

Determination of Molar Gibbs Energies and Entropies of Mixing of Melts in Binary Subsystems of the System $\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ — $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

III. The System $\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

J. STREČKO, I. NERÁD, L. KOSA, K. ADAMKOVIČOVÁ, and I. PROKS

Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava

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Composition and temperature dependences of component activities in the melt system $\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ were determined using the phase diagram as well as primary composition and temperature dependence of relative enthalpy of melts. The courses of Gibbs energy and entropy of mixing derived from the activities of both components have shown that these melts are general solutions.

This paper is linked with papers [1] and [2] in which the molar Gibbs energies ΔG_{mix} and entropies ΔS_{mix} of mixing in melts of the systems $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (C_2AS)— $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (CAS_2) and $\text{CaO} \cdot \text{SiO}_2$ (CS)— $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (CAS_2) were calculated. This calculation assumed the enthalpies of mixing of melts of these systems to be indirectly determined using the primary temperature and composition dependence of relative enthalpy of the CS — C_2AS — CAS_2 system [1] and therefore to be loaded with higher errors than if they were determined directly.

On the basis of the results from the previous papers it follows that in the temperature range 1600 K—1950 K the melts of the C_2AS — CAS_2 system behave as athermal solutions [1] while the melts of the CS — CAS_2 system are the general solutions [2].

The aim of this paper is to determine molar thermodynamic quantities of mixing in the melts of the CS — C_2AS system.

THERMODYNAMIC ANALYSIS OF MELTS IN THE CS — C_2AS SYSTEM

We will use symbols X for CS and Y for C_2AS in the following text. Chosen quantities will be denoted by subscript c and the ones corresponding to multiphase equilibria by subscript eq. Thermodynamic analysis is related to the phases in equilibrium state.

The base for this thermodynamic analysis is the primary dependence of relative enthalpy of the melts in the CS — C_2AS — CAS_2 system [1] and the phase diagram of the CS — C_2AS system (Fig. 1). Since this work is the basis for thermodynamic analysis of the ternary system CS — C_2AS — CAS_2 ,

measurements of Rankin and Wright [3], Osborn and Muan [4] as well as latest measurements of Gentile and Foster [5] were considered to optimize liquidus curves in the phase diagram of the CS — C_2AS system so that binary and ternary phase diagrams could be consistent. That is the reason why the liquidus curve at the region of C_2AS primary crystallization shown in Fig. 1 does not fit the experimental points of Osborn and Schairer [6].

Component activities at chosen composition and temperature $a_{X(Y)}(x_{Y,c}, T_c)$ were calculated from eqns (2) and (3) using the relation (1) in Ref. [1]. Temperature dependence $\Delta H_{\text{fus}, X(Y)}(T)$ is given by eqn (1) in [2]. Relative enthalpies $H_{\text{rel}, X(Y), \text{melt}}^\circ(T)$ were taken from [1], those of pure crystalline phases $H_{\text{rel}, X, \text{cryst}}^\circ(T)$ from [7, 8] and $H_{\text{rel}, Y, \text{cryst}}^\circ(T)$ from [9].

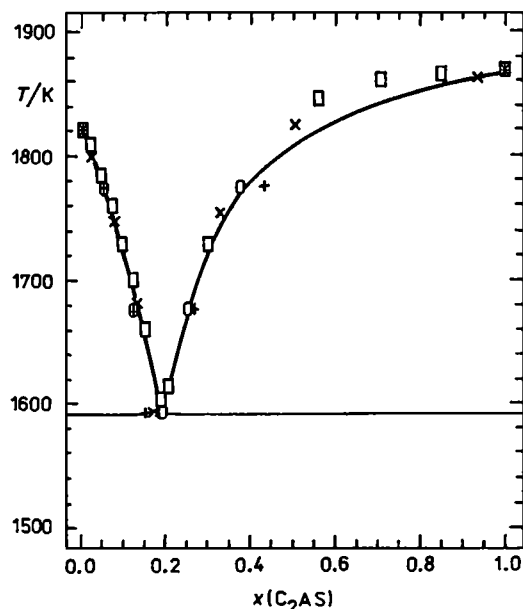


Fig. 1. Phase diagram of the CS — C_2AS system according to literature. \times [3], \circ [4], $+$ [5], \square [6].

