Determination of Molar Gibbs Energies and Entropies of Mixing of Melts in Binary Subsystems of the System CaO · SiO₂—2CaO · Al₂O₃ · SiO₂—CaO · Al₂O₃ · 2SiO₂ I. Theoretical Part. 2CaO · Al₂O₃ · SiO₂—CaO · Al₂O₃ · 2SiO₂ System

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Method for calculation of component activities in high-temperature binary melt systems is presented. For this purpose, phase diagrams and enthalpies of mixing were used. The latter ones were determined indirectly using primary composition and temperature dependence of relative enthalpy, found by means of multiple linear regression. The method was applied to the melts in the $2CaO \cdot Al_2O_3 \cdot SiO_2$—$CaO \cdot Al_2O_3 \cdot 2SiO_2$ system to find out that within the temperature range 1700 K to 1950 K and limits of experimental errors for enthalpy of mixing these melts behave as athermic solutions. Component activities are equal to equilibrium activities at any composition. The determined activities enabled to calculate the composition and temperature dependences of Gibbs energy and entropy of mixing.

Heats of fusion of pure components, as well as of all three binary eutectic mixtures and ternary eutectic mixture are known in the $CaO \cdot SiO_2$ (CS)—$2CaO \cdot Al_2O_3 \cdot SiO_2$ (C₂AS)—$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS₂) system. General temperature and composition dependence of relative enthalpy can be calculated using relative enthalpies of chosen melts in this system [1]. Relative enthalpy of the phase at given temperature is defined as a negative sum of the heat of cooling from the given temperature to the temperature of dissolution and heat of solution of the cooled sample, both measured by calorimetric methods [2].

These pieces of information together with the known phase diagrams were used to determine Gibbs energy and entropy of mixing of melts in binary subsystems of the ternary system as a function of composition and temperature.

This paper is dealing with the general thermodynamic analysis of melts in binary systems and its application to the C₂AS—CAS₂ system.

THEORETICAL

In the following text we use symbols X and Y for the system components, subscripts c and eq for the quantities chosen and those related to multiphase equilibria. Thermodynamic analysis is made for phases in equilibrium state.

Composition Dependence of Equilibrium Activities $a_{eq,X(Y)}(x_Y)$ for Both Components of the Melt in the System the Components of which do not Form Solid Solutions

The temperatures $T_{eq,X(Y)}(x_{Y,c})$ at which the melts of chosen composition $x_{Y,c}$ coexist with pure crystalline components X, Y were taken from phase diagrams. Corresponding equilibrium component activities at these temperatures were calculated from the Le Chatelier—Shreder equation

$$\ln a_{eq,X(Y)}(T_{eq,X(Y)}(x_{Y,c})) = \int_{T_{fus,X(Y)}}^{T_{eq,X(Y)}(x_{Y,c})} \frac{\Delta H_{fus,X(Y)}(T)}{RT^2} \, dT \quad (1)$$

where $a_{eq,X(Y)}(T_{eq,X(Y)}(x_{Y,c}))$ is the equilibrium activity of component X(Y) at the temperature $T_{eq,X(Y)}$, $T_{eq,X(Y)}(x_{Y,c}) \in \langle T_{fus,X(Y)}, T_{eut} \rangle$ is the temperature at which the melts of chosen composition $x_{Y,c}$ coexist with pure crystalline components X(Y), $T_{fus,X(Y)}$ is the equilibrium temperature of fusion for component X(Y), T_{eut} is eutectic temperature in the X—Y system, $\Delta H_{fus,X(Y)}(T)$ is enthalpy of fusion of X(Y) component at the temperature T. The temperature dependence of $\Delta H_{fus,X(Y)}(T)$ was derived using primary relative enthalpy dependence of melts in the CS—C₂AS—CAS₂ system and temperature dependence of relative enthalpy for the crystalline component X(Y).

Dependence $\ln a_{\text{eq}, X(Y)}(x_Y)$ was obtained from the calculated values of $\ln a_{\text{eq}, X(Y)}(T_{\text{eq}, X(Y)}(x_{Y, c}))$ according to eqn (1).

