Calculation of some types of phase diagrams of binary solutions in the framework of the generalized lattice model

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Abstract. A brief review of the methods of calculation of the basic types of binary phase diagrams is done in the framework of the generalized lattice model. The construction of binary phase diagrams with unlimited and limited solubility of the components in the solid state, the phase diagrams of the eutectic types is considered.

1. Introduction
Simulation of phase diagrams of binary and multicomponent solutions is an important direction of condensed matter physics and physical materials science. In particular, experimental diagrams of real systems allow predicting the physicochemical properties of solutions and alloys in a wide range of temperatures and compositions. In recent decades, in connection with the development of numerical methods and software, along with classical methods of physical and chemical analysis, the CALPHAD method has been actively developed (see, for example, [1–3]).

However, difficulties in adequately describing phase equilibria in complex condensed systems with different types of interatomic interactions can be overcome only by improving rigorous analytical methods of thermodynamics of multiphase systems.

Thus, within the framework of the generalized lattice model (GLM) (see, for example, [4–6]), methods were developed for calculating most types of diagrams of binary solutions, including those with intermediate phases of constant and variable compositions. The purpose of this work is a brief review and systematization of methods for calculating the main types of phase diagrams of binary systems in the framework of the GLM.

2. Model
Let us consider the first type of phase diagram of a binary system, a schematic representation of which is shown in figure 1.

Similar phase diagrams occur in systems with unlimited solubility of components in the liquid and solid states, provided that the mixing energy in the liquid state is less than the mixing energy in the solid state.

To calculate the state diagrams of the above type, it is necessary to know the concentration dependences of the liquidus and the solidus. Thus, according to the basic principles of the GLM, the curves of two-phase equilibria are determined by the following equations [7]:

\[ \text{Equations} \]
\[
T(x, y) = \frac{q_1 T_1 + W\lambda \left( \frac{1 - x}{x + \lambda (1 - x)} \right)^2 - U\lambda \left( \frac{1 - y}{y + \lambda (1 - y)} \right)^2}{q_1 - \ln \left( \frac{x}{y} \right)}.
\]

Where \( x \) and \( y \) are the mole fractions of the first component in the liquid and solid phases, respectively; \( T_i = t_i + 273.15 \) are the melting temperatures of the pure components, \( \lambda = \omega_i / \omega_j \), \( \omega \) is the characteristic atomic volume of the \( i \)th component, \( W \) and \( U \) are analogs of the energy of mixing in the liquid and solid phases, respectively; here \( \mu_{0i} \) is the standard chemical potential of the \( i \)th component in the corresponding phase, \( R \) is the universal gas constant, \( T \) is the temperature of the system.

\[
q_i T_i + W \lambda \left( \frac{1 - x}{x + \lambda (1 - x)} \right)^2 - U \lambda \left( \frac{1 - y}{y + \lambda (1 - y)} \right)^2
= \frac{q_1 T_1 + W\lambda \left( \frac{1 - x}{x + \lambda (1 - x)} \right)^2 - U\lambda \left( \frac{1 - y}{y + \lambda (1 - y)} \right)^2}{q_2 - \ln \left( \frac{1 - x}{1 - y} \right)}.
\]

Figure 1. Phase diagram of a binary system in the presence of unlimited solubility of components in solid and liquid states with a common minimum point of solidus and liquidus.

In order to calculate the quantities \( q_i \), it is necessary to determine the difference between the standard chemical potentials of the components in the solid and liquid phases. This problem can be solved using the conventional methods of statistical thermodynamics without invoking any specific solution model. For example, according to [8] (see also [7, 9]), we have

\[
q_i = \Delta H_i / RT_i,
\]

where \( \Delta H_i \) are the latent heats of the liquid–solid transition for the pure components.

The parameters \( \lambda \), \( W \) and \( U \) of the GLM can be determined from the known coordinates \((T_m, x_m)\) of the minimum point [7]; that is,

\[
\lambda = \frac{q_1 (T_m - T_1)}{q_2 (T_m - T_2)} \left( \frac{x_m}{1 - x_m} \right)^2.
\]
\[ U = \frac{Q_2 - q_2(T_m - T_2)}{x_0(x_m + \lambda(1-x_m))} \left( \frac{x_0}{x_0 + \lambda(1-x_0)} \right)^2 - \frac{y_0(y_m + \lambda(1-y_m))}{y_0 + \lambda(1-y_0)} \left( \frac{y_0}{y_0 + \lambda(1-y_0)} \right)^2 , \]  

(4)

\[ W = U + q_2(T_m - T_2) \left( \frac{x_m + \lambda(1-x_m)}{x_m} \right)^2 , \]  

(5)

where \( Q_2 = q_2(T_0 - T_2) - T_0 \ln \left( \frac{1-x_0}{1-y_0} \right) \), \( x_0 \) and \( y_0 \) are the compositions of the liquid and solid phases in equilibrium at the temperature \( T_0 \).

