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DETERMINING THE HEAT OF INCONGRUENT DECOMPOSITION OF MERWINITE

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Temperature dependences of the relative enthalpies of phases co-existing in equilibrium during incongruent decomposition of merwinite (merwinite, peritectic melt having the molar composition 1.193 CaO . *0.697* MgO . $1SiO_2$, α-Ca_2SiO_4, MgO) *and the material balance of this reaction were used for determining the heat of incongruent decomposition of merwinite at equilibrial temperature* $T_{eq} = 1848$ K: $\Delta H_{in.dis, C_3MS_2} = (125 \pm 15)$ *kJ . mole*$^{-1}$. *The temperature dependences of relative enthalpies of merwinite and those of the peritectic melt were determined by the method of "double calorimetry of the same sample". To determine the heat of incongruent decomposition of merwinite the same change in enthalpy during the cooling of* MgO *had to be measured and the heat of solution of* γ - Ca_2SiO_4 *and* MgO *had to be determined.*

The change in entropy due to incongruent decomposition of merwinite has the value $\Delta S_{in.dis, C_3MS_2} = (67.5 \pm 8.1)$ *J . mole*$^{-1}$ *. K*$^{-1}$.

INTRODUCTION

Merwinite is magnesium-calcium orthosilicate $Ca_3Mg(SiO_4)_2$ (further on designated C_3MS_2, where C, M and S are symbols for CaO, MgO and SiO_2 respectively) with a deformed structure of glaserite type ($K_3Na(SO_4)_2$) [1]. At 1848 K it decomposes incongruently producing a melt (p.m.), $Ca_2SiO_4(C_2S)$ and MgO (M) [2]. According to Gutt [3], decomposition of merwinite yields the α-modification of C_2S.

The material balance of CaO, MgO and SiO_2 in merwinite and in its decomposition products showed, that at 1848 K merwinite is decomposed according to the equation

$$1\ C_3MS_2 = 1.239\ \text{p.m.} + 0.761\ \alpha\text{-}C_2S + 0.136\ \text{M}, \tag{1}$$

where p. m. is the symbol of one formal mole of a peritectic melt having the composition 1.193 CaO . 0.697 MgO . 1 SiO_2 (the mole composition of the peritectic melt was calculated from its composition by weight (43.13% CaO; 18.12% MgO and 38.75% SiO_2), which was read from the phase diagram of the system CaO—MgO—SiO_2 [4]).

The heat of incongruent decomposition of 1 mole merwinite under atmospheric pressure at equilibrial temperature $T_{eq} = 1848$ K ($\Delta H_{in.dis, C_3MS_2}$) was calculated from the values of relative enthalpies of the individual phases $X(H_{rel, X})$ from equation (1) at this temperature according to the relationship

$$\Delta H_{in.dis, C_3MS_2} = 1.239 H_{rel, p.m.} + 0.761 H_{rel, \alpha\text{-}C_2S} + 0.136 H_{rel, M} - 1\ H_{rel, C_3MS_2} \quad [\text{kJ . mole}^{-1}]. \tag{2}$$

The relative enthalpy of 1 mole of the respective phase (H_{rel}), which represents the negative sum of change in enthalpy of 1 mole during its cooling down from a chosen temperature to 298 K (ΔH_{cool}) with the heat of solution at 298 K (ΔH_{sol}),

$$H_{rel} = -(\Delta H_{cool} + \Delta H_{sol}), \tag{3}$$

was determined in view of the state of the solution of the given phase in a mixture of concentrated HF with concentrated HNO_3 (2 : 1). This choice of the referent state has been necessitated by the variable phase composition of the sample obtained from a peritectic melt by its ill-reproducible cooling down in the drop calorimeter block. Determination of the relative enthalpy values by the method of "double calorimetry of the same sample" has been described in [5] and [6].

To determine the values of relative enthalpy of C_3MS_2, p.m. and M at the merwinite decomposition temperature it was necessary to measure the temperature dependence of relative enthalpies of these phases in suitably chosen temperature intervals. The temperature dependence of relative enthalpy of α-C_2S was determined from the relationship $\Delta H_{cool, \alpha\text{-}C_2S} = f(T)$, calculated from the tabellated data [7] and from the heat of solution of γ-C_2S measured.

