Computer Optimization of the Phase Diagrams of Alumino-Silicate Systems III. Regression Treatment of Peritectic Systems with Unknown Structural Parameters

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The phase diagram of the system CaO (C)—$12CaO \cdot 7Al_2O_3$ ($C_{12}A_7$) with incongruently melting compound $3CaO \cdot Al_2O_3$ (C_3A) is described by a thermodynamic model. Unknown structural and enthalpic parameters of the model were obtained by the nonlinear regression analysis. The least-squares method gave following estimates: $\alpha_4(Al) = 0.566 \pm 0.06$, $\Delta_{fus}H(C) = (140.7 \pm 2.6)$ kJ mol^{-1}, $\Delta_{fus}H(C_{12}A_7) = (57 \pm 8)$ kJ mol^{-1}, $\Delta_{fus}H(C_3A) = (223 \pm 21)$ kJ mol^{-1}, $T_{fus,hyp}(C_3A) = (1808 \pm 7)$ K. The inconsistency between the calorimetric and from the activity—composition relations deduced heats of fusion and/or heat of incongruent decomposition is critically discussed.

The phase diagrams involving peritectic points play a special role in interpretation of the phase diagrams of oxide systems. There are, however, no real values for the melting temperature and heat of fusion for incongruently melting compounds. The formalism of thermodynamic models describing such phase equilibria is therefore more complex. In a model described in the previous papers [1, 2], a peritectic compound is characterized by the hypothetical equilibrium temperature and the heat of fusion. These parameters can be determined from experimental phase diagram applying nonlinear regression analysis. This procedure we used in the previous paper [3] to determine the thermodynamic parameters of rankinite as well as dicalcium silicate in the system wollastonite—dicalcium silicate. The structural parameters were, however, in this case known *a priori* (all the silicon atoms are built into the tetrahedral network).

The present paper deals with the system CaO (C)—$Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) containing incongruently melting compound $Ca_3Al_2O_6$ (C_3A). A special emphasis is put on determining the unknown structural parameter $\alpha_4(Al)$ which is the fraction of Al^{3+} cations built into the tetrahedral network. The system CaO—Al_2O_3—SiO_2 was from this point of view studied by *Daněk* [2]. Comparing experimental and calculated phase diagrams within the region of primary crystallization of wollastonite, gehlenite, anorthite, and dicalcium silicate he showed that only approximately half of Al^{3+} cations are tetrahedrally coordinated, the remaining half shows a higher coordination, thus behaving as a modifier of tetrahedral network.

For the investigated system is of key importance from the point of view of applications such as metallurgical slags, ceramic materials, cement, *etc.* there were many attempts to interpret its phase diagram. Because of the high melting temperatures in the system, experimental determinations are often difficult or impossible to make. Some parts of the phase diagram and some thermodynamic properties — $\Delta_{fus}H$ and $\Delta_{fus}C_p$ of C_3A among them — are therefore still not unambiguously determined [4]. The purpose of this paper is to find within the limits of a given thermodynamic model a self-consistent set of both enthalpic and structural parameters characteristic of the investigated peritectic system.

METHOD

In our method a peritectic point is treated as a special case of more general approach in which at composition of incongruently melting compound, the temperature of primary crystallization of other crystalline phase is higher than the hypothetical melting temperature of pure, incongruently melting constituent. Such compound is therefore characterized by the hypothetical values of its temperature and enthalpy of fusion. From the point of view of input data we therefore need not distinguish between congruently and incongruently melting constituents. In this sense we also applied regression analysis to estimate unknown parameters that characterize incongruently melting compound(s).

We have considered the most simple temperature dependence of the heat of fusion given by

$$\Delta_{fus}H_i(T) = \Delta_{fus}H_i(T_{fus,i}) + \Delta_{fus}C_{p,i}(T - T_{fus,i}) \quad (1)$$

where $T_{fus,i}$ and $\Delta_{fus}H_i(T_{fus,i})$ are the temperature and enthalpy of fusion of the i-th constituent, respectively and $\Delta_{fus}C_{p,i}$ is the change in heat capacity of the liquid and solid constituent i which we assume to be constant. Substituting the last equation into the LeChatelier—Shreder equation

$$\left[\frac{\partial \ln a_i}{\partial T}\right]_p = \frac{\Delta_{fus}H_i(T)}{RT^2} \quad (2)$$

we obtain after integration and rearrangement a transcendental equation for the unknown liquidus temperature $T_{l,i}$

