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Isoplethic enthalpies of heating in the systems $CaO \cdot SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$, $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $2CaO \cdot Al_2O_3 \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$

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Abstract

Temperature dependences of the isoplethic enthalpy of heating $\Delta H_{\mathrm{isop,heat}}$ for compositions in the $CaO \cdot SiO_2$(CS)–$2CaO \cdot Al_2O_3 \cdot SiO_2$($C_2AS$), $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$($CAS_2$) and $2CaO \cdot Al_2O_3 \cdot SiO_2$–$CaO$ $Al_2O_3 \cdot 2SiO_2$ systems were determined. These quantities were determined using the non-isothermal Hess law, relative enthalpies of individual phases and phase diagrams. The resulting plots allow the direct evaluation of $\Delta H_{\mathrm{isop,heat}}$ values between any two temperatures for a chosen composition. In the CS–C_2AS and CS–CAS_2 systems, a narrow temperature range around 1800 K is present in which all mixtures with 0–0.4 CS have the same value of $\Delta H_{\mathrm{isop,heat}}$ of about 450 kJ mol^{-1}, but with different proportions of the coexisting phases. Within the single-phase melt region, the $\Delta H_{\mathrm{isop,heat}}$ value of all three systems varies linearly with temperature.

INTRODUCTION

Gehlenite, anorthite and wollastonite are silicate minerals that are common in nature and occur in many basic types of rocks. Chemical systems containing these minerals are important subjects of geochemical and geophysical research.

An evaluation of the complex enthalpy balance of processes in multicomponent multi-phase systems, which may include phase transformations, also requires determination of the isoplethic enthalpies of heating of phase assemblages. This paper provides a simple graphical estimation of the temperature dependence of the isoplethic enthalpy of heating.

THEORETICAL

Isoplethic enthalpies of heating can be calculated from the non-isothermal Hess law using relative enthalpies of the individual phases and the

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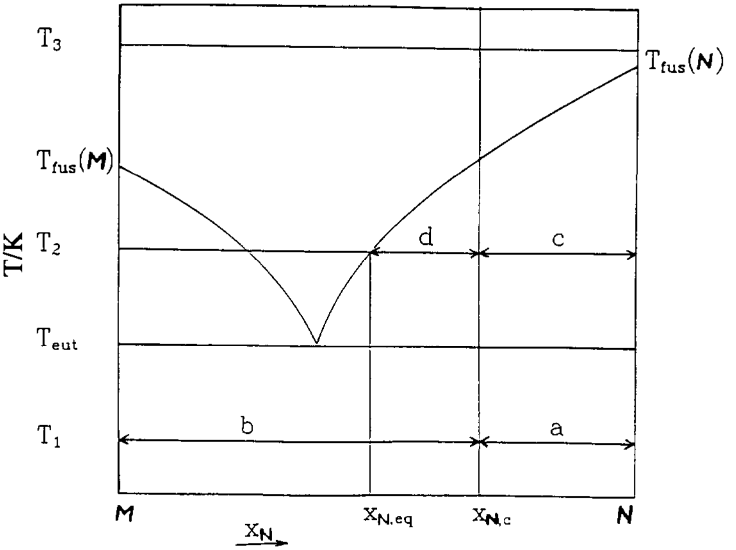

Fig. 1. The phase diagram of the M–N system with the labelled temperatures T_1, T_2 and T_3 being situated within the regions of crystalline phase coexistence, crystalline and liquid phase coexistence, and homogeneous melt, respectively.

corresponding phase diagrams. The isoplethic enthalpy of heating is a change in enthalpy in a system when processes during which the composition remains constant take place. The non-isothermal Hess law also involves cases when the initial and final states are not at the same temperature. The relative enthalpies of melts in two-component mixtures were obtained from primary temperature and composition dependences of this quantity in the $2CaO \cdot Al_2O_3 \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$–$CaO \cdot SiO_2$ system [1]. The experimental methods for the determination of relative enthalpies are also described in ref. 1. The relative enthalpies of the pure components gehlenite, anorthite and wollastonite were calculated using available measurements [2–6].