Equation (2), which was used for calculating the heat of incongruent decomposition of merwinite, was likewise used for calculating the error involved in the determination. As the errors involved in the determination of the relative enthalpies of the individual phases involved in equation (1) were determined $-\delta(H_{rel, X})$ — the error involved in the determination of the heat of incongruent decomposition of merwinite — $\delta(\Delta H_{in.\,dis, C_3MS_2})$ — was calculated by means of the "Gauss' law of errors propagation",

$$\delta(\Delta H_{in.\,dis, C_3MS_2}) = \sqrt{\sum [\nu_X \delta(H_{rel, X})]^2} \tag{4}$$

where ν_X is the stoichiometric coefficient of the respective phase X in equation (1), Σ is the algebraic sum.

The error involved in the determination of relative enthalpies of the individual phases as well as those involved in the determination of ΔH_{cool} and ΔH_{sol} of the crystalline phases were determined by the method described in [8].

EXPERIMENTAL

Sample preparation

The silicate phases — C_3MS_2, peritectic melt and γ-C_2S — were prepared by the precursor method, which has been described in detail in [9]. Merwinite was prepared by 12-hour heating of a precursor having the molar composition $3CaO \,.\, 1MgO \times \times 2\,SiO_2$ in a sealed crucible of Pt90Rh10 alloy at 1350 °C. The sample was identified by X-ray analysis by comparison with a calculated diffraction pattern [10]. To ensure suitable homogeneity of the peritectic melt during the measurement proper, the melt was prepared from the precursor by 4-hour heating at 1620 °C in a sealed crucible, followed by rapid quenching in liquid nitrogen in a copper cooling block. The following procedure was used in the preparation of γ-C_2S: a precursor having the molar composition $2\,CaO \,.\, 1\,SiO_2$ was heated for 4 hours at 1350 °C and then for 24 hours at 500—525 °C; the γ-C_2S obtained was identified by X-ray analysis.

In view of the slow dissolution of MgO in the HF + HNO_3 mixture, its heat of solution was measured on $Mg(OH)_2$ prepared by reacting MgO (Specpure JMC) with distilled water (after removing CO_2 by 3-hour boiling under reflux) in an autoclave at 190 °C for 48 hours. The $Mg(OH)_2$ obtained was dried at 160 °C in nitrogen atmosphere to prevent formation of $MgCO_3$. The phase composition of the sample was determined by X-ray analysis. Thermogravimetry has shown the $Mg(OH)_2$ sample to contain on the average 1.3 wt. % $MgCO_3$.

The equipment employed

The changes in enthalpy of the respective phases during their cooling down from the chosen temperatures to 298 K (ΔH_{cool}) were measured in a drop calorimeter described in detail in [11]. The specimen, which had been sealed in a crucible of Pt90Rh10 alloy, was tempered in the furnace of the drop calorimeter to the chosen temperature and then dropped into the calorimetric block kept before measurement at 298 K.

The heats of solution of the individual phases at 298 K (ΔH_{sol}) were determined in a solution calorimeter [12] in a solvent comprising a mixture of concentrated HF and concentrated HNO_3 (2 : 1). The solution calorimeter and the respective measuring procedure are described in [12].

THE MEASURING RESULTS AND CALCULATIONS

Determination of the temperature dependence of the relative enthalpy of merwinite

The experimentally established enthalpy change values obtained by cooling merwinite from a chosen temperature (in the 1480—1807 K temperature range) down to 298 K ($\Delta H_{\text{cool}, C_3MS_2}$) are listed in Table I. The temperature dependence of the enthalpy change due to the cooling down of merwinite was calculated by the least square method on the basis of the above experimental data and on that of the condition that the value of $\Delta H_{\text{cool}, C_3MS_2}$ is zero at 298 K:

$$-\Delta H_{\text{cool}, C_3MS_2, \varphi} = -7.29 \times 10^1 + 2.272 \times 10^{-1}\, T + 5.902 \times 10^{-5} T^2, \quad [\text{kJ . mole}^{-1}] \tag{5}$$

with an error $\delta(\Delta H_{\text{cool}, C_3MS_2, \varphi}) = 4.3$ kJ . mole^{-1} (φ designates the value of the quantity averaged by a regressive function). The $\Delta H_{\text{cool}, C_3MS_2, \varphi}$, values calculated for the chosen temperatures are likewise listed in Table I for the sake of comparison with the experimentally established values of $\Delta H_{\text{cool}, C_3MS_2}$.