Component Activities $a_{X(Y)}(x_{Y, c}, T_c)$ in the Melt at Chosen Temperature and Composition

To calculate both component activities at chosen temperature T_c from equilibrium activities it is necessary to know partial molar enthalpies of mixing $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T)$ as a function of temperature and chosen composition.

Activity of component X(Y) in the melt at composition $x_{Y, c}$ and temperature T_c is given by

$$\ln a_{X(Y)}(x_{Y, c}, T_c) = \ln a_{\text{eq}, X(Y)}(x_{Y, c}) + I_{X(Y)}(x_{Y, c}, T_c) \quad (2)$$

where

$$I_{X(Y)}(x_{Y, c}, T_c) = \int\limits_{T_{\text{eq}, X(Y)}(x_{Y, c})}^{T_c} -\frac{\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T)}{RT^2} \, dT \quad (3)$$

Enthalpies of mixing of melts in binary systems were calculated using primary temperature and composition dependence of relative enthalpy of melts in the CS—C_2AS—CAS$_2$ system, from the equation

$$\Delta H_{\text{mix}}(x_Y, T_c) = H_{\text{rel}}(x_Y, T_c) - (1 - x_Y)H^{\circ}_{\text{rel}, X}(T_c) - x_Y H^{\circ}_{\text{rel}, Y}(T_c) \quad (4)$$

where $\Delta H_{\text{mix}}(x_Y, T_c)$ is enthalpy of mixing when one mole of mixture at the temperature T_c and composition x_Y has been arisen, $H_{\text{rel}}(x_Y, T_c)$ is molar relative enthalpy of melt at the same temperature and composition, $H^{\circ}_{\text{rel}, X(Y)}(T_c)$ is molar relative enthalpy of pure component X(Y) melt at the temperature T_c. Using the method of intercepts, the values of $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T_c)$ for several chosen values of T_c were calculated from eqn (4). Temperature dependences of $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T)$ were obtained from these values by regression analysis.

The values $\Delta H_{\text{mix}}(x_Y, T_c)$ are loaded with considerable errors because of the high numerical values of relative enthalpies occurring in eqn (4). Partial molar enthalpies $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T_c)$ exhibit much higher errors because they are obtained using the derivative of composition dependence of $\Delta H_{\text{mix}}(x_Y, T_c)$. The quantities $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T_c)$, calculated in such manner, did not give monotonous isothermal composition dependences of activities resulting in nonequilibrium states of melts. To calculate $\Delta\overline{H}_{\text{mix}, X(Y)}(x_{Y, c}, T)$, substitute function $\Delta H_{\text{mix}}(x_Y, T_c)$ was selected, the course of which was identical with original equations within the limits of determined errors. Substitute function gives monotonous dependences of $a_{X(Y)}(x_Y, T_c)$ corresponding to equilibrium states of melts.

Dependences $a_{X(Y)}(x_Y, T_c)$ are deformed due to errors in ΔH_{mix}. Deformations occur in particular along the compositions with high values of derivative $d(\Delta H_{\text{mix}}(x_Y, T_c))/dx_Y$. Therefore the empirical developing function (5) was introduced

$$I_X(x_{Y, c}, T_c) = -\ln a_{\text{eq}, X}(x_{Y, c})[1 - \exp(-\kappa(T_c)(T_c - T_{\text{eq}, X}(x_{Y, c})))] \quad (5)$$

$\kappa(T_c)$ is composition independent parameter. The parameter $\kappa(T_c)$ was selected so that the dependence $\ln a_X(x_Y, T_c)$ had negative derivative for $x_Y \in <0, x_{Y, \text{eut}}>$.

If we divide the temperature range $(T_{\text{eq}, X}(x_{Y, c}) - T_c)$ for integration to temperature intervals $2\Delta T_i$ so that the ratio $2\Delta T_i/T_{c, i}$ would be sufficiently small, we can calculate $\Delta\overline{H}_{\text{mix}, X}(x_{Y, c}, T_{c, i})$ according to the formula

$$\Delta\overline{H}_{\text{mix}, X}(x_{Y, c}, T_{c, i}) = \kappa(T_{c, i})RT_{c, i}^2 \ln a_{\text{eq}, X}(x_{Y, c}) \exp[-\kappa(T_{c, i})(T_{c, i} - T_{\text{eq}, X}(x_{Y, c}))] \quad (6)$$

where $T_{c, i}$ is the temperature of the i-th interval centre.

