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Differential and integral enthalpies of solution of akermanite and pseudo-wollastonite in the melts of the system $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$. Isoplethal enthalpies in this system

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Abstract

It was found that the enthalpy of mixing at formation of the melts in the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system from melts of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and CaSiO_3 is zero within the temperature limits from 1673 to 1930 K. Consequently, the differential and integral heats of solution of akermanite and pseudo-wollastonite in the melts of this system are equal to their heats of fusion at the corresponding temperature. Using the non-isothermal Hess law and the phase diagram, isoplethal enthalpies were calculated in this system within the temperature range from 298 to 1920 K. The enthalpy and entropy of crystallization for the eutectic melt at the eutectic temperature $T_e = 1673$ K was determined to be $\Delta_{\text{cryst}}H(\text{eut. melt}, T_e) = (-78.3 \pm 2.4) \text{ J mol}^{-1}$ and $\Delta_{\text{cryst}}S(\text{eut. melt}, T_e) = (-46.8 \pm 1.4) \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Keywords: Akermanite; $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system; Differential and integral enthalpy of solution; Isoplethal enthalpy; Pseudo-wollastonite

1. Introduction

The $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system is a part of the geologically and technologically important CaO--MgO--SiO_2 system. It was shown that the enthalpy of mixing at formation of the melts in the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system from melts of the pure components is equal to zero over the entire compositional range and in the temperature region from 1760 to 1930 K within the experimental error limits. This result follows

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from the composition–temperature–relative enthalpy relation which was derived from experimental data obtained by high-temperature drop calorimetry and solution calorimetry measurements [1]. The present paper describes the determination of additional thermodynamic properties of this system based on experimental data from Ref. [1], namely:

(i) Verifying that the enthalpy of mixing of melts in this system is also zero in the temperature region of equilibrium coexistence of the liquid and crystalline phases, i.e. from the melting temperatures of end-members to the eutectic temperature T_e .

(ii) Finding the temperature dependences of the differential and integral heats of solution of akermanite and pseudo-wollastonite in the melts of this system.

(iii) Determining the isoplethal enthalpies in the studied system between 298 and 1920 K.

(iv) Calculating the enthalpy and entropy of crystallization of the eutectic melt at the eutectic temperature in this system, as well as the total heat of crystallization of this melt which is the sum of the heat of crystallization at the eutectic temperature and the enthalpy on cooling of the eutectic from T_e to 298 K.

2. Results and discussion

2.1. Properties of melts of the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system in the temperature region from 1673 to 1760 K

Recently, it was found that the enthalpy of mixing of melts in the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system is equal to zero over the entire range of compositions and temperatures between 1760 and 1930 K, within the experimental error limits [1]. The experimental values of relative enthalpy measured for 49 figurative points, only three of them below 1760 K, served as the input data for regression analysis in order to obtain the relative enthalpy as a function of temperature and composition [1]. Therefore, an extrapolation of relative enthalpy into the mentioned temperature region might be erroneous. The isoplethal ($x=0.6$) dependence of the relative enthalpy on temperature

$$H_{\text{rel.is}} = a + bT \quad (1)$$

was therefore used to verify the proposed zero value of the enthalpy of mixing of melts between 1673 and 1760 K. Least-squares analysis applied on six experimental points of H_{rel} between 1718 and 1925 K [1] resulted in the following best estimates: $a = 384.97$, $b = 0.268353$, with the standard errors $\sigma(a) = 12.65$, $\sigma(b) = 6.92 \times 10^{-3}$.

For the relative enthalpy, function (1) yields the value $(833.9 \pm 1.4) \text{ kJ mol}^{-1}$ at the eutectic temperature 1673 K. This value is close to that of $(834.3 \pm 1.7) \text{ kJ mol}^{-1}$ obtained on extrapolating the relative enthalpy–composition–temperature relation from Ref. [1] to the eutectic temperature. The difference is much smaller than the errors, which confirms the original assumption.

2.2. Temperature dependence of differential and integral heats of solution of crystalline components in the melts of the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system

Relations needed to calculate the differential enthalpy of solution ($\Delta_{\text{sol}}H_{\text{dif}}$) and the integral enthalpy of solution ($\Delta_{\text{sol}}H_{\text{int}}$) of pure crystalline components in the melts of binaries, using the composition dependences of the enthalpy of mixing are given in Refs. [2] and [3]. Because of the zero values of the enthalpy of mixing and the partial molar enthalpies of mixing of both end-members in the melts of the investigated system, the relations for the differential and integral enthalpies of solution of a crystalline component Y in the melt of the $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$ system are as follows