Table I

Merwinite

$\frac{T}{\text{K}}$	$\frac{-\Delta H_{\text{cool}, C_3MS_2}}{\text{kJ . mole}^{-1}}$	$\frac{-\Delta H_{\text{cool}, C_3MS_2, \varphi}}{\text{kJ . mole}^{-1}}$
1480	394.0	392.6
1546	421.7	419.4
1567	422.8	428.0
1730	500.6	496.8
1764	508.5	511.5
1807	530.7	530.4

The temperature dependence of the change in enthalpy during the cooling down of merwinite including numerical coefficients only slightly differring from the coefficients in equation (5) was dealt with in study [11] where it had been used to verify the function of the drop calorimeter by comparison with the measurements by

Pankratz and Kelley [13]. The $\Delta H_{\mathrm{cool, C_3MS_2}, \varphi}$ values calculated from the regressive function by Pankratz and Kelley [13] and from the regressive function established from our measurements (5) differ at the most by about 1.3 % within the temperature interval of 1480—1807 K.

The two mutually close experimentally established values of the heat of solution of merwinite:

$$\Delta H_{\mathrm{sol, C_3MS_2}} = -970.0 \text{ kJ . mole}^{-1} \text{ and } \Delta H_{\mathrm{sol, C_3MS_2}} = -973.6 \text{ kJ . mole}^{-1}$$

were used for determining the arithmetic mean of the heat of solution of merwinite,

$$\Delta H_{\mathrm{sol, C_3MS_2}, \varphi} = (-971.8 \pm 9.6) \text{ kJ . mole}^{-1}. \tag{6}$$

The temperature dependence of the relative enthalpy of merwinite was obtained by adding the negative value of the heat of solution of merwinite to the right side of equation (5):

$$H_{\mathrm{rel, C_3MS_2}, \varphi} = 8.989 \times 10^2 + 2.272 \times 10^{-1} T + 5.902 \times 10^{-5} T^2; \quad [\text{kJ . mole}^{-1}] \tag{7}$$

with an error $\delta(H_{\mathrm{rel, C_3MS_2}, \varphi}) = 11$ kJ . mole^{-1} (this error has been calculated by means of the "Gauss' law of propagation of errors" from errors $\delta(\Delta H_{\mathrm{cool, C_3MS_2}, \varphi})$ and $\delta(\Delta H_{\mathrm{sol, C_3MS_2}, \varphi})$).

Temperature dependence of the relative enthalpy of the peritectic melt

In view to the possible changes in the phase composition of the peritectic melt in the course of cooling, it was necessary to determine the heat of solution of the sample after each introduction of the sample at the chosen temperature into the drop calorimeter block (the X-ray patterns taken from the peritectic melt samples after their cooling in the block have shown, that merwinite is their prevailing crystalline phase). The measured value of relative enthalpy of the peritectic melt at each temperature is then the negative value of the sum of a change in enthalpy of cooling and the respective heat of solution of the same specimen.

The changes in enthalpy of the peritectic melt obtained by its cooling ($\Delta H_{\mathrm{cool, p.m.}}$) were measured within a comparatively narrow temperature interval of 1861—1934 K, which is restricted by the temperature of incongruent decomposition of merwinite. The heats of solution of the peritectic melt for each chosen temperature were determined as mean values from 3—5 measurements ($\Delta H_{\mathrm{sol, p.m.}, \varphi}$). The measured values of $\Delta H_{\mathrm{cool, p.m.}}$, $\Delta H_{\mathrm{sol, p.m.}, \varphi}$ as well as those of relative enthalpy $H_{\mathrm{rel, p.m.}}$ are listed

Table II

Peritectic melt

$\frac{T}{\mathrm{K}}$	$\frac{-\Delta H_{\mathrm{cool, p.m.}}}{\mathrm{kJ . mole^{-1}}}$	$\frac{-\Delta H_{\mathrm{sol, p.m.}, \varphi}}{\mathrm{kJ . mole^{-1}}}$	$\frac{H_{\mathrm{rel, p.m.}}}{\mathrm{kJ . mole^{-1}}}$	$\frac{H_{\mathrm{rel, p.m.}, \varphi}}{\mathrm{kJ . mole^{-1}}}$
1861	350.2	459.1	809.3	807.4
1889	355.8	458.3	814.1	818.1
1920	367.5	465.1	832.6	830.0
1934	371.3	463.4	834.7	835.3

in Table II, where all the values are given per one formal mole of peritectic melt having the molar compsition 1.193 CaO . 0.697 MgO . 1 SiO_2 and a molar weight of 155.084 g.mole^{-1}.

