Determination of the heat of fusion of $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (gehlenite)

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Dedicated to Corresponding Member M. Zikmund, in honour of his 65th birthday

Gehlenite ($\text{C}_2\text{AS}$) and the melt of composition corresponding to $\text{C}_2\text{AS}$ were prepared by a precursor method. The temperature dependences of the relative enthalpy of gehlenite and of the melt $\text{C}_2\text{AS}$ were determined in the temperature intervals $1519 \text{ K—1799 K}$ and $1873 \text{ K—1948 K}$, respectively. Combination of measurements in the drop calorimeter and in the calorimeter for determination of the heat of solution was used. On the basis of these data the value of the heat of fusion and the entropy of fusion of gehlenite were determined at the equilibrium temperature 1863 K. It was found that

$$\Delta H_{\text{fus}}(\text{C}_2\text{AS},\text{cryst}; 1863 \text{ K}) = (172.1 \pm 6.0) \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{fus}}(\text{C}_2\text{AS},\text{cryst}; 1863 \text{ K}) = (92.4 \pm 3.2) \text{ J mol}^{-1} \text{ K}^{-1}$$

Besides anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is the second ternary compound formed in the system CaO—Al$_2$O$_3$—SiO$_2$. (In this paper the formulas for oxides CaO, Al$_2$O$_3$, and SiO$_2$ will be abbreviated as C, A, and S, respectively.) The temperature of congruent melting of gehlenite given...
in literature by different authors ranges from 1584 °C to 1593 °C [1—3]. In this work as the most reliable the temperature of fusion 1863 K (1590 °C) was chosen [2].

The aim of this work is to obtain the calorimetric value of the heat of fusion of gehlenite at its equilibrium temperature of fusion. The only value of this quantity reported in literature [4] has not been probably determined by the calorimetric method. The system CaO—Al₂O₃—SiO₂ is fundamental in the technologies of cement clinker and glass and it forms base of blast-furnace slags. Thus this work is a contribution to the enthalpic analysis of this important system.

For determination of the heat of fusion of gehlenite an indirect calorimetric method was used [5, 6]. Using this method we need to know the relative values (these are related to a chosen reference state) of the enthalpy of crystalline C₂AS and of the melt C₂AS at the equilibrium melting temperature of gehlenite \( T_{\text{fus}} = 1863 \text{ K} \). The heat of fusion of gehlenite is calculated on the basis of the Hess law. The values of the relative enthalpy \( (H_{\text{rel}}) \) of crystalline C₂AS and of corresponding melt at \( T_{\text{fus}} = 1863 \text{ K} \) were determined by extrapolation from the temperature dependences of the relative enthalpy of both phases. These temperature dependences were determined from calorimetric measurements using the method of double calorimetry [5, 6]. The value of the relative enthalpy of the corresponding phase equals (except the sign) to the sum of changes in enthalpy of the sample when it is cooled from the chosen temperature to the temperature of 298 K in a drop calorimeter \( (\Delta H_{\text{cool}}) \) and then dissolved at 298 K in a calorimeter for determination of the heat of solution \( (\Delta H_{\text{sol}}) \)

\[ H_{\text{rel}} = -(\Delta H_{\text{cool}} + \Delta H_{\text{sol}}) \]  

It follows that this quantity is related to the state of the phase in the dissolving mixture. As the solvent aqueous solution of hydrofluoric acid \( (w(\text{HF}) = 40\%) \) and hydrochloric acid \( (1 \text{ volume part of the acid } (w(\text{HCl}) = 35—38\%) \) and 1 volume part of H₂O) in volume ratio 2 : 1 was used. As will be discussed later, the solvent was saturated with CaF₂. This mixture was used for measuring the heats of solution of both phases C₂AS.