Equations (1)–(5) form a closed system, whose solution allows us to find the concentration dependences of the liquidus and solidus branches in the framework of the GLM and, hence, to construct the phase diagrams corresponding to the type considered above. Within given approach, more than ten phase diagrams of real binary solutions were calculated [10] and compared with experimental data [11].

Further let us consider the second type of phase diagram of a binary system, a schematic representation of which is shown in figure 2. It is easy to see from this figure that the phase diagram is a conventional phase diagram with a simple eutectic. Such phase diagrams are characterized by negligible solubility of components in the solid state. At that the corresponding branches of the solidus and the solvus lie on the axes \( x = 0 \) and \( x = 1 \). Therefore, the calculation of diagrams of the type considered above is reduced to finding the concentration dependences of the two branches of the liquidus.

Figure 2. Phase diagram of the eutectic type in the absence of the mutual solubility of the components in the solid state.

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 [7]

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

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

(6)

For the phase diagrams under consideration, it is significant that, owing to the absence of the solubility of the components in the solid state, their chemical potentials in the solid phases do not depend on the composition (concentrations) and, hence, coincide with the corresponding standard chemical potentials: \( \mu_{10}^{\text{sol}} = \mu_{10} \) and \( \mu_{20}^{\text{sol}} = \mu_{20}^{\text{sol}} \). Taking into account the chemical equilibrium in the two-phase
system, i.e., equating the chemical potentials of the components in the solid and liquid phases, the concentration dependences of the right and left liquidus branches of the phase diagram for the binary system with the simple eutectic can be easily obtained in terms of the generalized lattice model [9]; that is,

$$T_R = \frac{q_1 T_1 + (W \lambda / R) \left( \frac{1-x}{x + \lambda (1-x)} \right)^2}{q_1 - \ln x}, \quad T_L = \frac{q_2 T_2 + (W / R) \left( \frac{x}{x + \lambda (1-x)} \right)^2}{q_2 - \ln (1-x)},$$

where \( q_i \) are determined by formulas (2).

At that the parameters \( \lambda \) and \( W \) of the GLM can be determined from the known coordinates \((T_0, x_0)\) of the eutectic point [9]; that is,

$$\lambda = \frac{x_0 \ln x_0 \left( \frac{x_0 + \lambda (1-x_0)}{1-x_0} \right)^2}{W q_2 (T_0 - T_2) - T_0 \ln (1-x_0)}, \quad R = \frac{q_2 (T_0 - T_1) - T_0 \ln x_0 \left( \frac{x_0 + \lambda (1-x_0)}{1-x_0} \right)^2}{\lambda q_1 (T_0 - T_1) - T_0 \ln x_0 \left( \frac{x_0 + \lambda (1-x_0)}{1-x_0} \right)^2}.$$

All the parameters of the GLM are calculated by formulas (2) and (8), and the temperature dependences of the liquidus branches are determined by equations (7). Within given approach, more than ten phase diagrams of real binary solutions were calculated [10] and compared with experimental data [11]. Further let us consider the third type of phase diagram of a binary system, a schematic representation of which is shown in figure 3. It is easy to see from this figure that such phase diagram of the eutectic type is characterized by negligible solubility of one of components in the solid state and limited solubility of another component in the solid state. Therefore, the calculation of diagrams of the type considered above is reduced to finding the concentration dependences of two branches of the liquidus, one (right) branch of solidus and one (right) branch of solvus.

**Figure 3.** Phase diagram of the eutectic type in the presence of limited solubility of one of the components in the solid state.