$$\begin{aligned}\Delta_{\text{sol}}H_{\text{dif}}(Y_{\text{cr}}, x, T) &= \Delta_{\text{sol}}H_{\text{int}}(Y_{\text{cr}}, x, T) = \Delta_{\text{fus}}H_{\text{m}}^0(Y_{\text{cr}}, T) \\ &= H_{\text{rel}}(Y_1, T) - H_{\text{rel}}(Y_{\text{cr}}, T)\end{aligned}\quad (2)$$

where Y stands for $\text{Ca}_2\text{MgSi}_2\text{O}_7$ or CaSiO_3 and x is the mole fraction of CaSiO_3 . Relation (2) is also an expression for the molar enthalpy of fusion ($\Delta_{\text{fus}}H_{\text{m}}^0$) of a corresponding end-member as a function of temperature. The first term on the right-hand side of Eq. (2) (relative enthalpy of a molten component $H_{\text{rel}}(Y_1, T)$) will be replaced by [1]

$$H_{\text{rel}} = (a_0 + a_1x) + (b_0 + b_1x)T \quad (3)$$

and the second by

$$H_{\text{rel}}(Y_{\text{cr}}, T) = -[\Delta_{\text{col}}H(Y_{\text{cr}}, T \rightarrow 298 \text{ K}) + \Delta_{\text{sol}}H(Y_{\text{cr}}, 298 \text{ K})] \quad (4)$$

Changes in enthalpy on cooling of a crystalline component Y from temperature T to 298 K, $\Delta_{\text{col}}H(Y_{\text{cr}}, T \rightarrow 298 \text{ K})$, were calculated from the temperature dependence of the heat capacity of akermanite and pseudo-wollastonite given in Refs. [4] and [5], respectively. Enthalpies of solution, $\Delta_{\text{sol}}H(Y_{\text{cr}}, 298 \text{ K})$, were taken from Refs. [6] and [7], respectively. This resulted in temperature dependences of the form

$$\begin{aligned}\Delta_{\text{sol}}H_{\text{dif}}(\text{Ca}_2\text{MgSi}_2\text{O}_{7,\text{cr}}, x, T) &= \Delta_{\text{sol}}H_{\text{int}}(\text{Ca}_2\text{MgSi}_2\text{O}_{7,\text{cr}}, x, T) \\ &= -7.753 + 3.659 \times 10^{-1}T - 8.2867 \times 10^{-5}T^2 \\ &\quad + 1.1146 \times 10^{-8}T^3 - 5.729T^{1/2} - 6.7905 \times 10^3T^{-1}\end{aligned}\quad (5)$$

and

$$\begin{aligned}\Delta_{\text{sol}}H_{\text{dif}}(\text{CaSiO}_{3,\text{cr}}, x, T) &= \Delta_{\text{sol}}H_{\text{int}}(\text{CaSiO}_{3,\text{cr}}, x, T) \\ &= -9.3727 + 5.5019 \times 10^{-2}T - 8.7405 \times 10^{-6}T^2 \\ &\quad - 2.2965 \times 10^3T^{-1}\end{aligned}\quad (6)$$

Table 1 shows the values obtained for both end-members at the temperatures 1693 K, 1723 K and at the temperatures of their fusion, 1727 K for $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and 1817 K for CaSiO_3 . These values can be compared with the measured values for the

Table 1

Differential and integral heats of solution of crystalline phases in the melts of the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – CaSiO_3 system at 1693, 1723 and 1727 K (for $\text{Ca}_2\text{MgSi}_2\text{O}_7$) and 1817 K (for CaSiO_3); Y_1 , akermanite; Y_2 , wollastonite

T/K	$\Delta_{\text{sol}}H_{\text{dir}}(Y_1)/\text{kJ mol}^{-1} = \Delta_{\text{sol}}H_{\text{in}}(Y_1)/\text{kJ mol}^{-1}$	$\Delta_{\text{sol}}H_{\text{dir}}(Y_2)/\text{kJ mol}^{-1} = \Delta_{\text{sol}}H_{\text{in}}(Y_2)/\text{kJ mol}^{-1}$
1693	118.8	57.4
1723	122.2	58.1
1727	122.6	
1817		60.5

enthalpy of fusion of akermanite: $\Delta_{\text{fus}}H(\text{Ca}_2\text{MgSi}_2\text{O}_7, 1727 \text{ K}) = (123.9 \pm 3.2) \text{ kJ mol}^{-1}$ [6] and of wollastonite $\Delta_{\text{fus}}H(\text{CaSiO}_3, 1817 \text{ K}) = (57.3 \pm 2.9) \text{ kJ mol}^{-1}$ [7].

