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Stolyarova T.A.[1], Brichkina E.A.[1], Osadchii E.G.[1], Baranov A.V.[1,2] Calorimetric determination of the standard enthalpy of mohite (Cu_2SnS_3) formation. UDC 544.332

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Abstract. Value of the standard reaction enthalpy of mohite (Cu_2SnS_3) formation from sulfides have been obtained experimentally according to the reaction 2CuS + SnS → Cu_2SnS_3: $\Delta_rH^0_{298.15}(Cu_2SnS_3) = -(50.83 \pm 0.47)$ kJ·mol^{-1}.The measurements were carried out with 10 run series in vacuum-block calorimeter. Using literature data for the binary sulfides the value of standard enthalpy of mohite formation from the elements were calculated $\Delta_fH^0_{298.15}(Cu_2SnS_3) = -(263.61 \pm 2.28)$ kJ·mol^{-1} .

Keywords: *standard enthalpy, mohite, Cu_2SnS_3, calorimetry*

Mohite is a rare mineral that occurs in hydrothermal veins, but the Cu_2SnS_3 compound can be used as a precursor for the synthesis of materials with photovoltaic properties. Also, the compound may appear as a result of dissociation of stannine or kesterite materials.

A calorimetric determination of the Cu_2SnS_3 standard enthalpy formation from sulfides CuS and SnS was carried out by comparing the amount of heat transferred to the sample system as an electrical energy for carrying out the reaction and the amount of heat obtained during the system cooling, which includes the heat released during the reaction. According to preliminary tests, the synthesis of Cu_2SnS_3 from the sulphides in evacuated quartz glass ampoules takes place at a temperature of ~ 850 ° C for 6–7 minutes, in consistent with the reaction (R1):

$$2CuS + SnS \rightarrow Cu_2SnS_3 \qquad (R1)$$

The sulfide (CuS and SnS) synthesis was carried out from the elements of high and especially high purity: high purity copper, powder (99.999%), high purity tin, bar (99.999%); crystalline sulfur (99.99%, Alfa Aesar). The CuS synthesis operations: synthesis 400 °C – regrinding – annealing 300 °C (with separated Cu) – regrinding – annealing 300 °C (with separated Cu). The SnS synthesis operations: synthesis 350 °C – synthesis 650 °C – regrinding – annealing 350 °C (with separated Sn) – regrinding – annealing 350 °C (with separated Sn). The sulfide compositions were confirmed with X-ray phase analysis (Bruker D2 PHASER diffractometer, $CoK_{\alpha 1}$ radiation, λ = 1.78897 Å) The total weight of the mixture in each of the samples is about 1.8 g.

Calorimetric studies were carried out in a high-temperature vacuum-block calorimeter, manufactured and improved in the Laboratory of Electrochemistry, Thermodynamics and Physics of Minerals IEM RAS (laboratory number VBC-3) and described previously in the works (Vasilyev, Soboleva, 1962; Fleisher, Stolyarova, 1978). The process of calorimeter operation control, visualization and data processing were carried out using especially developed control unit, interface and computer program (Zhdanov et al., 2005).

A quartz glass ampoule with a targeted mixture of the sulfides was pumped out to a residual pressure of 10^{-2} Pa, sealed in a flame of an oxygen torch, and placed in a resistance furnace inside a massive copper block. The block was filled with argon under a pressure of 10^6 Pa (to improve the heat exchange between the heater and the copper block). The vacuum block (isothermal shell, where the massive copper block was placed in) was pumped out to a residual pressure of 10^3 Pa, that was kept constant during the whole experiment. The temperature of the isothermal shell (298.15 ± 0.02) K was maintained with a 300-liter thermostat with a propeller stirrer. The set thermostat temperature was maintained using a special thermal controller.

Electric power was measured with an accuracy of 0.02%. The temperature rise during the experiment was measured with a resistance thermometer consisting of nine tiny platinum temperature sensors equally spaced along the massive block; the total resistance was 988 Ohms at 298.15 K. The calorimeter with an ampoule (where the investigated reaction had already occurred) in a resistance furnace was calibrated using electrical power in conditions identical to the conditions of the experiment (heating time, the amount of electrical power and the value of the start temperature).

The heating time of all experiments was fixed automatically. The total time of the experiment duration (50 min) was also fixed. The accuracy of thermal value is 0.05%. Reheating did not cause an additional thermal effect. This fact confirms the complete passage of the reaction during the first heating. X-ray phase analysis of the calorimetric experiments products has confirmed the presence of the only substance Cu_2SnS_3 in them.

There are only theoretically calculated (DFT - using density functional theory and DFT-D2 - based on the Van der Waals forces of molecular (atomic) interaction) data on the mohite formation enthalpy in the literature (Shigemi, Wada, 2018):

ΔH_f^{DFT}= -241.4 kJ·mol^{-1},

ΔH_f^{DFT-D2}= -338.8 kJ·mol^{-1}.

In this work, a series of 10 experiments was carried out in a shigh-temperature vacuum-block calorimeter. The measurement results are shown in **Table 1**.

The value of mohite formation enthalpy, according to the reaction of formation from sulfides (R1):

$\Delta_r H^0_{298.15\,K}(R1)$= -(50.83 ±0.47) kJ·mol^{-1}.

Using literature data of enthalpy formation from elements for sulfides CuS and SnS:

$\Delta_f H^0_{298.15\,K}$(CuS,cr)= -(53.14 ±2.28) kJ·mol^{-1} (Cemic, Kleppa, 1988),

$\Delta_f H^0_{298.15\,K}$(SnS,cr) = -(106.5 ±1.5) kJ·mol^{-1} (Robie, Hemingway, 1995),

the value of mohite formation enthalpy from elements:

$\Delta_f H^0_{298.15K}(Cu_2SnS_3,cr)$ =

$=\Delta_r H^0_{298.15\,K}(R1) + 2\Delta_f H^0_{298.15\,K}(CuS,cr) + \Delta_f H^0_{298.15\,K}(SnS,cr)$

$\Delta_f \mathbf{H}^0_{298.15K}(Cu_2SnS_3,cr)$ = -(263.61 ±2.28) kJ·mol^{-1}.

Table 1. The enthalpy of mohite formation from sulfides (M.M.= 342.0 g/mol).

Number of experiment	Sample weight (g)	ΔR+σ (Ohm)	The amount of heat, released during the experiment (J)			$-\Delta_f H^o_{298.15}$
			total	on the heater	in the reaction	kJ/mol
1	1.7977	28.3292	82154.7	81888.5	266.2	50.64
2	1.7975	28.3229	82136.4	81863.0	273.4	52.02
3	1.7994	28.3651	82258.8	81997.2	261.6	49.72
4	1.8031	28.436	82464.4	82192.2	272.2	51.63
5	1.7993	28.4376	82469.0	82202.6	266.4	50.64
6	1.8009	28.3179	82121.9	81851.0	270.9	51.45
7	1.8011	28.3329	82165.4	81904.6	260.8	49.52
8	1.8041	28.3289	82153.8	81880.9	272.9	51.73
9	1.8005	28.2948	82176.8	81905.6	271.2	51.51
10	1.8008	28.2916	82167.3	81906.9	260.4	49.45
The average:						50.83 ±0.47

Note: ΔR + σ – the thermometer resistance value with the correction for thermal exchange, 1-8– samples– calorimeter thermal value W = (2900.0 ±1.0) J·Ohm^{-1} , 9-10 W = (2904.3 ±1.0) J·Ohm^{-1}.

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