

Determination of the Enthalpy and Entropy of Peritectic Reaction in the $\text{CaO} \cdot \text{SiO}_2(\text{CS})$ — $2\text{CaO} \cdot \text{SiO}_2(\text{C}_2\text{S})$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2(\text{C}_2\text{AS})$ System at the Equilibrium Temperature 1588 K

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Inverse drop calorimetry performed in a SETARAM HTC 1800 K was used to measure the relative enthalpy value of the ternary peritectic melt (p.m.) in the CS—C₂S—C₂AS system at the temperature 1754 K with regard to the reference state of a mechanical mixture of β -C₂S, CS, and C₂AS crystals of corresponding composition at 298 K. The same method was applied to measure the relative enthalpy values of peritectic melt in the temperature interval 1624 K—1775 K with regard to the reference state of its glass at 298 K. From these data the temperature-independent value of specific heat capacity of the peritectic melt was determined

$$c_p(\text{p.m.}) = (1.8213 \pm 0.1318) \text{ J g}^{-1} \text{ K}^{-1}$$

Using these quantities and the literature data of some enthalpic quantities for crystalline phases of compounds in the CS—C₂S—C₂AS system, the specific enthalpy of peritectic reaction (p.r.) in this system at equilibrium temperature 1588 K was determined

$$\Delta_{\text{p.r.}}h(1588\text{K}) = (231 \pm 33) \text{ J g}^{-1}$$

For determination of this quantity the material balance of peritectic reaction and the material balance of dissociation of C₃S₂ to β -C₂S and CS were also used.

The $\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{SiO}_2$ — $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ system is a part of the CaO — Al_2O_3 — SiO_2 system, which is important for production of cement, glass and formation of slags. Further on the symbols C, A, and S will be used for the CaO , Al_2O_3 , and SiO_2 oxides, respectively. From theoretical point of view, the knowledge of the thermodynamic properties of the individual subsystems of the C—A—S system is substantial for the study of geochemical and geophysical processes.

Of thermodynamic properties of the CS—C₂S—C₂AS system, the heat capacities of crystalline phases of its components, the heats of fusion of pseudowollastonite (CS) [1, 2] and gehlenite (C₂AS) [3], and the heat capacities of the CS [1, 4], C₂AS [3], and C₂S [5] melts are known. The heat capacity and enthalpy of crystallization of the binary eutectic melt in the CS—C₂AS system [6] and of the ternary eutectic melt in the C₃S₂—CS—C₂AS system [7] are known, too. The relative enthalpies of melts in the CS—C₂AS system have been determined within the framework of the enthalpic analysis of melts in the CS—C₂AS—C₂AS

system [8].

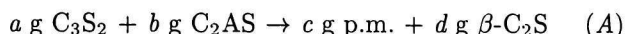
The presence of incongruently melting rankinite (C₃S₂) in the CS—C₂S—C₂AS system leads besides eutectic points also to two peritectic points in this system [9]. One of these peritectic points corresponds to the composition of the peritectic melt resulting from the incongruent melting of rankinite and the second one to the composition of the ternary peritectic melt. This peritectic melt, together with β -dicalcium silicate (β -C₂S), arises at temperature 1588 K, from such a mixture of rankinite and gehlenite the composition of which lies on the point of intersection of straight lines connecting rankinite—gehlenite and peritectic melt—C₂S [9]. Determination of the enthalpy and entropy of this peritectic reaction as well as of the heat capacity of the ternary peritectic melt (p.m.) using the indirect calorimetric method is the aim of this work.