$$f(T_{l,j}) = \Delta_{fus}H_i(T_{fus})\left(\frac{1}{T_{l,j}} - \frac{1}{T_{fus}}\right) + \\ + \Delta_{fus}C_{p,j} \ln (T_{fus}/T_{l,j}) - R \ln a_i = 0 \quad (3)$$

where a_i is the activity of the i-th constituent. The details of numerical iterative solution of eqn (*3*) are described in [3]. For the activity a_i occurring in eqn (*3*) we use the model introduced by Haase based on ideal mixing of considered ions

$$a_i = \prod_j \left(\frac{y_j}{y^o_{i,j}}\right)^{N_{i,j}} \quad (4)$$

where $y^o_{i,j}$ and y_j are mole fractions of the j-th kind atoms in the pure component i and in the melt, respectively, $N_{i,j}$ is the number of moles of elements j in one mole of the pure component i. Subscript j refers to the ions Ca^{2+}, Al^{3+}, $O°$, O^-, and O^{2-} in our particular case. The relative abundance of bridging ($O°$), nonbridging (O^-), and free (O^{2-}) oxygen atoms is determined by the composition of the melt and the value of α_4(Al) and can be calculated from one of the two sets of material balance equations [1]. These are in our case simplified to

$$N(O) = N(O°) + N(O^-) + N(O^{2-}) \quad (5)$$

$$N(O^-) + 2N(O°) = 4\alpha_4(Al)N(Al^{3+}) \quad (6)$$

$$N(O^{2-}) = 0 \quad (7)$$

or, if the solution of this system makes no physical sense (*i.e.* negative values of N), it is necessary to assume the oxygen atoms are present as nonbridging ones and as oxygen ions O^{2-}

$$N(O^-) = 2\alpha_4(Al)N(Al^{3+}) \quad (8)$$

$$N(O^{2-}) = N(O) - N(O^-) \quad (9)$$

$$N(O°) = 0 \quad (10)$$

For the total amount of oxygen atoms N(O) it holds

$$N(O) = N(CaO) + 3N(Al_2O_3) \quad (11)$$

It is evident from the above equations that the calculated phase diagram implicitly depends on the α_4(Al), (hypothetical) melting temperatures of pure components $T_{fus,i}$ and enthalpic parameters. Because of implicit dependence of liquidus temperature on these parameters, the minimization of the sum of squares of deviations between experimental and calculated liquidus temperature is a task of nonlinear regression analysis. It is, therefore, useful to use nonderivative minimization methods, *e.g.* the simplex method by *Nelder* and *Mead* [5].

The method described above was implemented into the original FORTRAN program presented in [1] and applied to the investigated binary system.

RESULTS AND DISCUSSION

The temperature of fusion of C and $C_{12}A_7$ [6] can be regarded as fixed experimental values for the presented thermodynamic model. A wide region of CaO primary crystallization allows reliably to determine the enthalpy and heat capacity of fusion for calcium oxide fitting the experimental phase diagram. The values of $\Delta_{fus}H$ = (140.7 ± 2.6) kJ mol^{-1} and $\Delta_{fus}C_p$ = (86 ± 6) J mol^{-1} K^{-1} were obtained fitting twelve experimental liquidus temperatures within the composition range from the pure calcium oxide to the eutectic composition. In this step the α_4(Al) was also optimized to yield the value of 0.566 ± 0.06. The last value is in principal harmony with the results of *Daněk* [2]. Unfortunately, there are not serious experimental data available that would enable to verify the obtained estimates of enthalpic parameters. Only the rough estimates of this value have been published, *e.g.* the JANAF estimate of 79 kJ mol^{-1}, obtained by analogy to a value for MgO estimated from phase equilibria [7, 8]. Another value, (68 ± 4) kJ mol^{-1}, was obtained by *Eliezer et al.* [9] from freezing point depression data on the CaO—MgO system. On the other hand, the fit of experimental phase diagram obtained as a result of regression analysis is very convincing (see Fig. 2). Taking this fit into consideration, low values of estimated standard deviations are not surprising.

