

CALORIMETRIC DATA AND PHASE EQUILIBRIA ASSESSMENT IN SILICATE SYSTEMS Optimization of mixing properties of silicate melts

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Abstract

The thermodynamic data are assessed by using molecular solution model with excess Gibbs energy of mixing expressed by Redlich Kister equation with temperature dependent parameters. The optimized data involve phase equilibria, 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. Thermodynamic quantities consistent with available experimental phase equilibria and calorimetric measurements are established for solid phases and liquids in the system $\text{CaO}\text{-SiO}_2$ (CS)– $\text{CaO}\text{-Al}_2\text{O}_3\text{-2SiO}_2$ (CAS₂)– $2\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ (C₂AS).

Keywords: data assessment, silicate melts, thermodynamic properties

Introduction

The experimental thermochemical data and phase diagrams may sometimes be inconsistent, i.e. it is impossible to reproduce experimental phase diagrams by using experimental thermochemical quantities. In thermodynamic optimization all available thermodynamic data and phase equilibrium data for a system are evaluated simultaneously, in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagram can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles [1]. These techniques have been applied to a large number of systems in recent years. Several different types of models have been used.

In this paper the thermodynamic data optimization is applied to the model system $\text{CaO}\text{-SiO}_2$ (CS)– $\text{CaO}\text{-Al}_2\text{O}_3\text{-2SiO}_2$ (CAS₂)– $2\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ (C₂AS) – a subsystem of the ternary system $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ (C–A–S) that is of considerable importance in geology, metallurgical slags, ceramics and cement chemistry.

Method of data treatment

In the present study molecular model with excess Gibbs energy expressed by Redlich-Kister polynomial with linearly temperature dependent coefficients is used. Gibbs energy of solid stoichiometric phases was expressed as

$$G = H_{298}^0 + \int_{298}^T C_p(T) dT - TS_{298}^0 - T \int_{298}^T \frac{C_p(T)}{T} dT \quad (1)$$

where H_{298}^0 is standard enthalpy and S_{298}^0 is standard entropy of a pure substance at 298 K. $C_p(T)$ is its heat capacity expressed as a function of temperature by a polynomial. Gibbs energy of liquid solution was described as follows

$$G = \sum_i x_i G_i^0 + RT \sum_i x_i \ln x_i + \Delta_{\text{mix}} G^E \quad (2)$$

x_i is mole fraction of component i , G_i^0 is Gibbs energy of pure liquid component i and $\Delta_{\text{mix}} G^E$ is excess Gibbs energy of mixing. By Redlich-Kister equation for binary solutions with components i and j

$$\Delta_{\text{mix}} G^E = \sum_0^n x_i x_j (x_i - x_j)^n L_{i,j} \quad (3)$$

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

$$\text{bin} \Delta_{\text{mix}} G^E = \sum_0^n x_i x_j (x_i - x_j)^n L_{i,j} + \sum_0^n x_i x_k (x_i - x_k)^n L_{i,k} + \sum_0^n x_j x_k (x_j - x_k)^n L_{j,k} \quad (4)$$

For ternary solutions with both binary and ternary interactions considered

$$\text{bin+ter} \Delta_{\text{mix}} G^E = \text{bin} \Delta_{\text{mix}} G^E + x_i x_j x_k L_{i,j,k} \quad (5)$$

PARROT program from THERMOCALC set [2, 3] was used to assess thermodynamic parameters. Thermochemical data for stoichiometric phases were not changed in the optimization.

The thermochemical data for pseudowollastonite and CS liquid by Saxena *et al.* [14] and Adamkovičová *et al.* [5], data for anortite and CAS_2 liquid by Richet and Fiquet [6] and Richet and Bottinga [7] and data for gehlenite and C_2AS liquid by Wang *et al.* [8] and Žigo *et al.* [9] have been used. The $\Delta_{\text{mix}} H$ temperature and composition dependence for CS– CAS_2 – C_2AS liquid by Proks *et al.* [10] has been applied.

Results and discussion

The calculated eutectic equilibria in the CS-CAS₂-C₂AS system in comparison with experimental data are summarised in Tables 1–3. For illustration the calculated phase diagrams and $\Delta_{\text{mix}}H$ functions for CS-CAS₂ system by model (3) and for CS-CAS₂-C₂AS system by model (4), in comparison with experimental data, are presented in Figs 1–5.

Table 1 Eutectic equilibria in the C₂AS-CAS₂ and CS-CAS₂ systems

	C ₂ AS-CAS ₂		CS-CAS ₂	
	experiment	assessed	experiment	assessed
<i>T/K</i>	1660 ^[12, 12]	1657	1582 ^[11]	1575
<i>x</i> (CAS ₂)	0.516	0.514	0.278	0.285
<i>T/K</i>	1660 ^[14]		1582 ^[12]	
<i>x</i> (CAS ₂)	0.511		0.311	
<i>T/K</i>	1661 ^[16]		1571 ^[13]	
<i>x</i> (CAS ₂)	0.516		0.291	
<i>T/K</i>			1574 ^[14]	
<i>x</i> (CAS ₂)			0.298	

Table 2 Eutectic equilibria in the CS-C₂AS system

	CS-C ₂ AS	
	experiment	assessed
<i>T/K</i>	1593 ^[12]	1591
<i>x</i> (C ₂ AS)	0.195	0.201
<i>T/K</i>	1593 ^[13]	
<i>x</i> (C ₂ AS)	0.179	
<i>T/K</i>	1591 ^[14]	
<i>x</i> (C ₂ AS)	0.186	
<i>T/K</i>	1603 ^[15]	
<i>x</i> (C ₂ AS)	0.189	

The optimization procedure has shown the enormous influence of the enthalpy of mixing on equilibria fit. The enthalpies of mixing are often determined as relatively small differences between quite large values of calorimetrically measured relative enthalpies. 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

unbeneficial in fit of phase equilibria. In some cases, on the other hand, 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.