For determination of the enthalpy of peritectic reaction in the CS—C₂S—C₂AS system using indirect calorimetric method we need to know the material balance of this process and the values of relative enthalpy (h_{rel}) of reactants and products taking part in the peri-

tectic reaction at the temperature of 1588 K. Applying the Hess law on the peritectic reaction (p.r.), we get for enthalpy of this process the relation

$$\Delta_{\text{p.r.}}h(1588 \text{ K}) = c h_{\text{rel}}(\text{p.m.}; 1588 \text{ K}) + d h_{\text{rel}}(\beta\text{-C}_2\text{S}; 1588 \text{ K}) - a h_{\text{rel}}(\text{C}_3\text{S}_2; 1588 \text{ K}) - b h_{\text{rel}}(\text{C}_2\text{AS}; 1588 \text{ K}) \quad (1)$$

where $\Delta_{\text{p.r.}}h(1588 \text{ K})$ is the specific enthalpy of peritectic reaction at equilibrium temperature of 1588 K, a , b and c , d are the mass fractions of the starting (C_3S_2 ; C_2AS) and final phases (p.m., $\beta\text{-C}_2\text{S}$), respectively, in the scheme (A) of the peritectic reaction



(in this scheme $a + b = c + d = 1$), and $h_{\text{rel}}(\text{X}; 1588 \text{ K})$ are the specific relative enthalpies of the individual phases of peritectic reaction at temperature of 1588 K ($\text{X} \equiv \text{C}_3\text{S}_2$; C_2AS ; p.m. and $\beta\text{-C}_2\text{S}$).

One of the methods useful for the determination of the relative enthalpy of glass-forming silicate melts is the method of "inverse drop calorimetry". When using this method the melt is formed at chosen temperature T_c directly in the calorimeter after dropping the sample of crystalline phase or the mixture of crystalline phases from temperature 298 K to T_c . The measured value of the relative enthalpy of melt at T_c is then related to the reference state of crystalline phase or to the mixture of crystalline phases at 298 K. Inverse drop calorimetry performed in a SETARAM HT 1500 calorimeter was used *e.g.* to measure the enthalpies of fusion of diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) [10], pseudowollastonite [2], and forsterite [11] and to determine the enthalpies of mixing in formation of melts from two- [11] or three-phase mixtures of minerals [2, 11] at 1773 K. A SETARAM HTC 1800 K was used to determine the heat capacity and the enthalpy of crystallization of ternary eutectic melt in the system $3\text{CaO} \cdot 2\text{SiO}_2\text{—CaO} \cdot \text{SiO}_2\text{—}2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ [7]. Based on the experience of the authors of [2, 10, 11] and our own one obtained within [7], we applied the method of inverse drop calorimetry to the determination of the enthalpy of peritectic reaction in the $\text{CS—C}_2\text{S—C}_2\text{AS}$ system at equilibrium temperature of 1588 K.

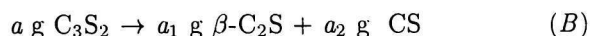
Application of the Inverse Drop Calorimetry to Determination of the Enthalpy of Peritectic Reaction

Contrary to the above-mentioned cases, in the measuring equipment at high temperature ($T_c > 1588 \text{ K}$) after dropping rankinite and gehlenite mixed in the ratio $a : b$ (scheme (A)) a two-phase equilibrium (melt— $\beta\text{-C}_2\text{S}$) was set. The peritectic melt arises together with $\beta\text{-C}_2\text{S}$ only at equilibrium temperature 1588 K. At any higher temperature a melt of such a composition is formed which is at the respective tem-

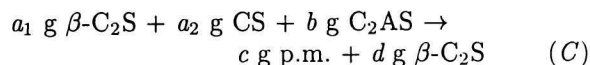
perature in equilibrium with $\beta\text{-C}_2\text{S}$ [9]. The relative enthalpy value of these phases at chosen temperature T_c , measured by the inverse drop calorimetry method, related to the reference state of the C_3S_2 and C_2AS mixture at 298 K includes several enthalpy changes. These are the increase of enthalpy on heating of C_3S_2 and C_2AS from 298 K to 1588 K, the enthalpy of peritectic reaction, the increase of enthalpy on heating the peritectic melt and $\beta\text{-C}_2\text{S}$ from 1588 K to T_c as well as the enthalpy of dissolution of $\beta\text{-C}_2\text{S}$ into a peritectic melt at T_c forming such melt which is at this temperature in equilibrium with the rest of $\beta\text{-C}_2\text{S}$. However, at this procedure the achievement of equilibrium is uncertain. Therefore, the way of the determination of the enthalpy of peritectic reaction was used which is based on two measured enthalpic quantities of peritectic melt. The first of them is the relative enthalpy of peritectic melt at chosen temperature T_c with regard to the reference state of the mixture of crystalline phases of $\beta\text{-C}_2\text{S}$, CS, and C_2AS at 298 K, mixed in the ratio necessary for the formation of peritectic melt ($h_{\text{rel},1}(\text{p.m.}; T_c)$), and the second one is the temperature dependence of heat capacity of the peritectic melt.

