Silikáty *XXII*, s. 109—116 (1978)

CALCULATION OF THE PHASE DIAGRAM OF THE TERNARY SYSTEM DIOPSIDE—AKERMANITE—LEUCITE

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Received 13. 1. 1977

The study was concerned with verifying the possibility of calculating the liquidus diagrams of eutectic ternary silicate systems containing anions with complex structures. The phase diagram calculation is based on knowledge of phase diagrams of the basic binary systems. The phase diagrams of binary systems serve for calculating excess functions defined as a difference between the actual and the ,ideal' ones. It is assumed that the excess functions in a ternary system can be estimated in satisfactory approximation as a sum of contributions of the basic binary systems. The relations employed in the calculation of phase diagrams meet the general requirements holding for the courses of liquidus curves and surfaces.

INTRODUCTION

Experimental study of phase equilibria in multicomponent systems is considerably time consuming. In addition to this one is mostly interested in a certain part of the multicomponent phase diagram only, for instance the eutectic point parameters. The present study is concerned with the possibility of approximate determination of the liquidus surface in simple eutectic systems comprising anions of complex structures.

In previous papers [1], [2] the present authors suggested a method for calculating the liquidus diagrams in three-component systems of molten salts and multicomponent cryolite-based systems. The principle of calculation was identical in all the studies.

1. With due respect to the system being studied a suitable reference state is chosen in terms of which the excess functions are defined. Excess functions are defined as a difference between the value of the given function in the real system and the value of the function following from the choice of the reference state. The basic requirement which each reference state must meet are the general rules for the courses of curves and liquidus areas (thermodynamic consistency criteria [3]). In the present case the concentration dependence of the coefficients should comply with the Gibbs-Duhem equation [4], [5].
2. The excess functions in binary systems are determined on the basis of known phase diagrams.
3. It is assumed that excess functions in a ternary system can be estimated at satisfactory approximation as a sum of contributions of the individual binary systems. (This assumption can be substantiated on the basis of the conforming solutions theory [6].)

In the previous studies mentioned above [1], [2] an ideal mixture as defined by Haase [7] was chosen as the reference state. This definition is suitable in particular in the case of ionic melts free from neutral molecules and ionic complexes. The present study is concerned with verifying the suitability of the formal approach to the calculation of liquidus diagrams in systems with which no experimental data on melting enthalpy of pure components are available and the liquid phase of which has a substantially complex structure so that utilization of models suitable for simple ionic systems would not be satisfactory.

THEORETICAL

The condition for an equilibrium of substance A in liquid and solid phase is the equality of chemical potentials μ_A of the substance in both phases. Transition of substance A from solid to liquid phase can be regarded as a reaction,

$$A(_s) \rightleftharpoons A(_l). \tag{1}$$

In a state of equilibrium,

$$\mu_{A},(_s) = \mu_{A},(_l).$$

The temperature dependence of the equilibrium constant of reaction (1) ($K = a_l/a_s$) is described by the van't Hoff reaction isobar equation [8]:

$$\mathrm{d}\ln \frac{a_l}{a_s} = \frac{\Delta H_{l/s}}{RT^2}\,\mathrm{d}T, \tag{2}$$

which in this case is identical with the differential form of the Le Chatelier-Shreder equation [9], [10].
a_l is the activity of component A in liquid phase, a_s is the activity of component A in solid phase; when component A does not form solid solutions, $a_s = 1$ and $\Delta H_{l/s}$ is the standard change of enthalpy of reaction (1) at temperature T (being identical with the melting enthalpy of component A at the given temperature).

When assuming that the difference in thermal capacities Δc_p of component A in solid and in liquid state is constant within the given temperature interval, integration of equation (2) (integrating from the limit point of interval $a_l = 1$, $T = T_f$) yields the known form of the liquidus curve

$$\ln a_l = \frac{\Delta H_f}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) + \frac{\Delta c_p}{R}\left(\frac{T_f}{T} - 1 - \ln\frac{T_f}{T}\right), \tag{3}$$

where ΔH_f is the melting enthalpy of pure component A at temperature T_f ($a_s = 1$).

