Thermodynamics and phase diagram calculation of the binary arsenic-tellurium system in the framework of the generalized lattice model

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Abstract. In this work we describe how to efficiently calculate thermodynamic properties and T-x diagram of binary As-Te solution in the generalized lattice model. All the thermodynamic parameters of the As-Te solution are obtained within framework of the generalized lattice model. The binary phase diagram of As-Te system is calculated and good agreement with experimental data is obtained.

1. Introduction
Theoretical and experimental investigations of the thermodynamic and chemical properties and phase equilibria in the arsenic-tellurium system is of great importance for materials science. In particular, the unique properties and functionalities of binary arsenic-tellurium solutions make them promising materials for microelectronics and photonic applications (see, for example, [1-3]). In this connection an important problem is to study the composition of the coexisting phases in the binary arsenic-tellurium system in a wide range of temperatures and/or various concentrations. However, it should be noted that most of the data on the phase equilibria of this binary system are experimental [4-6], which makes it difficult to predict the mechanical and thermal properties of the arsenic-tellurium alloys when changing their compositions and/or temperature. The purpose of this work was a theoretical calculation of the phase diagram of the arsenic-tellurium system in terms of the generalized lattice model (see, for example, [7, 8]).

2. Thermodynamic model
First of all, it should be noted that the phase diagram of the arsenic-tellurium system is eutectic phase diagram with intermetallic compound $As_2Te_3$ in the absence of the mutual solubility of the components in the solid state (see, for example, [4-6]). An example of a eutectic phase diagram with intermetallic compound $A_mB_n$ is shown in figure 1.

As seen from figure 1 the phase diagram has two eutectic points. In addition, the left and right parts of the initial phase diagram are morphologically similar to a conventional binary eutectic diagram. Moreover, it resembles two simple eutectic phase diagrams placed side by side. There is one important difference: the mole fractions $x$ of the $B$ component vary in the range $0 \leq x \leq n/(n + m)$ for the left system $A - A_mB_n$ and vary in the range $n/(n + m) \leq x \leq 1$ for the right system $A_mB_n - B$. As a result, the lengths of the segments that correspond in the concentration axis to the left and right parts of the initial diagram are not equal to unity. On the other hand, as a rule, the length of the
concentration axis in any phase diagram should be equal to unity. This difference do not permit to use directly the well-developed methods for calculating phase diagrams in the case of simulation of the components of phase diagrams for systems with intermetallic compounds. However, the given problem can be solved through the corresponding change in the concentration variables according to the procedure described in the works [9, 10]. This method of calculation of phase diagrams with intermetallic compounds is based on the transformations of the concentration axes and makes it possible to reduce the calculation of the phase diagrams with one or several intermediate phases (intermetallic compounds) to a sequence of phase diagrams of individual subsystems. These cases were studied in detail in the work [9] and, in this connection, one do not write out the explicit expressions for the transformations of the concentration axes.

![Figure 1](image)

**Figure 1.** A schematic binary eutectic phase diagram with intermetallic compound \( A_m B_n \) in the absence of the mutual solubility of the components in the solid state.

According to the generalized lattice model, the chemical potentials of the components of a homogeneous binary solution (per mole of a material) can be written in the form [11]

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

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

where \( \mu_{10} \) and \( \mu_{20} \) are the standard chemical potentials of the first and second components, respectively, \( R \) is the gas constant, \( T \) is the temperature of the binary system, \( x \) is the mole fraction of the first component, \( \lambda = \omega_2 / \omega_1 \), here \( \omega_1 \) and \( \omega_2 \) are the specific volumes of the first and second components, and, \( W \) is an analogue of the mixing energy in the generalized lattice model.
Now we consider the left system \( A - A_m B_n \) of the binary eutectic system (figure 1). Equating the chemical potentials of the components in the solid and liquid phases, one can obtain all the parameters of the generalized lattice model for the left system.