The temperature dependence of the relative enthalpy of the peritectic melt was determined from its measured values:

$$H_{\text{rel, p.m.}, \varphi} = 9.46 \times 10^{1} + 3.83 \times 10^{-1} T \qquad [\text{kJ . mole}^{-1}] \tag{8}$$

with error $\delta(H_{\text{rel, p.m.}, \varphi}) = 7.9$ kJ . mole^{-1}. The values of $H_{\text{rel, p.m.}, \varphi}$, calculated for the chosen temperatures according to equation (8) are likewise listed in Table II.

Temperature dependence of the relative enthalpy of α-C_2S

Another phase arising during incongruent decomposition of merwinite is α-C_2S [3]. As cooling down of α-C_2S to 298 K involves inversions of modifications, the temperature dependence of the change in enthalpy for the cooling of α-C_2S was determined by calculation from the temperature dependence of the molar heats of the individual C_2S modifications and from the heats of modification inversions of C_2S taken over from the tabellated data in [7]. The inversion temperatures of the individual C_2S modifications were also taken from these tables. The temperature dependence of the change in enthalpy for the cooling of α-C_2S between the temperatures $T > 1693$ K and 298 K, calculated by the method described above, is given by the following relationship (α-C_2S is stable above 1693 K)

$$-\Delta H_{\text{cool}, \alpha\text{-}C_2S, \varphi} = -3.17 \times 10^{1} + 1.347 \times 10^{-1} T + 2.307 \times 10^{-5} T^2 \ [\text{kJ . mole}^{-1}] \tag{9}$$

with error $\delta(\Delta H_{\text{cool}, \alpha\text{-}C_2S, \varphi}) = 1.9$ kJ . mole^{-1}. Its value was calculated by multiplying the mean relative error $\delta_{\text{rel}, \varphi}(\Delta H_{\text{cool}, \varphi}) = 0.0067$ by the value of $\Delta H_{\text{cool}, \alpha\text{-}C_2S}$ (T_φ) determined from function (9) for the mean temperature T_φ from the temperature interval 1693—1848 K. The value of the mean relative error $\delta_{\text{rel}, \varphi}(\Delta H_{\text{cool}, \varphi} = 0.0067$ was obtained from the values of relative errors $\delta_{\text{rel}}(\Delta H_{\text{cool}, \varphi})$ for merwinite, akermanite and wollastonite, and is considered of which are relevant for the calculation of $\delta(\Delta H_{\text{cool}, \varphi})$ for those substances, the regressive function of which are calculated on the basis of literary data.

The modification γ-C_2S is stable at 298 K. This modification was therefore used for measuring the heat of solution. Table III lists the measured values of the heat of solution of γ-C_2S which were used for determining the value of arithmetic mean heat of solution for γ-C_2S:

$$\Delta H_{\text{sol}, \gamma\text{-}C_2S, \varphi} = (-514.2 \pm 3.6) \qquad \text{kJ . mole}^{-1}. \tag{10}$$

Table III

The heat of solution of γ-C_2S

$-\Delta H_{\text{sol}, \gamma\text{-}C_2S}$/kJ . mole^{-1}	515.8	510.6	515.3	515.2

Equations (9) and (10) were used for determining the temperature dependence of relative enthalpy of α-C_2S

$$H_{\mathrm{rel},\alpha\text{-}\mathrm{C_2S},\varphi} = 4.825 \times 10^2 + 1.347 \times 10^{-1}T + 2.307 \times 10^{-5}T^2 \ [\mathrm{kJ\ .\ mole^{-1}}] \quad (11)$$

with error $\delta(H_{\mathrm{rel},\alpha\text{-}\mathrm{C_2S},\varphi}) = 4.1$ kJ . mole^{-1}. This error was calculated from errors $\delta(\Delta H_{\mathrm{cool},\alpha\text{-}\mathrm{C_2S},\varphi})$ and $\delta(\Delta H_{\mathrm{sol},\gamma\text{-}\mathrm{C_2S},\varphi})$ by means of the "Gauss' law of propagation of errors".

Relation (11) can be used for calculating the relative enthalpy of α-C_2S only for temperatures $T > 1693$ K.