Let \( x \) and \( y \) be the mole fraction of the first component in liquid phase and in \( \alpha \) solid solution, respectively. We introduce two new parameters \( W \) and \( U \), where \( W \) is an analog of the energy of mixing in the liquid phase, \( U \) is an analog of the energy of mixing in \( \alpha \) solid solution. Then relationships (6) determine the chemical potentials of components in liquid phase. The chemical potentials of components in \( \alpha \) solid solution are considered in a similar way. In this case for \( \alpha \) solid solution we have

$$\mu_1^\alpha = \mu_1^\beta + RT \ln y + U \lambda \left( \frac{1-y}{y + \lambda (1-y)} \right)^2, \quad \mu_2^\alpha = \mu_2^\beta + RT \ln (1-y) + U \left( \frac{y}{y + \lambda (1-y)} \right)^2.$$
For the phase diagrams under consideration, it is significant that the second solid phase is the pure second component \( B \). Therefore, the chemical potential of the second component in the second solid phase does not depend on the concentrations and coincides with the corresponding standard value, i.e.

\[
\mu^B_2 = \mu^S_2. \tag{10}
\]

For construction of the phase diagram, it is necessary to calculate three parameters of the GLM, namely, \( W, \ U, \) and \( \lambda \). For this purpose, we consider nonvariant three-phase equilibrium, which characterized by compositions of coexisting single liquid and two solid phases at the eutectic temperature \( T_0 \). In this case, we have

\[
\mu^L_1(x_0, T_0) = \mu^L_1(y_0, T_0), \quad \mu^L_2(x_0, T_0) = \mu^L_2(y_0, T_0), \quad \mu^L_2(x_0, T_0) = \mu^B_2 = \mu^S_2. \tag{11}
\]

Using relations for chemical potentials (6), (9), (10) and for chemical equilibrium conditions (11), it is easy to find the parameters \( W, \ U, \) and \( \lambda \) of the GLM model:

\[
q_1(T_0 - T_1) - T_0 \ln \frac{x_0}{y_0} = \lambda = \frac{(T_0 - T_2)q_2 - T_0 \ln(1-x_0)(x_0 + \lambda(1-x_0))}{(1-x_0)^2 A},
\]

\[
U_R = \frac{U}{R} = -\frac{T_0 \ln(1-y_0)}{y_0^2} \left( y_0 + \lambda(1-y_0) \right)^2, \tag{12}
\]

\[
W_R = \frac{W}{R} = \frac{(T_0 - T_2)q_2 - T_0 \ln(1-x_0)(x_0 + \lambda(1-x_0))}{x_0^2},
\]

where

\[
A = \frac{(T_0 - T_2)q_2 - T_0 \ln(1-x_0) + \left( 1 - y_0 \right)^2 T_0 \ln(1-y_0)}{y_0} \left( 1 - x_0 \right). \tag{13}
\]

A further calculation of the phase diagram reduces to modeling the corresponding two-phase equilibria above (or below) the temperature of the eutectic. Thus, in particular, the problem of calculating the liquidus and solidus curves splits into two:

i. Liquid—solid \( \alpha \) solution equilibrium \((x > x_0, \ y > y_0, \ T > T_0)\):

\[
T(x, y) = \frac{q_1T_1 + W\lambda \left( \frac{1-x}{x + \lambda(1-x)} \right)^2 - U\lambda \left( \frac{1-y}{y + \lambda(1-y)} \right)^2}{q_1 - \ln \left( \frac{x}{y} \right)} \tag{14}
\]

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

ii. Liquid—solid \( B \) component equilibrium \((x < x_0, \ T > T_0)\):

\[
q_2(T_2 - T(x)) + T \ln(1-x) + W\left( \frac{x}{x + \lambda(1-x)} \right)^2 = 0. \tag{15}
\]

iii. Finally, for a two-phase equilibrium of a solid \( \alpha \) solution — solid \( B \) component \((y > y_0, \ T < T_0)\), we have
\[ T(y) \ln(1 - y) + U \left( \frac{y}{y + \lambda(1 - y)} \right)^2 = 0. \]  
(16)

Equations (14)–(16) 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 in the framework of the GLM. Within given approach, more than ten phase diagrams of real binary solutions were calculated [10] and compared with experimental data [11].

Further let us consider the fourth type of phase diagram of a binary system, a schematic representation of which is shown in figure 4. It is easy to see from this figure that such phase diagram of the eutectic type is characterized by limited solubility of both components in the solid state. Therefore, the calculation of diagrams of the type considered above is reduced to finding the concentration dependences of two branches of the liquidus, two branches of the solidus and two branches of the solvus.

