Liquid binary metallic solutions containing components A and B may also be regarded as associated solutions. We may assume that associates of type $A_mB_n$ (heteroassociates) are mainly formed in solutions with negative deviation of the thermodynamic activity from Raoult’s law, and associates of type $A_m$ and $B_n$ (self-associates of order $m$ and $n$) are mainly formed in solutions with positive deviation from Raoult’s law. In the latter case, interaction between atoms of the same type in the solution predominates over interaction between atoms of different type.

Quantitative description of the thermodynamic properties of associated solutions with negative deviation from Raoult’s law is usually based on the model of ideal associated solutions [1]. If detailed thermodynamic information regarding the intermetallides present is available for such solutions, their properties may be correctly predicted without the need for fitting parameters [2].

However, for solutions with positive deviation from Raoult’s law, no such models exist, except for the approximate solution in [3]. In addition, all the known databases lack thermodynamic information regarding condensed compounds of type $A_m$. No experiments on this topic are planned. However, one option is to obtain such information by calculation on the basis of statistical thermodynamics. In that case, the proposed model of ideal associated solutions is well-founded.

Consider the system A–B, containing associates $A_m$ and $B_n$. The standard method in the model of ideal associated solutions calls for the solution of equations of three types:

1. the chemical–equilibrium equations (in terms of the effective-mass law)
   \[
   \frac{x_A}{x_A^m} = K_A, \quad \frac{x_B}{x_B^n} = K_B; \tag{1}
   \]

2. the mass-balance equations
   \[
   x_A + mx_A = b_A, \quad x_B + nx_B = b_B; \tag{2}
   \]

3. the normalization equations
   \[
   x_A + x_B + x_A + x_B = 1, \quad \frac{b_B}{b_A + b_B} = X_B. \tag{3}
   \]

Here $x_A$, $x_B$ are the mole fractions of the associates; $x_A$, $x_B$ are mole fractions of monomers; $K_A$, $K_B$ are the complex-formation coefficients of the associates; $b_A$, $b_B$ are the balanced contents of the components; $X_B$ is the mole fraction of component B in solution.

So as to specific, we use only a right-handed concentration variable $X_B$. We also assume that $m$ and $n$ are constant integers (the monodisperse approximation of actual ensembles of associated particles).

Equations (1)–(3) may be reduced to the following two equations

\[
-x_Bx_A + (1 - x_B)x_B - x_B^mK_Ax_A^m + (1 - x_B)nK_Bx_B^n = 0, \tag{4}
\]

\[
x_A + x_B + K_Ax_A^m + K_Bx_B^n = 1. \tag{5}
\]

In the analysis of systems with negative deviation from Raoult’s law, the basis of ideal associated solutions, the activities $a_A$ and $a_B$ of the components are
assumed equal to the concentrations of the corresponding monomers

$$a_A = x_A, \quad a_B = x_B.$$  \hspace{1cm} (6)

However, in systems with positive deviation from Raoult’s law, these equations do not apply. For the formation of self-associates, no mixing of components A and B in solution is required. Self-associates are formed in the greatest quantities in the pure liquids A and B. Mixing reduces their concentrations.

When \(x_A = 1\) and correspondingly \(x_B = 0\), Eq. (5) takes the form

$$x_A(1) + K_A x_A^n(1) = 1.$$  \hspace{1cm} (7)

Analogously, when \(x_B = 1\) and \(x_A = 0\)

$$x_B(1) + K_B x_B^n(1) = 1.$$  \hspace{1cm} (8)

Thus, the concentration of monomers at the boundaries of the concentration range will be less than one

$$x_A(1) = 1 - K_A x_A^n(1) = 1 - M_A,$$

$$x_B(1) = 1 - K_B x_B^n(1) = 1 - M_B.$$  \hspace{1cm} (9)

Here \(M\) denotes the maximum concentration of the associate in pure liquid.

Since the activity of the components in pure liquids is always assumed to be one (the standard state), renormalization of the variables is required to calculate the true activities of the components in solution

$$a_A = \frac{x_A}{x_A(1)} = \frac{x_A}{1 - M_A},$$

$$a_B = \frac{x_B}{x_B(1)} = \frac{x_B}{1 - M_B}.$$  \hspace{1cm} (10)

**Fig. 1.** Regular functions of binary solutions: (1) Ce–Cr (2073 K); (2) La–Cr (2273 K); (3) Y–Cr (2273 K); (4) Cu–Cr (2073 K); (5) Fe–Cr (2273 K).

**Fig. 2.** Activity isotherms of components and concentrations of associates in the Y–Cr (a) and Fe–Cr (b) systems at 2273 K: (1) \(a_Y\); (2) \(a_{Cr}^n\); (3) \(x_Y\); (4) \(x_{Cr}^n\); (5) \(x_Y\); (6) \(x_{Cr}^n\); (7) \(a_{Fe}^n\); (8) \(a_{Cr}^n\); (9) \(x_{Fe}^n\); (10) \(x_{Cr}^n\); (11) \(x_{Fe}^n\); (12) \(x_{Cr}^n\).