The course of peritectic reaction at 1588 K described by scheme (A) can be expressed by means of two reaction steps:

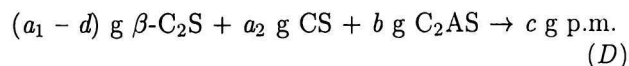
1. Rankinite dissociates at this temperature to $\beta\text{-C}_2\text{S}$ and pseudowollastonite



2. The products of dissociation of rankinite react at 1588 K with gehlenite forming peritectic melt and $\beta\text{-C}_2\text{S}$



The enthalpy of peritectic reaction at 1588 K is given by the sum of the reaction enthalpies of these two steps. Because $\beta\text{-C}_2\text{S}$ occurs on both sides of the reaction scheme (C) and since $a_1 > d$, we can rearrange the reaction (C) to the form



The enthalpies of the reactions (C) and (D) are the same. If we express the specific enthalpy of dissociation of rankinite at 1588 K $\Delta_{\text{r.}(B)}h(1588 \text{ K})$ with the aid of specific enthalpies of formation of rankinite, pseudowollastonite, and $\beta\text{-C}_2\text{S}$ at this temperature $\Delta_f h(\text{Y}; 1588 \text{ K})$ and if we indicate the enthalpy of reaction (D) at 1588 K with the symbol $\Delta_{\text{r.}(D)}h(1588 \text{ K})$, then we get for the specific enthalpy of peritectic reaction the relation

$$\begin{aligned} \Delta_{p.r.}h(1588\text{ K}) &= a \Delta_{r.(B)}h(1588\text{ K}) + \\ &+ c \Delta_{r.(D)}h(1588\text{ K}) = a_1 \Delta_f h(\beta\text{-C}_2\text{S}; 1588\text{ K}) + \\ &+ a_2 \Delta_f h(\text{CS}; 1588\text{ K}) - a \Delta_f h(\text{C}_3\text{S}_2; 1588\text{ K}) + \\ &+ c \Delta_{r.(D)}h(1588\text{ K}) \end{aligned} \quad (2)$$

If the value of specific relative enthalpy of peritectic melt at T_c related to the reference state of crystalline phases of $\beta\text{-C}_2\text{S}$, CS, and C_2AS mixed in the ratio $(a_1 - d):a_2:b$ at 298 K ($h_{\text{rel},1}(\text{p.m.}; T_c)$) and the temperature dependence of the specific heat capacity of peritectic melt have been measured and if the temperature dependences of the specific heat capacities of crystalline phases of $\beta\text{-C}_2\text{S}$, CS, and C_2AS are known from the literature, then the specific enthalpy of reaction (D) at 1588 K can be expressed with the aid of specific relative enthalpies of the individual phases of reaction at this temperature

$$\begin{aligned} \Delta_{r.(D)}h(1588\text{ K}) &= h_{\text{rel},1}(\text{p.m.}; T_c) - \int_{1588\text{ K}}^{T_c} c_p(\text{p.m.}; T) dT \\ &- \frac{(a_1 - d)}{c} \int_{298\text{ K}}^{1588\text{ K}} c_p(\beta\text{-C}_2\text{S}; T) dT - \frac{a_2}{c} \int_{298\text{ K}}^{1588\text{ K}} c_p(\text{CS}; T) dT \\ &- \frac{b}{c} \int_{298\text{ K}}^{1588\text{ K}} c_p(\text{C}_2\text{AS}; T) dT \end{aligned} \quad (3)$$

where $c_p(Z; T)$ are the temperature dependences of the specific heat capacities of phases of reaction (D). The values of the specific relative enthalpy of crystalline phases of $\beta\text{-C}_2\text{S}$, CS, and C_2AS expressed by three integrals of eqn (3) are related to the reference state of the pertinent crystalline phases at 298 K.

