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Thermodynamic properties of liquid phase in the $CaO{\cdot}SiO_2$–$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$–$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ system[☆]

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Abstract

Thermodynamic properties consistent with phase equilibria and calorimetric measurements were established for liquid phase in the system $CaO{\cdot}SiO_2$–$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$–$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ using molecular regular solution models. The assessed thermodynamic data set involves enthalpy and entropy of formation of crystalline phases, heat capacity (C_p) data of solid and liquid pure components, enthalpy of mixing of liquid pure components, enthalpy and entropy of fusion of solid phases and phase equilibria experiments. Considerable inconsistency was found between experimental phase equilibria and calorimetrically measured enthalpy of the liquid solution. To fix thermodynamic properties of melt in studied system, which reproduce phase diagrams satisfactorily, considerable changes in enthalpy of mixing with respect to the original calorimetric data must be accepted. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; CaO; Melts; SiO_2; Thermodynamic properties

1. Introduction

Modeling of many natural and technical processes needs a reasonable set of internally consistent thermodynamic data. A considerable effort has been devoted in recent decades by systematizing and critical assessments of thermodynamic quantities. Assessment procedures have been widely discussed in literature (e.g. Refs. 1–3). Most of the published databases[1–5] are usually large and have wide impact. The present paper deals with the system $CaO{\cdot}SiO_2$ (CS) – $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ (CAS2) – $2CaOa{\cdot}Al_2O_3{\cdot}SiO_2$ (C2AS) — a subsystem of the ternary system CaO–Al_2O_3–SiO_2 (C–A–S) which is of considerable importance in oxide ceramics, cement chemistry, metallurgical slags and geochemistry.

The assessment in the C–A–S system was done by Pelton[6] using a quasichemical model and Wang et al.[7] using an ionic sublattice model. In the present study we are using a molecular model with excess Gibbs energy expressed by the Redlich–Kister polynomial. In addition to the usual data e.g. standard enthalpy, entropy and Gibbs energy of formation and heat capacities of solid stoichiometric phases, there is an extensive data set on enthalpy of liquid phase in the whole ternary system region as well as data on melting of pure components and crystallization of both binary and ternary eutectic melts available from detailed calorimetric studies[8–14] in the studied system, which are involved in this assessment.

The thermodynamic analysis of all three particular binary subsystems has already been performed using a quite complicated empirical model, based on phase diagrams and enthalpy measurements, resulting in Gibbs energy of mixing and activities.[15–17] However, the data determined in these analyses have not been optimized simultaneously. The analysis of data in the ternary system has not yet been performed.

The present study relies upon data on known thermodynamic properties of solid components, data on

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phase equilibrium experiments in binary subsystems and ternary system and on calorimetric data on high temperature enthalpy of liquids. The aim of this study is to assess the thermodynamic quantities in the system under study and to evaluate the thermodynamic properties of the liquid phase, maintaining consistency of all considered thermodynamic quantities.

2. Experimental data

Phase relations in CS–CAS2–C2AS system were experimentally studied by Rankin and Wright,[18] and Osborn and Shairer.[19] The binary system C2AS–CAS2 was first investigated by Rankin and Wright[18] and revised by Osborn, whose unpublished data were presented by Goldsmith.[20] Data for CS–CAS2 phase diagram are from Osborn,[21] data for CS–C2AS system measured Rankin and Wright[18] and Osborn and Shairer.[19] The other data used in this study are taken from phase diagrams of the C–A–S system by Osborn and Muan[22] and Gentil and Foster.[23] In binary systems only particular experimental points are accepted as input phase equilibria data. The considered experimental points are presented below in the phase diagrams along with optimized liquidus curves.

The phase equilibrium data for binary systems used in this assessment are consistent with that used by Proks et al.,[15] Kosa et al.,[16] Strečko at al.[17] and Eliašová et al.[24] Note that the binary phase equilibria projected from ternary C–A–S phase diagram are also included in binary data sets, making an effort to achieve better consistency between binary phase diagrams and the ternary one.

The calorimetric data accepted for solid phases and liquids are summarized in Table 1. Enthalpies of mixing for binary and ternary melts have been measured by Kosa et al.,[10] the statistical treatment of the experimental data was revised by Proks et al.[15] The function describing the dependence of relative enthalpy of melt on temperature and composition published by Proks et al.[15] was used to calculate any enthalpic quantities of melts in the studied systems.

3. Thermodynamic description

The approach of computer coupling of phase diagrams and thermochemical data was used for data treatment. That means, both phase equilibria and calorimetric data are included in the procedure of assessment of thermodynamic parameters. Nowadays, there are several computer programs for data assessments available, which allow including diverse experimental data simultaneously, e.g. BINGSS and TERGSS of Lukas et al.,[27] THERMOCALC of Sundman et al.,[1] etc. In this study PARROT program from the THERMOCALC set[1,28] was used to assess thermodynamic parameters. To calculate phase diagrams the method of minimization of Gibbs energy is most commonly used, e.g. THERMOCALC, F*A*C*T of Pelton et al.,[4] CHEMSAGE of Eriksson and Hack[29] etc. In this study the POLY-3 program from the THERMOCALC set was used for phase diagram calculation.

Table 1
Thermochemical quantities for solids and liquids in the system CS–CAS2–C2AS, included in optimization

CS pseudowollastonite
$H°(298\ \mathrm{K}) = -1629.54\ \mathrm{kJ\ mol^{-1}}$ Saxena et al.[5]
$S°(298\ \mathrm{K}) = 84.46\ \mathrm{J\ (mol\ K)^{-1}}$ Saxena et al.[5]
$Cp(\mathrm{J\ (mol\ K)^{-1}}) = 63.58 + 0.05724\ T$ Adamkovičová et al.[8]
$\Delta_{\mathrm{fus}}H(1821\ \mathrm{K}) = 57.3\ \mathrm{kJ\ mol^{-1}}$ Adamkovičová et al.[8]

CS liquid
$Cp = 149.84\ \mathrm{J\ (mol\ K)^{-1}}$ Adamkovičová et al.[8]

CAS2 anorthite
$H°(298\ \mathrm{K}) = -4232.5\ \mathrm{kJ\ mol^{-1}}$ Saxena et al.[5]
$S°(298\ \mathrm{K}) = 203\ \mathrm{J\ (mol\ K)^{-1}}$ Saxena et al.[5]
$Cp(\mathrm{J\ (mol\ K)^{-1}}) = 406.813 - 2733.6/(T)^{0.5} - 4546200/(T)^2$
$+ 377140000/(T)^3$ Richet and Fiquet[25]
$\Delta_{\mathrm{fus}}H(1830\ \mathrm{K}) = 133\ \mathrm{kJ\ mol^{-1}}$ Richet and Bottinga[26]