Within the region of coexistence of the crystalline phases (Fig. 1, T_1), the isoplethic enthalpy of heating from temperature T_0 to temperature T_1 was calculated from

$$\Delta H_{\mathrm{isop,heat}}(x_{\mathrm{N,c}},T_0 \rightarrow T_1) = aH_{\mathrm{rel}}(\mathrm{M,cr},T_1) + bH_{\mathrm{rel}}(\mathrm{N,cr},T_1) - aH_{\mathrm{rel}}(\mathrm{M,cr},T_0) - bH_{\mathrm{rel}}(\mathrm{N,cr},T_0) \qquad (1)$$

where $\Delta H_{\mathrm{isop,heat}}(x_{\mathrm{N,c}},T_0 \rightarrow T_1)$ is the isoplethic enthalpy of heating of one mole of mixture at composition $x_{\mathrm{N,c}}$, $H_{\mathrm{rel}}(\mathrm{X},T_c)$ is molar relative enthalpy of component X at the temperature T_c, and a and b are mole fractions of component M and N, respectively. N is the component chosen to express the composition of a system (in the CS–CAS_2 and C_2AS–CAS_2 systems, N is CAS_2, while in the CS–C_2AS system, N is C_2AS).

Within the region of coexistence of crystalline and liquid phases (Fig. 1, T_2), the isoplethic enthalpy of heating from T_0 to T_2 was calculated from

$$\Delta H_{\mathrm{isop,heat}}(x_{\mathrm{N,c}},T_0 \rightarrow T_2) = \frac{c}{c+d}H_{\mathrm{rel}}(1,x_{\mathrm{N,eq}},T_2) + \frac{d}{c+d}H_{\mathrm{rel}}(\mathrm{N,cr},T_2) - aH_{\mathrm{rel}}(\mathrm{M,cr},T_0) - bH_{\mathrm{rel}}(\mathrm{N,cr},T_0) \qquad (2)$$

where $H_{\mathrm{rel}}(1,x_{\mathrm{N,eq}},T_2)$ is the molar relative enthalpy of the melt at composition $x_{\mathrm{N,eq}}$ which, at T_2, is in equilibrium with crystals of component N; $c/(c+d)$ and $d/(c+d)$ are the mole fractions of melt at composition $x_{\mathrm{N,eq}}$ and for crystals of component N, respectively (Fig. 1).

Within the region of homogeneous melt (Fig. 1, T_3), the isoplethic enthalpy of heating from T_0 to T_3 was calculated from

$$\Delta H_{\mathrm{isop,heat}}(x_{\mathrm{N,c}},T_0 \rightarrow T_3) = H_{\mathrm{rel}}(1,x_{\mathrm{N,c}},T_3) - aH_{\mathrm{rel}}(\mathrm{M,cr},T_0) - bH_{\mathrm{rel}}(\mathrm{N,cr},T_0) \qquad (3)$$

where $H_{\mathrm{rel}}(1,x_{\mathrm{N,c}},T_3)$ is the molar relative enthalpy of the melt at a chosen composition $x_{\mathrm{N,c}}$ at the temperature T_3.

In a manner analogous to that used before, isoplethic enthalpies of heating for any temperature variations within considered temperature range, can be calculated.

RESULTS AND DISCUSSION

Plots of isoplethic enthalpies of heating versus temperature and composition between 298 K and the chosen temperature in the CS–C_2AS, CS–CAS_2 and C_2AS–CAS_2 systems are shown in Figs. 2–4, respectively. The high-temperature region of the latter plot is shown in expanded scale in Fig. 5. The values of $\Delta H_{\mathrm{isop,heat}}$ for any pair of temperatures selected at a chosen isopleth can be evaluated directly from these figures. For other compositions these values can be estimated by interpolation.

Figures 2 and 3 show that in the systems wollastonite–gehlenite and wollastonite–anorthite, in a narrow temperature range around 1800 K, a range of two-phase mixtures occurs that have the same value of $\Delta H_{\mathrm{isop,heat}}$, approximately 450 kJ mol^{-1}, but with different ratios of coexisting crystals and melt. The same value of $\Delta H_{\mathrm{isop,heat}}$ is also found for assemblages of gehlenite and anorthite at corresponding temperatures, respectively. In order to obtain the same value of $\Delta H_{\mathrm{isop,heat}}$ for two different compositions $x_{\mathrm{N}} \in \langle 0.6-1.0 \rangle$ at around 1800 K, the differences in the relative enthalpies of the coexisting phases at this temperature and at 298 K have to be equal according to eqn. (2).

