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Integral enthalpies of solution of components in the binary systems $2CaO \cdot Al_2O_3 \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$, $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$

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Abstract

Integral enthalpies of solution for crystalline phases of one component in the melt of the second one were determined in the $2CaO \cdot Al_2O_3 \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$, $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$ systems. Determinations were based on the composition and temperature dependences of the enthalpies of mixing for the binary systems, and on the temperature dependences of the heats of fusion for single components. In the $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$, systems we found out that the composition dependences of the integral enthalpy of solution go through extrema at low dilutions; this is due to characteristic composition dependences of the enthalpies of mixing.

INTRODUCTION

We have determined the differential enthalpies of solution for components in the binary systems $2CaO \cdot Al_2O_3 \cdot SiO_2$ (C_2AS)–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2), $CaO \cdot SiO_2$ (CS)–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$ based on the enthalpies of mixing $\Delta H_{mix}(x, T)$ and heats of fusion $\Delta H_{fus}(T)$ [1]. Knowing these quantities, we can determine the composition and temperature dependences of the integral enthalpies of solution for the components of these systems; this is presented here.

THEORETICAL

The integral enthalpy of solution $\Delta H_{sol,int}(M,cr,x_M)$ of a crystalline component M, cr is equal to the increase in enthalpy accompanying the isobaric-isothermal dissolution of 1 mole of crystalline component M, cr in

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an amount of liquid component N, l such that a liquid solution of known composition x_M is produced. It can be derived from the relationship

$$\Delta H_r(x_M) = (n_N + n_M)H_m(l,x_M) - n_N H_m^{\ominus}(N,l) - n_M H_m^{\ominus}(M,cr) \tag{1}$$

where $H_m(l, x_M)$ is the molar enthalpy of the liquid solution at composition x_M, and $H_m^{\ominus}(M, cr)$ and $H_m^{\ominus}(N, l)$ are the molar enthalpies of the reactants. If we substitute

$$H_m^{\ominus}(M,cr) = H_m^{\ominus}(M,l) - \Delta H_{fus,m}^{\ominus}(M) \tag{2}$$

into eqn. (1) we obtain

$$\frac{\Delta H_r(x_M)}{n_M} = \Delta H_{sol,int}(M,cr,x_M)$$

$$= \frac{1}{x_M} H_m(l,x_M) - \frac{x_N}{x_M} H_m^{\ominus}(N,l) - \frac{x_M}{x_M} H_m^{\ominus}(M,l) + \frac{x_M}{x_M} \Delta H_{fus,m}^{\ominus}(M)$$

$$= \frac{\Delta H_{mix,m}(l, x_M)}{x_M} + \Delta H_{fus,m}^{\ominus}(M) \tag{3}$$

The first term on the right side of eqn. (3) was substituted by the functions $\Delta H_{mix,m}(l,x_M)$ from refs. 2–4 that are consistent with the phase diagrams and the Gibbs–Duhem equation for ΔG_{mix}. The second term was substituted by the heat of fusion of component M, $\Delta H_{fus,m}(M)$, at the chosen temperature T_c obtained using both the relative enthalpies of component melts [5] and of the crystalline phases [6–10]. In this way, integral heats of solution of all the crystalline components in these systems were calculated. Experimental methods used to determine the relative enthalpies are described in detail in ref. 5.

RESULTS AND DISCUSSION

Example plots of the integral enthalpies of solution $\Delta H_{sol,int}(M,cr,x_M,T_c)$ versus composition x_N/x_M for both components in the C_2AS–CAS_2 system at 1700 and 1800 K, are shown in Fig. 1. Plots at 1600 and 1800 K for the CS–CAS_2 and CS–C_2AS systems are shown in Figs. 2 and 3, respectively.

Tables 1 and 2 present the integral enthalpies of solution for component M, cr corresponding to $x_M = 0$; these are the integral heats of solution at infinite dilution, i.e. the first differential enthalpies of solution for this component [1]. The integral enthalpies of solution for component M, cr at compositions corresponding to saturated solutions of component N are given in Tables 3 and 4. The integral enthalpies of solution for component M,cr at compositions corresponding to saturated solutions of component M are presented in Tables 5 and 6.