Table 3 Eutectic equilibrium in the CS-CAS₂-C₂AS system

	CS-CAS ₂ -C ₂ AS		
	experiment	assessed	
		model (4)	model (5)
<i>T</i> /K	1540 ^[12, 14]	1466	1490
<i>x</i> (CAS ₂)	0.185	0.170	0.160
<i>x</i> (C ₂ AS)	0.135	0.146	0.136
<i>x</i> (CS)	0.680	0.683	0.704

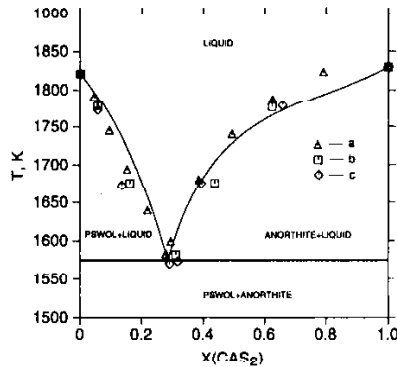


Fig. 1 Phase equilibria in the system CS-CAS₂. Experimental data are by Osborn [11] (a), Osborn and Muan [12] (b), Gentile and Foster [13] (c). Solid lines are optimized liquidus curves

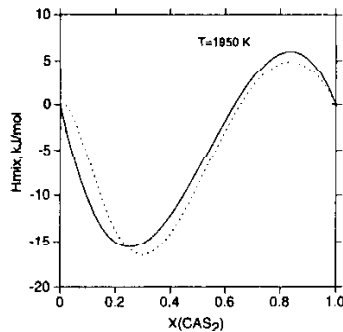


Fig. 2 Enthalpy of mixing in the system CS-CAS₂ at 1950 K. Solid line is calculated in this work, dotted line is experimental by Proks *et al.* [10]

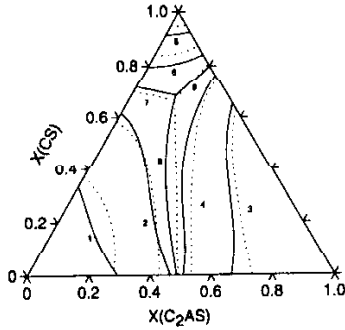


Fig. 3 Phase equilibria in the system CS-CAS₂-C₂AS. Experimental data (dotted lines) are taken from phase diagram of the system C-A-S by Osborn and Muan [12]. Solid lines are calculated according to model (4). Line couples 1, 3 and 5 are isotherms 1500°C, line couples 2, 4 and 6 are isotherms 1400°C, and line couples 7, 8 and 9 represent 3-phase equilibria

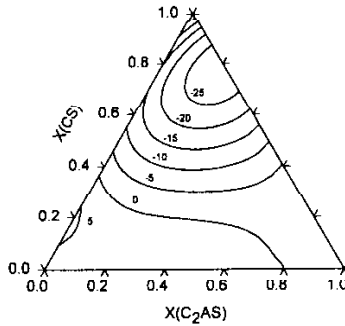


Fig. 4 Enthalpy of mixing in the system CS-CAS₂-C₂AS at 1950 K according to model (4) in kJ mol⁻¹

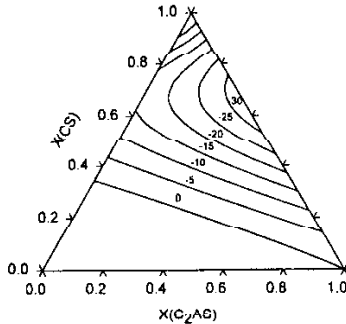


Fig. 5 Enthalpy of mixing in the system CS-CAS₂-C₂AS at 1950 K according to experimental data by Proks *et al.* [10], in kJ mol⁻¹

Conclusions

A molecular solution model with excess Gibbs energy of mixing expressed by Redlich-Kister equation with temperature dependent parameters, optimized on the basis of phase equilibria data and calorimetric data on enthalpy of liquid phase, can be successfully used to describe consistently thermodynamic quantities of the studied system.

Both models for ternary system describe the phase equilibria quite well without considerable differences. The model with eliminated ternary interaction parameter gives better accord with experimental enthalpy of mixing, however, the temperature of the ternary eutectic point is better fitted by a more complicated model.

To describe thermodynamic properties of the melts in the system under study in a way consistent with experimental phase equilibria, except for $\text{CaS}_2\text{-C}_2\text{AS}$ system, considerable changes in enthalpy of mixing with respect to the experimental data by Proks *et al.* [14] had to be accepted.

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