In this thermodynamic analysis the temperature range 1575 K—1975 K was divided into eight intervals, every of 50 K. The quantities $\Delta\overline{H}_{\text{mix}, X}(x_{Y, c}, T_{c, i})$ were calculated from eqn (6) for the temperatures at the centres of these intervals. Using these values the regression functions at compositions $x_{Y, c}$ were determined and substituted into eqn (3).

For $x_{Y, c} \in <0, x_{Y, \text{eut}}>$ we obtained discrete function values using the method of intercepts and eqn (6). For $x_{Y, c} \in <x_{Y, \text{eut}}, 1>$ the substitute function was represented by a polynomial, the values and derivatives of which at compositions $x_{Y, \text{eut}}$ and $x_Y = 1$ were identical with corresponding values and their derivatives of substitute function and $\Delta H_{\text{mix}}(x_Y, T_c)$ according to eqn (4), respectively. The substitute function has to satisfy the condition that its values have to lie within the error limits of the function $\Delta H_{\text{mix}}(x_Y, T_c)$ given by eqn (4).

Isothermal Composition Dependences of Component Activities $a_{X(Y)}(x_Y, T_c)$

These dependences have to satisfy the following conditions:
a) if standard states of chemical potentials are related to pure components, the following expressions have to be valid

$$a_{X(Y)}(x_{X(Y)} = 0, T_c) = 0 \quad (7)$$

$$a_{X(Y)}(x_{X(Y)} = 1, T_c) = 1 \quad (8)$$

b) in the case of low contents of admixture M in solvent N, ΔH_{mix} is given by the formula

$$\lim_{x_M \to 0} \Delta H_{\text{mix}} = x_M \Delta\overline{H}_{\text{mix}, M} \quad (9)$$

where

$$\lim_{x_M \to 0} \Delta\overline{H}_{\text{mix}, M} = \text{const} \quad (10)$$

Eqn (9) also implies

$$\lim_{x_N \to 1} \Delta\overline{H}_{\text{mix}, N} = 0 \quad (11)$$

Eqns (2), (3) and (11) imply at any temperature T_c two further conditions (according to selection of M and N)

$$\frac{\mathrm{d}\ln a_N(x_N = 1, T_c)}{\mathrm{d}x_M} = \frac{\mathrm{d}\ln a_{eq,N}(x_N = 1, T_{fus,N})}{\mathrm{d}x_M} \quad (12)$$

The right side of eqn (12) was obtained by deriving $\ln a_{eq,N}(x_M)$ from the first section at $x_N = 1$.

c) at $T_c = T_{eq}(x_{X(Y),c})$, the values of $a_{X(Y)}(x_{X(Y),c}, T_c)$ are given by

$$a_{X(Y)}(x_{X(Y),c}, T_c) = a_{eq,X(Y)}(x_{X(Y),c}) \quad (13)$$

d) isothermal dependences $a_{X(Y)}(x_Y, T_c)$ have to satisfy the Gibbs—Duhem equation

$$\frac{\mathrm{d}\ln a_Y(T_c)}{\mathrm{d}x_Y} = -\frac{1-x_Y}{x_Y}\frac{\mathrm{d}\ln a_X(T_c)}{\mathrm{d}x_Y} \quad (14)$$

Function $a_{X(Y)}(x_Y, T_c)$ was expressed by the Margules equation [3]

$$\ln a_{X(Y)}(x_Y, T_c) = \alpha_{X(Y)}(T_c)\ln x_{X(Y)} + \beta_{X(Y)}(T_c) +$$
$$+ \sum_{i=1}^{r} K_{X(Y),i}(T_c)x_Y^i \quad (15)$$

where i and r are natural numbers. Eqn (15) identically fulfils the conditions (7) for definite values $\beta_{X(Y)}(T_c)$ and $K_{X(Y),i}(T_c)$.