It is evident from Figs. 2 and 3 that within the composition range $x_{\mathrm{N}} \approx 0.6-1.0$, the isopleths showing the temperature dependence of $\Delta H_{\mathrm{isop,heat}}$ cross twice or, in a limiting case, they touch at one point. Every

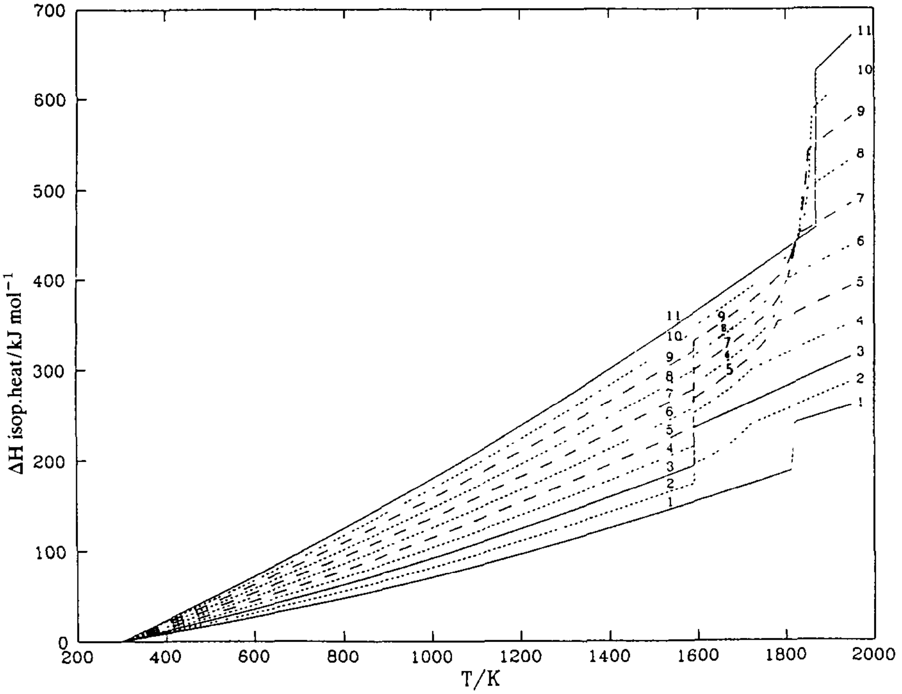

Fig. 2. Plots of isoplethic enthalpies of heating against temperature in the CS–C_2AS system. Isopleths are labelled 1–11 in the direction of increasing mole fraction $x(C_2AS)$ from 0 to 1 in 0.1 increments, except the isopleth labelled 3, which corresponds to the eutectic mixture.

intersection corresponds to the same temperature and $\Delta H_{\mathrm{isop,heat}}$ for two systems of different composition. At lower temperatures in these systems, crystals coexist with the melt of corresponding composition. One of these systems can also consist of a pure component. At higher temperatures, one of these systems can be just a melt of corresponding composition. Above about 1800 K, $\Delta H_{\mathrm{isop,heat}}$ increases rapidly with increasing temperature.

In the C_2AS–CAS_2 system, the temperature dependences of $\Delta H_{\mathrm{isop,heat}}$ corresponding to compositions $x_N \in \langle 0, x_{\mathrm{eut}} \rangle$ can cross with those of compositions $x_N \in \langle x_{\mathrm{eut}}, 1 \rangle$, as can be seen in Fig. 5. In this case every intersection corresponds to the same values of $\Delta H_{\mathrm{isop,heat}}$ and temperature for two systems of different composition.

Because the molar heat capacities of gehlenite and anorthite are approximately the same in the temperature range of 298 K to T_{eut} [2, 3], isothermal differences between $\Delta H_{\mathrm{isop,heat}}$ over the whole composition range are small (Fig. 4). The $\Delta H_{\mathrm{isop,heat}}$ of a eutectic mixture of crystalline phases is not too different from the arithmetic mean of these quantities for both components over the whole temperature range. This is a consequence of the relatively symmetrical liquidus curves in the phase diagram of the C_2AS–CAS_2 system ($x_{\mathrm{eut}} = 0.52$) [7].