The necessity to use two calorimeters for determination of the heat of fusion of gehlenite follows from unreproducibility of the phase composition of the samples formed at cooling of the melt C₂AS in the drop calorimeter. The quantities of glass and crystal phases and their structure in cooled sample may differ. As the result of that \( \Delta H_{\text{cool}} \) and \( \Delta H_{\text{sol}} \) of the sample depend on the regime of cooling of the sample. The value of \( H_{\text{rel}} \) however, is only the function of temperature.

At the measurement of the heat of solution of gehlenite or of the cooled melt C₂AS it is important that the ions Ca²⁺ be quantitatively removed by precipita-
tion in the form of fluoride or fluoroaluminate as their formation is accompanied with a heat effect. To ensure this 150 mg CaCO₃ was added to 1 dm³ of the dissolving mixture. This was sufficient for saturation of the mixture with CaF₂. (Surplus of calcium ions is precipitated in the form of CaF₂.)

Experimental

Preparation of samples

Both gehlenite and the melt C₂AS were prepared by the precursor method described in [7]. As starting substances at the synthesis sol of silicic acid, CaCO₃ (Specpure, JMC), and metal aluminium (w(Al) = 99.999 %, The Research Institute of Metals, Panenské Březany) were used. Sol of silicic acid was prepared from water glass as follows. Water glass was diluted with water in the ratio 1:8—1 10 and flowed through the layer of the ion exchanger DOWEX 50W × 8. The cations were replaced by protons, which resulted in formation of sol of silicic acid. Concentration of solution expressed in content of SiO₂ was approx. 3 mass %. The analysis by the atomic emission spectroscopy proved that no alkalis are present in the dried sample. As the sol of silicic acid polymerizes quite quickly (from several minutes to one week depending on the content of silicic acid) it was necessary to stabilize it by addition of ammonia. When approx. 8 cm³ NH₄OH (w(NH₃) ≥ 25 %) to 1 dm³ of sol was added (pH = 10 was achieved) the sol was stable and during one year no changes in its properties were observed.

By heating the precursor to the temperature of 500 °C—600 °C the ideally homogenized mixture of oxides CaO, Al₂O₃, and SiO₂ was obtained. When this mixture was heated for 4 h at the temperature of 1000 °C gehlenite with the addition of ca. 2 mole % of other minerals was formed. X-Ray diffraction pattern of the sample indicates that the admixtures can be formed by CS and calcium aluminates which at the temperature 1000 °C have not reacted under formation of gehlenite. (The amount of the admixtures was estimated from the X-ray pattern. As the admixtures should form gehlenite, their mass % in the mixture equal their mole %.) For diminishing the amount of the admixtures the sample should be heated up to 1300 °C. However, the sample calcined at 1300 °C dissolves much worse than the sample calcined only at 1000 °C. For this reason the calorimetric measurements of heat of solution of crystalline phase were done with the sample prepared at 1000 °C. As it will be shown the effect of impurities on the values of ΔHₕₗ and ΔHₕᵢ can be neglected.

Molten C₂AS was obtained by melting of gehlenite in sealed crucible (PtRh 10) at the temperature 1650 °C for 4 h. After quenching the sample in liquid nitrogen the sample of glass with partly crystallized gehlenite was obtained. Crystallization of gehlenite from the C₂AS melt makes no trouble because at measurement in the drop calorimeter the sample is again melted at high temperature. The described procedure was used for better homogenization of the sample.
Changes in enthalpy at cooling of gehlenite and of the melt $C_2AS$ from chosen temperatures to the temperature of 298 K ($\Delta H_{\text{cool}}$) were measured in the drop calorimeter [8]. The heat of solution of gehlenite and of products of the cooled melt $C_2AS$ in the mixture of acids was measured in “solution” calorimeter at the temperature of 298 K. The apparatus is described in [9].