When the condition of thermodynamic consistency is to be met the following should hold in the binary system in the boundary concentration regions:

$$\gamma_A \to 1, \quad \text{when} \quad x_B \to 0$$

and at the same time

$$\mathrm{d}\gamma_A/\mathrm{d}x_B = 0, \quad \text{when} \quad x_B \to 0.$$

Let us therefore determine the slope of the tangent to the liquidus curve in binary systems. The differential equation of the liquidus curve of a binary system can be written in the form [4]

$$\frac{\mathrm{d}T}{\mathrm{d}x_B} = \frac{T}{L}\left(\frac{\partial \mu_A}{\partial x_B}\right)_{T,p}, \tag{4}$$

where x_B is the mol fraction of the other component in the system ($x_A + x_B = 1$) and L is the differential heat of fusion, that is the difference between partial molar enthalpy of component A in the melt and molar enthalpy of pure solid component A; $L = \bar{H}_A - H^\circ_{A,s}$ (also called final heat of dissolution). When $x_B \to 0$, then $L \to \Delta H_f$.

The slope of the tangent to the liquidus curve at the point of melting of pure component A is defined as lim ($x_B \to 0$): $\mathrm{d}T/\mathrm{d}x_B$. Having defined the chemical potential of component A as $\mu_A = \mu_A^0 + RT \ln a_A$ and $a_A = x_A \gamma_A$, then from equation (4) it follows that

$$\lim_{x_B \to 0} \mathrm{d}T/\mathrm{d}x_B = \frac{RT_f^2}{\Delta H_f} \left(-1 + \frac{\mathrm{d}\gamma_A}{\mathrm{d}x_B} \right)_{T_{f,p}} \tag{5}$$

and since $\mathrm{d}\gamma_A/\mathrm{d}x_B$ must be equal to zero for $x_B \to 0$,

$$\lim_{x_B \to 0} \mathrm{d}T/\mathrm{d}x_B = -RT_f^2/\Delta H_f .$$

However, as each molecule of substance B introduces into the melt of pure component A a number of particles which differs from 1 (so that the actual molar fraction of new-foreign-particles being introduced is not equal to the formal mole fraction calculated on the basis of weighed—in amount of substance B), equation (5) will not be complied with.

It holds generally that [11]

$$\lim_{x_B \to 0} \mathrm{d}T/\mathrm{d}x_B = (-RT_f^2 \Delta H_f)\, k , \tag{6}$$

where k is the number of new-foreing-particles introduced by each molecule of substance B into the melt of substance A.

The activity vs. concentration dependence should therefore be defined by such an expression that the following equation would hold:

$$\lim_{x_A \to 1} \mathrm{d}a_A/\mathrm{d}x_A = k . \tag{7}$$

In the case of ionic melts this result is provided by the application of the Temkin model [12] or by the procedure suggested by Haase [4, 11].

The calculation principle

In the case of systems comprising anions of complex structures the application of the ideal ionic melt model [1], [2] would obviously be considerably formal; at the same time, the mathematical expressions employed are comparatively complex. A formal approach, which is mathematically simpler and likewise meets the requirements of thermodynamic consistency, has therefore been suggested for the description of liquidus curves and areas of systems containing anions with complex structures.

Let us define the quantity

$$M_A = \Delta H_f/k . \tag{8}$$

For the integral form of the liquidus equation one can then write an equation analogous to equation (3),

$$\ln x_A f_A = \frac{M_A}{R}\left(\frac{1}{T_{f,A}} - \frac{1}{T}\right). \tag{9}$$

The temperature dependence of M_A is not considered (even if it actually arises in practice, it is included in the numerical value of correction factor f_A). The reference state is defined by equation (9) and by the condition $f_A = 1$ holding within the entire concentration range (and thus also the temperature range since the relationship holds for the solidus-liquidus equilibrium only).

Let us define the supplementary characteristic φ^E so that

$$\varphi^E - x_B\left(\frac{\partial \varphi^E}{\partial x_B}\right)_{T,p} = RT \ln f_A. \tag{10}$$

This characteristic is thus a formal analogy of the excess Gibbs energy, with which it is identical when f is the activity coefficient. Let us assume that the concentration dependence of φ^E can be expressed by the relation [1]:

$$\varphi^E = x_A x_B[\lambda_\alpha + \lambda_\beta(x_B - x_A)]. \tag{11}$$

The following relations can be obtained by combining equations (10) and (11):

$$\begin{aligned} RT \ln f_A &= x_B^2[\lambda_\alpha + \lambda_\beta(4x_B - 3)], \\ RT \ln f_B &= x_A^2[\lambda_\alpha + \lambda_\beta(4x_B - 1)]. \end{aligned} \tag{12}$$

For given temperature the values f_A, f_B may be determined from two branches of the liquidus curve of the binary phase diagram using equation (9).

