CALORIMETRIC STUDY OF NATURAL POLLUCITE Ogorodova L.P., Melchakova L.V., Kiseleva I.A.

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Pollucite is found in rare-element-rich granitic pegmatites having lithium and niobium-tantalum mineralization. It is an aluminosilicate phase with a cubic lattice representing the Cs end-member of the analcime NaAlSi₂O₆ H_2O - leucite KAlSi₂O₆ - pollucite CsAlSi₂O₆ series. The knowledge of the thermodynamic properties of pollucite, analcime, leucite and their solid solutions is of geological and technological interest. We have determined previously the thermodynamic properties of analcime [1] and leucite [2]. This work is concerned with an experimental investigation of the thermodynamic properties of pollucite. Experimental data on the heat capacities, enthalpies of formation from the oxides and elements of the natural pollucites: Cs_{0.77}Na_{0.14}Rb_{0.04}Al_{0.91}Si_{2.08}O₆·0.34H₂O (Minas Gerais, Brazil) (I) and Cs_{0.84}Na_{0.11}Al_{0.88}Si_{2.10}O₆·0.17H₂O (East Siberia, Russia) (II) have been determined. The heat capacities of the pollucite (II) were measured by DSC method from T=250 K to 810 K. A value of $C_{p,m}^{o}$ (298.15 K)=172.2 J K⁻¹ mol⁻¹ was obtained and the resultant $C_{p,m}^{o}(T)$ equation in the interval T=298.15-610 K was calculated: $C_{nm}^{o}=131.37+181.97\cdot10^{-3}T-11.84\cdot10^{5}T^{2}$, J K⁻¹ mol⁻¹ (±0.36%). The standard enthalpies of formation were determined by a set of thermochemical cycles using decomposition and subsequent dissolution of the dehydration products in molten lead borate at T=973 K. Values of $\Delta_{\rm f} H_{\rm m}^{\rm o}$ (298.15 K) are found to be -3104 ± 13 (pollucite I) and -3090 ± 14 (pollucite II) kJ mol⁻¹. The standard entropies for pollucites were estimated from adiabatic calorimetric data [3] for natural pollucite, taking into account their composition variations. Using these values we calculated the molar Gibbs free energies of formation $\Delta_{\rm f} G_{\rm m}^{\rm o}$ (298.15 K) to be equal -2921 (I) and -2911(II) kJ mol^{-1} .

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