**Determination of the temperature dependence of the relative enthalpy of gehlenite ($H_{\text{rel.}}(C_2AS,\text{cryst})$)**

Using the drop calorimeter the enthalpic changes at cooling of gehlenite from six temperatures lying in the temperature range 1519 K—1799 K to the temperature of 298 K were measured. These values are given in Table I ($\Delta H_{\text{cool}}(C_2AS,\text{cryst})$). Owing to the Neumann—Kopp rule on the summation of molar heat capacities the influence of admixtures of CS and of calcium aluminates on the values of $\Delta H_{\text{cool}}(C_2AS,\text{cryst})$ is negligible.

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$-\Delta H_{\text{cool}}(C_2AS,\text{cryst})$ kJ mol$^{-1}$</th>
<th>$-\Delta H_{\text{cool.}}(C_2AS,\text{cryst})$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1519</td>
<td>335.9</td>
<td>337.3</td>
</tr>
<tr>
<td>1567</td>
<td>354.1</td>
<td>353.0</td>
</tr>
<tr>
<td>1582</td>
<td>359.5</td>
<td>358.0</td>
</tr>
<tr>
<td>1691</td>
<td>393.2</td>
<td>394.6</td>
</tr>
<tr>
<td>1730</td>
<td>407.5</td>
<td>407.9</td>
</tr>
<tr>
<td>1799</td>
<td>432.5</td>
<td>431.8</td>
</tr>
</tbody>
</table>

The temperature dependence of $\Delta H_{\text{cool.}}(C_2AS,\text{cryst})$ ($\varphi$ denotes the mean value) was calculated from the experimental data on enthalpy of cooling of gehlenite using the least-squares method. It follows

$$\frac{-\Delta H_{\text{cool.}}(C_2AS,\text{cryst})}{\text{kJ mol}^{-1}} = -6.38 \times 10^1 + 2.019 \times 10^{-1} \frac{T}{K} + 4.090 \times 10^{-5} \frac{T^2}{K^2}$$

The error in determination of the change in enthalpy at cooling of gehlenite $\delta(\Delta H_{\text{cool.}}(C_2AS,\text{cryst})) = 1.6 \text{ kJ mol}^{-1}$ was determined in the following way.
The error of the regression function (2) was divided by the square root of the number of measurements and multiplied by the Student coefficient for the given degree of freedoms of the regression and for the reliability coefficient $(1 - \alpha) = 0.95$ [10]. The values of $\Delta H_{\text{cool,} \varphi}(C_2AS, \text{cryst})$ calculated according to eqn (2) at temperatures used for measurements are compared with experimental data in Table 1.

The heat of solution of gehlenite was measured in the “solution” calorimeter at 298 K. Because the samples contained impurities we shall denote the measured quantity as $\Delta H_{\text{sol}}(C_2AS, \text{cryst, impur})$. The negative values of the heat of solution of samples, the negative value of the arithmetic mean of these values ($- \Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur})$), and the error of determination of the arithmetic mean of the heat of solution of sample in the mixture of acids ($\delta(\Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur}))$) are presented in Table 2. The error of $\Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur})$ was determined as the error of the arithmetic mean of the heat of solution of the sample of gehlenite containing admixtures using the Student distribution of errors. For the given number of measurements and chosen reliability coefficient $(1 - \alpha) = 0.95$ the Student coefficient was read from [10].

### Table 2

Experimental values of the heat of solution of the samples consisting of gehlenite and unreacted admixtures and the error in determination of this quantity

<table>
<thead>
<tr>
<th>$- \Delta H_{\text{sol}}(C_2AS, \text{cryst, impur})$</th>
<th>$- \Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur})$</th>
<th>$\delta(\Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur}))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>851.6</td>
<td>850.5</td>
<td>4.9</td>
</tr>
<tr>
<td>854.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>845.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>848.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>845.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>857.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determination of the arithmetic mean of the heat of solution of gehlenite ($\Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst})$) from the experimentally determined value of $\Delta H_{\text{sol,} \varphi}(C_2AS, \text{cryst, impur})$ is based on the assumption that the admixtures CS and CA are present in equimolar ratio. (Composition of the precursor was identical with the composition of gehlenite so this assumption has to be fulfilled.) Then the experimental value of the arithmetic mean of the heat of solution of the sample of gehlenite containing admixtures can be composed of two parts: $\Delta H_{\text{sol,} \varphi}$ of gehlenite and $\Delta H_{\text{sol,} \varphi}$ of admixtures. Taking into account their mole fractions in the sample ($x$ is the mole fraction of C$_2$AS, $(1 - x)$ is the...
mole fraction of admixture) and the reaction heat $\Delta H_r$ of the reaction $\text{CS} + \text{CA} \rightarrow \text{C}_2\text{AS}$ and $\Delta H_{\text{sol}, \varphi}$ of gehlenite we obtain