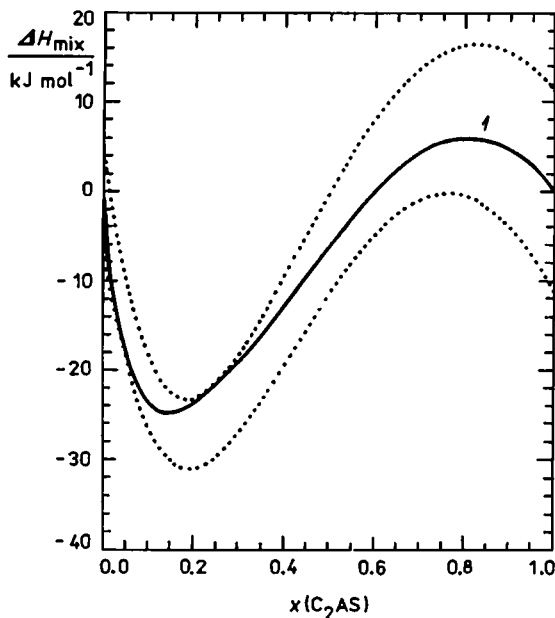


Fig. 2. Substitute function $\Delta H_{\text{mix}}(x(\text{C}_2\text{AS}))$ (1) at the temperature 1600 K and error interval ($\pm 3\sigma$) related to $\Delta H_{\text{mix}}(x(\text{C}_2\text{AS}))$ calculated using primary dependence $H_{\text{rel}}(x_Y, T)$.

The dependence $\Delta H_{\text{mix}}(x_Y, T_c)$ calculated from primary dependence of relative enthalpy of the melts in the CS—C₂AS—CAS₂ system [1] gives at the compositions close to the pure CS so low values of $\Delta H_{\text{mix}, x}(x_Y, T_c)$ that the regression function $a_x(x_Y, T_c)$ was not monotonous. Therefore we used substitute function to calculate $\Delta H_{\text{mix}}(x_Y, T_c)$. At compositions $x_Y \in \langle 0, x_{Y, \text{eut}} \rangle$ this function was obtained by the iterative method using the developing function [1] with $\kappa(T_c) \in \langle 0.0007 \text{ K}^{-1}, 0.0026 \text{ K}^{-1} \rangle$ and at $x_Y \in \langle x_{Y, \text{eut}}, 1 \rangle$ it was expressed by a third-order polynomial [1]. The substitute function did not differ more than 3σ from the original function over the entire composition range and temperature range from 1600 K to 1950 K. Plot of substitute function $\Delta H_{\text{mix}}(x_Y, T_c)$ and error limits related to the original function at the temperatures 1600 K and 1950 K is shown in Figs. 2 and 3.

Dependence $\ln a_{x(Y)}(x_Y, T_c)$ was expressed by the Margules equation (15) in Ref. [1]. Coefficients in