By introducing the relation for the specific enthalpy of formation of $\beta\text{-C}_2\text{S}$, pseudowollastonite, and rankinite at 1588 K expressed according to the Kirchhoff law

$$\Delta_f h(Y; 1588\text{ K}) = \Delta_f h(Y; 298\text{ K}) + \int_{298\text{ K}}^{1588\text{ K}} c_p(Y; T) dT \quad (4)$$

and eqn (3) for $\Delta_{r.(D)}h(1588\text{ K})$ into eqn (2) we get the relation for the determination of the specific enthalpy of peritectic reaction at 1588 K

$$\begin{aligned} \Delta_{p.r.}h(1588\text{ K}) &= a_1 \Delta_f h(\beta\text{-C}_2\text{S}; 298\text{ K}) + \\ &+ a_2 \Delta_f h(\text{CS}; 298\text{ K}) - a \Delta_f h(\text{C}_3\text{S}_2; 298\text{ K}) + \\ &+ c h_{\text{rel},1}(\text{p.m.}; T_c) - c \int_{1588\text{ K}}^{T_c} c_p(\text{p.m.}; T) dT + \\ &+ d \int_{298\text{ K}}^{1588\text{ K}} c_p(\beta\text{-C}_2\text{S}; T) dT - a \int_{298\text{ K}}^{1588\text{ K}} c_p(\text{C}_3\text{S}_2; T) dT - \\ &- b \int_{298\text{ K}}^{1588\text{ K}} c_p(\text{C}_2\text{AS}; T) dT \end{aligned} \quad (5)$$

The relation (5) differs from the relation (1) only in the way of expressing the relative enthalpies of starting and final phases of peritectic reaction at 1588 K. The expression

$$[h_{\text{rel},1}(\text{p.m.}; T_c) - \int_{1588\text{ K}}^{T_c} c_p(\text{p.m.}; T) dT]$$

is the specific relative enthalpy of peritectic melt at 1588 K related to the reference state of the mixture of crystalline phases $\beta\text{-C}_2\text{S}$, CS, and C_2AS at 298 K. This is converted with the aid of specific enthalpy of formation of $\beta\text{-C}_2\text{S}$, CS, and C_3S_2 at 298 K, the expression

$$\int_{298\text{ K}}^{1588\text{ K}} c_p(\beta\text{-C}_2\text{S}; T) dT$$

and the pertinent material balances of reactions (A) and (B) into the relative enthalpy of final phases of peritectic reaction at 1588 K, related to the reference state of the mixture of rankinite and gehlenite at 298 K.

The mass fractions of the starting phases C_3S_2 ($a = 0.7982$) and C_2AS ($b = 0.2018$) and the final phases p.m. ($c = 0.6332$) and $\beta\text{-C}_2\text{S}$ ($d = 0.3668$) of peritectic reaction (A) have been obtained on the basis of material balance of oxides C, A, and S in the individual phases of peritectic reaction. The composition of peritectic melt (in mass fractions): $w(\text{C}) = 0.4885$, $w(\text{A}) = 0.1185$, and $w(\text{S}) = 0.393$ was read from the phase diagram of the C—A—S system revised and redrawn by Osborn and Muan [9]. The stoichiometric coefficients for the products of dissociation of rankinite described by the scheme (B) are $a_1 = 0.4767$ and $a_2 = 0.3215$.

It can be concluded that determination of the enthalpy of peritectic reaction on the basis of the relation (5) requires to measure the relative enthalpy value of the peritectic melt at a chosen temperature $T_c > 1588\text{ K}$ and to measure the temperature dependence of the heat capacity of the peritectic melt. The other quantities in the relation (5) are known from the literature.