$$\Delta H_{\text{sol}, \varphi}(\text{C}_2\text{AS}, \text{cryst}) = \Delta H_{\text{sol}, \varphi}(\text{C}_2\text{AS}, \text{cryst}, \text{impur}) - (1 - x) \cdot \Delta H_r \quad (3)$$

The value of $\Delta H_r$ can be calculated from heats of formation of $\text{C}_2\text{AS}$, CS [2], and CA [11], the value of $\Delta H_{\text{sol}, \varphi}(\text{C}_2\text{AS}, \text{cryst}, \text{impur})$ is given in Table 2, and the mole fraction $(1 - x)$ was estimated to be 0.02. Then from the relationship (3) we can obtain the value of the arithmetic mean of the heat of solution of gehlenite

$$\Delta H_{\text{sol}, \varphi}(\text{C}_2\text{AS}, \text{cryst}) = (-849.9 \pm 4.9) \text{kJ mol}^{-1} \quad (4)$$

It can be seen that this value differs from the experimental value obtained for gehlenite containing admixtures only by 0.6 kJ mol$^{-1}$.

Adding the negative value of the arithmetic mean of the heat of solution of gehlenite (eqn (4)) to the experimental values of $(-\Delta H_{\text{cool}}(\text{C}_2\text{AS}, \text{cryst}))$ (given in Table 1) we obtain the values of relative enthalpy of gehlenite ($H_{\text{rel}}(\text{C}_2\text{AS}, \text{cryst})$).

**Table 3**

Experimental values of $H_{\text{rel}}$ and calculated values of $H_{\text{rel}, \varphi}$ of gehlenite at different temperatures from the interval $<1519 \text{K}; 1799 \text{K}>$

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$H_{\text{rel}}(\text{C}_2\text{AS}, \text{cryst})$ kJ mol$^{-1}$</th>
<th>$H_{\text{rel}, \varphi}(\text{C}_2\text{AS}, \text{cryst})$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1519</td>
<td>1185.8</td>
<td>1187.2</td>
</tr>
<tr>
<td>1567</td>
<td>1204.0</td>
<td>1202.9</td>
</tr>
<tr>
<td>1582</td>
<td>1209.4</td>
<td>1207.9</td>
</tr>
<tr>
<td>1691</td>
<td>1243.1</td>
<td>1244.5</td>
</tr>
<tr>
<td>1730</td>
<td>1257.4</td>
<td>1257.8</td>
</tr>
<tr>
<td>1799</td>
<td>1282.4</td>
<td>1281.7</td>
</tr>
</tbody>
</table>

These data are summarized in Table 3. In this table there are also presented the values of $H_{\text{rel}, \varphi}(\text{C}_2\text{AS}, \text{cryst})$ calculated for given temperatures from the temperature dependence of the relative enthalpy of gehlenite according to the following equation

$$\frac{H_{\text{rel}, \varphi}(\text{C}_2\text{AS}, \text{cryst})}{\text{kJ mol}^{-1}} = 7.861 \times 10^2 + 2.019 \times 10^{-1} \frac{T}{\text{K}} + 4.090 \times 10^{-5} \frac{T^2}{\text{K}^2} \quad (5)$$