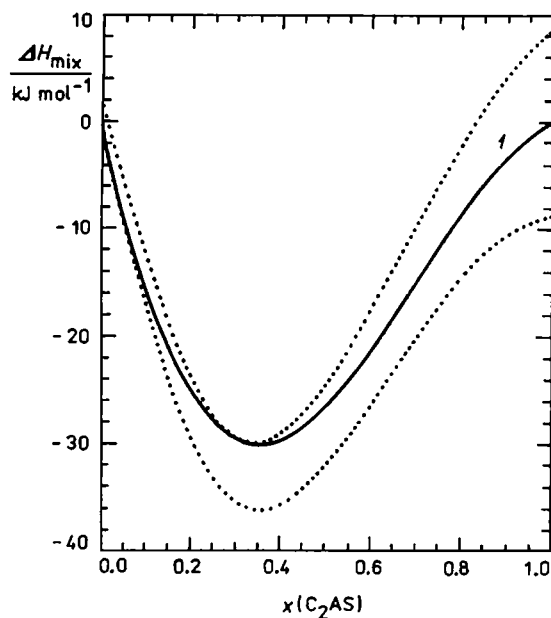


Fig. 3. Substitute function $\Delta H_{\text{mix}}(x(\text{C}_2\text{AS}))$ (1) at the temperature 1950 K and error interval ($\pm 3\sigma$) related to $\Delta H_{\text{mix}}(x(\text{C}_2\text{AS}))$ calculated using primary dependence $H_{\text{rel}}(x_Y, T)$.

this equation were found using the conditions (2) and (3) in [2] and nine values of activities were calculated from eqns (2) and (3) in [1]; two of them at compositions $x_Y \in \langle 0, x_{Y, \text{eut}} \rangle$ and seven at compositions $x_Y \in \langle x_{Y, \text{eut}}, 1 \rangle$ at the temperatures 1600 K to 1950 K by 50 K (Table 1).

Comparing the number of conditions [1] and number of coefficients in the Margules equation we get r equal to 10. There are two temperature independent and ten temperature dependent coefficients in the Margules equation. Temperature dependences of the coefficients were expressed by the relation (4) in [2]. Plot of dependences $a_{x(Y)}(x_Y, T_c)$ at the temperatures 1600 K and 1950 K is shown in Fig. 4.

The dependence of Gibbs energy of mixing $\Delta G_{\text{mix}}(x_Y, T)$ was calculated using the Margules equation. The dependences for entropy of mixing $\Delta S_{\text{mix}}(x_Y, T)$ and enthalpy of mixing $\Delta H_{\text{mix}}(x_Y, T)$ were found by partial deriving of $\Delta G_{\text{mix}}(x_Y, T)$ and $\Delta G_{\text{mix}}(x_Y,$

Table 1. Starting Values of CS and C₂AS Activities Used for the Margules Equation Coefficients Calculation

$x(\text{C}_2\text{AS})$	a	T/K							
		1600	1650	1700	1750	1800	1850	1900	1950
0.1	(CS)	0.742	0.770	0.792	0.810	0.823	0.833	0.840	0.846
0.19		0.573	0.611	0.644	0.671	0.693	0.711	0.724	0.735
0.3	(C ₂ AS)	0.411	0.397	0.394	0.400	0.414	0.436	0.465	0.498
0.4		0.655	0.621	0.600	0.590	0.589	0.596	0.609	0.627
0.5		0.812	0.767	0.736	0.714	0.700	0.692	0.690	0.694
0.6		0.897	0.857	0.825	0.800	0.781	0.767	0.757	0.752
0.7		0.933	0.905	0.883	0.863	0.847	0.833	0.822	0.814
0.8		0.946	0.935	0.925	0.916	0.907	0.898	0.890	0.884
0.9		0.959	0.955	0.951	0.948	0.945	0.942	0.940	0.938

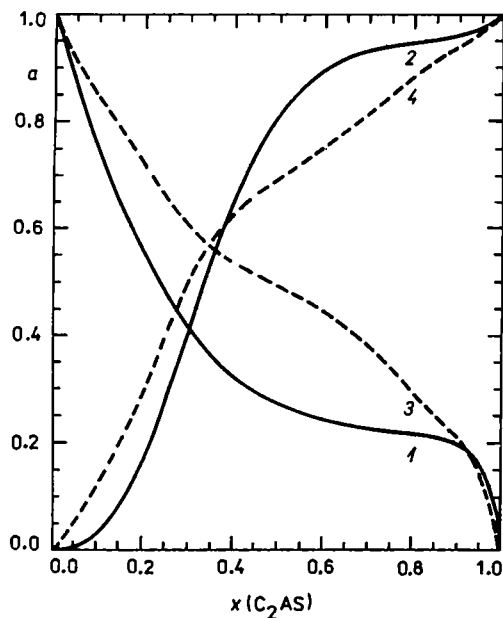


Fig. 4. Composition dependence of activities for CS (1 and 3) and C₂AS (2 and 4) at the temperature 1600 K and 1950 K, respectively.