Then, it is possible to calculate the empirical constants λ_α, λ_β, which are functions of temperature only (and generally also functions of pressure), using equation (12).

Calculation of the liquidus areas of a ternary system $A - B - C$ is based on the assumption that the supplementary function φ^E may be determined as a sum of contributions of the supplementary functions of the binary systems:

$$\begin{aligned} \varphi^E &= \varphi^E{}_{AB} + \varphi^E{}_{AC} + \varphi^E{}_{BC} = \\ &= x_A x_B[\lambda_{\alpha,AB} + \lambda_{\beta,AB}(x_B - x_A)] + x_B x_C[\lambda_{\alpha,BC} + \lambda_{\beta,BC}(x_C - x_B)] + \\ &\quad + x_A x_C[\lambda_{\alpha,AC} + \lambda_{\beta,AC}(x_C - x_A)]. \end{aligned} \tag{13}$$

The correction factor f as a function of composition in the ternary system is obtained by combining equations (10) and (13) (being located over the liquidus area, temperature is likewise a function of composition). For a chosen temperature T the equilibrium value of concentration of components A, B, C was then determined from equation (9). However, for this calculation it is first necessary to define the value of quantity M_A in the given section through the ternary system (Fig. 1). Let us choose a first type section passing from pure component A (dashed in the diagram). Throughout this section the ratio of components x_B/x_C is constant. Quantity M_A can be estimated in first approximation as a linear combination of values M_{AB} and M_{AC}, obtained from binary phase diagrams $A - B$ and $A - C$. (The M_A values in the corresponding binary systems are therefore designated M_{AB} and M_{AC} respectively.)

$$M_A = (M_{AB}x_B + M_{AC}x_C) / (x_B + x_C) \tag{14}$$

As regards the actual technique of calculating the liquidus surface it should be noted that when considering the constant λ as a function of temperature, the equilibrium composition has to be determined by the iteration procedure.

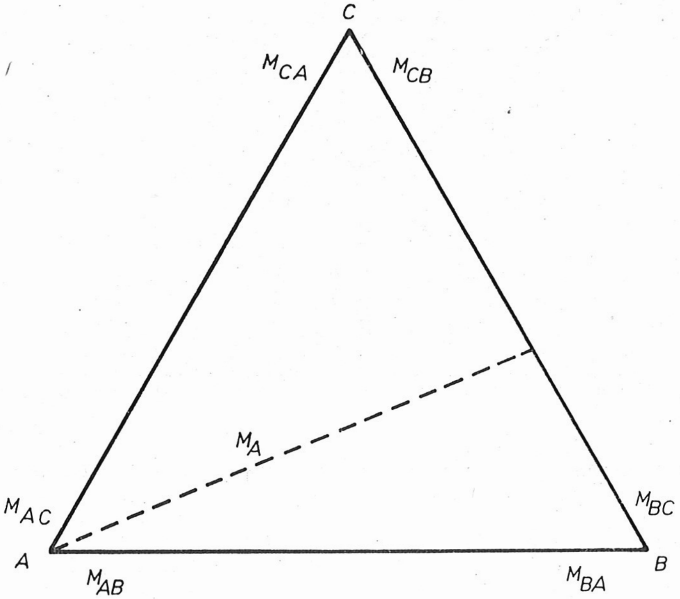

Fig. 1. Designation of components and M characteristics in the ternary system.