CAS2 liquid
$Cp(\mathrm{J\ (mol\ K)^{-1}}) = 400.772 + 0.020243\ T$ Richet and Bottinga[26]

C2AS gehlenite
$H°(298\ \mathrm{K}) = -3980.31\ \mathrm{kJ\ mol^{-1}}$ Wang et al.[7]
$S°(298\ \mathrm{K}) = 209.78\ \mathrm{J\ (mol\ K)^{-1}}$ Wang et al.[7]
$Cp(\mathrm{J\ (mol\ K)^{-1}}) = 201.9 + 0.0818\ T$ Žigo et al.[9]
$\Delta_{\mathrm{fus}}H(1868\ \mathrm{K}) = 172.9\ \mathrm{kJ\ mol^{4-1}}$ Žigo et al.[9]

C2AS liquid
$Cp = 518.2\ \mathrm{J\ (mol\ K)^{-1}}$ Žigo et al.[9]

The following expressions were used in thermodynamic modeling in this study. Gibbs energy of liquid stoichiometric phases was expressed as

$$G_{\mathrm{i}}^{\mathrm{o}}(T) = H_{\mathrm{cr,298K}}^{\mathrm{o}} - TS_{\mathrm{cr,298K}}^{\mathrm{o}} + \int_{298\mathrm{K}}^{T_{\mathrm{fus}}} C_{p,\mathrm{cr}}(T)\mathrm{d}T - T\int_{298\mathrm{K}}^{T_{\mathrm{fus}}} \frac{C_{p,\mathrm{cr}}(T)}{T}\mathrm{d}T - (T - T_{\mathrm{fus}})\frac{\Delta_{\mathrm{fus}}H_{T_{\mathrm{fus}}}}{(T_{\mathrm{fus}})} + \int_{T_{\mathrm{fus}}}^{T} C_{p,1}(T)\mathrm{d}T - T\int_{T_{\mathrm{fus}}}^{T} \frac{C_{\mathrm{p},1}(T)}{T}\mathrm{d}T \quad (1)$$

where $H_{\mathrm{cr,298K}}^{\mathrm{o}}$ and $S_{\mathrm{cr,298K}}^{\mathrm{o}}$ are the standard enthalpy, and the standard entropy of crystalline phase. $C_{p,\mathrm{cr}}$ and $C_{p,1}$ are heat capacities of crystalline and liquid phases, expressed as a function of temperature by a polynomial. $\Delta_{\mathrm{fus}}H_{T_{\mathrm{fus}}}$ is the enthalpy of fusion at the temperature of fusion. Gibbs energy of liquid solution was described by the formula

$$G_l = \sum_i x_i G_i^o + \Delta_{\mathrm{mix}}G \quad (2)$$

where x_i is the mole fraction of component i and $G_i{}^{o}$ is the Gibbs energy of pure liquid component i. The Gibbs energy of mixing is defined as

$$\Delta_{\mathrm{mix}}G = RT\sum_{i} x_i \ln x_i + \Delta_{\mathrm{mix}}{}^{G^E} \tag{3}$$

where $\Delta_{\mathrm{mix}}G^{E}$ is the excess Gibbs energy of mixing expressed by Redlich–Kister equation. For binary solutions with components i and j is the model as follows

$$\Delta_{\mathrm{mix}}G^E = \sum_{0}^{n} x_i x_j \left(x_i - x_j\right)^{n}\,{}^{n}L_{i,j} \tag{4}$$

where ${}^{n}L_{i,j}$ are mixing parameters between components i and j. For ternary solution with components i, j and k, with only binary interaction mixing parameters considered we have

$$\begin{aligned} {}^{\mathrm{bin}}\Delta_{\mathrm{mix}}G^E = {} & \sum_{0}^{n} x_i x_j \left(x_i - x_j\right)^{n}\,{}^{n}L_{i,j} \\ & + \sum_{0}^{n} x_i x_k (x_i - x_k)^{n}\,{}^{n}L_{i,k} \\ & + \sum_{0}^{n} x_j x_k \left(x_j - x_k\right)^{n}\,{}^{n}L_{j,k} \end{aligned} \tag{5}$$

This model will be called bellow model 1.

For ternary solution for which the excess Gibbs energy of mixing was considered to be composed of binary interaction contributions as well as of ternary interaction one, additional ternary interaction term was added to the right side of the Eq. (5).

$${}^{\mathrm{bin+ter}}\Delta_{\mathrm{mix}}G^E = {}^{\mathrm{bin}}\,\Delta_{\mathrm{mix}}G^E + x_i x_j x_k L_{ij,k} \tag{6}$$

This model will be called bellow model 2.

In the first step data on solid–liquid phase equilibria and calorimetric data on $\Delta_{\mathrm{mix}}H$ were included in optimization simultaneously to assess binary mixing parameters ${}^{n}L_{i,j}$ separately for each binary subsystem. In the second step the resulting binary mixing parameters and ternary data only were used to assess ternary mixing parameter $L_{i,j,k}$. Data on solid–solid–liquid phase equilibria and data on solid–liquid phase equilibria at 1573, 1673 and 1773 K, along with calorimetric data on $\Delta_{\mathrm{mix}}H$ for ternary solutions were included in optimization in this step. Thermochemical data for stoichiometric phases were not changed during the optimization.

4. Results and discussion

The optimized mixing parameters of the CS–CAS2–C2AS melts are presented in Table 2. The calculated eutectic equilibria in the CS-CAS2-C2AS system in comparison with experimental data are summarized in Table 2.

4.1. System C2AS–CAS2

4.1.1. Phase equilibria

The evaluated liquidus curves along with the experimental points are shown in Fig. 1. The optimized liquidus curves fit the experimental data within error limits, usual in solidus–liquidus equilibria measurements in the entire composition range of the system. The calculated temperature of crystallization and the composition of the eutectic melt are 1657 K and x(CAS2) = 0.514, respectively. They are in quite good agreement with experimental data as presented in Table 3. The probable maximum inaccuracy in the assessed phase diagram was estimated as ±2 mol% and ±15 K.

4.1.2. Mixing properties

In Fig. 2 the optimized enthalpy of mixing of C2AS–CAS2 melts at 1950 K in comparison with experimental curve based on data by Kosa et al.[10] as interpreted by Proks et al.[15] is presented. The postulated composition independent enthalpy of mixing was used in thermodynamic analysis by Proks et al.,[15] The optimized $\Delta_{\mathrm{mix}}H$ curve does not exceed the error limits of experimental data, ±4.3 kJ mol^{-1}, given by Proks et al.[15] From this viewpoint the different character of the calculated dependence with respect to the experimental data (minima on the $\Delta_{\mathrm{mix}}H$ curve) may be considered as not significant.