Because the C_2AS–CAS_2 system displays athermic behavior within the

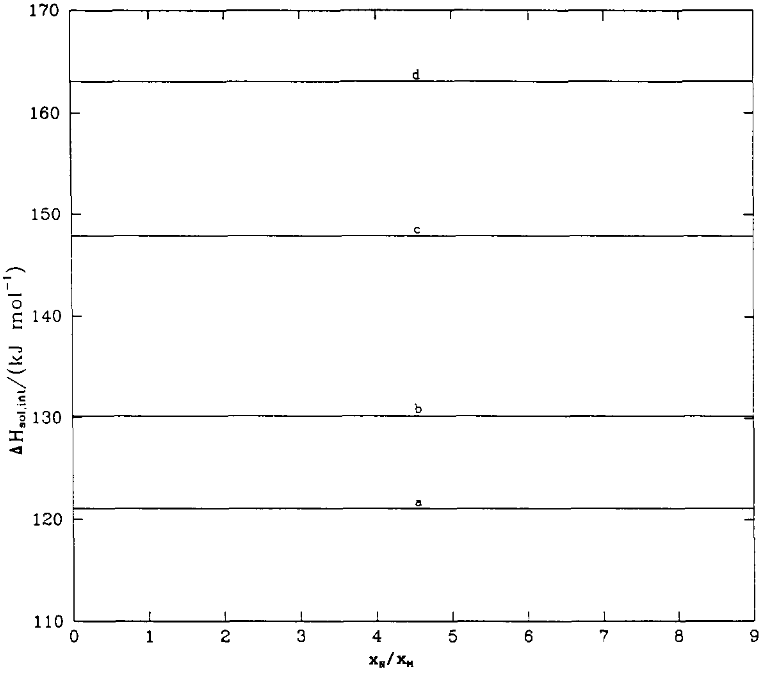

Fig. 1. Plots of $\Delta H_{sol,int}(CAS_2)$ at 1700 K (a) and 1800 K (b), and of $\Delta H_{sol,int}(C_2AS)$ at 1700 K (c) and 1800 K (d), versus composition in the C_2AS–CAS_2 system.

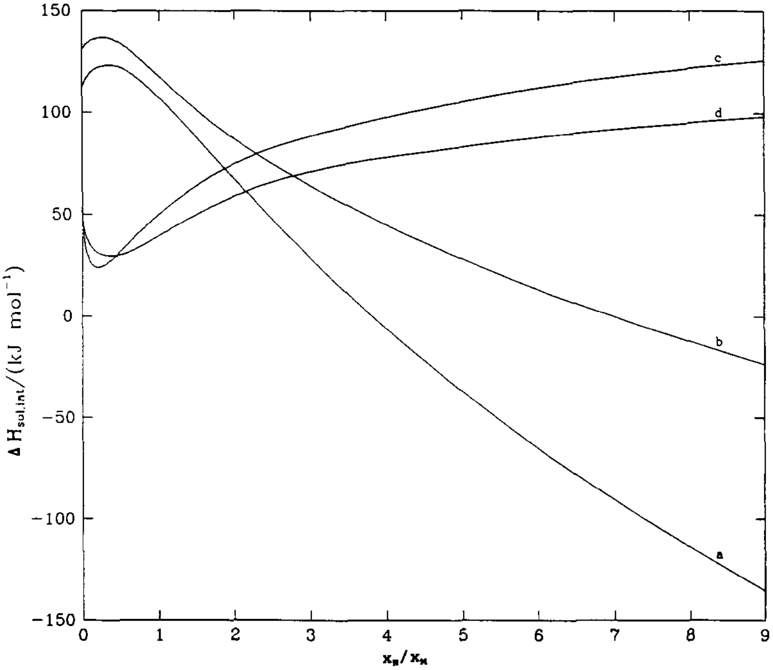

Fig. 2. Plots of $\Delta H_{sol,int}(CAS_2)$ at 1600 K (a) and 1800 K (b), and of $\Delta H_{sol,int}(CS)$ at 1600 K (c) and 1800 K (d), versus composition in the CS–CAS_2 system.

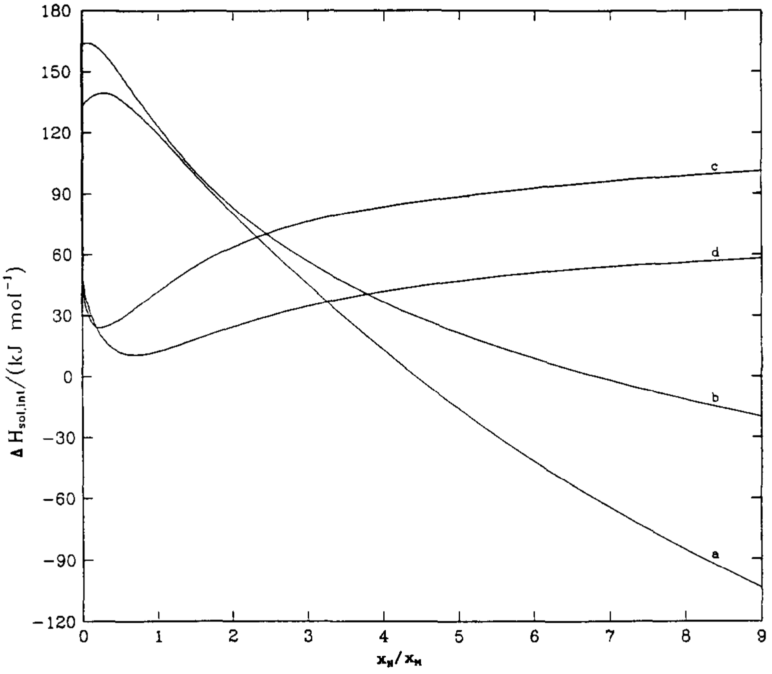

Fig. 3. Plots of $\Delta H_{\mathrm{sol,int}}(C_2AS)$ at 1600 K (a) and 1800 K (b), and of $\Delta H_{\mathrm{sol,int}}(CS)$ at 1600 K (c) and 1800 K (d), versus composition in the CS–C_2AS system.