Substituting eqn (15) into (14) and comparing coefficients with the same powers of mole fractions we get next $r + 1$ conditional expressions among coefficients $\alpha_{X(Y)}(T_c)$, $\beta_{X(Y)}(T_c)$, and $K_{X(Y),i}(T_c)$.

e) Eqn (15) has to be fulfilled for n chosen values of both activities $a_{X(Y)}(x_{X(Y),c}, T_c)$ calculated from eqns (2) and (3). The condition (13) is within the errors of activities determination for sufficiently large n fulfilled and therefore it was not considered.

Comparing number of conditions ($2 \times 2 + r + 1 + n$) and number of coefficients ($2 \times (2 + r)$) in the equations, we get unambiguous relation between r and n

$$r = 1 + n \quad (16)$$

Composition and Temperature Dependences of Gibbs Energy of Mixing $\Delta G_{mix}(x_Y, T)$ and Entropy of Mixing $\Delta S_{mix}(x_Y, T)$ in the Melt

Composition and temperature dependence of component activities $a_{X(Y)}(x_Y, T)$ was calculated at suitably chosen temperatures T_c from the isothermal dependences of $a_{X(Y)}(x_Y, T_c)$. $\Delta G_{mix}(x_Y, T)$ were calculated from the formulas that are by the definition

$$\Delta G_{mix}(x_Y, T) = RT\,[(1 - x_Y)\ln a_X(x_Y, T) +$$
$$+ x_Y\ln a_Y(x_Y, T)] \quad (17)$$

and

$$\Delta S_{mix}(x_Y, T) = -\left[\frac{\partial(\Delta G_{mix}(x_Y, T))}{\partial T}\right]_{x_Y, p} \quad (18)$$

APPLICATION

General Composition and Temperature Dependence of Relative Enthalpy in the CS—C$_2$AS—CAS$_2$ System

To determine this dependence, the arithmetic means of relative enthalpies of eleven melts of various compositions measured at several temperatures were used as the input data [1]. This dependence was determined by multiple linear regression [4] in the form

$$H_{rel} = \sum_i B_i[x(CaO)]^{b_i}[x(Al_2O_3)]^{c_i}T^{d_i} \quad (19)$$

Parameters in this equation are shown in Table 1. The weights of the input data were proportional to $1/\sigma^2$ and normalized to the number of input data. Errors of relative enthalpy and enthalpy of mixing were determined according to the formulas (20) and (21), respectively

$$\sigma(H_{rel}) = \left\{\sum_{i=1}^{11}\left(\frac{\partial H_{rel}}{\partial B_i}\right)^2[\sigma(B_i)]^2 +\right.$$
$$\left.+\sum_{i=1}^{11}\sum_{j>i}^{11}2\frac{\partial H_{rel}}{\partial B_i}\frac{\partial H_{rel}}{\partial B_j}[\sigma(B_i, B_j)]^2\right\}^{1/2} \quad (20)$$

$$\sigma(\Delta H_{mix}) = \left\{\left(\frac{\partial\Delta H_{mix}}{\partial H_{rel}}\right)^2[\sigma(H_{rel})]^2 +\right.$$
$$\left.+\sum_{k=1}^{3}\left(\frac{\partial\Delta H_{mix}}{\partial H_{rel,k}^{\circ}}\right)^2[\sigma(H_{rel,k}^{\circ})]^2 x_k^2\right\}^{1/2} \quad (21)$$

Table 1. Exponents b_i, c_i, d_i, Coefficients B_i, and Standard Deviations $\sigma(B_i)$ of Regression Polynomial (19) in the CS—C$_2$AS—CAS$_2$ System

i	b	c	d	B kJ mol^{-1} K^{-d}	$\sigma(B)$ kJ mol^{-1} K^{-d}
1	0	0	1	0.3189	0.0018
2	2	0	1	− 0.6751	0.0201
3	0	2	1	− 13.3859	0.9778
4	0	3	1	51.9769	3.1716
5	1	1	1	3.9222	0.1957
6	1	2	1	− 11.1714	0.6126
7	1	3	1	29.4333	2.0100
8	2	0	0	1104.7	32.1
9	0	2	0	38483.2	1096.6
10	0	3	0	− 101352.3	6218.1
11	1	1	0	− 4374.8	353.7

where k denotes the components of the CS—C_2AS—CAS_2 system.

Relative errors of H_{rel} were less than 0.5 %.