The calculated Gibbs energy of mixing and entropy of mixing of liquids in comparison with data by Proks et al.[15] are presented in Fig. 3. The calculated activities of both components in the liquid of the system in comparison with data by Proks et al.[15] are presented in Fig. 4. The agreement at the considered temperature is good.

Table 2
Optimized mixing parameters of the melt in the system CS–CAS2–C2AS

System C_2AS–CAS_2
${}^{0}L_{12}$ (kJ mol^{-1}) = 10995.9346–18.2605746 T
${}^{1}L_{12}$ (kJ mol^{-1}) = –362.582207 + 4.76257739 T
${}^{2}L_{12}$ (kJ mol^{-1}) = –29200.0104 + 24.7140653 T

System CS–CAS2
${}^{0}L_{13}$ (kJ mol^{-1}) = –29093.2418 + 16.2291939 T
${}^{1}L_{13}$ (kJ mol^{-1}) = 108446.014–55.0501135 T

System CS–C2AS
${}^{0}L_{23}$ (kJ mol^{-1}) = –42707.8711 + 28.3250564 T
${}^{1}L_{23}$ (kJ mol^{-1}) = 143227.623–71.0200283 T
${}^{2}L_{23}$ (kJ mol^{-1}) = –134187.036 + 71.4098651 T

System CS–CAS2–C2AS
${}^{0}L_{123}$ (kJ mol^{-1}) = 366072.453–213.738085 T

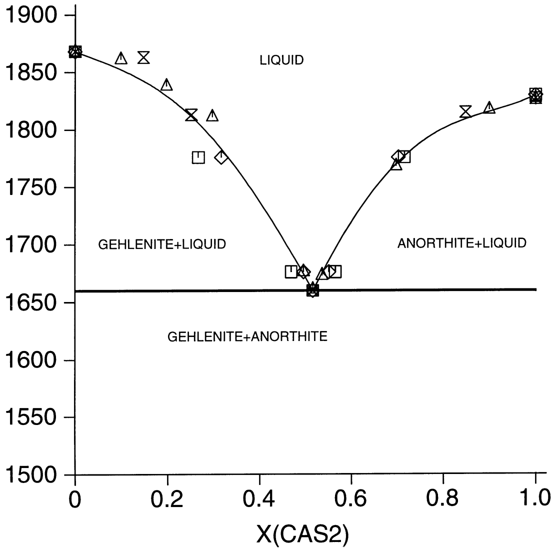

Fig. 1. Phase equilibria in the system C2AS–CAS2. Experimental data points are from Osborn after Goldsmith[20] (△), Osborn and Muan[22] (□), Gentil and Foster[23] (◇), and Rankin and Wright[18] (⊠). Solid lines are optimized curves.

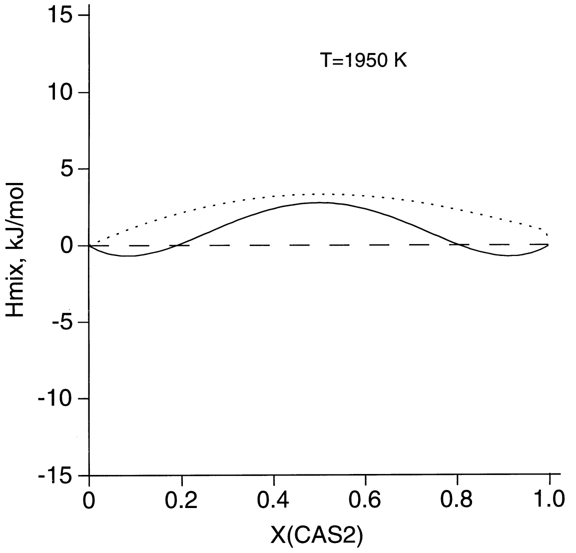

Fig. 2. Enthalpies of mixing in the system C2AS–CAS2 at 1950 K. Dotted line represents experimental data by Kosa et al.[10] interpreted by Proks et al.,[15] dashed line is postulated in thermodynamic analysis by Proks et al.[15] and solid line is optimized in this study.

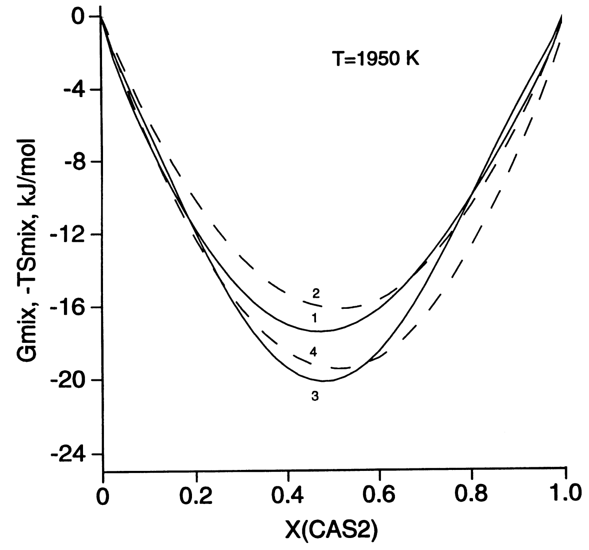

Fig. 3. Gibbs energy of mixing (1,2) and $-T\Delta_{\mathrm{mix}}S$ (3, 4) of liquids in the system C2AS–CAS2 at 1950 K. Dashed curves are calculated by Proks et al.,[15] solid lines are calculated in this study.

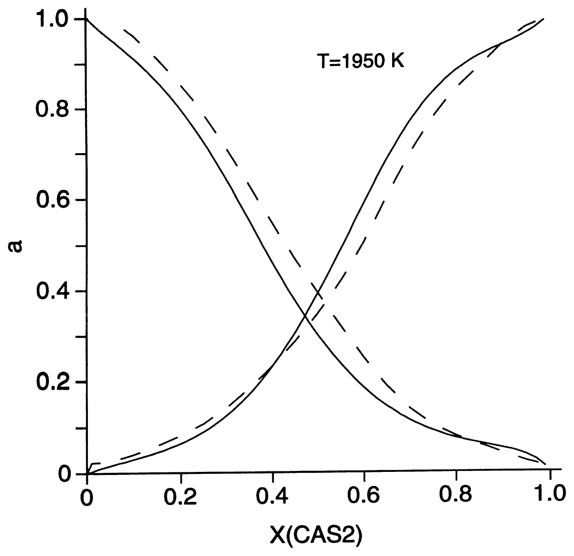

Fig. 4. Activities of components in the system C2AS–CAS2 at 1950 K. Dashed lines are calculated by Proks et al.,[15] solid lines are calculated in this study.

