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Thermochemical investigation of natural antlerite

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Abstract Thermal and thermochemical investigations of natural hydroxyl-bearing copper sulfate $Cu_3SO_4(OH)_4$—antlerite have been carried out. The stages of its thermal decomposition have been studied employing the Fourier-transform IR spectroscopy. The enthalpy of formation of antlerite from the elements $\Delta_f H_m^o$ (298.15 K) = (−1750 ± 10) kJ mol^{-1} has been determined by the method of oxide melt solution calorimetry. Using value of S_m^o (298.15 K), equal to (263.46 ± 0.47) J K^{-1} mol^{-1}, obtained earlier by the method of adiabatic calorimetry, the Gibbs energy value of $\Delta_f G_m^o$ (298.15 K) = (−1467 ± 10) kJ mol^{-1} has been calculated.

Keywords Antlerite · Thermochemistry · Thermal analysis · Enthalpy of formation

Introduction

Antlerite, a copper hydroxyl sulfate mineral, with the formula $Cu_3(SO_4)(OH)_4$, occurs in the oxidized zones of copper ore veins in the arid areas such as Chuquicamata in Chili, Mohave in the South-West of the USA; within the territory of the former USSR antlerite has been found at the Zhezkazgan deposit in Central Kazakhstan. Atacamite, brochantite, chalcosine, linarite, malachite, and gypsum occur in the oxidized copper ores as accompanying minerals to antlerite.

Previously the investigations of thermal stability of antlerite were performed on synthetic samples in [1–4]. Temperature ranges of dehydration, dehydroxylation, and desulfation were determined in [1] in dynamic, quasi-isothermal, and quasi-isobaric modes. X-ray diffraction and IR spectroscopy showed that the product of antlerite dehydroxylation is a mixture of crystalline dolerophanite Cu_2OSO_4 and tenorite CuO. The investigations [2, 3] are devoted to the research of thermal decomposition of antlerite and determination of kinetic parameters of this process. In these studies, the composition of decomposition products has been controlled by means of the X-ray phase analysis. In work [2], the data on activation energy of the reactions of dehydroxylation and desulfation of antlerite have been obtained. In work [3], in addition to kinetic investigations a calorimetric evaluation of enthalpy of water removing and enthalpy of antlerite formation in the temperature range of 430–510 °C has been carried out. No other experimental determination of enthalpy of antlerite formation have been performed. However, the literature contains thermodynamic data for antlerite ($\Delta_f G_m^o$ (298.15 K), $\Delta_f H_m^o$ (298.15 K), and S_m^o (298.15 K)) calculated from the equilibrium constant of experimentally studied reaction: $Cu_3SO_4(OH)_4 \cdot nH_2O\ (s) + 4H^+(aq) \rightarrow 3Cu^{2+}(aq) + (4+n)H_2O\ (l) + SO_4^{2-}(aq)$ using the computer program COMICS [5]. The value of Gibbs energy of formation as noted in the mentioned paper agrees with the results of an unpublished work [6].

The present investigation has studied the step character of thermal decomposition of a natural antlerite employing the Fourier-transform IR spectroscopy; and new data on

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standard enthalpy of formation of antlerite by the method of Calvet microcalorimetry have been obtained.

Experimental

A sample of natural antlerite (Zhezkazgan deposit, Central Kazakhstan) in the form of a fine-crystalline powder of a light-green color from A.E. Fersman Mineralogical museum RAS (No. 57917) has been selected to carry out the research. A chemical analysis of antlerite has been made by the X-ray spectrum method using a microprobe analyzer "Camebax SX-50" at the chair of Mineralogy of Geology Department of M.V. Lomonosov Moscow State University; the content of sulfur trioxide and water has been determined according to the data of a thermal analysis.

X-ray diagnostics of the specimen has been carried out in a monochromatic Fe_{α} emission (DRON-2; an anode tube current 15 mA; slots 1.0, 1.0, 0.25; scale 1000 impulse/s; response time 5 s).

IR spectroscopy investigation of studied sample was done in a Fourier spectrometer FSM-1201 (LOMO, Russia) over the range from 400 up to 4000 cm^{-1} with a wavenumber accuracy of ±1 cm^{-1}. The spectra (Fig. 1) were recorded at room temperature in the air. The specimens were prepared in the form of suspensions in petrolatum.

The study of antlerite thermal behavior was carried out on derivatograph "Q-1500D" (Hungary) over the temperature range from room temperature up to 1223 K. The temperature rise was performed at the rate of 5 K min^{-1}, the specimen mass was 45 mg. The obtained heating curves are given in Fig. 2.