2.3. Isolethal enthalpies

Isolethal enthalpy is the change in enthalpy when a system passes from an initial equilibrium state to the final equilibrium state without any change of chemical composition. Isolethal enthalpies were calculated using the non-isothermal Hess law, the relative enthalpies of individual phases and the phase equilibrium data. The phase diagram used was obtained by recalculating that from Ref. [8] to mole fractions (Fig. 1). The relative enthalpies of melts, inclusive of the pure components, were obtained using Eq. (3). The above-mentioned temperature dependence of the relative enthalpy of

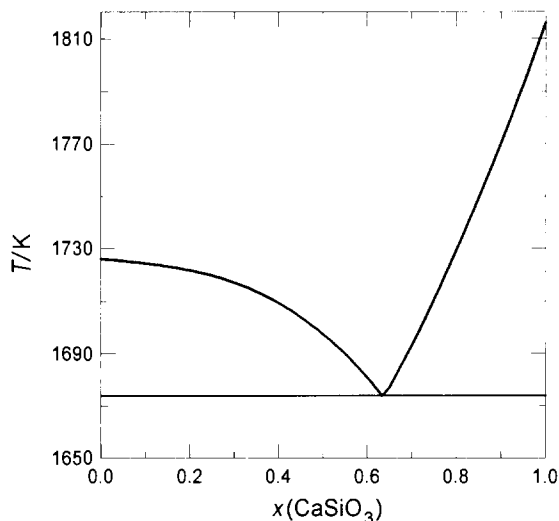


Fig. 1. Phase diagram of the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – CaSiO_3 system after recalculating composition to mole fractions.

akermanite and pseudo-wollastonite (Eq. (4)) was used. The calculation procedure was described in Ref. [9]. Fig. 2 shows a plot of the isoplethal enthalpy of equilibrium systems at various compositions between 298 K and T . The value of the isoplethal enthalpy for any pair of temperatures selected at the chosen isopleth can be evaluated directly from this diagram. In Fig. 3, a two-phase section of the diagram in Fig. 2 is

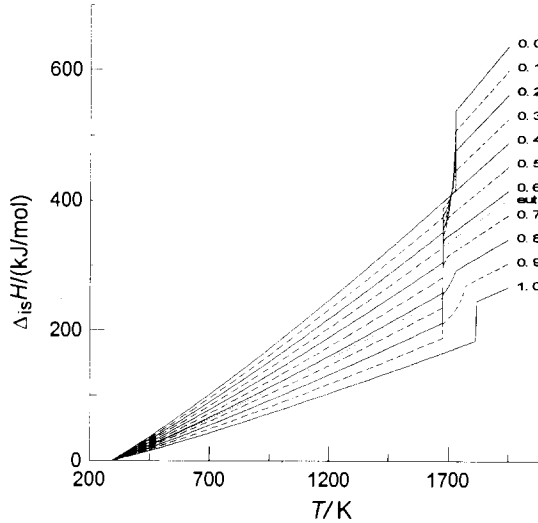


Fig. 2. Isoplethal enthalpy versus temperature for various isopleths of the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ – CaSiO_3 system between 298 K and T . Mole fractions of CaSiO_3 are specified at individual isopleths.

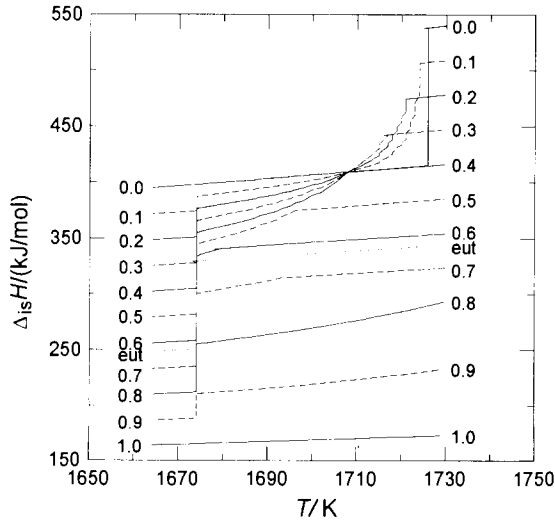


Fig. 3. Detailed section of Fig. 2.

shown in expanded scale. It can be seen in Figs. 2 and 3 that within a certain composition range isopleths showing the temperature dependence of $\Delta_{\text{is}}H$ for systems of different composition cross, or in a limiting case, touch each other at a single point. This intersection point corresponds to the same temperature and $\Delta_{\text{is}}H$ value for systems of different chemical composition. It is evident that in this system at the mentioned temperature, a range of two-phase mixtures occurs, with the same $\Delta_{\text{is}}H$ value but with different ratios of coexisting crystals and melt. The same phenomenon was observed in the systems $\text{CaSiO}_3\text{--Ca}_2\text{Al}_2\text{SiO}_7$ and $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8$ [9].