TABLE 1

Integral heats of solution of CS and CAS_2 at infinite dilution in the CS–CAS_2 system

T/K	$\Delta H_{\mathrm{sol,int}}(\mathrm{CS,cr},x(\mathrm{CS}) = 0)$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{CAS_2,cr},x(\mathrm{CAS_2}) = 0)$/ kJ mol^{-1}
1600	163	−418
1800	129	−165

TABLE 2

Integral heats of solution of CS and C_2AS at infinite dilution in the CS–C_2AS system

T/K	$\Delta H_{\mathrm{sol,int}}(\mathrm{CS,cr},x(\mathrm{CS}) = 0)$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{C_2AS,cr},x(\mathrm{C_2AS}) = 0)$/ kJ mol^{-1}
1600	124	−324
1800	71	−117

TABLE 3

Integral enthalpies of solution of CS and CAS_2 at compositions $x_{eq}(CS)$ and $x_{eq}(CAS_2)$ corresponding to saturated solutions of components CAS_2, cr and CS, cr, respectively, in the CS–CAS_2 system

T/K	$\Delta H_{\mathrm{sol,int}}(\mathrm{CS,cr},x_{\mathrm{eq}}(\mathrm{l,CAS_2,cr}))$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{CAS_2,cr},x_{\mathrm{eq}}(\mathrm{l,CS,cr}))$/ kJ mol^{-1}
1600	32	50
1800	71	−164

TABLE 4

Integral enthalpies of solution of CS and C_2AS at compositions $x_{eq}(CS)$ and $x_{eq}(C_2AS)$ corresponding to saturated solutions of components C_2AS, cr and CS, cr, respectively, in the CS–C_2AS system

T/K	$\Delta H_{\mathrm{sol,int}}(\mathrm{CS,cr},x_{\mathrm{eq}}(\mathrm{l,C_2AS,cr}))$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{C_2AS,cr},x_{\mathrm{eq}}(\mathrm{l,CS,cr}))$/ kJ mol^{-1}
1600	24	5
1800	11	−116

TABLE 5

Integral enthalpies of solution of CS and CAS_2 at compositions $x_{eq}(CS)$ and $x_{eq}(CAS_2)$ corresponding to saturated solutions of components CS, cr and CAS_2, cr, respectively, in the CS–CAS_2 system

T/K $\Delta H_{\mathrm{sol,int}}$	$(\mathrm{CS,cr},x_{\mathrm{eq}}(\mathrm{l,CS,cr}))$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{CAS_2,cr},x_{\mathrm{eq}}(\mathrm{l,CAS_2,cr}))$/ kJ mol^{-1}
1600	29	67
1800	42	137

TABLE 6

Integral enthalpies of solution of CS and C_2AS at compositions $x_{eq}(CS)$ and $x_{eq}(C_2AS)$ corresponding to saturated solutions of components CS, cr and C_2AS, cr, respectively, in the CS–C_2AS system

T/K	$\Delta H_{\mathrm{sol,int}}(\mathrm{CS,cr},x_{\mathrm{eq}}(\mathrm{l,CS,cr}))$/ kJ mol^{-1}	$\Delta H_{\mathrm{sol,int}}(\mathrm{C_2AS,cr},x_{\mathrm{eq}}(\mathrm{l,C_2AS,cr}))$/ kJ mol^{-1}
1600	24	13
1800	45	116

limits of our experimental errors, the integral heats of solution are composition independent and equal to the heats of fusion for the corresponding components at the temperature considered (Fig. 1).

As indicated in Figs. 2 and 3, the composition dependences of $\Delta H_{\text{sol,int}}$ go through the extrema at low values of x_N/x_M. In the case of $\Delta H_{\text{sol,int}}(\text{CS,cr})$ in the CAS_2 and C_2AS melt, this dependence goes through a minimum, while in the case of $\Delta H_{\text{sol,int}}(\text{CAS}_2\text{,cr})$ and of $\Delta H_{\text{sol,int}}(\text{C}_2\text{AS,cr})$ in the CS melt, the dependence goes through a maximum. The extremum values of $\Delta H_{\text{sol,int}}$ and the corresponding compositions are temperature dependent.

The $\Delta H_{\text{sol,int}}(\text{CS,cr})$ values in the CS–CAS_2 and CS–C_2AS systems at higher values of dilutions x_N/x_M decrease with increasing temperature, while the values of $\Delta H_{\text{sol,int}}(\text{CAS}_2\text{,cr})$ and $\Delta H_{\text{sol,int}}(\text{C}_2\text{AS,cr})$ under the same conditions increase with increasing temperature. With increasing dilution these values approach asymptotically the first differential heats of solution of component M.

The value of $\Delta H_{\text{sol,int}}$ in all three cases is a consequence of eqn. (3) and the composition dependence of ΔH_{mix} in the considered systems.

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