This equation was obtained by adding the values of arithmetic mean of the heat of solution of gehlenite (eqn (4)) to the right-hand side of eqn (2). Error in determination of the relative enthalpy of gehlenite $\delta(H_{\text{rel}, \varphi}(\text{C}_2\text{AS}, \text{cryst}))$ was determined from the errors $\delta(\Delta H_{\text{cool}, \varphi}(\text{C}_2\text{AS}, \text{cryst}))$ and $\delta(\Delta H_{\text{sol}, \varphi}(\text{C}_2\text{AS}, \text{cryst}))$ on the basis of the Gauss law of spreading of errors and it equals $\delta(H_{\text{rel}, \varphi}(\text{C}_2\text{AS}, \text{cryst})) = 5.2 \text{kJ mol}^{-1}$.  

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Table 4

Experimental values \((-\Delta H_{\text{cool}})\), \((-\Delta H_{\text{sol,p}})\), and \(H_{\text{rel}}\) of the melt \(\text{C}_2\text{AS}\) and the calculated values of \(H_{\text{rel,p}}(\text{C}_2\text{AS},\text{melt})\) at different temperatures from the interval \(\langle 1873 \text{ K} ; 1948 \text{ K} \rangle\)

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(-\Delta H_{\text{cool}}(\text{C}_2\text{AS,melt})) (kJ mol(^{-1}))</th>
<th>(-\Delta H_{\text{sol,p}}(\text{C}_2\text{AS,melt})) (kJ mol(^{-1}))</th>
<th>(H_{\text{rel}}(\text{C}_2\text{AS,melt})) (kJ mol(^{-1}))</th>
<th>(H_{\text{rel,p}}(\text{C}_2\text{AS,melt})) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1873</td>
<td>545.1</td>
<td>937.1</td>
<td>1482.2</td>
<td>1481.5</td>
</tr>
<tr>
<td>1888</td>
<td>548.9</td>
<td>938.2</td>
<td>1487.1</td>
<td>1489.3</td>
</tr>
<tr>
<td>1908</td>
<td>561.5</td>
<td>939.9</td>
<td>1501.4</td>
<td>1499.6</td>
</tr>
<tr>
<td>1932</td>
<td>571.7</td>
<td>941.9</td>
<td>1513.6</td>
<td>1512.1</td>
</tr>
<tr>
<td>1948</td>
<td>584.3</td>
<td>934.7</td>
<td>1519.0</td>
<td>1520.4</td>
</tr>
</tbody>
</table>
Determination of the temperature dependence of the relative enthalpy of the melt $\text{C}_2\text{AS}$ ($H_{\text{rel,} \varphi}(\text{C}_2\text{AS,melt})$)

For determination of the temperature dependence of the relative enthalpy of the melt $\text{C}_2\text{AS}$ it was necessary to measure the changes in enthalpy at cooling of the melt from chosen temperatures to 298 K and then to determine the heat of solution of cooled samples. Five samples cooled from temperatures from the range 1873 K—1948 K were investigated. The results ($\Delta H_{\text{cool}}(\text{C}_2\text{AS,melt})$) are summarized in Table 4.

Because of partial crystallization of gehlenite at cooling the melt $\text{C}_2\text{AS}$ in drop calorimeter and/or change in structure of formed glasses (this change takes place in the region of transformation temperature) it was necessary to determine the heat of solution of each sample studied in the drop calorimeter. Negative values of the arithmetic mean of three or four measurements of heat of solution made for each sample are given in Table 4 ($-\Delta H_{\text{sol,} \varphi}(\text{C}_2\text{AS,melt})$). By adding these values to the values of ($-\Delta H_{\text{cool}}(\text{C}_2\text{AS,melt})$) (they are also given in this table) the relative enthalpies of the melt $\text{C}_2\text{AS}$ for chosen temperatures were obtained. They are denoted as $H_{\text{rel}}(\text{C}_2\text{AS,melt})$ and they are also presented in Table 4.