4.2. System CS-CAS2

4.2.1. Phase equilibria

The evaluated liquidus curves along with the experimental points are shown in the Fig. 5. The liquidus curves do not fit experimental data as well as in the above system. The maximum difference between calculated liquidus curves and experimental points is about 30 K. The attempt to bring the fitted curves closer to the experimental data results in an increase of differences between calculated and experimental enthalpy of mixing, in particular at lower temperatures. The calculated temperature of crystallization and the composition of the eutectic melt are 1575 K and x(CAS2) = 0.285, respectively. They are in a good agreement with experimental data presented in Table 3. The probable maximum inaccuracy in the assessed phase diagram was estimated as ± 4 mol% and ± 30 K.

4.2.2. Mixing properties

The evaluated enthalpy of mixing at 1950 K in comparison with experimental data by Kosa et al.[10] as interpreted by Proks et al.[15] and calculated data by

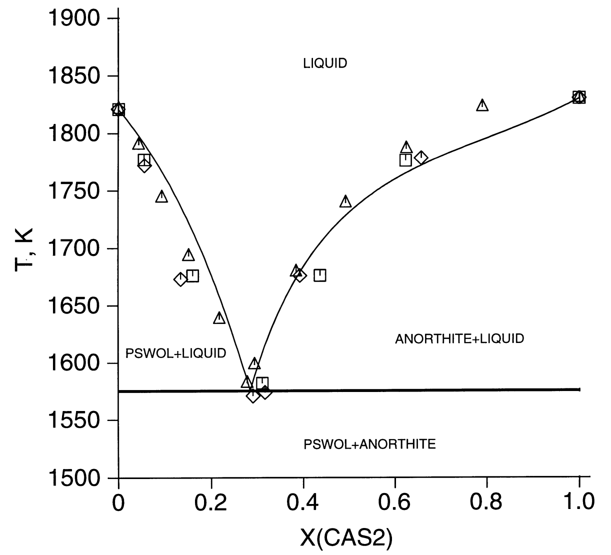

Fig. 5. Phase equilibria in the system CS–CAS2. Experimental data points are from Osborn[21] (△), Osborn and Muan[22] (□), Gentil and Foster[23] (◇). Solid lines are optimized liquidus curves.

Table 3
Eutectic equilibria in the CS–CAS2–C2AS system. The experimental temperatures are corrected by IPTS–68

C2AS–CAS2	Experiment	Assessed
T	1660[22,23]	1657
x(CAS2)	0.516	0.514
T	1660[18]	
x(CAS2)	0.511	
T	1661[20]	
x(CAS2)	0.516	
CS–CAS2		
T	1582[21]	1575
x(CAS2)	0.278	0.285
T	1582[22]	
x(CAS2)	0.311	
T	1571[23]	
x(CAS2)	0.291	
T	1574[18]	
x(CAS2)	0.298	
CS–C2AS		
T	1593[22]	1591
x(C2AS)	0.195	0.201
T	1593[23]	
x(C2AS)	0.179	
T	1591[18]	
x(C2AS)	0.186	
T	1603[19]	
x(C2AS)	0.189	

CS–CAS2–C2AS		Model 1	Model 2
T	1540[22,18]	1466	1490
x(CAS2)	0.185	0.1703	0.1603
x(C2AS)	0.135	0.1465	0.1361
x(CS)	0.680	0.6832	0.7038

Kosa et al.[16] is presented in Fig. 6. At this temperature the coincidence with experimental data is good. At lower temperatures, however, the experimental data on enthalpy of mixing show more expressive temperature dependence than those assessed in this study.

The calculated Gibbs energy of mixing and entropy of mixing of liquids in comparison with data by Kosa et al.[16] are presented in Fig. 7. Both assessed dependencies are quite similar to those by Kosa et al.[16] The activities of both components in the liquid of the system are presented in Fig. 8, along with data of Kosa et al.[16] Calculations

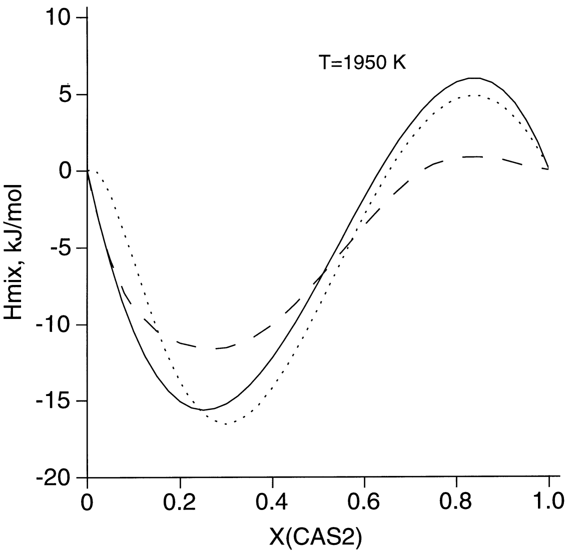

Fig. 6. Enthalpies of mixing in the system CS–CAS2 at 1950 K. Dotted line represents experimental data by Kosa et al.[10] interpreted by Proks et al.,[15] dashed line is calculated in thermodynamic analysis by Strečko et al.[17] and solid line is optimized in this study.

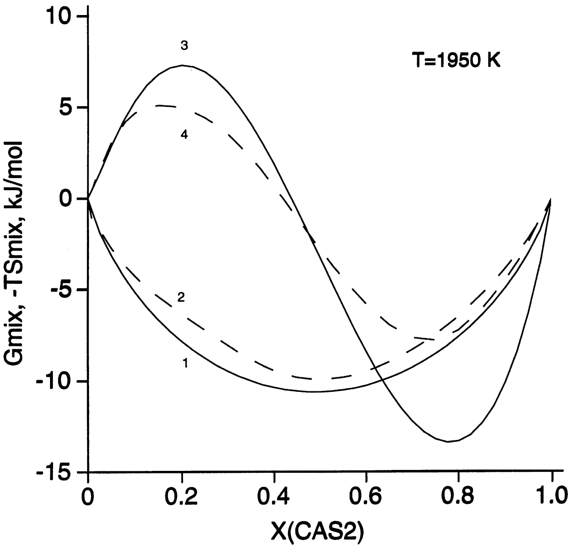

Fig. 7. Gibbs energy of mixing (1,2) and $-T\Delta_{\mathrm{mix}}S$ (3,4) of liquids in the system CS–CAS2 at 1950 K. Dashed lines are calculated by Kosa et al.,[16] solid lines are calculated in this study.

made in this study do not show any tendency to groundless extremes in activity curves found by Kosa et al.[16] The activity-composition relations are much smoother and closer to the ideal course.

