

HIGH TEMPERATURE HEAT CAPACITY OF NATURAL PROTOLITHIONITE (LITHIAN SIDEROPHYLLITE)

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Protolithionite (lithian siderophyllite) is Li,Fe- mica, containing 1.3-2.8 % Li₂O (formula unit of Li = 0.4-0.8). For calorimetric study the sample of natural protolithionite (chamber pegmatites, Volyn', Ukraine) was chosen. Using its chemical composition (%): SiO₂–42.40; TiO₂–0.50; Al₂O₃–20.83; Fe₂O₃–0.10; FeO–15.84; MnO–0.39; MgO–0.10; ZnO–0.11; CaO–0.04; K₂O–8.85; Na₂O–0.25; Rb₂O–0.70; Cs₂O–0.08; Li₂O–2.50; F–4.83; H₂O⁺–1.72; H₂O[–]–1.75 (Σ=100.99), the chemical formula based on 22 charges was calculated as (K_{0.84}Na_{0.04}Rb_{0.03})(Li_{0.75}Al_{0.99}Fe³⁺_{0.01}Fe²⁺_{0.99}Mn_{0.03}Mg_{0.01}Ti_{0.03})[Si_{3.16}Al_{0.84}O₁₀](OH)_{0.86}F_{1.14}. High temperature heat contents of protolithionite were determined on the heat flux Tian-Calvet microcalorimeter ("Setaram", France) by the "drop" method. The samples weighing 3-8 (±2 · 10^{–3}) mg were dropped directly from room temperature into the calorimeter at experiment temperatures from 472 to 781 K and the enthalpy increments [*H*^o(*T*)-*H*^o(298.15 K)] (Table) were measured. Calibration was performed by dropping standard substance - corundum α-Al₂O₃, the required thermochemical data were taken from [1]. The experimental results were fitted by least-squares method yielding:

$$H^o(T)-H^o(298.15K) = 863.317T-307.030\cdot 10^{-3}T^2+430.837\cdot 10^5T^{-1}-374608 \text{ (J/mol);}$$

$$C_p^o=863.317-614.060\cdot 10^{-3}T-430.837\cdot 10^5T^2 \text{ (J/mol K) in the range 298.15-800 K.}$$

Table. Experimental calorimetric data

Temperature, K	472	566	663	736	781
<i>H</i> ^o (<i>T</i>)- <i>H</i> ^o (298.15K), kJ/mol	56.35±2.44 (6)*	91.03±2.00 (9)	128.84±4.60 (9)	155.60±3.96 (9)	166.17±3.31 (8)

*- experimental errors are expressed at the 95 per cent confidence level, number of determinations is given in parentheses.

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Reference

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