure 1.
Let \( x, y \) and \( z \) be the mole fraction of the first component in liquid phase, in \( \alpha \) solid solution and in \( \beta \) solid solution, respectively. We introduce three new parameters \( W, U \) and \( G \), where \( W \) is an analog of the energy of mixing in liquid phase, \( U \) is an analog of the energy of mixing in \( \alpha \) solid solution and \( G \) is an analog of the energy of mixing \( \beta \) solid solution. Then relationships (1) determine the chemical potentials of components in liquid phase. The chemical potentials of components in solid solutions are considered in a similar way. In these cases for \( \alpha \) solid solution we have

\[
\mu_{\alpha 1} = \mu_{S_10}^S + RT \ln y + U \lambda \left( \frac{1 - y}{y + \lambda (1 - y)} \right)^2,
\]

\[
\mu_{\alpha 2} = \mu_{S_20}^S + RT \ln(1 - y) + U \left( \frac{y}{y + \lambda (1 - y)} \right)^2,
\]

and for \( \beta \) solid solution we obtain

\[
\mu_{\beta 1} = \mu_{S_10}^S + RT \ln z + G \lambda \left( \frac{1 - z}{z + \lambda (1 - z)} \right)^2,
\]

\[
\mu_{\beta 2} = \mu_{S_20}^S + RT \ln(1 - z) + G \left( \frac{z}{z + \lambda (1 - z)} \right)^2.
\]

We can obtain all parameters of generalized lattice model for binary solutions of the peritectic type taking into account the chemical equilibrium in the three-phase system, i.e., equating the chemical potentials of the components in the solid and liquid phases

\[
\mu_{\alpha 1}^L(x_0, T_0) = \mu_{\alpha 2}^S(y_0, T_0) = \mu_{\beta 1}^S(z_0, T_0),
\]

\[
\mu_{\beta 2}^L(x_0, T_0) = \mu_{\beta 1}^S(y_0, T_0) = \mu_{\beta 2}^S(z_0, T_0).
\]

Taking into account the chemical equilibrium in the two-phase systems gives

\[
\mu_{\alpha 2}^L(x_0, T_0) = \mu_{\beta 2}^S(y_0, T_0) = \mu_{\beta 2}^S(z_0, T_0).
\]
i) Liquid—\(\alpha\) solid solution \((x > x_0, y > y_0, T > T_0)\):

\[
T(x, y) = \frac{q_1T_1 + \tilde{W}\lambda \left( \frac{1-x}{x+\lambda(1-x)} \right)^2 - \tilde{U}\lambda \left( \frac{1-y}{y+\lambda(1-y)} \right)^2}{q_1 - \ln\left( \frac{x}{y} \right)}
\]

\[
= \frac{q_2T_2 + \tilde{W}\left( \frac{x}{x+\lambda(1-x)} \right)^2 - \tilde{U}\left( \frac{y}{y+\lambda(1-y)} \right)^2}{q_2 - \left( \frac{1-x}{1-y} \right)}.
\]

(5)

ii) Liquid—\(\beta\) solid solution \((x < x_0, z < z_0, T < T_0)\):

\[
T(x, z) = \frac{q_1T_1 + \tilde{W}\lambda \left( \frac{1-x}{x+\lambda(1-x)} \right)^2 - \tilde{G}\lambda \left( \frac{1-z}{z+\lambda(1-z)} \right)^2}{q_1 - \ln\left( \frac{x}{z} \right)}
\]

\[
= \frac{q_2T_2 + \tilde{W}\left( \frac{x}{x+\lambda(1-x)} \right)^2 - \tilde{G}\left( \frac{z}{z+\lambda(1-z)} \right)^2}{q_2 - \left( \frac{1-x}{1-z} \right)}.
\]

(6)

iii) \(\alpha\) solid solution—\(\beta\) solid solution \((y > y_0, z > z_0, T < T_0)\):

\[
T(y, z) = \frac{\tilde{G}\lambda \left( \frac{1-z}{z+\lambda(1-z)} \right)^2 - \tilde{U}\lambda \left( \frac{1-y}{y+\lambda(1-y)} \right)^2}{\ln\left( \frac{y}{z} \right)}
\]

\[
= \frac{\tilde{G}\left( \frac{z}{z+\lambda(1-z)} \right)^2 - \tilde{U}\left( \frac{y}{y+\lambda(1-y)} \right)^2}{\ln\left( \frac{1-y}{1-z} \right)}.
\]

(7)

Here \(\tilde{W} = W/R, \tilde{G} = G/R, \tilde{U} = U/R\), and \(q_i = \Delta H_i/RT_i\), where \(\Delta H_i\) are the latent heats of the liquid–solid transition for the pure components, \(T_i\) stands for the melting temperatures of the pure components.

Equations (4)–(7) form a closed system, whose solution allows us to find the concentration dependences of the liquidus branches, solidus branches and solvus branches and, hence, to construct the phase diagrams of peritectic binary systems in the framework of the generalized lattice model.

3. Phase diagram calculation

The table presents the calculated parameters of the generalized lattice model for two of binary systems with the phase diagrams corresponding to the type considered above. The parameters \(q_i\) were determined with the use of the reference data on the latent heats of the liquid–solid transition.

The corresponding phase diagrams calculated with these parameters are depicted in Figure 2. It should be noted that the results obtained from the theoretical calculations are in agreement with the experimental data available in the literature [10, 11].
Table 1. Parameters of the generalized lattice model of binary systems.

| A–B   | q₁   | q₂   | λ   | Ŵ, K | Ū, K | Š, K |
|-------|------|------|-----|------|------|------|
| Ag–Pt | 1.282| 1.164| 2.858| 3411 | 4556 | 4721 |
| Au–Cr | 1.182| 1.140| 1.705| 2831 | 5091 | 4109 |

Figure 2. Phase diagrams of the Ag–Pt and Au–Cr systems. Dashed lines are the experimental data taken from [10, 11]. Solid lines indicate the results obtained from theoretical calculations.

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