4.3. System CS–C2AS

4.3.1. Phase equilibria

The optimized liquidus curves as well as the experimental points are shown in Fig. 9. The liquidus curves do not fit the experimental data as expected, in particular in the gehlenite-rich region of composition. There is a groundless inflex on the liquidus curve on C2AS rich side of the phase diagram. Similar, but a less conspicuous inflex can also be seen in the CAS2 side of phase diagram of the CS–CAS2 system. The attempt to correct the courses of the liquidus curves by changing the enthalpies of fusion failed.

The calculated temperature of crystallization and composition of eutectic melt are 1591 K and x(C2AS) = 0.201, respectively. They are in a good agreement with available experimental data (Table 3).

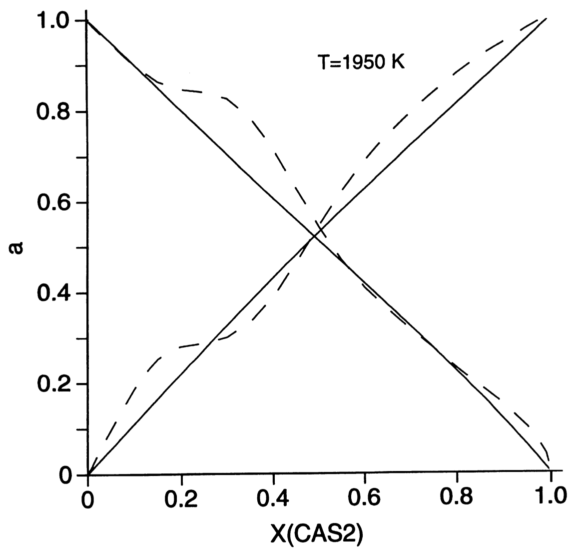

Fig. 8. Activities of components in the system CS–CAS2 at 1950 K. Dashed lines are calculated by Kosa et al.,[16] solid lines are calculated in this study.

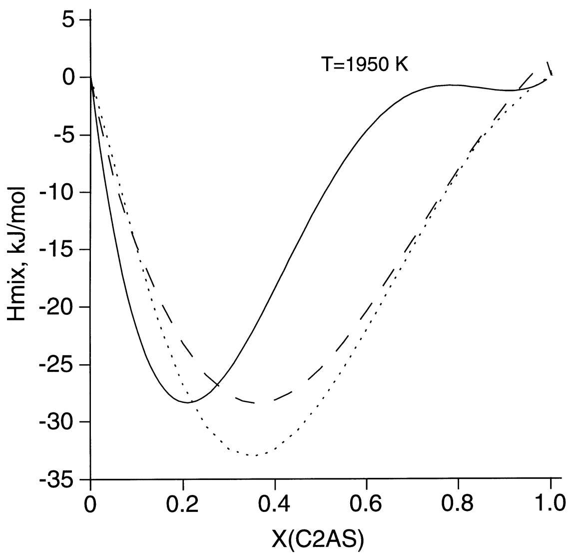

Fig. 10. Enthalpies of mixing in the system CS–C2AS at 1950 K. Dotted line represents experimental data by Kosa et al.[10] interpreted by Proks et al.,[15] dashed line is calculated in thermodynamic analysis by Kosa et al.[16] and solid line is optimized in this study.

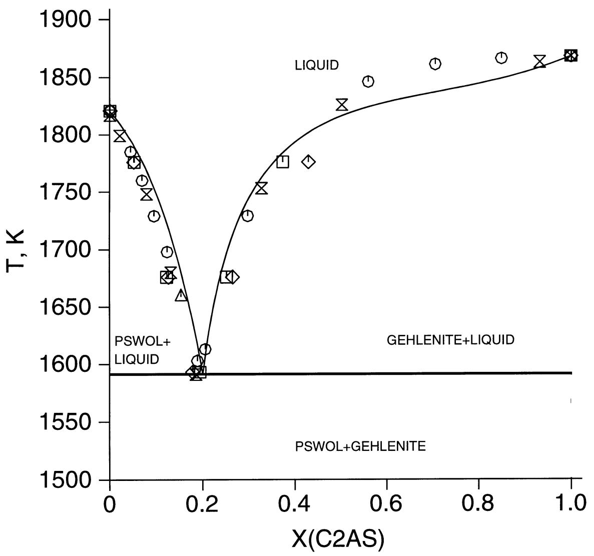

Fig. 9. Phase equilibria in the system CS–C2AS. Experimental data points are from Osborn and Muan[22] (□), Gentil and Foster[23] (◇), Rankin And Wright[18] (☒) and Osborn and Shairer[19] (○). Solid lines are optimized liquidus curves.

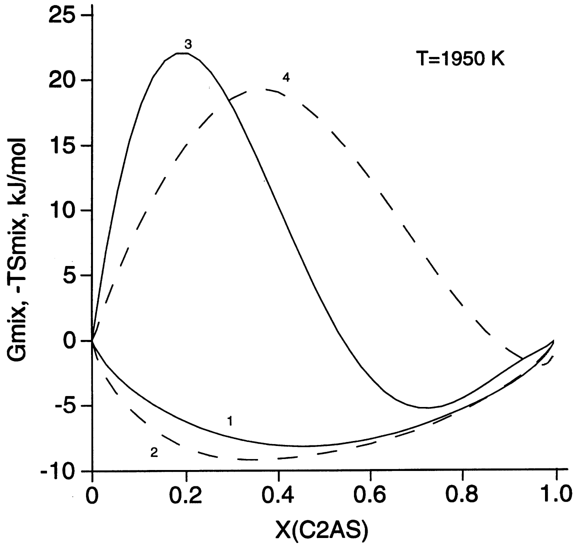

Fig. 11. Gibbs energy of mixing (1, 2) and $-T\Delta_{\mathrm{mix}}S$ (3, 4) of liquid in the system CS–C2AS at 1950 K. Dashed lines are calculated by Strečko et al.,[17] solid lines are calculated in this study.

The probable maximum inaccuracy in the assessed phase diagram was estimated as ±3 mol% and ±20 K.

4.3.2. Mixing properties

The optimized enthalpy of mixing at 1950 K in comparison with experimental data by Kosa et al.[10] as interpreted by Proks et al.[15] and calculated data by Strečko et al.[17] is presented in Fig. 10. The consistency between optimized and experimental curves is not very good at this temperature. Calculated minimum in $\Delta_{\mathrm{mix}}H$ is moved towards CS component. The maximum difference between experimental and calculated $\Delta_{\mathrm{mix}}H$ is about 18 kJ mol^{-1}. However, the optimized $\Delta_{\mathrm{mix}}H$ curve fits the experimental data quite well at higher temperatures. At 1800 K the maximum difference is about 5 kJ mol^{-1}.