Temperature dependence of relative enthalpy of MgO

The temperature dependence of the change in enthalpy of MgO during its cooling down was determined on MgO (Specpure, JMC). The values of $(-\Delta H_{\mathrm{cool,M}})$, measured in the temperature interval of 1481—1871 K are listed in Table IV. The values of $(-\Delta H_{\mathrm{cool,M},\varphi})$ listed in Table IV were calculated from regressive function of (12) established from the measured values of $\Delta H_{\mathrm{cool,M}}$ by the least square method

Table IV
MgO

$\frac{T}{\mathrm{K}}$	$\frac{-\Delta H_{\mathrm{cool,M}}}{\mathrm{kJ\ .\ mole^{-1}}}$	$\frac{-\Delta H_{\mathrm{cool,M},\varphi}}{\mathrm{kJ\ .\ mole^{-1}}}$
1481	57.73	57.58
1520	59.55	59.53
1566	62.44	61.83
1656	65.64	66.36
1673	66.64	67.21
1754	71.69	71.30
1871	77.42	77.23

$$-\Delta H_{\mathrm{cool,M},\varphi} = -1.402 \times 10^1 + 4.672 \times 10^{-2}T + 1.097 \times 10^{-6}T^2 \ [\mathrm{kJ\ .\ mole^{-1}}] \quad (12)$$

with error $\delta(\Delta H_{\mathrm{cool,M},\varphi}) = 0.52$ kJ.mole^{-1}.

As a result of the slow dissolution of MgO in the mixture of acids employed $HF + HNO_3$ (2 : 1), the heat of solution of MgO was determined indirectly from the experimentally established heats of solution of $Mg(OH)_2$ and H_2O (1) in this mixture (1 — designation of the liquid phase) and from the heats of formation of $Mg(OH)_2$, MgO and H_2O (1), listed in Tables [7], using the relationship

$$\Delta H_{\mathrm{sol,M},\varphi} = \Delta H_{\mathrm{f,Mg(OH)_2}} - \Delta H_{\mathrm{f,M}} - \Delta H_{\mathrm{f,H_2O}(l)} - \Delta H_{\mathrm{sol,H_2O}(l),\varphi} + \Delta H_{\mathrm{sol,Mg(OH)_2},\varphi}, \quad (13)$$

where $\Delta H_{f,X}$ is the heat of formation of substance X. In view of a contamination of the $Mg(OH)_2$ sample with $MgCO_3$ (the sample contained about 1.3% $MgCO_3$) the arithmetic mean of the heat of solution of $Mg(OH)_2$ obtained from five measurements was corrected for the $MgCO_3$ content (the heat of solution of $MgCO_3$ was measured in the mixture of acids mentioned above). The following value of heat of solution for $Mg(OH)_2$ was obtained after the correction:

$$\Delta H_{\mathrm{sol,Mg(OH)_2},\varphi} = (-139.8 + 0.9) \ \mathrm{kJ\ .\ mole^{-1}}. \quad (14)$$

By substituting this heat of solution of $Mg(OH)_2$, the measured heat of solution of H_2O ($\Delta H_{\mathrm{sol},\,H_2O(l),\,\varphi} = -3.0$ kJ . mole^{-1} and the heats of formation of $Mg(OH)_2$, MgO and $H_2O(1)$ from [7] into equation (13), the value of the heat of solution of MgO was obtained:

$$\Delta H_{\mathrm{sol},\,\mathrm{M},\,\varphi} = (-174.5 \pm 1.1)\ \mathrm{kJ\ .\ mole^{-1}}. \tag{15}$$

In the calculation of the error $\delta(\Delta H_{\mathrm{sol},\,\mathrm{M},\,\varphi})$, the relative error of the arithmetic mean of MgO solution heat was considered to be the same as the relative error of the arithmetic mean of $Mg(OH)_2$ solution heat.

The temperature dependence of the relative enthalpy of MgO is obtained by combining equations (12) and (15):

$$H_{\mathrm{rel},\,\mathrm{M},\,\varphi} = 1.605 \times 10^2 + 4.672 \times 10^{-2}T + 1.097 \times 10^{-6}T^2, \quad [\mathrm{kJ\ .\ mole^{-1}}] \tag{16}$$

where the error involved in the determination of the relative enthalpy of MgO is $\delta(H_{\mathrm{rel},\,\mathrm{M},\,\varphi}) = 1.2$ kJ . mole^{-1} (the value has again been calculated by means of the "Gauss' law of the propagation of errors").