THE RESULTS AND DISCUSSION

The suggested calculation method was applied in the calculation of liquidus surface of the ternary system diopside—akermanite—leucite. The system was chosen because the boundary binary systems are known. The literature references to these binary systems as well as the temperature and composition of eutectic points are listed in Table I. In the binary system diopside—akerma-

Table I

Composition and temperature of eutectic points of the basic binary systems

System	Eutectic point composition and temperature		
	% by wt.	°C	Ref.
Leucite — akermanite	49.5 , 50.0	1 297 ∓ 3	13
Diopside — akermanite	59.0 , 41.0	1 361	14
Diopside — leucite	61.5 , 38.5	1 302 ∓ 2	13

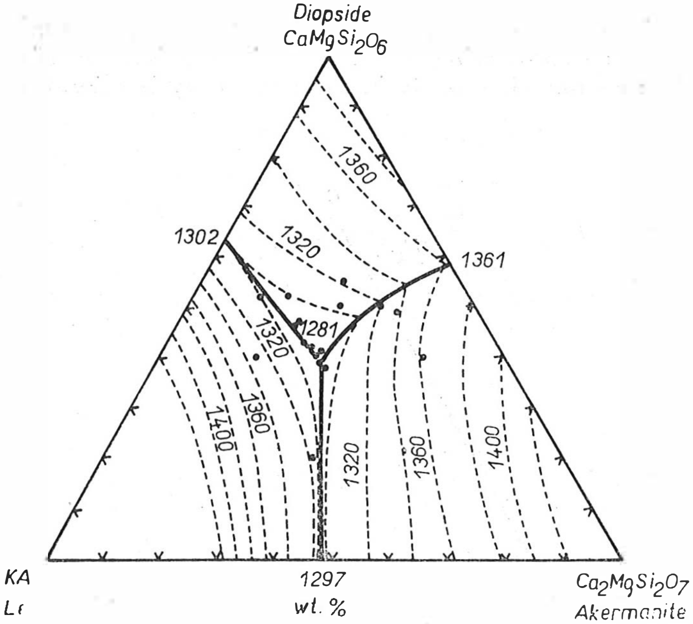

Fig. 2. Phase diagram of the system diopside—akermanite—leucite, according to [13].

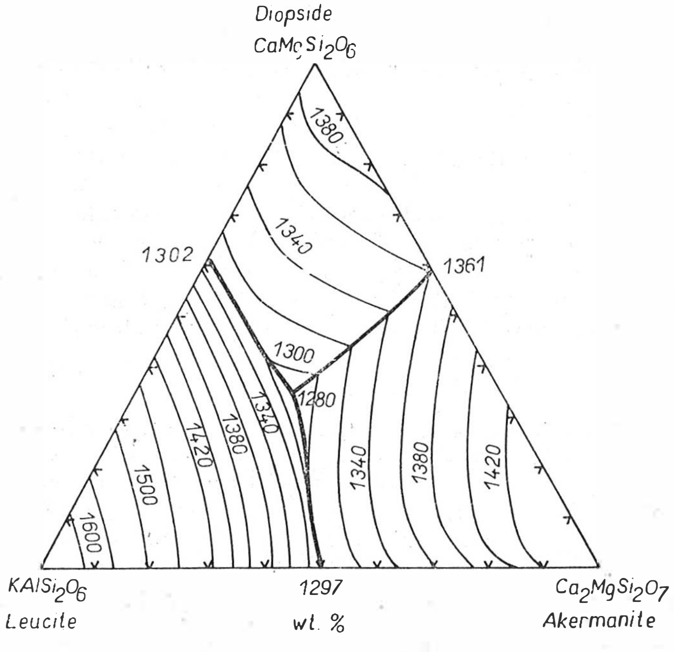

Fig. 3. Calculated phase diagram of the system diopside—akermanite—leucite.

nite the diopside side contains a region of solid solutions up to about 5 wt. % of akermanite. The fusion points of pure components were taken from study [13]. The calculations were carried out on the CDC 3 300 computer (Research Computer Center, Bratislava). A phase diagram of the ternary system diopside—akermanite—leucite was determined experimentally by Gupta [13] (Fig. 2). The calculated phase diagram is shown in Fig. 3. As indicated by the graphic representation of the given system the agreement between the experimental sections of the phase diagram and the calculated ones is satisfactory. In the determination of composition and temperature of the ternary eutectic the agreement is very satisfactory:

experimentally determined values	39 % D, 29 % A, 32 % L, $T_e = 1\,281 \pm 4$ °C
calculated values	35 % D, 29 % A, 36 % L, $T_e = 1\,280$ °C.

The calculation described implies that the suggested formalism employed in the calculation of phase diagrams of ternary systems comprising anions of complex structures provides a very satisfactory approximation for estimating the eutectic point parameters and those of the fields of primary crystallization. The procedure allows to reduce considerably the number of necessary experimental measurements in the study of three-component phase diagrams.