The calculated Gibbs energy of mixing and entropy of mixing of liquid in comparison with data by Strečko et al.[16] are presented in Fig. 11. The calculated activities of both components in the liquid of the system at 1950 K

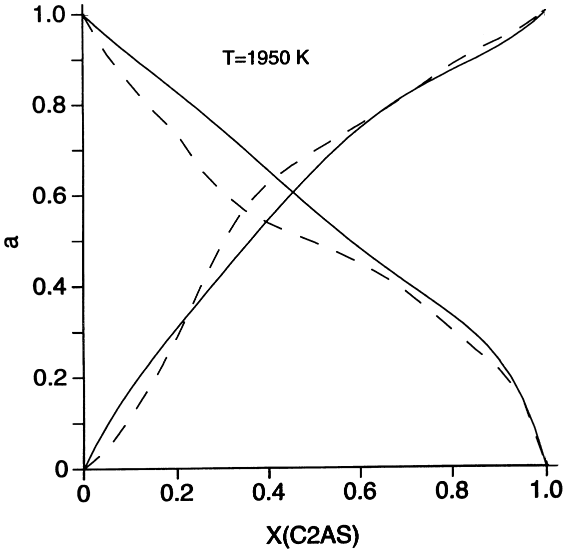

Fig. 12. Activities of components in the system CS–CAS2 at 1950 K. Dashed lines are calculated by Strečko at al.,[17] solid lines are calculated in this study.

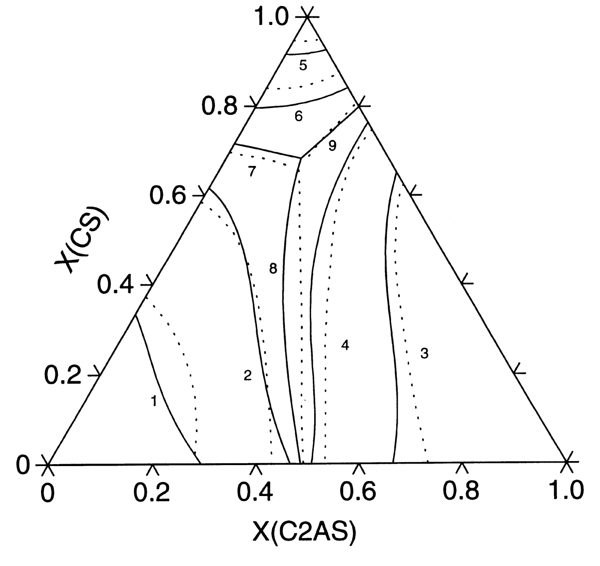

Fig. 13. Phase equilibria in the system CS–CAS2–C2AS. Dotted lines are taken from phase diagram of the system C–A–S by Osborn and Muan.[22] Solid lines are calculated according to model 1. Couples of corresponding solid and dotted lines are isotherms at 1773 K (1, 3 and 5), and 1673 K (2, 4 and 6). Experimental and optimized 3-phase equilibria are represented by couples of lines 7, 8 and 9.

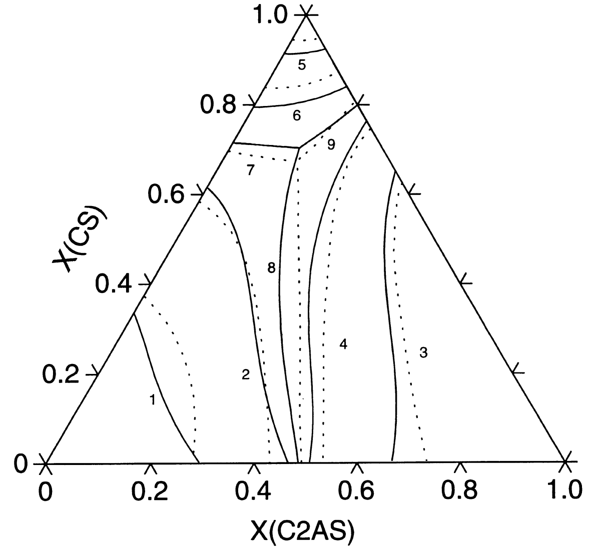

Fig. 14. Phase equilibria in the system CS–CAS2–C2AS. Dotted lines are taken from phase diagram of the system C–A–S by Osborn and Muan.[22] Solid lines are calculated according to model 2. Couples of corresponding solid and dotted lines are isotherms at 1773 K (1, 3 and 5), and 1673 K (2, 4 and 6). Experimental and optimized 3-phase equilibria are represented by couples of lines 7, 8 and 9.

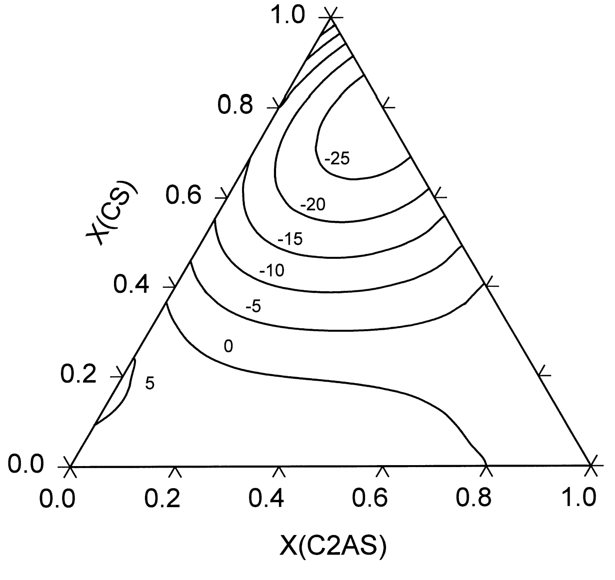

Fig. 15. Enthalpy of mixing in the system CS–CAS2–C2AS at 1950 K according to model 1, in kJ mol^{-1}.

are presented in Fig. 12. The activity curves are smoother than those obtained by Strečko et al.[17]

4.4. System CS–CAS2–C2AS

4.4.1. Phase equilibria

The optimized phase diagrams of the system constructed according to both considered models, in comparison with that of Osborn and Muan[26] are shown in Figs. 13 and 14. Calculated and experimental data on temperature and composition of invariant points are compared in Table 3. Both models, with and without ternary term, give similar resulting phase diagrams. Calculated and experimental phase compositions are in good agreement. However, there is a substantial difference between the calculated and the experimental temperature of the ternary eutectic point, especially for the model without ternary interaction (model 1), presented in Table 3. For the model with ternary interaction parameter included (model 2) the difference approaches to that, usual for assessments of larger systems by the use of more complicated models e.g. by Pelton.[6] The