The existence of a common cross-section point of several isoplethal enthalpy curves in the two-phase region in all three mentioned systems can be explained by the fact that in this region there is a temperature at which the pure crystalline component and the coexisting melt have the same value of isoplethal enthalpy. This condition is satisfied inside the composition interval bordered by the equilibrium melt composition at the cross-section temperature, on the one hand, and the corresponding crystalline end-member composition on the other.

The co-ordinates of the cross-section of isoplethal curves $x_{\text{eq.c.p.}}$ and $T_{\text{c.p.}}$ can be calculated from the condition of equality of isoplethal enthalpies between the coexisting liquid and crystalline phases

$$\begin{aligned} H_{\text{rel}}(l, x_{\text{eq.c.p.}}, T_{\text{c.p.}}) - x_{\text{eq.c.p.}} H_{\text{rel}}(Y_{2,\text{cr}}, T_0) - (1 - x_{\text{eq.c.p.}}) H_{\text{rel}}(Y_{1,\text{cr}}, T_0) \\ = H_{\text{rel}}(Y_{1,\text{cr}}, T_{\text{c.p.}}) - H_{\text{rel}}(Y_{1,\text{cr}}, T_0) \end{aligned} \quad (7)$$

where $T_{\text{c.p.}} \in \langle T_e, T_{\text{fus}}(Y_1) \rangle$. The value of $x_{\text{eq.c.p.}}$ must satisfy the temperature dependence of x_{eq} of the primary crystallization of the end-member $Y_{1,\text{cr}}$

$$x_{\text{eq}} = f(T) \quad (8)$$

The function in Eq. (8) is explicitly obtained from the liquidus curve in the phase diagram. If $Y_1 = \text{Ca}_2\text{MgSi}_2\text{O}_7$ and $Y_2 = \text{CaSiO}_3$, substituting from Eq. (3), Eq. (7) transforms into

$$\begin{aligned} (a_0 + a_1 x_{\text{eq.c.p.}}) + (b_0 + b_1 x_{\text{eq.c.p.}}) T_{\text{c.p.}} - x_{\text{eq.c.p.}} H_{\text{rel}}(\text{CaSiO}_{3,\text{cr}}, T_0) \\ - (1 - x_{\text{eq.c.p.}}) H_{\text{rel}}(\text{Ca}_2\text{MgSi}_2\text{O}_{7,\text{cr}}, T_0) = H_{\text{rel}}(\text{Ca}_2\text{MgSi}_2\text{O}_{7,\text{cr}}, T_{\text{c.p.}}) \\ - H_{\text{rel}}(\text{Ca}_2\text{MgSi}_2\text{O}_{7,\text{cr}}, T_0) \end{aligned} \quad (9)$$

After substitution from Eq. (8), relation (9) transforms into an equation of the single unknown $T_{\text{c.p.}}$. Solving this equation, the value $T_{\text{c.p.}} = 1708.1$ K was obtained for the system $\text{Ca}_2\text{MgSi}_2\text{O}_7\text{--CaSiO}_3$. The limiting value of $x_{\text{eq.c.p.}} = 0.395$ of the composition interval of systems with a common cross-section of isoplethal enthalpy curves was computed by substituting $T_{\text{c.p.}} = 1708.1$ K back into Eq. (8). The cross-section enthalpy $\Delta_{\text{is}}H_{\text{c.p.}} = 409.4$ kJ mol⁻¹ was finally calculated from the difference in the relative enthalpy of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ at $T_{\text{c.p.}}$ and T_0 .

2.4. Enthalpy and entropy of crystallization of the eutectic melt at the eutectic temperature, and the total heat of crystallization of the eutectic melt

The enthalpy of crystallization of the eutectic melt at its equilibrium temperature of crystallization $T_e = 1673$ K

$$\Delta_{\text{cryst}} H(\text{eut. melt, 1673 K}) = (-78.3 \pm 2.4) \text{ kJ mol}^{-1} \quad (10)$$

was calculated as the difference between the relative enthalpies of the eutectic and the eutectic melt, both at T_e . The corresponding entropy value is

$$\Delta_{\text{cryst}} S(\text{eut. melt, 1673 K}) = (-46.8 \pm 1.4) \text{ J mol}^{-1} \text{ K}^{-1} \quad (11)$$

The difference between the relative enthalpies of the eutectic at 298 K and the eutectic melt at T_e , is the heat of total crystallization of the eutectic melt

$$\Delta_{\text{cryst.tot}} H(\text{eut. melt, 1673 K} \rightarrow 298 \text{ K}) = (-327.3 \pm 2.2) \text{ kJ mol}^{-1} \quad (12)$$

The heat of equilibrium crystallization at the eutectic temperature covers only about 24% of the total heat of crystallization revealed on cooling of the eutectic melt from T_e to 298 K.

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