The narrow range of $C_{12}A_7$ primary crystallization allowed us to take only four relatively close experimental points into consideration. These figurative points were confined to the composition range from x(C) = $x_{e,1}$ to x(C) = $x_{e,2}$, where $x_{e,1}$ and $x_{e,2}$ are the eutectics of $C_{12}A_7$ with CA and C_3A, respectively. Little range of liquidus temperature allows to neglect the change in heat capacity on fusion for this compound. In this case the regression analysis had only three degrees of freedom, which from the statistical

point of view considerably decreases the reliability of the obtained estimate for $C_{12}A_7$, $\Delta_{fus}H$ = (76 ± 12) kJ mol^{-1}

There are various ways how to obtain the parameters characterizing tricalcium aluminate that melts incongruently. The first one is to exploit the enthalpy balance of the reaction

$$9C + C_{12}A_7 = 7C_3A \qquad (A)$$

for the estimation of the enthalpy of fusion from the hypothetical melting temperature $T_{fus,hyp}(C_3A)$

$$9[\Delta_{fus}H(C, T_{fus}(C)) + \Delta_{fus}C_p(C)(T_{fus,hyp}(C_3A) - T_{fus}(C))] + 1[\Delta_{fus}H(C_{12}A_7, T_{fus}(C_{12}A_7)) + \Delta_{fus}C_p(C_{12}A_7)(T_{fus,hyp}(C_3A) - T_{fus}(C_{12}A_7))] = 7\Delta_{fus}H(C_3A, T_{fus,hyp}(C_3A)) \qquad (12)$$

and then apply the regression to fit 17 experimental points of the phase diagram to optimize this temperature at the fixed $\Delta_{fus}H$. The estimate of the enthalpy of fusion is, however, a rough approximation which assumes that the relation

$$\Delta_r H(s, 298\ K) = \Delta_{mix}H(l, T_{fus}(C_3A)) \approx 0$$

where $\Delta_r H$ is the heat of the reaction (*A*) and the Neumann—Kopp's rule are valid. The remaining parameters for C and $C_{12}A_7$ were taken from the previous estimates. When we tried, in addition, to optimize the change in heat capacity on fusion for this compound it turned out to be zero. The optimization procedure has been carried out cyclically. First, from the enthalpy balance of the reaction scheme (*A*) we had calculated enthalpy of fusion at an initial hypothetical melting temperature. In the second step we optimized this temperature and compared experimental and calculated phase diagrams. Then we repeated this procedure until the self-consistency was achieved to end up with the values $\Delta_{fus}H$ = 88.9 kJ mol^{-1} and $T_{fus,hyp}$ = 1913 K. The experimental and calculated phase diagrams are shown in Fig. 1. As it can be seen, there is a significant difference between them which might suggest the incorrectness in obtained estimates. The second procedure to obtain these parameters was that four experimental points around tricalcium aluminate primary crystallization were fit to give the values $T_{fus,hyp}$ = (1808 ± 7) K, $\Delta_{fus}H$ = (215 ± 15) kJ mol^{-1} and $\Delta_{fus}C_p$ = 0. These values were used as the input ones to make the regression analysis with all 17 experimental points involved. In this step the enthalpy of fusion for $C_{12}A_7$ was also optimized. The regression analysis resulted in the following estimates: $\Delta_{fus}H(C_{12}A_7)$ = (57 ± 8) kJ mol^{-1}, $\Delta_{fus}H(C_3A)$ = (223 ± 21) kJ mol^{-1}, $T_{fus,hyp}(C_3A)$ = (1802 ± 9) K. It turned out that including α_4(Al) into regression procedure does not make any significant effect except the negative influence of a strong linear bond between α_4(Al) and $\Delta_{fus}H(C_3A)$ on overall statistics. This fact simultaneously confirms the admittance of using a single mean α_4(Al) value in the studied composition range. The experimental and calculated phase diagrams are compared in Fig. 2.

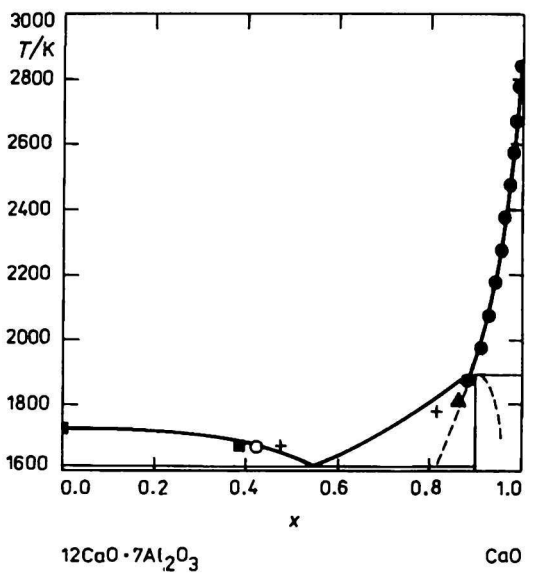

Fig. 1. Plot of experimental (points) and calculated (solid line) phase diagram of the system $C_{12}A_7$—C using $\Delta_{fus}H(C_3A)$ estimated from eqn (*12*). ● Experimental points within the region of calcium oxide primary crystallization, ■ experimental points within the region of dodecacalcium aluminate primary crystallization, + experimental points within the region of tricalcium aluminate primary crystallization, ○ eutectic point, ▲ peritectic point, dashed lines — calculated, hypothetical liquidus curves of undercooled phases.