Calculation of the heat of incongruent decomposition of merwinite ($\Delta H_{\mathrm{in.\,dis.},\,C_3MS_2,\,\varphi}$)

Equations (7), (8), (11) and (16) were used for determining the following values of the relative enthalpy of all the phases co-existing in equilibrium during incongruent decomposition of merwinite at $T_{\mathrm{eq}} = 1848$ K:

$$H_{\mathrm{rel},\,C_3MS_2,\,\varphi} = (1520 \pm 11)\ \mathrm{kJ\ .\ mole^{-1}} \tag{17}$$

$$H_{\mathrm{rel},\,\mathrm{p.}m.,\,\varphi} = (802.4 \pm 7.9)\ \mathrm{kJ\ .\ mole^{-1}} \tag{18}$$

$$H_{\mathrm{rel},\,\alpha-C_2S,\,\varphi} = (810.2 \pm 4.1)\ \mathrm{kJ\ .\ mole^{-1}} \tag{19}$$

$$H_{\mathrm{rel},\,\mathrm{M},\,\varphi} = (250.6 \pm 1.2)\ \mathrm{kJ\ .\ mole^{-1}} \tag{20}$$

By substituting these values from equations (17—20) into equation (2) the heat of incongruent decomposition of merwinite at the equilibrium temperature $T_{\mathrm{eq}} = 1848$ K was calculated:

$$\Delta H_{\mathrm{in.\,dis},\,C_3MS_2,\,\varphi} = (125 \pm 15)\ \mathrm{kJ\ .\ mole^{-1}}. \tag{21}$$

The relative enthalpy values of the individual phases multiplied by the stoichiometric coefficients from equation (1) are plotted in Fig. 1 (rings), while the temperature dependence of the relative enthalpies of these phases multiplied by these coefficients are plotted as lines.

By dividing the heat of incongruent decomposition of merwinite by the temperature of its decomposition ($T_{\mathrm{eq}} = 1848$ K) the following change in entropy of incongruent decomposition of merwinite was obtained

$$\Delta S_{\mathrm{in.\,dis},\,C_3MS_2,\,\varphi} = (67.5 \pm 8.1)\ \mathrm{J\ .\ mole^{-1}\ .\ K^{-1}}. \tag{22}$$

The great value involved in the determination of the heat of incongruent decomposition of merwinite is due to the great errors in the determination of the relative enthalpy of merwinite and that of the peritectic melt. The inaccuracy involved in reading the composition of the peritectic melt from the phase diagram of the system

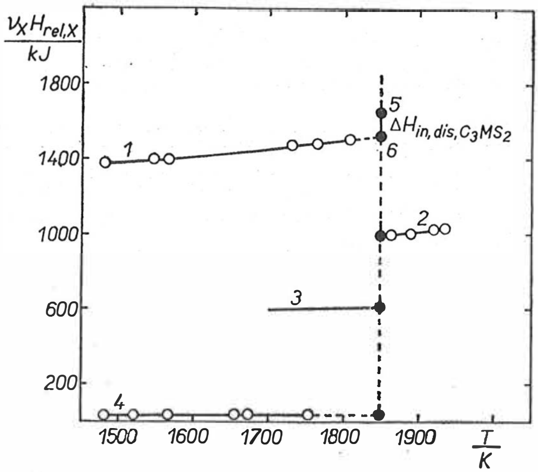

Fig. 1. The temperature dependences of ($\nu_X H_{rel,X,\varphi}$); 1 — C_3MS_2, 2 — p.m., 3 — α-C_2S, 4 — M. *Point 5 represents the value* $\Sigma\nu_X H_{rel,X,\varphi}$ (X *is p.m.,* α-C_2S, M) *at the equilibrium temperature* T_{eq} = *1848 K* (ν_X — *stoichiometric coefficients of p.m.,* α-C_2S *and M in equation* (*1*)). *Point 6 represents the value of relative enthalpy of* C_3MS_2 *at the equilibrial temperature* T_{eq} = *1848 K. The value of* $\Delta H_{in,dis,C_3MS_2}$ *is given by the difference of co-ordinates of points 5 and 6.*

CaO—MgO—SiO_2 [4] has an only minor effect on the value of the heat of incongruent decomposition of merwinite, as indicated by its calculation for the peritectic melt composition reported by Osborn in study [2] (43% CaO; 18.2% MgO; 38.8% SiO_2 — wt. %). The heat of incongruent melting of merwinite calculated (when considering the higher given composition of the peritectic melt) has the following value: $\Delta H_{in.dis,C_3MS_2,\varphi} = (124 \pm 15)$ kJ . mole^{-1}, which differs only a little from the value $\Delta H_{in.dis,C_3MS_2,\varphi} = (125 \pm 15)$ kJ . mole^{-1} (equation (21)).

