Application of the Haase functional relationship for activity to the systems with complete miscibility in both solid and liquid phase

Systems without common ion

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The mathematic and thermodynamic analysis of the course of liquidus and solidus curves in binary systems of the 2nd kind (the systems formed by components M_pA_q—N_rB_t) was carried out. The existence of unlimited solid solutions was assumed. The activities of components of the system were estimated using the Haase relations. The limit values of slopes of the tangents to liquidus and solidus curves at the melting points of pure components as well as the general character of these systems were determined. The course of liquidus and solidus curves is practically the same regardless of that the activity is expressed by means of the Haase or Temkin relationships. However, utilizing Haase's approach the mathematical expressions are substantially simpler.

Выполнен математический и термодинамический анализ хода кривых ликвидуса и солидуса в бинарных системах 2-го рода, образованных компонентами типа M_pA_q—N_rB_t. Предполагалось существование неограниченных твердых растворов в этой системе. Активности компонентов системы выражены посредством соотношения Гаазе. Определены предельные значения наклонов касательных кривых ликвидуса и солидуса в точках плавления чистых компонентов, а также общий характер систем. Ход кривых ликвидуса и солидуса получается практически одинаковый, безразлично от использования соотношения Гаазе или Темкина. Расчеты становятся, однако, гораздо проще в случае соотношения Гаазе.

In the preceding papers [1—4] the analysis of the course of liquidus and solidus curves in binary systems with a complete series of solid and liquid solutions has been presented. The functional relationship between activity and composition has been expressed by classical relation $a_i = x_i$, by relation following from Temkin's model of ideal ionic solution [5], and by the universal relationship [6].

In this work a similar procedure as in the quoted papers is applied but the activity is calculated using Haase's approach [7]. The analysis is based on the concepts of "characteristic equation" and "equation of extremum" which have been defined in [2, 3]. The systems of the type H/K, K/H, and H/H (see list of symbols) are analyzed. For each type the Haase functional relationship between activity and composition is given and the characteristic equation of liquidus and solidus curve, respectively, is derived. In the cases H/K and K/H the equation for extremum is derived as well. Further, the limit values of slopes of tangents at the melting points of pure components are calculated. The results obtained in this work, based on Haase's relationships, are compared with those following from an analysis based on Temkin's model [2]. This comparison results in a recommendation for using one of these models in research practice.

With respect to the extent of calculations only results of the mathematical analysis are presented (Tables 1—3). An example of the mathematic procedure used has been published in [1]. (It has been applied to the system U/K.) From this work it follows that the results obtained using both the Haase and Temkin model are very similar, which is illustrated in Figs. 1 and 2. Here the courses of liquidus and solidus curves calculated according to both

Table 1

System M_pA_q—N_rB_t without common ion, type H/K

$$a_1^l = (p+q)^{p+q} \left[\frac{x_1^l}{r+t+(p+q-r-t)x_1^l} \right]^{p+q} ; \quad a_1^s = x_1^s$$

$$a_2^l = (r+t)^{r+t} \left[\frac{1-x_1^l}{r+t+(p+q-r-t)x_1^l} \right]^{r+t} ; \quad a_2^s = 1 - x_1^s$$

Characteristic equation of liquidus curve

$$MQ[r+t+(p+q-r-t)x_1^l]^{p+q} - Q(p+q)^{p+q}(x_1^l)^{p+q} - \\ - M(r+t)(1-x_1^l)^{r+t}[r+t+(p+q-r-t)x_1^l]^{p+q-r-t} = 0$$

$$\lim_{T \to T_1^f} dT/dx_1^l = \frac{r+t}{\Delta H_1^f} R(T_1^f)^2 ; \quad \lim_{T \to T_2^f} dT/dx_1^l = -\frac{p+q}{\Delta H_2^f} R(T_2^f)^2$$

$$\lim_{T \to T_1^f} dT/dx_1^s = +\infty ; \quad \lim_{T \to T_2^f} dT/dx_1^s = -\infty$$

