On the choice of standard state at the calculation of phase diagrams of multicomponent molten systems

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Transformation of concentration coordinates in n-component system is proposed which assures that 1 mole of a mixture consisting of $n-1$ components added to the melt of the remaining component yields just 1 mole of new (foreign) particles. The activity calculated according to this model is compared with the value of activity resulting from the Haase, Temkin, and universal models.

Предлагается преобразование концентрационных координат, при помощи которого 1 моль смеси $n-1$ компонентов прибавляемой к расплаву остального компонента приводит к образованию 1 моля новых (посторонних) частиц. Активность, рассчитанная по этой модели сравнивается с активностью, рассчитанной по моделям Хаазе и Темкина и универсальному соотношению.

The calculation of phase diagrams of molten systems having three or more components is an effective way for obtaining preliminary information on the temperature of primary crystallization of technically important systems and it can serve as a base for planning and controlling experiments [1].

If we investigate systems having more complicated anions, *e.g.* fluoroaluminates or silicates, then using the model of *Temkin* [2] or of *Haase* [3, 4] for the description of standard state is rather formal because the assumptions, on which the models are based, are not fulfilled. Besides, these models give for multicomponent mixtures rather complicated mathematical expressions describing the relation between molar composition of the systems and activities of the corresponding components.

In this paper another approach to the choice of standard state for the special case of calculation of phase equilibria solidus—liquidus is discussed. The proposed model is simple, general and it gives a correct value for the limit

$$\lim_{x_i \to 1} (\mathrm{d}a_i/\mathrm{d}x_i) = k \tag{1}$$

which is in agreement with the requirements of thermodynamic consistency [5, 6]. In eqn (1) a_i is the activity of the i-th component calculated according to the chosen model, x_i is the formal mole fraction of the component. In systems having more than two components the relationship (1) still holds assuming that the ratio among the other components $j \neq i$ is constant. The constant k equals the number of moles of new (foreign) particles (*i.e.* particles which do not exist in the liquid phase) brought into the melt of pure component i by 1 mole of a mixture of the other components of the system. The necessity to introduce this factor has been pointed out by *Stortenbeker* [7] and it is discussed also in papers [6, 8, 9]. The Temkin model, Haase model, and the universal model [10] as well satisfy eqn (1) and yield the value k which is in agreement with experiment. However, the fulfillment of the condition (1) can be assured also in another way, by making suitable transformation of concentration coordinates. For the special case of Temkin model the possibility of the restoration of Rault law and Henry law by using suitable transformation of coordinates in binary systems is outlined in [11].

Let us do such a transformation of concentration coordinates which assures that 1 mole of a mixture added to the melt of pure component yields just 1 mole of new (foreign) particles. Then the constant k will be equal to 1 and, therefore, the ideal behaviour of the concentration-transformed system can be described by the relationships valid for classically ideal solution. From the formal point of view this transformation is very simple.

Let us consider the n-component system in which the mole fractions and molar masses of its components are denoted by x_i and M_i, respectively. Each of the components $(i > 1)$ brings into the melt of the first component k_i of new (foreign) particles. It follows that the resulting mixture contains x_1 moles of the first component, $x_2 k_2$ moles of new (foreign) particles of the second component, $x_3 k_3$ moles of new (foreign) particles of the third component, *i.e.* generally $x_i k_i$ moles of new (foreign) particles. If we denote the mole fraction of the first component in this mixture as x_1^+ then according to the definition

$$x_1^+ = \frac{x_1}{x_1 + \sum_{i=2}^{n} k_i x_i} \qquad (2)$$

It can be shown that the relation (2) satisfies the condition (1). (The differentiation is to be carried out at constant ratio of concentrations of the components $i > 1$.)

As an example of application of the relation (2) the activity of the first component in the system $MA + N_2A + MC_2$ was calculated according to different models (Table 1).

Table 1

Activity of the first component in the system $MA + N_2A + MC_2$
calculated according to different models

x_1	x_2	x_3	a_1^+	a_H	a_T	a_U
1.0	0.0	0.0	1.000	1.000	1.000	1.000
0.9	0.1	0.0	0.818	0.816	0.818	0.810
0.9	0.0	0.1	0.818	0.816	0.818	0.810
0.8	0.2	0.0	0.667	0.661	0.667	0.640
0.8	0.1	0.1	0.667	0.669	0.669	0.640
0.8	0.0	0.2	0.667	0.661	0.667	0.640
0.7	0.3	0.0	0.538	0.529	0.538	0.490
0.7	0.2	0.1	0.538	0.544	0.545	0.490
0.6	0.4	0.0	0.429	0.417	0.429	0.360
0.6	0.3	0.1	0.429	0.438	0.441	0.360
0.6	0.2	0.2	0.429	0.444	0.444	0.360
0.5	0.5	0.0	0.333	0.320	0.333	0.250
0.5	0.4	0.1	0.333	0.346	0.351	0.250
0.5	0.3	0.2	0.333	0.358	0.359	0.250
0.4	0.6	0.0	0.250	0.237	0.250	0.160
0.4	0.5	0.1	0.250	0.266	0.273	0.160
0.4	0.4	0.2	0.250	0.284	0.286	0.160
0.4	0.3	0.3	0.250	0.290	0.290	0.160
0.3	0.7	0.0	0.176	0.165	0.176	0.090
0.3	0.4	0.3	0.176	0.230	0.231	0.090
0.2	0.4	0.4	0.111	0.184	0.184	0.040
0.0	0.5	0.5	0.000	0.111	0.111	0.000

$$a_1^+ = \frac{x_1}{x_1 + 2x_2 + 2x_3} \tag{3}$$

$$a_H = \frac{4(x_1 + x_3)(x_1 + x_2)}{(2x_1 + 3x_2 + 3x_3)^2} \tag{4}$$

$$a_T = \frac{x_1 + x_3}{x_1 + 2x_2 + x_3} \frac{x_1 + x_2}{x_1 + x_2 + 2x_3} \tag{5}$$

$$a_U = x_1^k ; \quad k = \frac{2x_2 + 2x_3}{x_2 + x_3} = 2 \tag{6}$$

On the basis of numerical analysis of different systems it can be concluded that the agreement between the proposed model and Temkin model or Haase model is good for mole fractions of the first component higher than 0.5. At lower concentrations of the first component this model does not take into account mutual interactions of the other components of reciprocal systems. It should be also advised upon the restrictions following from the Gibbs—Duhem relation for the activity of the other components.

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