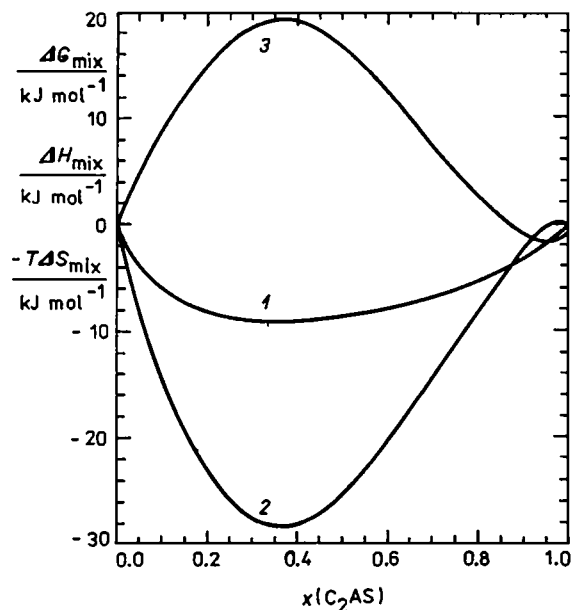


Fig. 6. Isothermal dependences of the quantities $\Delta G_{\text{mix}}(x_\gamma)$ (1), $\Delta H_{\text{mix}}(x_\gamma)$ (2), and $-T\Delta S_{\text{mix}}(x_\gamma)$ (3) of the system CS—C₂AS at the temperature 1950 K.

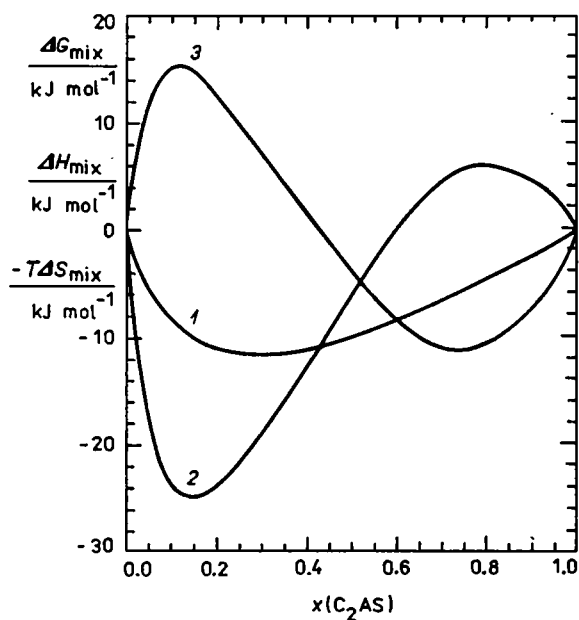


Fig. 5. Isothermal dependences of the quantities $\Delta G_{\text{mix}}(x_\gamma)$ (1), $\Delta H_{\text{mix}}(x_\gamma)$ (2), and $-T\Delta S_{\text{mix}}(x_\gamma)$ (3) of the system CS—C₂AS at the temperature 1600 K.

$T)/T$ with respect to T , respectively. Plots of these quantities vs. composition at the temperatures 1600 K and 1950 K are shown in Figs. 5 and 6.

As follows from these figures the melts of the CS—C₂AS system behave over the temperature range under study as general solutions. Nonzero values of enthalpies of mixing are the consequence of reactions between particles of both components and therefore of their structural difference.

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