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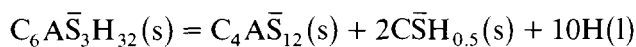
DIRECT DETERMINATION OF STANDARD ENTHALPIES AND GIBBS ENERGIES OF FORMATION AND ABSOLUTE ENTROPIES OF HYDRATED CALCIUM SULPHOALUMINATES AND CARBOALUMINATES

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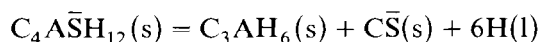
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The differential hydrothermal analysis (DHA) method [1–3] was used to determine the reaction enthalpies for the following reactions (where C = CaO, S = SiO₂, A = Al₂O₃, H = H₂O, \bar{C} = CO₂ and \bar{S} = SO₃)



$$\Delta_r H = (188.41 \pm 4.19) \text{ kJ mol}^{-1} \quad (1)$$



$$\Delta_r H = (50.66 \pm 4.19) \text{ kJ mol}^{-1} \quad (2)$$



$$\Delta_r H = (52.40 \pm 2.1) \text{ kJ mol}^{-1} \quad (3)$$

On the assumption of a zero value of ΔC_p for the reactions, the standard enthalpies of formation were calculated from these values using the standard enthalpies of formation of the substances involved [4]

$$\Delta_f H^\ominus (C_4A\bar{S}_3H_{32}) = -17527.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus (C_4A\bar{S}H_{12}) = -8752.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus (C_4A\bar{C}H_{11}) = -8241.0 \text{ kJ mol}^{-1}$$

The equilibrium temperatures of the reactions were determined by extrapolating the dependence of the onset of the corresponding DHA peak on the heating rate ϕ towards $\phi \rightarrow 0$: $T_{r_1} = (384 \pm 1) \text{ K}$, $T_{r_2} = (450 \pm 2) \text{ K}$ and $T_{r_3} = (403 \pm 2) \text{ K}$.

From the established values of $\Delta_r H$ and the corresponding equilibrium temperatures it follows for reaction entropies

$$\Delta_r S = \frac{\Delta_r H}{T_r} \quad (4)$$

On the assumption that $\Delta C_p = 0$, the values of the standard absolute entropies were calculated from these values using the standard entropies of the substances involved

$$S^\ominus(\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}) = 1916.73 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}) = 816.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}) = 717.52 \text{ J K}^{-1} \text{ mol}^{-1}$$

From the values of $\Delta_r H$ and $\Delta_r S$ it follows

$$\Delta_r G = \Delta_r H - T\Delta_r S \quad (5)$$

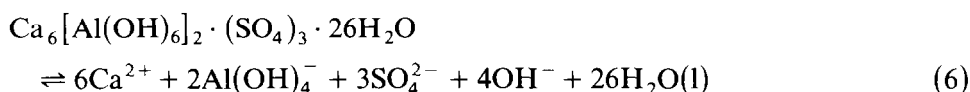
The standard Gibbs energies of formation were then calculated using the values of $\Delta_r G^\ominus$ [4]

$$\Delta_r G^\ominus(\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}) = -15\,202.0 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus(\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}) = -7779.86 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus(\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}) = -7348.55 \text{ kJ mol}^{-1}$$

The solubility products K_a correspond to the equilibria of the reactions



Then

$$K_a = \prod_i a_i^{\nu_i} \quad (9)$$

when a_i is the activity of the solvated species and the activity $a_{\text{H}_2\text{O}} \approx 1$.

The K_a value can be calculated using the equation

$$\Delta_r G^\ominus = -RT \ln K_a \quad (10)$$

in which the values of $\Delta_r G^\ominus$ evaluated above were used. Then, $\Delta_r G^\ominus =$

TABLE 1

Concentrations (mmol dm^{-1})

	CaO	CaSO ₄	Al ₂ O ₃	CaCO ₃
C ₆ A $\bar{\text{S}}$ ₃ H ₃₂	1.223	1.303	0.358	–
C ₄ A $\bar{\text{S}}$ H ₁₂	2.977	0.330	0.920	–
C ₄ A $\bar{\text{C}}$ H ₁₁	1.403	–	–	0.702

235.8 kJ and $K_{a_6} = 4.72 \times 10^{-42}$; $\Delta_{r_7} G^\ominus = 157.24$ kJ and $K_{a_7} = 2.76 \times 10^{-28}$; $\Delta_{r_8} G^\ominus = 179.35$ kJ and $K_{a_8} = 3.71 \times 10^{-32}$.