EXPERIMENTAL

Sample Preparation

Pseudowollastonite and gehlenite were prepared by the precursor method [12]. This method was employed to prepare also the glass of peritectic melt used to measure the temperature dependence of the heat capacity of peritectic melt. As starting components CaCO_3 (Specpure, JMC), metallic Al ($w(\text{Al}) = 99.999$, Research Institute of Metals, Panenské Břežany, Czech Republic), and sol of silicic acid stabilized by ammonia were used. The sol of silicic acid was prepared from commercial water glass using the ion exchanger DOWEX 50 W \times 8 [3]. The homogeneous mixtures

of oxides C, A, and S were obtained by heating (at 500°C–600°C) the dry residue of aqueous solutions prepared from citric acid and weighed in amounts of sol of silicic acid, $\text{Ca}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$ corresponding to the desired composition.

Pseudowollastonite was prepared by heating the homogeneous mixture of oxides C, A, and S of pertinent composition first at 1000°C (4 h) and then at 1300°C for 4 h [13]. When preparing gehlenite, the respective homogeneous mixture of oxides was heated at 1300°C for 8 h and subsequently at 1400°C for the same time [7]. The purity of both crystalline phases as well as of $\beta\text{-C}_2\text{S}$ (OZNC, Podolsk, Russia) was verified by X-ray diffraction analysis.

The glass of peritectic melt was prepared by quenching the melt (in liquid nitrogen), obtained by two-step heating of the homogeneous mixture of oxides first at 1100°C (4 h) and after sealing it into a Pt90Rh10 crucible by further heating at 1400°C. X-Ray diffraction analysis revealed that there is no crystalline phase in the glass of the peritectic melt and so this state is a suitable reference state for measurement of the relative enthalpy values of peritectic melt at several temperatures ($h_{\text{rel},2}(\text{p.m.}; T_c)$). These values are necessary for the determination of the temperature dependence of heat capacity of the peritectic melt.

The mechanical mixture of $\beta\text{-C}_2\text{S}$, pseudowollastonite, and gehlenite, mixed in the ratio $(a_1 - d)/c$ a_2/c $b/c = 0.1736$ 0.5077 0.3187 (1 g) and suspended in toluene, was homogenized by stirring for 4 h. After being dried at 60°C, cylindrical pellets of 4 mm diameter and *ca.* 2 mm height (≈ 50 mg) were prepared from the mixture by pressing. These pellets were used for calorimetric measurement of the relative enthalpies of peritectic melt at chosen temperature. The same procedure was applied to make the pellets from the glass of the peritectic melt.

To control the completeness of melting of the pellets prepared from the mixture of crystalline phases after dropping them into the calorimeter at high temperature, the conditions of melting have been simulated outside the calorimeter. The Pt90Rh10 crucible with the pellets was put into the furnace heated at 1480°C and was held at this temperature for 15 min. The time of heating was chosen with regard to the fact that a typical calorimetric peak is finished within 10 min. Then the crucible was quickly cooled in liquid nitrogen. The subsequent X-ray diffraction analysis showed that the sample was at 1480°C completely

melted (no crystalline phase was observed in the glass after cooling the sample). On the basis of this result the value of relative enthalpy of the peritectic melt was measured at this temperature (*ca.* 1480°C) related to the reference state of crystalline phases $\beta\text{-C}_2\text{S}$, CS, and C_2AS at 298 K ($h_{\text{rel},1}(\text{p.m.}; 1754 \text{ K})$).

Apparatus

The method of inverse drop calorimetry, performed in a SETARAM HTC 1800 K, was used to measure $h_{\text{rel},1}(\text{p.m.}; 1754 \text{ K})$ value as well as $h_{\text{rel},2}(\text{p.m.}; T_c)$ values in the temperature interval 1624–1775 K. In this calorimeter the temperature difference between two crucibles of the calorimetric cell placed one above the other in vertical calorimetric furnace was measured. The crucibles of calorimetric cell, made from sintered alumina, were lined by Pt90Rh10 crucibles. In the lower (reference) crucible there were pieces of sintered alumina as reference material, while into the upper crucible of calorimetric cell, held on constant temperature, the pellets of the sample and bodies of the calibration substance were dropped alternatively, using a special dropping equipment.

During the experiment, the temperature and the temperature difference between the middle parts of the crucibles measured by a set of thermocouples connected in series were recorded in constant time intervals. From the measured data (their treatment is described in [14]) the area below the curve of the time dependence of the temperature difference between the crucibles was calculated which is proportional to the heat flow between the crucibles.