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STANOVENIE TEPLA INKONGRUENTNÉHO ROZKLADU MERWINITU

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Namerali sa hodnoty zmeny entalpie pri ochladzovaní merwinitu, peritektickej taveniny mólového zloženia 1,193 CaO . 0,697 MgO . 1 SiO_2 a MgO medzi zvolenými teplotami a teplotou 298 K a hodnoty rozpúšťacích tepiel merwinitu, peritektickej taveniny, $\gamma-Ca_2SiO_4$, $Mg(OH)_2$ a H_2O pri teplote 298 K v rozpúšťacej zmesi koncentrovanej HF a koncentrovanej HNO_3 (2 : 1). Z nich, ako aj z vypočítanej teplotnej závislosti zmeny entalpie pri ochladzovaní $\alpha-C_2S$ (na podklade tabelizovaných hodnôt [7]) medzi teplotami $T > 1693$ K a teplotou 298 K, sa určili teplotné závislosti relatívnej entalpie merwinitu, peritektickej taveniny, $\alpha-Ca_2SiO_4$ a MgO (t.j. fáz, ktoré rovnovážné koexistujú pri inkongruentnom rozklade merwinitu):

$H_{\mathrm{rel},\,C_3MS_2,\,\varphi} = 8{,}989 \,.\, 10^2 + 2{,}272 \,.\, 10^{-1}T + 5{,}902 \,.\, 10^{-5}T^2$ [kJ . mol^{-1}]
s chybou $\delta(H_{\mathrm{rel},C_3MS_2,\varphi}) = 11$ kJ . mol^{-1},

$H_{\mathrm{rel,p.m.},\varphi} = 9{,}46 \,.\, 10^1 + 3{,}83 \,.\, 10^{-1}T$ [kJ . mol^{-1}]
s chybou $\delta(H_{\mathrm{rel,p.m.},\varphi}) = 7{,}9$ kJ . mol^{-1},

$H_{\mathrm{rel},\,\alpha-C_2S,\,\varphi} = 4{,}825 \,.\, 10^2 + 1{,}347 \,.\, 10^{-1}T + 2{,}307 \,.\, 10^{-5}T^2$ [kJ . mol^{-1}]
s chybou $\delta(H_{\mathrm{rel},\,\alpha-C_2S,\,\varphi}) = 4{,}1$ kJ . mol^{-1} a

$H_{\mathrm{rel},\,M,\,\varphi} = 1{,}605 \,.\, 10^2 + 4{,}672 \,.\, 10^{-2}T + 1{,}097 \,.\, 10^{-6}T^2$ [kJ . mol^{-1}]
s chybou $\delta(H_{\mathrm{rel},\,M,\,\varphi}) = 1{,}2$ kJ . mol^{-1}.

Teplo inkongruentného rozkladu merwinitu pri rovnovážnej teplote 1848 K sa stanovilo na základe hodnôt relatívnej entalpie C_3MS_2, peritektickej taveniny, $\alpha-C_2S$ a MgO pri tejto teplote a na základe materiálovej bilancie reakcie inkongruentného rozkladu merwinitu a dostala sa hodnota: $\Delta H_{\mathrm{in.\,dis},\,C_3MS_2,\,\varphi} = (125 \pm 15)$ kJ . mol^{-1}. Zmena entropie pri inkongruentnom rozklade merwinitu $\Delta S_{\mathrm{in.\,dis},\,C_3MS_2,\,\varphi} = (67{,}5 \pm 8{,}1)$ J . mol^{-1}. K^{-1}.

Obr. 1. Teplotné závislosti ($\nu_X H_{\mathrm{rel},\,X,\,\varphi}$); 1 — C_3MS_2, 2 — p.m., 3 — α-C_2S, 4 — M. *Bod 5 predstavuje hodnotu* $\Sigma\,\nu_X H_{\mathrm{rel},\,X,\,\varphi}$ (*X je p.m.,* α-C_2S, *M*) *pri rovnovážnej teplote* $T_{\mathrm{eq}} = 1848$ *K* (ν_X — *stechiometrické koeficienty p.m.,* α-C_2S *a M v rovnici (1)*). *Bod 6 predstavuje hodnotu relatívnej entalpie* C_3MS_2 *pri rovnovážnej teplote* $T_{\mathrm{eq}} = 1848$ *K. Hodnota* $\Delta H_{\mathrm{in.\,dis},\,C_3MS_2}$ *je daná rozdielom poradníc bodov 5 a 6.*