Let us discuss the most significant differences between the two approaches that will be further referred to as the case A (Fig. 1) and B (Fig. 2). Comparing Figs. 1 and 2 we can conclude that the fit of experimental data is much better in the case B. The value of $T_{fus,hyp}(C_3A)$ = (1802 ± 9) K obtained in the case B is acceptable regarding the liquidus curve in the experimental phase diagram. Extrapolating the experimental liquidus curve linearly to the pure substance C_3A the value ≈ 1819 K is obtained. The value of (1913 ± 18) K reached in the case A appears to be too high.

$\Delta_{fus}H$ = 88.9 kJ mol^{-1} obtained for tricalcium aluminate in the case A from the enthalpy balance equation (*12*) seems to be in a good agreement with experimental determinations of *Adamkovičová et al.* [10] and *Hallstedt* [4]. The value of (223 ± 21) kJ mol^{-1} obtained in the case B is supported by the better fit of the experimental phase diagram. Moreover, within 3-σ range this value coincides with the one of 157 kJ mol^{-1} determined by *Eliezer et al.* [9]

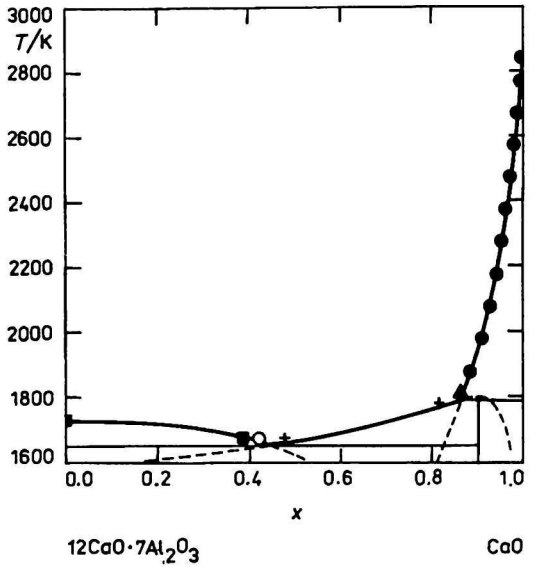

Fig. 2. Plot of experimental (points) and calculated (solid line) phase diagram of the system $C_{12}A_7$—C. $\Delta_{fus}H(C_3A)$ has been also optimized. ● Experimental points within the region of calcium oxide primary crystallization, ■ experimental points within the region of dodecacalcium aluminate primary crystallization, + experimental points within the region of tricalcium aluminate primary crystallization, ○ eutectic point, ▲ peritectic point, dashed line — calculated, hypothetical liquidus curves of undercooled phases.

and of 151 kJ mol^{-1} reported by *Scholze* and *Kumm* [11]. The difference between the $\Delta_{fus}H(C_{12}A_7)$ = (76 ± 12) kJ mol^{-1} used in the case A and the $\Delta_{fus}H(C_{12}A_7)$ = (57 ± 8) kJ mol^{-1} used in the case B may be considered statistically insignificant. Both these values differ appreciably from the value of 209 kJ mol^{-1} published in [11]. It is not clear, however, how this value was gained.

Summarizing the previous comparison we can see that both the theoretical and experimental approaches lead to equivalent dichotomic situation in determination of the $\Delta_{fus}H(C_3A)$ and $T_{fus}(C_3A)$ values. Both cases give the zero heat capacity of fusion for C_3A which enables to use the LeChatelier—Shreder equation derived for constant heat of fusion in the form

$$T = \frac{T_{fus}\Delta_{fus}H}{\Delta_{fus}H - RT_{fus}\ln a} \qquad (13)$$

to cope with this situation. Within the limits of the presented thermodynamic model, the activity of tricalcium aluminate is a function of composition in a melt as well as of structural parameter α_4(Al). Two equations with two unknowns $\Delta_{fus}H(C_3A)$ and $T_{fus}(C_3A)$ can be written for the eutectic and peritectic compositions. Solving them we express the unknowns as functions of the corresponding activities a_e, a_p

$$T_{fus} = T_pT_e\frac{\ln a_p - \ln a_e}{T_p\ln a_p - T_e\ln a_e} \qquad (14)$$

$$\Delta_{fus}H = RT_pT_e\frac{\ln a_p - \ln a_e}{T_p - T_e} \qquad (15)$$

where T_p and T_e are the peritectic and eutectic temperatures. Giving the value α_4(Al), the activities a_p, a_e can be calculated from the peritectic and eutectic compositions (see eqns (*4*—*14*)). Using the values of T_e = 1668 K and T_p = 1808 K, Table 1 was