Equation for extremum

$$\left[\frac{r+t}{r+t+(p+q-r-t)x} \right]^{r+t} (1-x)^{r+t-1} \left\{ \left[\frac{p+q}{r+t+(p+q-r-t)x} \right]^{p+q} x^{p+q-1} \right\}^{-\Delta H_2^f \Delta H_1^f} - \\ - Q_0 = 0$$

Table 2

System $M_pA_q - N_rB_t$ without common ion, type K/H

$$a_1^l = x_1^l; \quad a_1^s = (p+q)^{p+q} \left[\frac{x_1^s}{r+t+(p+q-r-t)x_1^s} \right]^{p+q}$$

$$a_2^l = 1 - x_1^l; \quad a_2^s = (r+t)^{r+t} \left[\frac{1-x_1^s}{r+t+(p+q-r-t)x_1^s} \right]^{r+t}$$
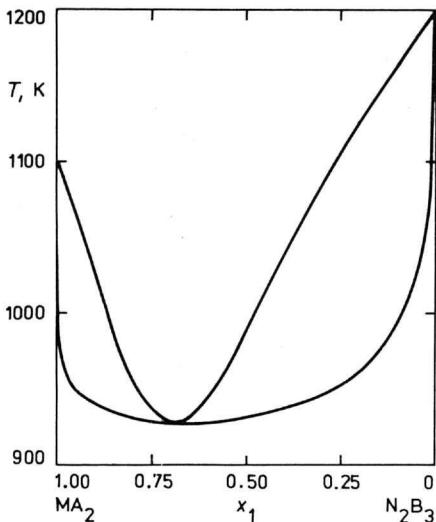
Characteristic equation of solidus curve

$$Q(r+t)^{r+t}[r+t+(p+q-r-t)x_1^s]^{p+q}(1-x_1^s)^{r+t} +$$
$$+ M(p+q)^{p+q}[r+t+(p+q-r-t)x_1^s]^{r+t}(x_1^s)^{p+q} - [r+t+(p+q-r-t)x_1^s]^{p+q+r+t} = 0$$

$$\lim_{T \to T_1^f} dT/dx_1^l = -\infty; \quad \lim_{T \to T_2^f} dT/dx_1^l = +\infty$$

$$\lim_{T \to T_1^f} dT/dx_1^s = -\frac{r+t}{\Delta H_1^f} R(T_1^f)^2; \quad \lim_{T \to T_2^f} dT/dx_1^s = \frac{p+q}{\Delta H_2^f} R(T_2^f)^2$$
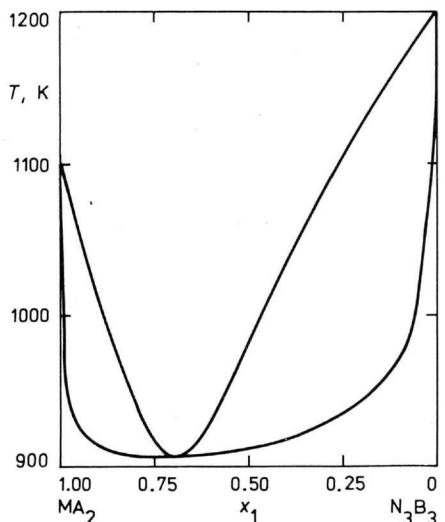
Equation for extremum

$$\left[\frac{r+t+(p+q-r-t)x}{r+t} \right]^{r+t} (1-x)^{1-r-t} \left\{ \left[\frac{r+t+(p+q-r-t)x}{p+q} \right]^{p+q} x^{1-p-q} \right\}^{-\Delta H_2^f/\Delta H_1^f} -$$
$$- Q_0 = 0$$

Fig. 1. Phase diagram of the binary system
MA_2—N_2B_3 of the type H/K and T/K.
$T_1^f = 1100$ K, $\Delta H_1^f = 6.276 \times 10^4$ J mol^{-1}.
$T_2^f = 1200$ K, $\Delta H_2^f = 10.46 \times 10^4$ J mol^{-1}.
$x_{1,ex} = 0.693$, $T_{ex} = 926$ K.