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VÝPOČET FÁZOVÉHO DIAGRAMU TERNÁRNEJ SÚSTAVY DIOPSID—AKERMANIT—LEUCIT

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Zo znalosti fázových diagramov základných binárnych sústav sa počíta fázový diagram ternárnej sústavy. Výpočet je založený na predpoklade, že dodatkovú Gibbsovu energiu ternárnej sústavy je možné s dobrým priblížením určiť ako sumu príspevkov základných binárnych sústav. V práci sa rieši problém výpočtu fázových rovnováh v sústavách s komplikovanou štruktúrou aniónov a navrhuje sa formálny model, vzhľadom ku ktorému sa počítajú dodatkové veličiny (rozdiel medzi skutočnou hodnotou a hodnotou získanou na základe modelu). Vzťahy použité pre výpočet fázových diagramov spĺňajú obecné termodynamické zákony platné pre priebeh kriviek a plôch likvidus.

Pri vlastnom výpočte rovnovážnej teploty sa používa rovnica (9). Veličinu M_A v každej binárnej sústave stanovíme s využitím vzťahov (6) a (8). Na základe experimentálnych údajov určíme podľa rovnice (9) v binárnych sústavách pre každú teplotu a zloženie hodnotu f_A. Riešením sústavy rovníc (12) stanovíme konštanty λ_α, λ_β, ktoré sú len funkciou teploty. Dodatkovú veličinu φ^E v ternárnej sústave získame pre každú teplotu a zloženie použitím rovnice (13). Korekčný faktor f_A v ternárnej sústave získame využitím vzťahov (10) a (13). Veličinu M_A v ternárnej sústave určíme použitím rovnice (14) (obr. 1). Získané údaje umožňujú potom z rovnice (9) vypočítať teplotu primárnej kryštalizácie zložky A. Postup výpočtu sa overil pri určení plôch primárnej kryštalizácie sústavy diopsid—akermanit—leucit (obr. 2, 3).

Obr. 1. Označenie zložiek a veličín M v ternárnej sústave.
Obr. 2. Fázový diagram sústavy diopsid—akermanit—leucit podľa [13].
Obr. 3. Vypočítaný fázový diagram sústavy diopsid—akermanit—leucit.

РАСЧЕТ ФАЗОВОЙ ДИАГРАММЫ ТЕРНАРНОЙ СИСТЕМЫ ДИОПСИД—АКЕРМАНИТ—ЛЕЙЦИТ

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Зная фазовые диаграммы основных бинарных систем, можно рассчитывать фазовую диаграмму тернарной системы. Расчет основываестя на предположении, что добавочную энергию Гиббса тернарной системы можно с хорошей апроксимацией определить как сумму энергий отдельных бинарных систем. В работе решается проблема расчета фазовых равновесий в системах со сложной структурой анионов и предлагается формальная модель, на основании которой рассчитываются добавочные величины (разность между действительной величиной и величиной, полученной на основании модели). Отношения, применяемые для расчета фазовых диаграмм соответствуют общим термодинамическим законам, действующим для хода кривых и поверхностей ликвидус.

Для собственного расчета равновесной температуры применяется уравнение (9). Величину M_A в каждой бинарной системе определяют, используя отношения (6) и (8). На основании экспериментальных данных определяют согласно уравнению (9) в бинарных системах для каждой температуры и состава величину f_A. Решением системы уравнений (12) определяют константы λ_α, λ_β, являющиеся только функцией температуры. Добавочную величину φ^E в тернарной системе получают для каждой температуры и состава при помощи уравнения (13). Поправочный коэффициент f_A в тернарной системе определяют применением уравнения (14) (рис. 1). На основании полученных данных можно из уравнения (9) рассчитать температуру первичной кристаллизации компонента A. Способ расчета проверяли при определении поверхностей первичной кристаллизации системы диопсид—акерманит—лейцит (рис. 2,3).

Рис. 1. Обозначение компонентов и величин M в тернарной системе.
Рис. 2. Фазовая диаграмма системы диопсид—акерманит—лейцит согласно [13].
Рис. 3. Рассчитанная фазовая диаграмма системы диопсид—акерманит—лейцит.