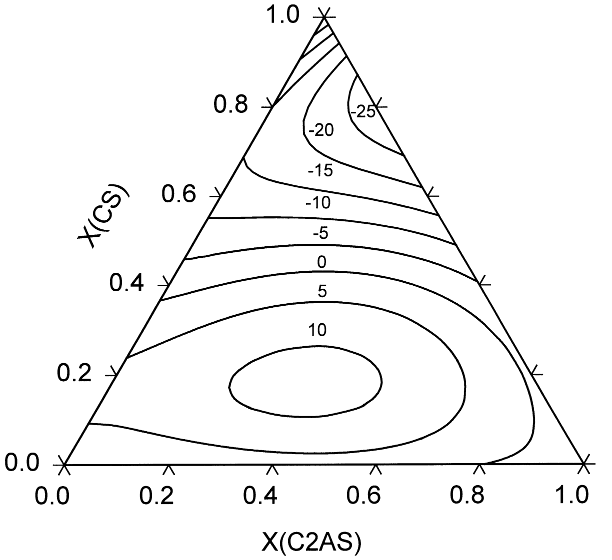

Fig. 16. Enthalpy of mixing in the system CS–CAS2–C2AS at 1950 K according to model 2, in kJ mol^{-1}.

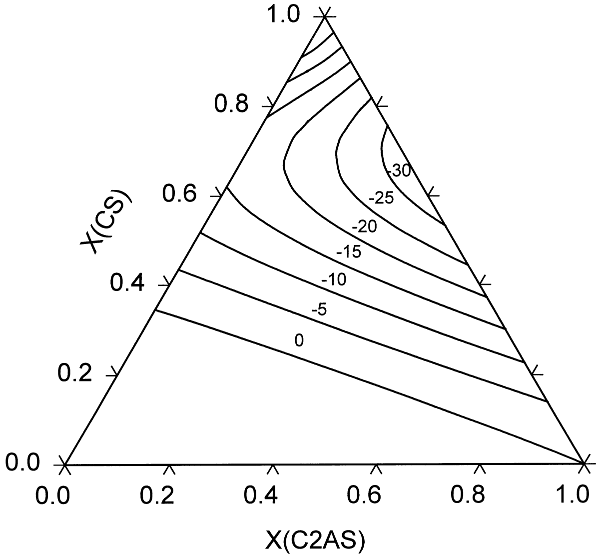

Fig. 17. Enthalpy of mixing in the system CS–CAS2–C2AS at 1950 K obtained using temperature and composition dependence of the relative enthalpy by Proks et al.,[15] based on experimental data by Kosa et al.,[10] in kJ mol^{-1}.

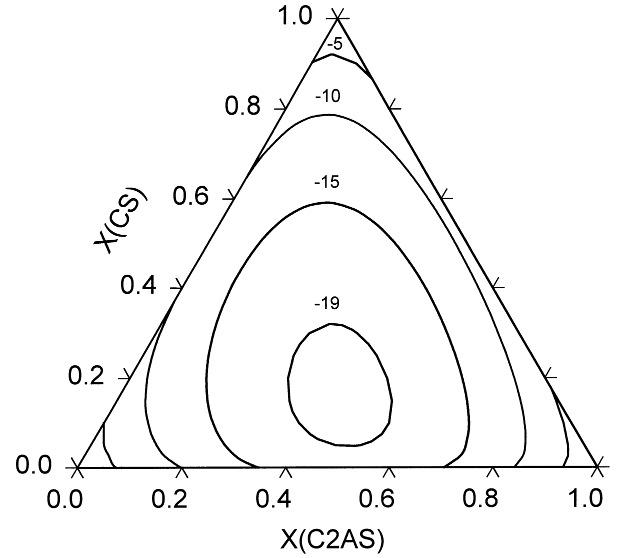

Fig. 18. Gibbs energy of mixing in the system CS–CAS2–C2AS at 1950 K according to model 1, in kJ mol^{-1}.

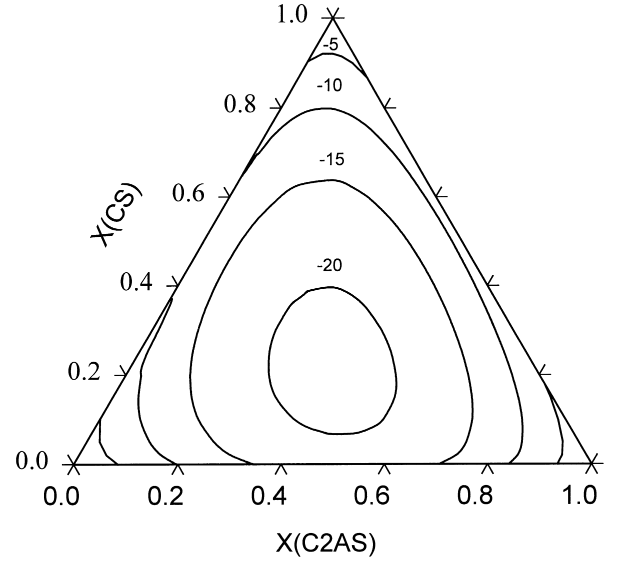

Fig. 19. Gibbs energy of mixing in the system CS–CAS2–C2AS at 1950 K according to model 2, in kJ mol^{-1}.

probable maximum inaccuracy in the assessed phase diagrams was estimated as ± 5 mol% and ± 70 K for model 1, and ± 5 mol% and ± 50 K for model 2.

4.4.2. Mixing properties

The composition dependencies of the enthalpy of mixing in the system CS–CAS2–C2AS at 1950 K, calculated according to models 1 and 2 in the form of iso-enthalpy curves are presented in Figs. 15 and 16, respectively. For comparison, the composition dependence of the $\Delta_{\mathrm{mix}}H$ at the same temperature, calculated using regression polynomial by Proks et al.,[15] based on experimental data of Kosa et al.[10] is given in Fig. 17. The results from model 1 are in better agreement with data by Proks et al.[15] than that from model 2, especially, when the flat composition dependence in the CS poor part of the composition region is considered. The Gibbs energy of mixing at 1950 K, according to models 1 and 2 are presented in Figs. 18 and 19, respectively. The composition dependence of $-T\Delta_{\mathrm{mix}}S$ at 1950 K calculated using optimized mixing parameters of both models are presented in Figs. 20 and 21 for models 1 and 2, respectively. The differences in $\Delta_{\mathrm{mix}}H$ between both models are projected in these diagrams.