Fig. 2. Phase diagram of the binary system
MA_2—N_3B_3 of the type H/K and T/K.
$T_1^f = 1100$ K, $\Delta H_1^f = 6.276 \times 10^4$ J mol^{-1}.
$T_2^f = 1200$ K, $\Delta H_2^f = 10.46 \times 10^4$ J mol^{-1}.
$x_{1,ex} = 0.700$, $T_{ex} = 903$ K.

Table 3

System M_pA_q—N_rB_t without common ion, type H/H

$$a_1^1 = (p+q)^{p+q} \left[\frac{x_1^1}{r+t+(p+q-r-t)x_1^1} \right]^{p+q} ;$$

$$a_1^s = (p+q)^{p+q} \left[\frac{x_1^s}{r+t+(p+q-r-t)x_1^s} \right]^{p+q}$$

$$a_2^1 = (r+t)^{r+t} \left[\frac{1-x_1^1}{r+t+(p+q-r-t)x_1^1} \right]^{r+t} ;$$

$$a_2^s = (r+t)^{r+t} \left[\frac{1-x_1^s}{r+t+(p+q-r-t)x_1^s} \right]^{r+t}$$

Characteristic equation of liquidus curve

$$M^{1/(p+q)}(r+t)(1-x_1^1)(Q^{1/(r+t)}-1) + Q^{1/(r+t)}x_1^1(p+q)(M^{1/(p+q)}-1) = 0$$

$$\lim_{T\to T_1^f} dT/dx_1^1 = \frac{(r+t)(Q_0^{1/(r+t)}-1)}{Q_0^{1/(r+t)}\Delta H_1^f} R(T_1^f)^2$$

$$\lim_{T\to T_2^f} dT/dx_1^1 = \frac{(p+q)(1-M_0^{1/(p+q)})}{M_0^{1/(p+q)}\Delta H_2^f} R(T_2^f)^2$$

$$\lim_{T\to T_1^f} dT/dx_1^s = \frac{(r+t)(Q_0^{1/(r+t)}-1)}{\Delta H_1^f} R(T_1^f)^2$$

$$\lim_{T\to T_2^f} dT/dx_1^s = \frac{(p+q)(1-M_0^{1/(p+q)})}{\Delta H_2^f} R(T_2^f)^2$$

models are compared. (The numerical calculations were carried out using computer Siemens 4004, at the Calculating Centre of Universities, Mlynská dolina, Bratislava, and computer Minsk 22 at the Faculty of Electrotechnical Engineering, Bratislava.) It should be mentioned that for the numerical solution of the characteristic equation of the liquidus curve as well as of nonalgebraic equation of extremum the method of "dividing the interval in half" [8] was used. The error in calculated composition range (in mole fraction) was less or equal to 5×10^{-5}.

Comparison of Haase's and Temkin's functional relationships between activity and composition

1. For solutions of the type H/K and K/H only the courses of liquidus and solidus curves with extremum are possible. In agreement with the principle of monotonicity [3] the type H/H has always a monotonic course of liquidus curves.

The same results have been also found for the types T/K, K/T, and T/T.

2. The expressions and equations when utilizing Haase's approach are from the formal point of view simpler than those of Temkin's model.

3. The limit values of slopes of tangents at the melting points of pure components are the same as for the corresponding types T/K, K/T, and T/T.

4. The courses of liquidus and solidus curves are practically the same regardless the model applied. However, it cannot be stated that the lines are exactly identical for the following reasons:

a) The equations which are used for calculation of curves are different according to functional relationship (Temkin's or Haase's) employed. The exact equality of the roots of these equations cannot be proved since the calculations are performed by approximate methods. A solution of algebraic equations of higher degrees is the problem. *E.g.* the following equations (for the above functional relationships) hold for the system MA_2—NB_3

Type	Characteristic equation
H/K	$MQ(4-x)^4 - 3^3x^3Q(4-x) - M4^4(1-x)^4 = 0$
T/K	$MQ(3-x)^3 - 2^2x^3Q(3-x) - M3^3(1-x)^4 = 0$

b) For the sake of completeness it may be stated that the calculations based on Temkin's model were carried out on computer Minsk 22 (using Algol 60) and those based on Haase's approach on computer Siemens 4004 (using Fortran).