Molar Gibbs Energy and Entropy of Mixing in the C_2AS—CAS_2 Melt System

In the following text we will use symbol X for C_2AS and Y for CAS_2.

The base for thermodynamic analysis was the phase diagram of this system constructed by the optimization of data taken from [5—7] (Fig. 1). All experimental data published since 1915 to 1963, including information about the conditions and ways of their measurements, were taken into account. Simultaneously the binary phase diagram of this system was correlated with that of the ternary system CaO—Al_2O_3—SiO_2 [8]. We can assume that systematic errors of data taken from various authors differ and correspond to experimental technology level of the era they were measured at. Therefore we could not process these data by means of common statistical methods.

To determine the dependence $\ln a_{eq, X(Y)}(x_Y)$, the relation

$$\Delta H_{fus, X(Y)}(T) = H^\circ_{rel, X(Y), melt}(T) - H^\circ_{rel, X(Y), cryst}(T) \quad (22)$$

was substituted into eqn (1). $H^\circ_{rel}(C_2AS, cryst, T)$ was taken from [9]. Temperature dependence of molar heat capacity $C_p(CAS_2, cryst)$ from [10] and

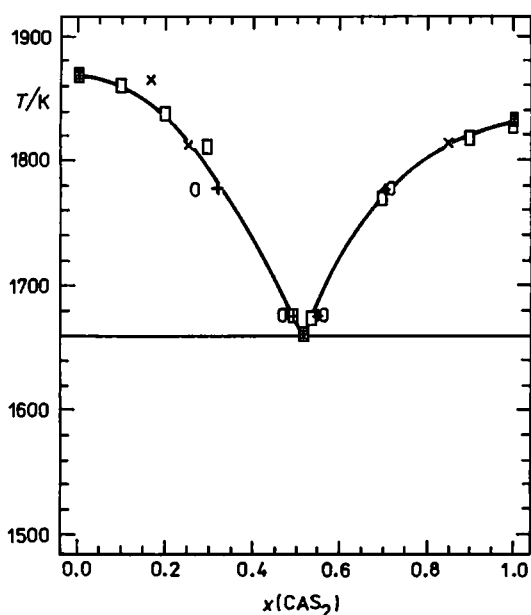the value of heat of solution $\Delta H_{sol}(CAS_2, cryst)$ from [11] were used to calculate $H^\circ_{rel}(CAS_2, cryst, T)$.

Enthalpy of mixing was calculated from eqn (4) into which the relative enthalpies of melts of the C_2AS—CAS_2 system and the pure components C_2AS and CAS_2, calculated from eqn (19), were substituted. Enthalpy of mixing was within the error limits 2σ equal to zero at any composition and temperature 1700 K—1950 K. The highest error limit did not exceed the value of 4.32 kJ mol^{-1}. Thus for the melts of the C_2AS—CAS_2 system the following relations are valid within the framework of regression function (19)

$$\Delta H_{mix}(x_Y, T_c) = 0 \quad (23)$$

and

$$\Delta \bar{H}_{mix, X(Y)}(x_{Y, c}, T) = 0 \quad (24)$$

If we substitute from the relation (24) into eqn (3) we get

$$I_{X(Y)}(x_{Y, c}, T_c) = 0 \quad (25)$$

and eqn (2) will be then of the form

$$\ln a_{X(Y)}(x_{Y, c}, T_c) = \ln a_{eq, X(Y)}(x_{Y, c}) \quad (26)$$

As follows from eqn (26) the activities of C_2AS and CAS_2 in their solutions are equal to their equilibrium activities in the melts coexisting with their corresponding crystalline phases. The dependence $\ln a_{eq, X(Y)}(x_Y)$ can be used within the interval $x_Y \in <x_{Y, eut}, 1>$ for C_2AS and $x_Y \in <0, x_{Y, eut}>$ for CAS_2 to integrate Gibbs—Duhem equation isothermally

$$d \ln a_Y = -\frac{1-x_Y}{x_Y} d \ln a_X \quad (27)$$

But in our case we used the procedure described in the paragraph d of the theoretical part. To determine coefficients in eqn (15) we have considered the conditions (8) and (12) for both components, nine values of activities calculated from eqn (1) and presented in Table 2 — five of them (a_X) corresponding to compositions $x_Y \in <0, x_{Y, eut}>$ and four (a_Y) corresponding to compositions $x_Y \in <x_{Y, eut}, 1>$.