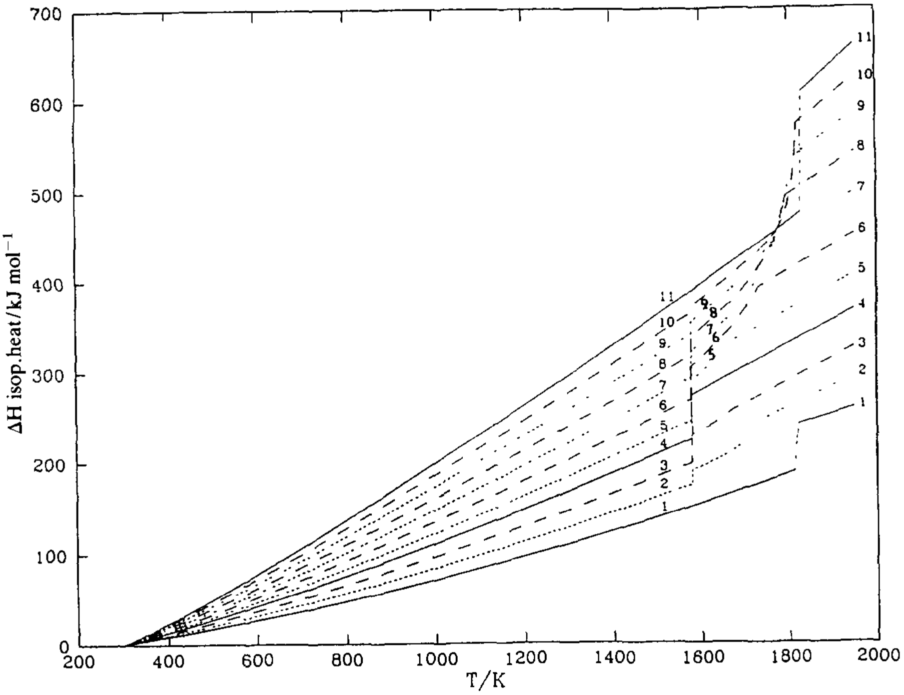

Fig. 3. Plots of isoplethic enthalpies of heating against temperature in the CS–CAS$_2$ system. Isopleths are labelled 1–11 in the direction of increasing mole fraction $x(\mathrm{CAS_2})$ from 0 to 1 in 0.1 increments, except the isopleth labelled 4, which corresponds to the eutectic mixture.

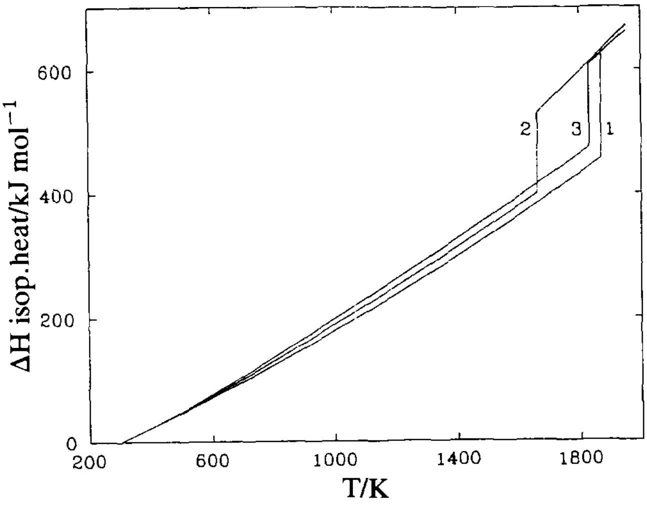

Fig. 4. Plots of isoplethic enthalpies of heating against temperature in the C$_2$AS–CAS$_2$ system. Curves 1, 2 and 3 correspond to $x(\mathrm{CAS_2})$ equal to 0, x_{eut} and 1, respectively.

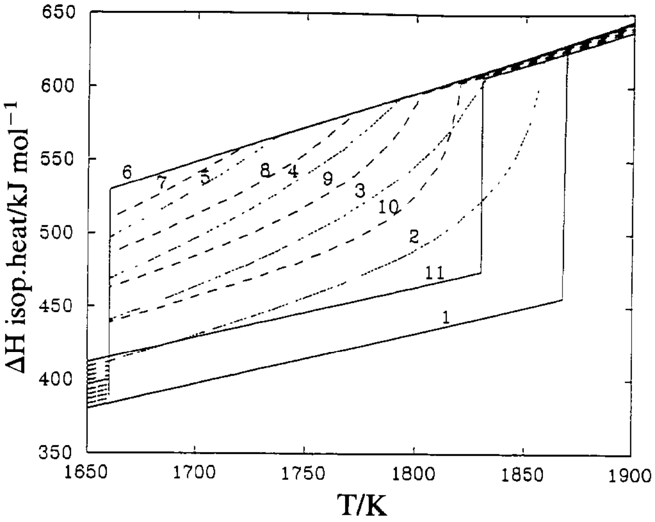

Fig. 5. High-temperature sections of the plots in Fig. 4. Isopleths are labelled 1–11 in the direction of increasing mole fraction $x(\mathrm{CAS_2})$ from 0 to 1 in 0.1 increments, except the isopleth labelled 6, which corresponds to the eutectic mixture.

The heat capacity of anorthite at any temperature is larger than that of gehlenite. This is in agreement with the larger number of atoms in the formula of anorthite and with the equipartition law of energy.

$\Delta H_{\mathrm{isop,heat}}$ varies linearly with temperature in a single-phase melt region because the heat capacities of silicate melts do not depend on the temperature if the temperature interval is not too large. It can be seen in Fig. 5 that within the melt region, the temperature dependences of $\Delta H_{\mathrm{isop,heat}}$ are similar to each other over the whole compositional range.

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