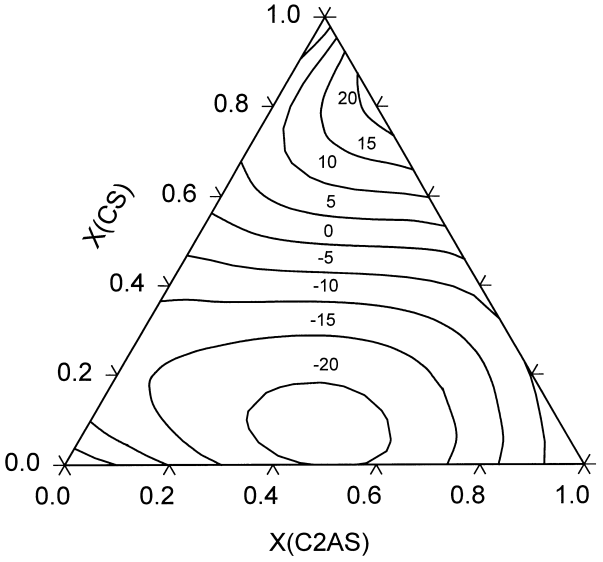

Fig. 20. $-T\Delta_{\mathrm{mix}}S$ in the system CS–CAS2–C2AS at 1950 K according to model 1, in kJ mol^{-1}.

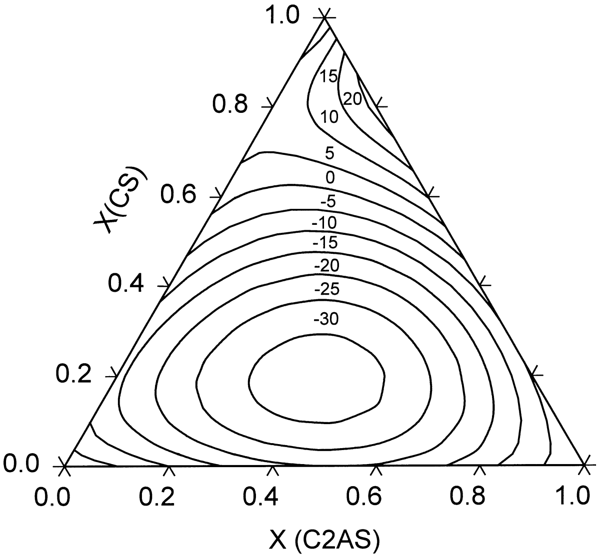

Fig. 21. $-T\Delta_{\mathrm{mix}}S$ in the system CS–CAS2–C2AS at 1950 K according to model 2, in kJ mol^{-1}.

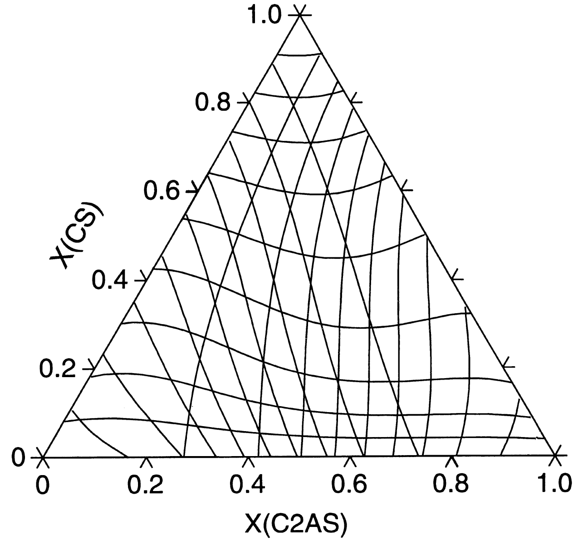

Fig. 22. Isoactivity lines (step 0.1) of components in the system CS–CAS2–C2AS at 1950 K according to model 1.

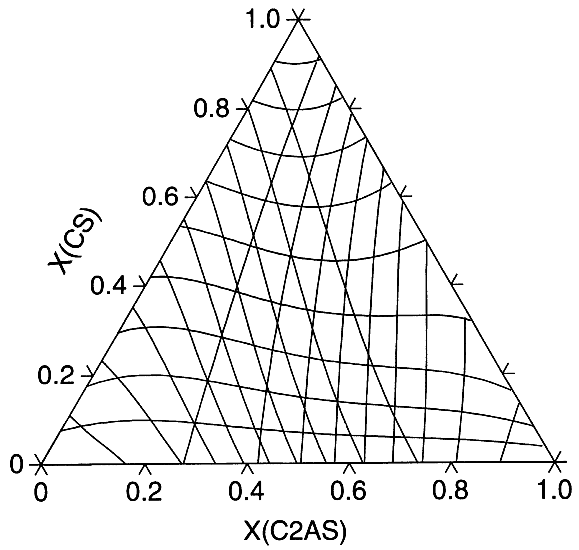

Fig. 23. Isoactivity lines (step 0.1) of components in the system CS–CAS2–C2AS at 1950 K according to model 2.

The isoactivity lines of components in step 0.1 in the system CS–CAS2–C2AS at 1950 K by models 1 and 2 are displayed in Figs. 22 and 23, respectively. There are no considerable differences between dependencies by both models.

5. Conclusion

The molecular solution model with excess Gibbs energy of mixing expressed by the Redlich–Kister equation with temperature dependent parameters, calculated from phase equilibria data and calorimetric data on enthalpy of liquid phase can be successfully used to describe phase equilibria in the studied system. In binary subsystems, except of the CS–C2AS system, the mixing parameters optimized in this study fit better the experimental enthalpy of mixing at 1950 K, than that calculated by Proks et al.[15] and Kosa et al.[16] The activity–composition relations do not have the probably groundless meanders by our model. The consideration of the ternary interaction parameter is not explicitly beneficial for description of thermodynamic properties of ternary melts. Both models provide a reasonable description of the phase equilibria. There are no significant differences in Gibbs energy of mixing and activities between both models. The model without ternary interaction parameter gives better accord with the experimental enthalpy of mixing, however, the temperature of the ternary eutectic point is better fitted by the more complicated model.

The optimization procedure has shown an enormous influence of the enthalpy of mixing on equilibria fit and activity composition relation curves. The enthalpies of mixing are often determined as relatively small differences between quite large values of calorimetrically measured relative enthalpy. In this case even small errors in relative enthalpy may cause quite large uncertainties in $\Delta_{\text{mix}}H$ data. The errors are often too large, making the enthalpy data unuseable in the fitting of phase equilibria. The function of activity upon composition may, in this case, show groundless extremes. On the other hand, in some cases the errors from fitting the equilibria data are about the same magnitude or larger as those of calorimetric data. In this case $\Delta_{\text{mix}}H$ data are very useful.

The study has also shown a considerable inconsistency between experimental phase equilibria and calorimetrically measured enthalpy of the liquid solution. To get thermodynamic properties of melts in the CS–C2AS–CAS2 system (except of CAS2–C2AS system), which reproduce phase equilibria satisfactorily, considerable changes in enthalpy of mixing with respect to the experimental data had to be accepted in the assessment. Similar consequences follow also from Proks et al.,[15] Kosa et al.[16] and Strečko et al.[17]

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