![Figure 4. Phase diagram of the eutectic type in the presence of limited solubility of both components in the solid state.](image)

Let \( x, y \) and \( z \) be the molar fractions of the first component in the liquid phase, in the solid \( \alpha \)-solution and in the solid \( \beta \)-solution, respectively. We also agree to denote the mixing energies of the melt and solid-and-solution by the letters \( W, U \) and \( G \). Then the relations (6) determine the concentration dependences of the chemical potentials of the components in the liquid phase. According to (9), the chemical potentials of components in \( \alpha \) solid solution are considered in a similar way. Finally, in this case for \( \beta \) solid solution we have

\[ \mu_1^\beta = \mu_{10}^\beta + RT \ln z + G\lambda \left( \frac{1 - z}{z + \lambda(1 - z)} \right)^2, \quad \mu_2^\beta = \mu_{20}^\beta + RT \ln(1 - z) + G \left( \frac{z}{z + \lambda(1 - z)} \right)^2. \]  
(17)

For construction of the phase diagram, it is necessary to calculate four parameters of the GLM, namely, \( W, U, G \) and \( \lambda \). For this purpose, we consider nonvariant three-phase equilibrium, which characterized by compositions of coexisting single liquid and two solid phases at the eutectic temperature \( T_0 \). In this case, we have

\[ \mu_1^L(x_0, T_0) = \mu_{10}^\alpha (x_0, T_0), \quad \mu_2^L(x_0, T_0) = \mu_{20}^\alpha (x_0, T_0), \quad \mu_{10}^\beta (x_0, T_0) = \mu_{20}^\beta (x_0, T_0). \]  
(18)

Using the expressions for the chemical potentials (6), (9) and (173) and the chemical equilibrium conditions (18), it is not difficult to express the parameters \( W, U, G \) and \( \lambda \) through the coordinates of the
ends of the eutectic conode. These cases were studied in detail in paper [12]. For this reason, we do not write out the explicit expressions, which can be found in the paper mentioned above.

A further calculation of the phase diagram reduces to modeling the corresponding two-phase equilibria above (or below) the temperature of the eutectic. Thus, in particular, the problem of calculating the liquidus and solidus curves splits into two:

i. Liquid—solid $\alpha$-solution equilibrium $(x > x_0, y > y_0, T > T_0)$:

$$T(x, y) = \frac{q_1 T_1 + W \lambda \left(1 - \frac{x}{x + \lambda(1 - x)}\right)^2 - U \lambda \left(1 - \frac{y}{y + \lambda(1 - y)}\right)^2}{q_1 - \ln \left(\frac{x}{y}\right)}$$

$$= \frac{q_2 T_2 + W \left(1 - \frac{x}{x + \lambda(1 - x)}\right)^2 - U \left(1 - \frac{y}{y + \lambda(1 - y)}\right)^2}{q_2 - \ln \left(\frac{1 - x}{1 - y}\right)}.$$  \hspace{1cm} (19)

ii. Liquid—solid $\beta$-solution equilibrium $(x < x_0, z < z_0, T > T_0)$:

$$T(x, z) = \frac{q_1 T_1 + W \lambda \left(1 - \frac{x}{x + \lambda(1 - x)}\right)^2 - G \lambda \left(1 - \frac{z}{z + \lambda(1 - z)}\right)^2}{q_1 - \ln \left(\frac{x}{z}\right)}$$

$$= \frac{q_2 T_2 + W \left(1 - \frac{x}{x + \lambda(1 - x)}\right)^2 - G \left(1 - \frac{z}{z + \lambda(1 - z)}\right)^2}{q_2 - \ln \left(\frac{1 - x}{1 - z}\right)}.$$  \hspace{1cm} (20)

Finally, for a two-phase equilibrium of a solid $\alpha$-solution—solid $\beta$-solution $(y > y_0, z < z_0, T < T_0)$, we have

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

$$= \frac{G \left(1 - \frac{z}{z + \lambda(1 - z)}\right)^2 - U \left(1 - \frac{y}{y + \lambda(1 - y)}\right)^2}{\ln \left(\frac{1 - y}{1 - z}\right)}.$$  \hspace{1cm} (21)

Equations (19)–(21) 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 in the framework of the GLM. Within given approach, more than ten phase diagrams of real binary solutions were calculated [10] and compared with experimental data [11].
3. Conclusion
In conclusion, we note that the GLM can be used to construct phase diagrams of practically any real binary solutions of the eutectic type both in the absence of solubility of the components in the solid state and in the presence of mutual solubility of the components.

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