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Note

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

VLADIMÍR ŠATAVA
Institute of Chemical Technology, Prague 6, Suchbatarova 5 (Czechoslovakia)

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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 = SiO_2, A = Al_2O_3, H = H_2O, $\bar{C} = CO_2$ and $\bar{S} = SO_3$)

$$C_6A\bar{S}_3H_{32}(s) = C_4A\bar{S}_{12}(s) + 2C\bar{S}H_{0.5}(s) + 10H(l)$$

$$\Delta_{r_1}H = (188.41 \pm 4.19)\ \text{kJ mol}^{-1} \qquad (1)$$

$$C_4A\bar{S}H_{12}(s) = C_3AH_6(s) + C\bar{S}(s) + 6H(l)$$

$$\Delta_{r_2}H = (50.66 \pm 4.19)\ \text{kJ mol}^{-1} \qquad (2)$$

$$C_4A\bar{C}H_{11}(s) = C_3AH_6(s) + C\bar{C}(s) + 5H(l)$$

$$\Delta_{r_3}H = (52.40 \pm 2.1)\ \text{kJ mol}^{-1} \qquad (3)$$

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]

$$\Delta_f H^{\ominus}(C_4A\bar{S}_3H_{32}) = -17\,527.7\ \text{kJ mol}^{-1}$$

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

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

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 $\phi \rightarrow 0$: $T_{r_1} = (384 \pm 1)$ K, $T_{r_2} = (450 \pm 2)$ K and $T_{r_3} = (403 \pm 2)$ K.

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

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

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

$$S^{\ominus}(C_4A\bar{S}_3H_{32}) = 1916.73 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^{\ominus}(C_4A\bar{S}H_{12}) = 816.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^{\ominus}(C_4A\bar{C}H_{11}) = 717.52 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$\Delta_r G = \Delta_r H - T\Delta_r S \tag{5}$$

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

$$\Delta_f G^{\ominus}(C_6A\bar{S}_3H_{32}) = -15\,202.0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^{\ominus}(C_4A\bar{S}H_{12}) = -7779.86 \text{ kJ mol}^{-1}$$

$$\Delta_f G^{\ominus}(C_4A\bar{C}H_{11}) = -7348.55 \text{ kJ mol}^{-1}$$

The solubility products K_a correspond to the equilibria of the reactions

$$Ca_6[Al(OH)_6]_2 \cdot (SO_4)_3 \cdot 26H_2O$$
$$\rightleftharpoons 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O(l) \tag{6}$$

$$Ca_4[Al(OH)_6]_2 \cdot (SO_4) \cdot 6H_2O$$
$$\rightleftharpoons 4Ca^{2+} + 2Al(OH)_4^- + SO_4^{2-} + 4OH^- + 6H_2O(l) \tag{7}$$

$$Ca_4[Al(OH)_6]_2 \cdot (CO_3) \cdot 5H_2O$$
$$\rightleftharpoons 4Ca^{2+} + Al(OH)_4^- + CO_3^{2-} + 4OH^- + 5H_2O(l) \tag{8}$$

Then

$$K_a = \prod_i a_i^{\nu_i} \tag{9}$$

when a_i is the activity of the solvated species and the activity $a_{H_2O} \simeq 1$.

The K_a value can be calculated using the equation

$$\Delta_r G^{\ominus} = -RT \ln K_a \tag{10}$$

in which the values of $\Delta_f G^{\ominus}$ evaluated above were used. Then, $\Delta_{r_6} G^{\ominus} =$

TABLE 1

Concentrations (mmol dm^{-1})

	CaO	$CaSO_4$	Al_2O_3	$CaCO_3$
$C_6A\bar{S}_3H_{32}$	1.223	1.303	0.358	–
$C_4A\bar{S}H_{12}$	2.977	0.330	0.920	–
$C_4A\bar{C}H_{11}$	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 $C_6A\bar{S}_3H_{32}$

$$[Ca^{2+}] = [CaO] + [CaSO_4]$$

$$[Al(OH)_4^-] = 2[Al_2O_3]$$

$$[SO_4^{2-}] = [CaSO_4]$$

$$[OH^-] = 2[CaO] \tag{11}$$

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

$$K_a = K_s K_\gamma \tag{12}$$

where

$$K_\gamma = \prod_i \gamma_i^{\nu_i} \tag{13}$$

and γ_i are the activity coefficients.

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

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

where ionic strength I is defined as

$$I = 0.5 \sum_i m_i z_i^2 \tag{15}$$

and m_i is the molality of the ith disolved ionic species and z_i is the charge of this species. The calculated values of K_a are then

$$K_{a_6}(\text{calc}) = \gamma^6_{Ca^{2+}} \gamma^2_{Al(OH_4)^-} \gamma^3_{SO_4^{2-}} \gamma^4_{OH^-} K_{s_6} = 4.3 \times 10^{-42}$$

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

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

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
$C_6A\bar{S}_3H_{32}$	-15202.0	1.1×10^{-40}	4.72×10^{-42}	4.3×10^{-42}
$C_4A\bar{S}H_{12}$	-7779.8	1.7×10^{-28}	2.76×10^{-28}	1.4×10^{-29}
$C_4A\bar{C}H_{11}$	-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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