From the experimental values of the relative enthalpy of the melt $\text{C}_2\text{AS}$ the temperature dependence of this quantity was obtained using the least-squares method. It holds

$$H_{\text{rel,} \varphi}(\text{C}_2\text{AS,melt}) = 5.109 \times 10^2 + 5.182 \times 10^{-1} \frac{T}{K}$$ \hspace{1cm} (6)

Error $\delta(H_{\text{rel,} \varphi}(\text{C}_2\text{AS,melt})) = 2.9 \text{kJ mol}^{-1}$ This error was calculated from the error of the regression function (6) by dividing it by the square root of the number of measurements and multiplying it by the Student coefficient taken for the given degree of freedoms of the regression and for the reliability coefficient $(1 - \alpha) = 0.95$ [10]. The values of $H_{\text{rel,} \varphi}(\text{C}_2\text{AS,melt})$ calculated according to eqn (6) are compared with experimental data in Table 4.

Calculation of the heat of fusion of gehlenite

From the temperature dependences of the relative enthalpy of the melt $\text{C}_2\text{AS}$ (relationship (6)) and of gehlenite (relationship (5)) the relative enthalpies of both phases at the equilibrium temperature of fusion of gehlenite ($T_{\text{fus}} = 1863 \text{K}$) were calculated. It follows $H_{\text{rel,} \varphi}(\text{C}_2\text{AS,melt}; \text{1863 K}) = (1476.3 \pm 2.9) \text{kJ mol}^{-1}$ and $H_{\text{rel,} \varphi}(\text{C}_2\text{AS,cryst}; \text{1863 K}) = (1304.2 \pm 5.2) \text{kJ mol}^{-1}$. The heat of fusion of gehlenite equals the difference of these two values.
The error of $\Delta H_{\text{fus}, \varphi}(C_2\text{AS,cryst}; 1863 \text{ K})$ was determined from $\delta(H_{\text{rel}, \varphi}(C_2\text{AS,melt}; 1863 \text{ K}))$ and $\delta(H_{\text{rel}, \varphi}(C_2\text{AS,cryst}; 1863 \text{ K}))$ using the Gauss law of spreading of errors.

Dividing the heat of fusion of gehlenite by the equilibrium temperature of its fusion the entropy of melting of gehlenite was obtained

$$\frac{\Delta S_{\text{fus}, \varphi}(C_2\text{AS,cryst}; 1863 \text{ K})}{\text{J mol}^{-1} \text{K}^{-1}} = \frac{\Delta H_{\text{fus}, \varphi}(C_2\text{AS,cryst}; 1863 \text{ K})}{\text{J mol}^{-1} 1863} = 92.4 \pm 3.2 \quad (8)$$

In Fig. 1 both the experimental and calculated values of the relative enthalpy of gehlenite and of the melt $C_2\text{AS}$ are plotted as function of temperature (curve 1 and curve 2, respectively). The value of $\Delta H_{\text{fus}, \varphi}(C_2\text{AS,cryst}; 1863 \text{ K})$ is given in this figure as the difference of relative enthalpy of the melt $C_2\text{AS}$ at the temperature of 1863 K (point $B$) and the relative enthalpy of gehlenite at the same temperature (point $A$).

![Fig. 1. The temperature dependences of $H_{\text{rel}}(C_2\text{AS})$.](image)

1. Gehlenite; 2. the melt $C_2\text{AS}$.

The enthalpy of fusion $\Delta H_{\text{fus}}(C_2\text{AS}; 1863 \text{ K})$ is given as the difference of the relative enthalpies at the points $B$ and $A$.

**Results and discussion**

Form of the regression relationship $H_{\text{rel}, \varphi}(C_2\text{AS,cryst}) = f(T)$ is given by the form of the regression relationship ($-\Delta H_{\text{cool}, \varphi}(C_2\text{AS,cryst}) = f(T)$). These two dependences differ by the value of ($-\Delta H_{\text{sol}, \varphi}(C_2\text{AS,cryst})$). In literature it is
common to use the regression function in the form of \((-\Delta H_{\text{cool, } \varphi}(X)) = A + BT + CT^2 + DT^{-1}\). In this work it has been found that the simpler form (eqn (2)) of the regression relationship fits well with experimental data. These two functions differ less than 0.1 kJ mol\(^{-1}\) in the investigated temperature region. Thus it follows that the simpler form of eqn (2) is suitable for description of the temperature dependence of changes in enthalpy of gehlenite at its cooling.

