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Note

Heat capacities of C_3AH_6, $C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$*

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Babushkin et al.[1, 2] have reported the heat capacities of C_3AH_6, $C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$ in the form of $c_p = 61.68 + 139{,}9 \times 10^{-3}T$, $c_p = 108.62 + 273 \times 10^{-3}T$ and $c_p = 186.00 + 717.2 \times 10^{-3}T$ cal mole^{-1}, respectively. These functions were calculated by using the method of structural analogy[3] and it was shown for some cases[2] that such an approximation is useful. The semi-empirical c_p data however can lead to a great error, especially when used for the calculation of heterogeneous chemical equilibria[4]; for this reason experimentally determined data are needed.

PREPARATION AND CHARACTERISATION

Samples were prepared by the following methods.

C_3AH_6 was prepared by heating C_3A in distilled water at 180 °C in an autoclave for 120 h according to the method described by Thorwaldson et al.[5].

$C_4A\bar{S}H_{12}$ was prepared by heating C_3A and gypsum (molar ratio 1:1) in distilled water at 150 °C in an autoclave for 50 h, as reported by Kuzel[6].

$C_6A\bar{S}_3H_{32}$ (ettringite) was prepared by a modification of the method of Jones[7] by shaking suitable stoichiometric quantities of C_3A and gypsum in excess of water at 25 °C for 3 weeks in a stoppered bottle.

All reagents were of analytical purity and the necessary precautions were taken against carbonation. The products were rapidly filtered and dried in a desiccator filled with the saturated solution of $NaClO_3$ (RH = 75% at 20 °C).

The compounds were characterized by X-ray diffraction, chemical analysis, scanning electron microscopy and thermogravimetric analysis. Chemical analysis and TG curves showed that only a small quantity of $CaCO_3$ was present in the ettringite sample.

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* In the formulae, the cement chemist's notation (C = CaO, A = Al_2O_3, S = SO_3, H = H_2O) is used.

APPARATUS AND TECHNIQUE

The heat capacities were measured using a Perkin–Elmer Differential Scanning Calorimeter (Type DSC-1B). For the calibration of the temperature scale the melting of gallium and indium was employed. For the evaluation of heat capacities from DSC data and their temperature dependences the method described by O'Neill[8] was applied using a single crystal of sapphire as a standard sample. The reproducibility of the results, however, was not satisfactory enough where pulverized sample was used. Improved results were achieved when the suspension of the sample in alcohol was directly evaporated in the sample holder[9] so that a layer of the material was created in intimate contact with the metal surface. The temperature gradient between the sample and the sample holder was thus diminished and the accuracy of individual measurements of c_p was better as ± 3 relative percent. Each DSC run was made at least five times.

Experimentally obtained c_p data for ettringite were corrected on the content of $CaCO_3$ in the sample.

The determination of c_p data from DSC curves was limited by the thermal decomposition of the sample, i.e. the decomposition of ettringite begins at 70°C in air and the temperature dependences of c_p were thus established only up to 60°C, similarly for $C_4A\bar{S}H_{12}$ up to 80°C and for C_3AH_6 up to 200°C.

RESULTS AND DISCUSSION

The method of least squares was utilized to fit constants in linear relations between c_p and temperature (T), i.e., $c_p = a + bT$. The results obtained are graphically illustrated in Figs. 1–3.

From the C_3AH_6 plots in Fig. 1 it can be seen that the experimentally determined data are in good agreement with the calculated data. In contrast, the differences

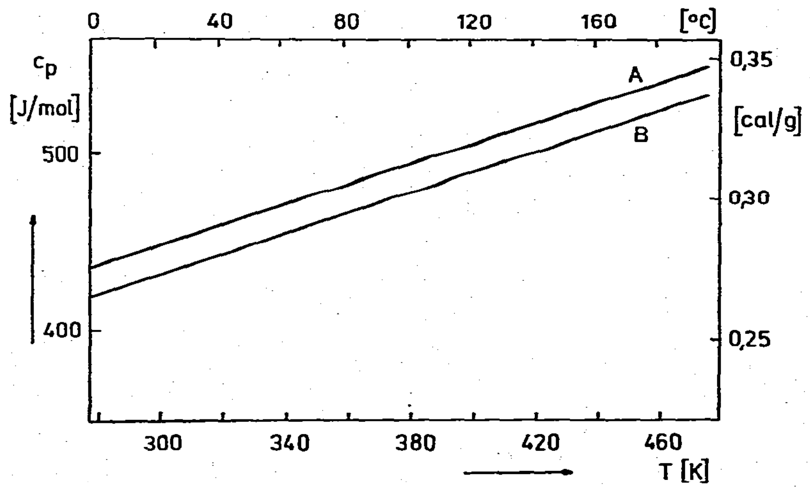
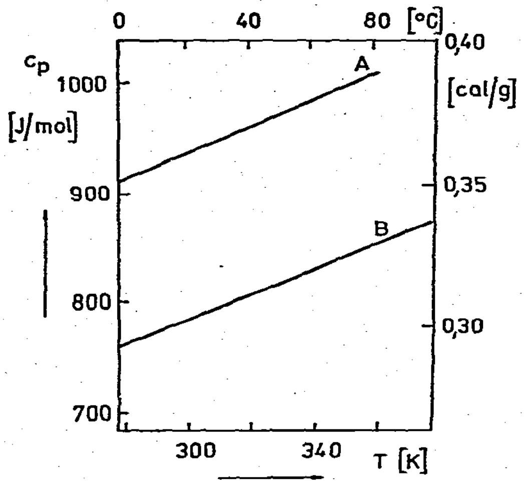


Fig. 1. The c_p–temperature dependence of C_3AH_6. A, experimental; B, calculated.



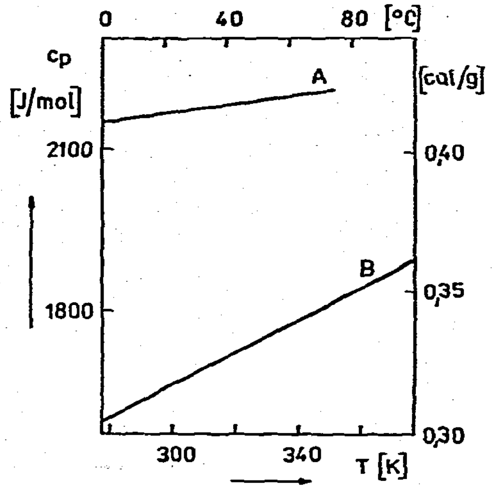


Fig. 2. The c_p–temperature dependence of $C_4A\check{S}H_{12}$. A, experimental; B, calculated.

Fig. 3. The c_p–temperature dependence of $C_6A\check{S}H_{32}$. A, experimental; B, calculated.

TABLE 1

TEMPERATURE DEPENDENCES OF c_p

Substance	c_p *(J mole*$^{-1}$*)*	c_p *(cal mole*$^{-1}$*)*	*Temp. interval (K)*
C_3AH_6	$292.09 + 561 \times 10^{-3}T$	$69.76 + 134 \times 10^{-3}T$	273–473
$C_4A\check{S}H_{12}$	$594.18 + 1168 \times 10^{-3}T$	$141.91 + 279 \times 10^{-3}T$	273–353
$C_6A\check{S}_3H_{32}$	$1939.12 + 789 \times 10^{-3}T$	$463.13 + 188 \times 10^{-3}T$	273–333

are noticeable for the remaining two hydrates (Figs. 2 and 3). In addition the ettringite exhibits a considerable deviation in c_p temperature dependence (compare Fig. 3).

The temperature dependences of c_p are given in Table 1.

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