ОПРЕДЕЛЕНИЕ ТЕПЛОТЫ ИНКОНГРУЕТНОГО РАСПАДА МЕРВИНИТА

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Измеряли величины изменения энтальпии при охлаждении мервинита, перитектического расплава молярного состава 1,193 CaO. 0,697 MgO . 1 SiO_2 и MgO между подобранными температурами и температурой 298 K и величины теплоты растворения мервинита, перитектического расплава, γ-Ca_2SiO_4, $Mg(OH)_2$ и H_2O при температуре 298 K в растворяющей смеси концентрированной HF и концентрированной HNO_3 (2 : 1). На основании полученных величин и расчитанной температурной зависимости изменения энтальпии при охлаждении $\alpha - C_2S$ (на основании табелизированных величин [7]) между температурами $T > 1693$ K и температурой 298 K, определяли температурные зависимости относительной энтальпии мервинита, перитектического расплава, α-Ca_2SiO_4 и MgO (т. е. фаз, которые равновесно сосуществуют при инконгруентном распаде мервинита):
$H_{\mathrm{rel},\,C_3MS_2,\,\varphi} = 8{,}989 \,.\, 10^2 + 2{,}272 \,.\, 10^{-1}\,T + 5{,}902 \,.\, 10^{-5}T^2$ [кДж. моль$^{-1}$]
с погрешностью $\delta(H_{\mathrm{rel},\,C_3MS_2,\,\varphi}) = 11$ кДж. моль$^{-1}$,
$H_{\mathrm{rel,p.m.},\varphi} = 9{,}46 \,.\, 10^1 + 3{,}83 \,.\, 10^{-1}T$ [кДж. моль$^{-1}$]
с погрешностью $\delta(H_{\mathrm{rel,p.m.},\varphi}) = 7{,}9$ кДж. моль$^{-1}$,
$H_{\mathrm{rel},\,\alpha\text{-}C_2S,\,\varphi} = 4{,}825 \,.\, 10^2 + 1{,}347 \,.\, 10^{-1}T + 2{,}307 \,.\, 10^{-5}T^2$ [кДж. моль$^{-1}$]
с погрешностью $\delta(H_{\mathrm{rel},\,\alpha\text{-}C_2S,\,\varphi}) = 4{,}1$ кДж. моль$^{-1}$ и

$H_{\mathrm{rel,M},\varphi} = 1{,}605 \,.\, 10^2 + 4{,}672 \,.\, 10^{-2}T + 1{,}097 \,.\, 10^{-6}T^2$ [кДж. моль$^{-1}$]
с погрешностью $\delta(H_{\mathrm{rel,M},\varphi}) = 1{,}2$ кДж. моль$^{-1}$.

Теплоту инконгруентного распада мервинита при равновесной температуре 1848 К устанавливали на основании величин относительной энтальпии C_3MS_2, перитектического расплава, α-C_2S и MgO при этой температуре и на основании массового баланса реакции инконгруентного распада мервинита и получали величину:
$\Delta H_{\mathrm{in.dis},C_3MS_2,\varphi} = (125 \pm 15)$ кДж. моль$^{-1}$.
Изменение энтропии при инконгруентном распаде мервинита $\Delta S_{\mathrm{in.dis},C_3MS_2,\varphi} = (67{,}5 \pm 8{,}1)$ Дж. моль$^{-1}$. К$^{-1}$.

Рис. 1. Температурные зависимости ($\nu_X H_{\mathrm{rel,X},\varphi}$); *1* — C_3MS_2, *2* — *p.m.*, *3* — α-C_2S, *4* — *M*. *Точка 5 представляет собой величину* $\Sigma\nu_X H_{\mathrm{rel},X,\varphi}$($X$ — p.m., α-C_2S, M) *при равновесной температуре* $T_{\mathrm{eq}} = 1848$ К(ν_X — *стехиометрические коэффициенты* p.m., α-C_2S *и* M *в уравнении* (*1*)). *Точка 6 представляет собой величину относительной энтальпии* C_3MS_2 *при равновесной температуре* $T_{\mathrm{eq}} = 1848$ К. *Величина* $\Delta H_{\mathrm{in.dis},C_3MS_2}$ *дана различием координат точек 5 и 6.*