The literature data [2] on the temperature dependence of the molar heat capacity of gehlenite are given in the form from which it follows \((-\Delta H_{\text{cool, } \varphi}(C_2\text{AS,cryst})) = A + BT + CT^2 + DT^{-1}\). From the comparison of the values of \((-\Delta H_{\text{cool, } \varphi}(C_2\text{AS,cryst}))\) calculated according to eqn (2) with literature data [2] it follows that the values obtained in this work (eqn (2)) are in the temperature interval \(<1519\text{ K}; 1799\text{ K}\rangle\) lower than the values calculated from tabulated constants [2]. The difference between these two sets of values decreases with increasing temperature. At the temperature of 1519 K this difference is 2.68 \% while at 1799 K it is only 0.94 \%. At the temperature of melting of gehlenite, \(i.e. 1863\text{ K}\), the values of \((-\Delta H_{\text{cool, } \varphi}(C_2\text{AS,cryst}; 1863\text{ K}))\) calculated according to eqn (2) and literature [2] differ only by 0.53 \%, which corresponds to 2.4 kJ mol\(^{-1}\). If we used at the calculation of the temperature dependence of the relative enthalpy of gehlenite \((-\Delta H_{\text{cool, } \varphi}(C_2\text{AS,cryst})) = f(T)\) the literature data instead of the experimental values found in this work, then at the temperature of 1863 K the value of relative enthalpy of gehlenite would be by 2.4 kJ mol\(^{-1}\) higher and the heat of fusion of gehlenite would be by this value lower. It follows that this difference is smaller than the numerical error in determination of the heat of fusion of gehlenite (eqn (7)). For description of the temperature dependence of the relative enthalpy of the melt \(C_2\text{AS}\) a linear relationship was used (eqn (6)). This is because the relative enthalpy of the melt \(C_2\text{AS}\) could be measured in relatively narrow temperature interval \(<1873\text{ K}; 1948\text{ K}\rangle\). This form of regression equation follows, however, also from the fact that the molar heat capacity of melts is usually considered as constant [2].

Determination of the heat of fusion by the indirect method used in this work is influenced also by uncertainty in the temperature of fusion of gehlenite [1—3]. We can estimate this influence so that we calculate the heat of fusion at the lowest and the highest temperature of fusion given in literature, \(i.e. 1584\text{ °C}\) and 1593 °C, respectively. At \(T_{\text{fus}} = 1857\text{ K}\) (the lowest value) we obtain \(\Delta H_{\text{fus, } \varphi}(C_2\text{AS,cryst}; 1857\text{ K}) = (171.1 \pm 6.0)\text{ kJ mol}^{-1}\) For \(T_{\text{fus}} = 1866\text{ K}\) (the highest value) \(\Delta H_{\text{fus, } \varphi}(C_2\text{AS,cryst}; 1866\text{ K}) = (172.6 \pm 6.0)\text{ kJ mol}^{-1}\) The difference of these values is smaller than the error of determination of the heat of fusion of gehlenite. Thus the uncertainty in the temperature of fusion of gehlenite does not influence significantly the value of the heat of its fusion. This is caused by that the slopes of the temperature dependences of relative enthalpy of gehlenite
and the melt C$_2$AS in the vicinity of the melting point have relatively similar values.

According to paper [4] the enthalpy of fusion of gehlenite $\Delta H_{\text{fus}}$(C$_2$AS,-cryst) = 156.2 kJ mol$^{-1}$. This is by 10% lower than the value determined by calorimetric method in this work.

**References**