Table 1. Heat of Fusion $\Delta_{fus}H$ and Temperature of Fusion T_{fus} of Tricalcium Aluminate Calculated Using Eqns (*14*, *15*) for Various Values of α_4(Al)

α_4(Al)	a_e	a_p	T_{fus} / K	$\Delta_{fus}H$ / kJ mol^{-1}
0.50	0.5332	0.9621	1818.0	105.7
0.51	0.5083	0.9603	1817.7	113.9
0.52	0.4805	0.9583	1817.4	123.6
0.53	0.4491	0.9560	1817.1	135.3
0.54	0.4133	0.9536	1816.7	149.7
0.55	0.3722	0.9508	1816.2	168.0
0.56	0.3244	0.9477	1815.6	192.0
0.57	0.2681	0.9442	1815.0	225.5
0.58	0.2008	0.9401	1814.1	276.5
0.59	0.1191	0.9355	1812.9	369.1

constructed to demonstrate the strong dependence of the heat of fusion on the α_4(Al) value. This dependence is the steeper, the greater is the value of α_4(Al). It can be seen from Table 1 that around the optimal α_4(Al) = 0.566 the $\Delta_{fus}H(C_3A)$ varies from 192 kJ mol^{-1} for α_4(Al) = 0.56 to 225 kJ mol^{-1} for α_4(Al) = 0.57, which is in agreement with the case B estimate of $\Delta_{fus}H(C_3A)$ = (223 ± 21) kJ mol^{-1}.

We realize that the regression character of $\Delta_{fus}H(C_3A)$ estimation disables to use the experimental phase diagram fit as the only correctness criterion. Moreover, the situation is complicated by the bonds between α_4(Al) and $\Delta_{fus}H(C_3A)$ values explicitly given in Table 1.

Therefore we tried to estimate the enthalpy of fusion of tricalcium aluminate by an independent way based on the additive scheme for the entropy of fusion [12]

$$\Delta_{fus}S(C_3A,\ T_{fus,hyp}(C_3A)) = 3\Delta_{fus}S(C,\ T_{fus}(C)) + 3\Delta_{fus}S(A,\ T_{fus}(A)) + 3\int_{T_{fus}(C)}^{T_{fus,hyp}(C_3A)}\Delta_{fus}C_p(C,\ T)\,d\ln T + \int_{T_{fus}(A)}^{T_{fus,hyp}(C_3A)}\Delta_{fus}C_p(C,\ T)\,d\ln T \qquad (16)$$

where

$\Delta_{fus}C_p(X, T) = C_p(X, l, T) - C_p(X, s, T) = C_p(X, l) - [a(X) + b(X)T + c(X)T^{-2} + d(X)T^2]$, for X = C, A (*17*)

Temperature-independent $C_p(X, l)$ values and the coefficients $a(X)$—$d(X)$ were taken from *Barin* and *Knacke* [13]. The value of 1819 K, obtained by the linear extrapolation of liquidus curve, was taken for the hypothetical temperature of fusion in eqn (*16*). From the equation

$$\Delta_{fus}H = T_{fus}\Delta_{fus}S \qquad (18)$$

the value of 214 kJ mol^{-1} was obtained for $\Delta_{fus}H(C_3A)$. This estimate is relatively insensitive of the $T_{fus,hyp}$ selection, *e.g.* for $T_{fus,hyp}(C_3A)$ = 1913 K and 1700 K we get $\Delta_{fus}H(C_3A)$ = 218 kJ mol^{-1} and 202 kJ mol^{-1}, respectively. In this sense, the presented estimate may be considered not to depend on the experimental phase diagram.

CONCLUSION

On the basis of the above arguments we adopt the results obtained in the case B. Summarizing these results with those in our previous paper [3], the general conclusion may be proposed that the computational procedure employed is suitable to describe phase equilibria in oxide systems containing incongruently melting compounds. It is worth to note in connection with our method that, in addition, some structural information (at least semi-quantitative) is obtained. On the other hand, the present paper pointed out some problems that may be encountered due to the strong bond between some structural and enthalpic parameters of the model. Therefore the need of sufficiently large, precise, and mutually consistent number of experimental phase diagram data is emphasized.

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