ENTHALPY OF FORMATION AND HEAT CAPACITY OF MUSCOVITE

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The sample of natural muscovite from East Siberia with composition (%): SiO_2 - 44.80; TiO_2 - сл.; Al_2O_3 -35.77; Fe_2O_3 - 0.94; FeO - 1.16; CaO - сл.; MgO - 0.90; K_2O - 10.40; Na_2O - 0.86; H_2O^+ - 4.38; H_2O^- - 0.30 ($\sum$=99.51) was used for calorimetric investigations. The chemical formula calculated on the basis of 22 negative charges is following:
$(K_{0.89}Na_{0.11})_{1.00}(Al_{1.84}Mg_{0.09}Fe^{2+}_{0.07}Fe^{3+}_{0.05})_{2.05}(Si_{3.01}Al_{0.99})_{4.00}O_{10}[(OH)_{1.96}O_{0.02}]_{1.98}$.

The thermo-chemical investigations were performed on Tian-Calvet high-temperature heat-flux microcalorimeter ("Setaram", France). The "transposed temperature drop solution calorimetry" method was used to obtain the enthalpies of formation of muscovite. In each run 3-10 mg of sample was dropped from room temperature into molten $2PbO{\cdot}B_2O_3$ at T=973K. The heat effect measured was thus the sum of the heat content and the enthalpy of solution of the mineral [H^o(973 K)-H^o(298.15 K) + $\Delta_{sol}H^o$(973 K)]. The enthalpy increments of muscovite [$H^o(T)$-H^o(298.15 K)] at T=474, 670, 943 K were measured by "drop" method. Calibration of the calorimeter was performed by dropping pieces of platinum wire (in the solution experiments) and α-Al_2O_3 (in the "drop" experiments) and using their known enthalpies [1].

The standard molar enthalpy of formation of studied natural muscovite from oxides and elements at T=298.15 K was calculated from experimental data using the reference thermodynamic characteristics for needed compounds [1] according to the following equations:

$$\Delta_f H^o_{ox}(298.15\ K)muscovite = \sum\nu_i[H^o(973\ K)-H^o(298{,}15\ K) + \Delta_{sol.}H^o(973\ K)]ox_i - [H^o(973\ K)-H^o(298{,}15\ K) + \Delta_{раств.}H^o(973\ K)]muscovite \quad (1)$$

$$\Delta_f H^o_{el}(298.15\ K)\ muscovite = \Delta_f H^o_{ox}(298.15\ K)\ muscovite + \sum\nu_i\Delta_f H^o_{el}(298.15\ K)ox_i \quad (2)$$

It is taken that all iron in formula is ferric. The obtained values are following: $\Delta_f H^o_{ox}$(298.15 K)= –234.5±10.4 and $\Delta_f H^o_{el}$(298.15 K)= –5915.0±11.0 kJ/mol for muscovite $(K_{0.89}Na_{0.11})_{1.00}(Al_{1.84}Mg_{0.09}Fe^{2+}_{0.07}Fe^{3+}_{0.05})_{2.05}(Si_{3.01}Al_{0.99})_{4.00}O_{10}[(OH)_{1.96}O_{0.02}]_{1.98}$.

Based on the experimental data for natural muscovite, we determined the enthalpy of formation of muscovite with theoretical composition. The specific heats of drop solution were corrected on ideal formula weight. The values of enthalpies of formation of muscovite with composition $KAl_3Si_3O_{10}(OH)_2$ from oxides (-240.2±10.4 kJ/mol) and elements (–5953.2±11.0 kJ/mol) are calculated using equations (1,2) and are in a good agreement with HF-acid calorimetry results (-233.5±5.4 и -5946.2±5.4 kJ/mol respectively) [2]. A correction for difference of real and theoretical muscovite compositions to calorimetric data on enthalpy increments was –0.6%. The corrected values of [H^o(973 K)-H^o(298,15 K)] were combined with the literature data on the heat capacities [3,4] and heat contents [5,6] and the resultant equations for muscovite $KAl_3Si_3O_{10}(OH)_2$ were obtained:

$$C^o_p = 376.90 + 156.87{\cdot}10^{-3}T - 86.83{\cdot}10^5T^{-2}\ J/K\ mol; \quad (3)$$

$$H^o(973\ K)-H^o(298{,}15\ K) = 376.90{\cdot}T + 78.44{\cdot}10^{-3}T^2 + 86.83{\cdot}10^5T^{-1} - 148.47\ kJ/mol; \quad (4)$$

C^o_p(298.15)=325.99 J/K mol; deviation of approximation ±1.4%.

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