Zhang et al. [5] measured experimentally the equilibrium concentrations corresponding to reactions (6)–(8) (see Table 1).

The concentrations of ionic species were calculated using the stoichiometry of reactions (6), (7) and (8). For $C_6A\bar{S}_3H_{32}$

$$\begin{aligned} [Ca^{2+}] &= [CaO] + [CaSO_4] \\ [Al(OH)_4^-] &= 2[Al_2O_3] \\ [SO_4^{2-}] &= [CaSO_4] \\ [OH^-] &= 2[CaO] \end{aligned} \quad (11)$$

Then, $K_{s_6}(C_6A\bar{S}_3H_{32}) = [Ca^{2+}]^6 [Al(OH)_4^-]^2 [SO_4^{2-}]^3 [OH^-]^4 = 1.1 \times 10^{-40}$. The values $K_{s_7}(G_4A\bar{S}H_{12}) = 1.7 \times 10^{-28}$ and $K_{s_8}(C_4A\bar{C}H_{11}) = 1.4 \times 10^{-30}$ were obtained in a similar way. The K_a value can be calculated using the equation

$$K_a = K_s K_\gamma \quad (12)$$

where

$$K_\gamma = \prod_i \gamma_i^{\nu_i} \quad (13)$$

and γ_i are the activity coefficients.

The Davies equation [6] which simplifies the calculation of the activity coefficients was used

$$\log \gamma_i = -0.507 |z_i^2| \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \quad (14)$$

where ionic strength I is defined as

$$I = 0.5 \sum_i m_i z_i^2 \quad (15)$$

and m_i is the molality of the i th dissolved ionic species and z_i is the charge of this species. The calculated values of K_a are then

$$K_{a_6}(\text{calc}) = \gamma_{Ca^{2+}}^6 \gamma_{Al(OH)_4^-}^2 \gamma_{SO_4^{2-}}^3 \gamma_{OH^-}^4 K_{s_6} = 4.3 \times 10^{-42}$$

$$K_{a_7}(\text{calc}) = \gamma_{Ca^{2+}}^4 \gamma_{Al(OH)_4^-}^2 \gamma_{SO_4^{2-}}^4 \gamma_{OH^-} K_{s_7} = 1.4 \times 10^{-29}$$

$$K_{a_8}(\text{calc}) = \gamma_{Ca^{2+}}^4 \gamma_{Al(OH)_4^-}^2 \gamma_{CO_3^{2-}}^4 \gamma_{OH^-} K_{s_8} = 1.98 \times 10^{-31}$$

The values of K_a calculated using the values of the standard Gibbs energies of formation of $C_6A\bar{S}_3H_{32}$, $C_4A\bar{S}H_{12}$ and $C_4A\bar{C}H_{11}$ are in satisfac-

TABLE 2

Substance	$\Delta_f G^\ominus$ (kJ mol ⁻¹)	K_s	K_a	
			From $\Delta_f G^\ominus$	From K_s
C ₆ A \bar{S} ₃ H ₃₂	-15202.0	1.1 × 10 ⁻⁴⁰	4.72 × 10 ⁻⁴²	4.3 × 10 ⁻⁴²
C ₄ A \bar{S} H ₁₂	-7779.8	1.7 × 10 ⁻²⁸	2.76 × 10 ⁻²⁸	1.4 × 10 ⁻²⁹
C ₄ A \bar{C} H ₁₁	-7348.5	1.4 × 10 ⁻³⁰	3.71 × 10 ⁻³²	2.0 × 10 ⁻³¹

tory agreement with the values calculated from the experimental measurement of equilibrium concentrations (see Table 2).

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