As the calibration substance Pt cylindrical bodies (*ca.* 400 mg) of 4 mm diameter and 1 mm height were used. The temperature dependence of the heat capacity of Pt was taken from [15]. From the values of the heat necessary for the heating of the calibration bodies and from the corresponding areas the calibration factor as an average value of one-day series of measurements was calculated. The one-day series of measurements means 5 drops of the sample pellets and 4 drops of the calibration bodies.

RESULTS AND DISCUSSION

The specific relative enthalpy values of the peritectic melt at temperature $T_c = 1754 \text{ K}$ related to the reference state of the crystalline phases $\beta\text{-C}_2\text{S}$, CS,

Table 1. The Measured Values of $h_{\text{rel},1}(\text{p.m.}; 1754 \text{ K})$, the Value of their Arithmetic Mean, and the Doubled Value of the Error of Arithmetic Mean

$h_{\text{rel},1}(\text{p.m.}; 1754 \text{ K})/(\text{J g}^{-1})$	1859	1841	1896	1898	1970	1855	1837
	1933	1931	1857	1858	1834	1891	
$h_{\text{rel},1,\Phi}(\text{p.m.}; 1754 \text{ K})/(\text{J g}^{-1})$	1882						
$2\sigma_{\Phi}(h_{\text{rel},1,\Phi}(\text{p.m.}; 1754 \text{ K}))/(\text{J g}^{-1})$	24						

Table 2. The Values of Arithmetic Mean of the Relative Enthalpy of Peritectic Melt at T_c ($h_{\text{rel},2,\Phi}(\text{p.m.}; T_c)$) and the Doubled Values of the Error of Arithmetic Mean for Pertinent Number of Measurements of the Relative Enthalpy Values

T_c	$h_{\text{rel},2,\Phi}(\text{p.m.}; T_c)$	$2\sigma_{\Phi}(h_{\text{rel},2,\Phi}(\text{p.m.}; T_c))$	n
K	J g ⁻¹	J g ⁻¹	
1624	1546	19	11
1654	1593	41	9
1684	1638	13	9
1714	1701	32	9
1775	1830	36	9

and C₂AS at 298 K, obtained from several series of measurements, are given in Table 1. In this table the value of the arithmetic mean of the relative enthalpy of peritectic melt at 1754 K ($h_{\text{rel},1,\Phi}(\text{p.m.}; 1754 \text{ K})$) and the doubled value of the error of the arithmetic mean of this quantity ($2\sigma_{\Phi}(h_{\text{rel},1,\Phi}(\text{p.m.}; 1754 \text{ K}))$) are given, too. The scattering of the measured data of the relative enthalpy of peritectic melt is mainly due to certain instability of the base line of the measured curves of the time dependence of the temperature difference between the crucibles.

From the measured values of the relative enthalpy of peritectic melt at five temperatures in the interval 1624–1775 K related to the reference state of the glass of peritectic melt at temperature 298 K ($h_{\text{rel},2}(\text{p.m.}; T_c)$), the values of the arithmetic means ($h_{\text{rel},2,\Phi}(\text{p.m.}; T_c)$) have been determined. These values and the doubled values of the error of arithmetic mean of relative enthalpy ($2\sigma_{\Phi}(h_{\text{rel},2,\Phi}(\text{p.m.}; T_c))$) for pertinent number of measurements n are given in Table 2.

Using the method of weighted least squares, from the measured data, the temperature dependence of the relative enthalpy of peritectic melt with regard to the reference state of its glass at 298 K was calculated.

$$h_{\text{rel},2}(\text{p.m.}; T)/(\text{J g}^{-1}) = (-1422.0 \pm 221.3) + (1.8213 \pm 0.1318) T/\text{K} \quad (6)$$

The values of standard deviation of the relative enthalpy of peritectic melt calculated on the basis of the relation

$$\sigma(h_{\text{rel},2}(\text{p.m.}; T)) = (\text{var}(b)T^2 + 2T\text{cov}(a, b) + \text{var}(a))^{1/2} \quad (7)$$

are in the measured temperature interval smaller than 15 J g⁻¹. The covariance of coefficients of eqn (6) is (-26.161).