Substituting for n into eqn (16) we get r being equal to 10. Margules' series (15) for both components have therefore 24 coefficients independent of temperature. The dependence $a_{X(Y)}(x_Y, T)$, which in this case agrees with the dependence $a_{eq, X(Y)}(x_Y)$, is for both components shown in Fig. 2.

Substituting eqn (15) into (17) for both components we get for the melts of the C_2AS—CAS_2 system the dependence $\Delta G_{mix}(x_Y, T)$ and from eqn (18) $\Delta S_{mix}(x_Y, T)$. The dependences $\Delta G_{mix}(x_Y)$ and

Fig. 1. Phase diagram of the C_2AS—CAS_2 system. □ [5], + [6], x [7], O [8] (taken off from the ternary phase diagram).

Table 2. Starting Values of C_2AS and CAS_2 Activities Used for the Margules Equation Coefficients Calculation

Activity	$x(CAS_2)$								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$a(C_2AS)$	0.960	0.853	0.709	0.544	0.391				
$a(CAS_2)$						0.503	0.693	0.839	0.938
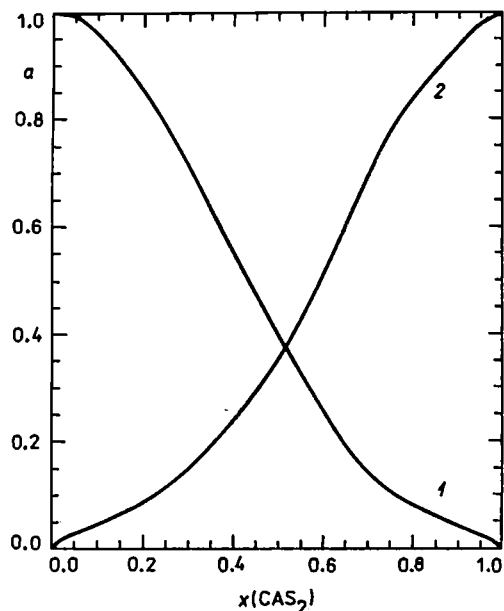
Fig. 2. Composition dependences of activities for C_2AS (1) and CAS_2 (2).

$T\Delta S_{mix}(x_Y)$ at the temperature 1700 K are shown in Fig. 3.

As follows from eqn (23) the melts of the C_2AS—CAS_2 system behave at all compositions and all temperatures under study as athermic solutions within the limits of errors for $\Delta H_{mix}(x_Y, T)$. This property is obviously the consequence of the fact that the melts C_2AS and CAS_2 have similar structure.
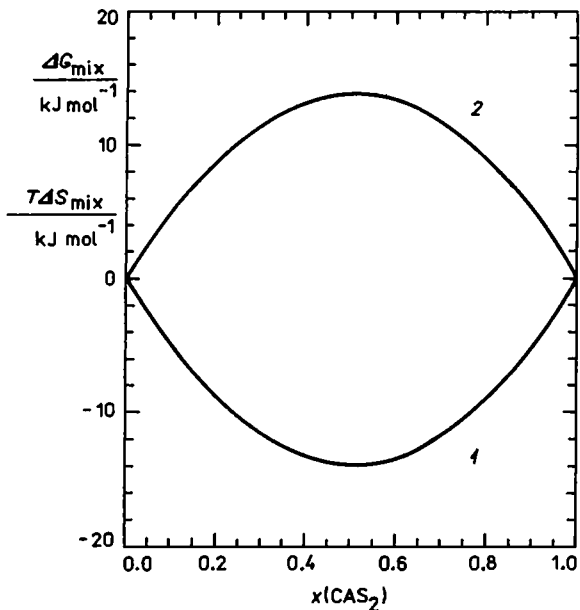
Fig. 3. Isothermal composition dependences of the quantities of mixing $\Delta G_{mix}(x_Y)$ (1) and $T\Delta S_{mix}(x_Y)$ (2) of the C_2AS—CAS_2 system at 1700 K.

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