The chemical equilibrium of the components of a solution at constant temperature is determined from the conditions of constancy of the corresponding chemical potentials. In this connection, using the relationships (1) and (2) determining the chemical potentials of the components of this solution, we can obtain a closed set of equations describing the complete chemical equilibrium in the the left system \( A - A_m B_n \) under isothermal conditions. This thermodynamic description permits us to find the concentration dependences of the liquidus curves and, therefore, to calculate the phase diagrams of binary eutectic system \( A - A_m B_n \) in terms of the generalized lattice model. We should also note that the chemical equilibrium in the right system \( A_m B_n - B \) can be considered in a similar way.

Further note 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 concentrations and, therefore, coincide with the corresponding standard chemical potentials, i.e. \( \mu_{1m}^{sol} = \mu_{10}^{sol} \) and \( \mu_{2m}^{sol} = \mu_{20}^{sol} \). Taking into account the chemical equilibrium in the two-phase system, the concentration dependences of the right and left liquidus curves of the phase diagram for the binary system with the simple eutectic can be obtained in terms of the generalized lattice model [11, 12]:

\[
T_R(x) = \frac{q_1 T_1 + \lambda W}{q_1 - \ln x} \left( \frac{1-x}{x+\lambda(1-x)} \right)^2,
\]

(3)

\[
T_L(x) = \frac{q_2 T_2 + W}{q_2 - \ln(1-x)} \left( \frac{x}{x+\lambda(1-x)} \right)^2,
\]

(4)

where \( T_i (i = 1,2) \) are the melting temperatures of the pure components, reduced to an absolute scale, and

\[
q_i = \frac{\Delta H_i}{RT_i},
\]

(5)

here \( \Delta H_i (i = 1,2) \) are the latent heats of the liquid–solid phase transition for the pure components.

According to [12], the parameters \( \lambda \) and \( W \) of the generalized lattice model can be determined from the known coordinates \( (T_0, x_0) \) of the eutectic point, namely,

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

(6)

\[
W = \frac{q_1(T_0 - T_1) - T_0 \ln x_0}{\lambda} \left( \frac{x_0 + \lambda(1-x_0)}{1-x_0} \right)^2.
\]

(7)

Thus, all the parameters of the generalized lattice model are calculated by formulas (5)-(7), whereas the temperature dependences of the liquidus curves are determined by equations (3) and (4).

On the basis of the given thermodynamic description, we pass to calculation of phase diagram of the arsenic-tellurium system.
3. The arsenic-tellurium system and comparison with experiment

Using the method of the paper [9] and relationships (5)-(7), all the thermodynamic parameters of the arsenic-tellurium system were calculated (see, table 1). It should be emphasized here we use the notation introduced in the work [9].

Table 1. Parameters of the generalized lattice model.

|                  | The arsenic-tellurium system |
|------------------|-----------------------------|
|                  | As – As₂Te₃                | As₂Te₃ – Te                |
| q₁₁              | 70.480                     | q₂₁                        | 2.893                     |
| q₁₂              | 2.269                      | q₂₂                        | 106.699                   |
| λ₁               | 35.940                     | λ₂                         | 0.339                     |
| Wₚ / R, K        | 3608                       | Wₚ / R, K                  | -6512                     |

Figure 2 shows the results of the phase diagram calculation of the arsenic-tellurium system, taking into account the parameters given above. At that the temperature dependences of the liquidus curves were determined by equations (3) and (4).

**Figure 2.** Phase diagram of the arsenic-tellurium system. Solid lines are the calculated phase diagram, dashed lines are the experimental data [6].

It can be seen that the phase diagram of the arsenic-tellurium system (solid lines) is consistent with the experimental data (dashed lines) [3-6].

In addition it should be noted that explicit account of “volume” effects in the arsenic-tellurium system with intermediate phase of constant composition As₂Te₃ was carried by introducing specific volumes of As and Te in terms of the generalized lattice model.
4. Conclusion
In closing, let us formulate the main results of the work. Within the framework of the generalized lattice model, the phase diagram of the arsenic-tellurium system was calculated in the entire concentration range. The phase diagram of the arsenic-tellurium system is compared qualitatively with the experimental data. Finally, we also note that the generalized lattice model can be used to construct phase diagrams of practically any real binary solutions of the considered type.

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