The values of arithmetic mean of the specific relative enthalpy of peritectic melt at chosen temperatures as well as their temperature dependence are plotted in Fig. 1. The bars represent two-fold values of the errors.

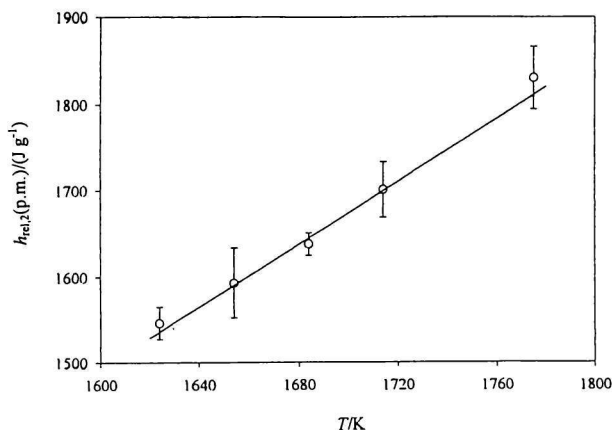


Fig. 1. The temperature dependence of $h_{\text{rel},2}(\text{p.m.}; T)$ with the two-fold errors of inlet data.

Differentiating eqn (6) with regard to temperature, the value of the specific heat capacity of peritectic melt is

$$c_p(\text{p.m.}) = (1.8213 \pm 0.1318) \text{ J g}^{-1} \text{ K}^{-1} \quad (8)$$

This value is independent of the choice of reference state in measurement of the relative enthalpy of peritectic melt and that is why the index at c_p in eqn (8) is omitted.

By introducing the value of arithmetic mean of specific relative enthalpy of peritectic melt at 1754 K, the value of its specific heat capacity, the values of the enthalpy of formation of β -C₂S, CS, and C₃S₂ crystals at 298 K taken from [5], coefficients of temperature dependences of heat capacities of β -C₂S, rankinite, and gehlenite taken from [16] as well as the respective stoichiometric coefficients of reaction schemes (A) and (B) into eqn (5), the value of the specific enthalpy of the peritectic reaction was determined

$$\Delta_{\text{p.r.}}h(1588 \text{ K}) = (231 \pm 33) \text{ J g}^{-1} \quad (9)$$

The error of determination of the enthalpy of peritectic reaction was calculated on the basis of the Gauss law of spreading of errors considering besides the errors of determination of the measured quantities also 1 % relative errors of specific enthalpy of heating the β -C₂S, C₃S₂, and C₂AS crystals from 298 K to 1588 K. The errors of determination of specific enthalpies of formation of crystal phases were neglected.

The specific entropy of peritectic reaction was obtained by dividing the value of specific enthalpy of peritectic reaction by the equilibrium temperature 1588 K as follows

$$\Delta_{\text{p.r.}}s(1588 \text{ K}) = (0.145 \pm 0.021) \text{ J g}^{-1} \text{ K}^{-1} \quad (10)$$

The peritectic reaction in the CS—C₂S—C₂AS system described by scheme (A) is thus an endother-

mic process. This corresponds with the fact that the melt is formed in the system. The method used for determination of enthalpy of peritectic reaction allows to calculate the enthalpy of formation of peritectic melt from the crystalline phases of β -C₂S, CS, and C₂AS described by scheme (D) at temperature 1588 K. From the relation (3) we obtain for the enthalpy of this process the value $\Delta_{r.(D)}h(1588\text{ K}) = 249\text{ J g}^{-1}$ which is relatively close to the numeric value of the enthalpy of crystallization of ternary eutectic melt in the C₃S₂—CS—C₂AS system at temperature 1583 K (-324.6 J g^{-1} [7]).

Determination of the enthalpy of peritectic reaction in the CS—C₂S—C₂AS system is a further contribution to the enthalpy balances of the processes taking part in this system. It can be utilized in optimization of the consistency of phase diagrams of the systems of inorganic oxide materials.

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