From the items 1—3 the following conclusions for practical application can be drawn:

The course of liquidus and solidus curves is practically the same regardless the functional relationship (Haase's or Temkin's) used. Therefore for description of the system we shall use the simpler relationship, in our case the Haase relationship.

The advantages of the Haase relationship are evident from a comparison of the types H/H and T/T. The relationships for the type H/H are presented in Table 3; those for the type T/T are as follows

$$a_1^l = \{px_1^l/[r + x_1^l(p-r)]\}^p\{qx_1^l/[t + x_1^l(q-t)]\}^q \tag{1}$$

$$a_2^l = \{r(1-x_1^l)/[r + x_1^l(p-r)]\}^r\{t(1-x_1^l)/[t + x_1^l(q-t)]\}^t \tag{2}$$

$$a_1^s = \{px_1^s/[r + x_1^s(p-r)]\}^p\{qx_1^s/[t + x_1^s(q-t)]\}^q \tag{3}$$

$$a_2^s = \{r(1-x_1^s)/[r + x_1^s(p-r)]\}^r\{t(1-x_1^s)/[t + x_1^s(q-t)]\}^t \tag{4}$$

The characteristic equation results after elimination of x_1^l and x_1^s from basic thermodynamic relations (see [3]).

In our case

$$M = a_1^l/a_1^s = (x_1^l/x_1^s)^{p+q}\{[r + x_1^s(p-r)]/[r + x_1^l(p-r)]\}^p \cdot$$
$$\cdot \{[t + x_1^s(q-t)]/[t + x_1^l(q-t)]\}^q \tag{5}$$

$$Q = a_2^l/a_2^s = [(1-x_1^l)/(1-x_1^s)]^{r+t}\{[r+x_1^s(p-r)]/[r+x_1^l(p-r)]\}^r \cdot$$
$$\cdot \{[t+x_1^s(q-t)]/[t+x_1^l(q-t)]\}^t \tag{6}$$

The elimination in this case is not possible and thus the characteristic equation does not exist. We have only two nonlinear equations with two variables x_1^l and x_1^s which are to be solved by a numerical method. But it is not simple to find the best numerical method for solving these equations and the calculation involves great numerical difficulties.

The type H/H has a characteristic equation of the first degree for liquidus curve. Therefore the function $x_1^l = f(T)$ can be expressed explicitly and the calculation of liquidus curve is very simple in this case.

Symbols

T	Temkin's relationship
H	Haase's relationship
K	classically ideal $(a_i = x_i)$
U	universal relationship

T, H, K, U denote the relationship which is used to describe the dependence between activity and composition. *E.g.* T/K denotes that for liquid solution the Temkin relationship for activity was used and solid solution is assumed to be classically ideal.

a_i^l, a_i^s	activity of the i-th component in liquid or in solid state
ΔH_i^f	molar enthalpy of fusion of pure i-th component at temperature T_i^f
T_i^f	temperature of fusion of the i-th component
l_i, s_i	corresponding liquidus and solidus curves
M	$\exp[(\Delta H_1^f/R)(1/T_1^f - 1/T')]$
Q	$\exp[(\Delta H_2^f/R)(1/T_2^f - 1/T')]$
M_0	$\exp[(\Delta H_1^f/R)(1/T_1^f - 1/T_2^f)]$
Q_0	$\exp[(\Delta H_2^f/R)(1/T_2^f - 1/T_1^f)]$
p, q, r, t	stoichiometric coefficients
R	gas constant
T	temperature, K
T_{ex}	temperature of extremum
x_i^l, x_i^s	mole fraction of the i-th component in liquid or in solid state
$x_{i,ex}$	composition of extremum

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