Thermochemical investigation was performed using a high-temperature heat-flux Tian-Calvet microcalorimeter "Setaram" (France) [7]. Enthalpy of formation was determined by the oxide melt solution calorimetry method. Solution was prepared by the method of "drop" permitting to measure simultaneously both increment of the specimen enthalpy and enthalpy of its solution $[(H^{o}_{973} - H^{o}_{298.15}) + \Delta_{sol}H^{o}_{973}] = \Delta H$. For this purpose, the tablets compressed from the ground natural mineral (mass of 2.5–6.0 ($\pm 2 \times 10^{-3}$) mg) were dropped into the molten solvent ($2PbO{\cdot}B_2O_3$) in the calorimeter at $T = 973$ K. To remove a small amount of "low" (adsorption) water (0.4% according to thermogravimetry data), before the experiments the specimens had been heated for an hour at 373–393 K. Calibration of the apparatus was made by the same method of "drop" of a reference substance—platinum. Necessary thermochemical data for the reference substance had been borrowed from [8]. The results of calorimetric measurements are represented in Table 2.

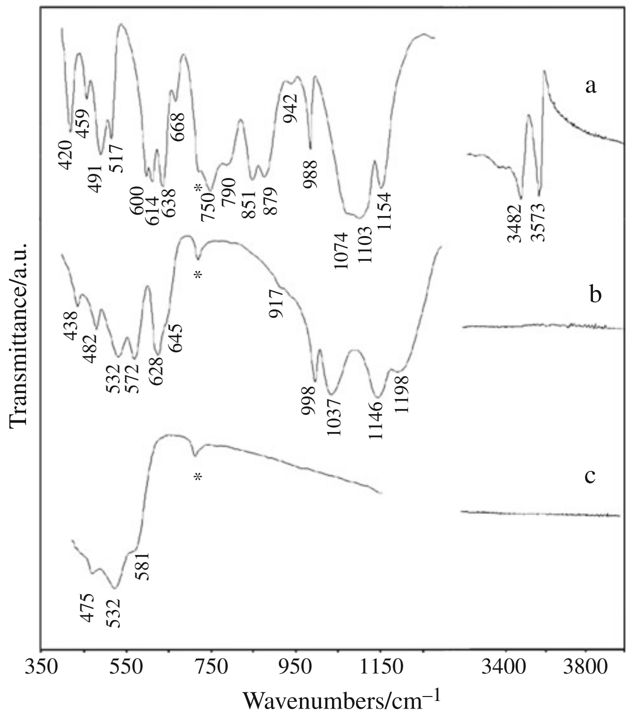

Fig. 1 Spectra of the IR absorption of a natural antlerite: *a* an initial state, *b* after heating up to 873 K, and *c* after heating up to 1223 K

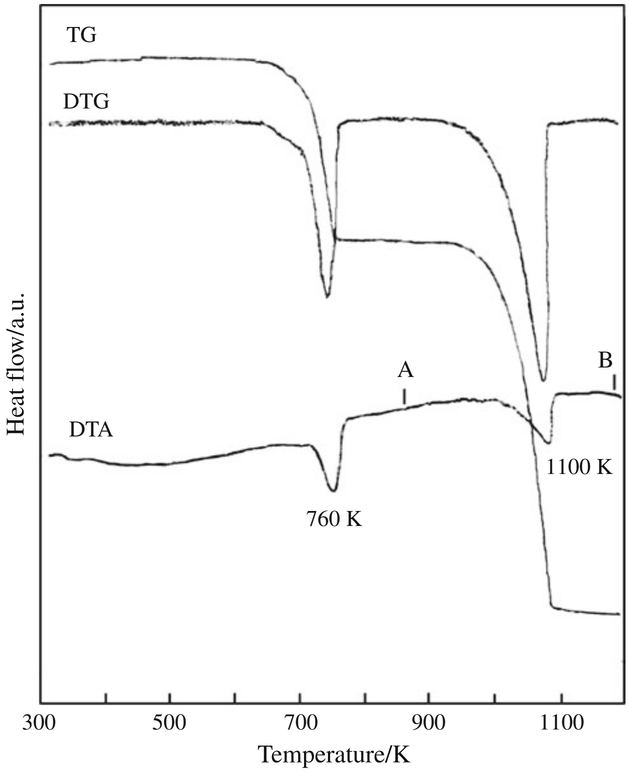

Fig. 2 The thermal analysis curves for natural antlerite: *A* 873 K and *B* 1223 K

Results and discussion

The mineral investigated had the following composition (mass%): 66.8 CuO, 22.6 SO_3, 0.3 P_2O_5, and 10.7 H_2O. The obtained chemical formula calculated for three cations is close to the theoretical one; in this connection, the calculation of thermodynamic properties of the studied mineral was based on its ideal formula $Cu_3SO_4(OH)_4$ (molar mass = 354.73 g mol^{-1}). Identification of a crystalline phase as antlerite has been performed according to the interplanar spacing and corresponding intensities of the X-ray spectrum (ASTM 7-407). The IR-absorption spectrum of antlerite (Fig. 1a) is identical to the spectral data given in generally known reference books [9, 10]. A detailed interpretation of antlerite absorption bands is given in [11], where the band assignment has been carried out according to the results of the IR-absorption study of a number of copper-bearing sulfate minerals and accompanying compounds. Table 1 presents the values of absorption bands wavenumbers of the natural antlerite studied by us, and their assignment in accordance with [11].

Figure 2 shows two stages of the mass loss on TG curve: removal of water over the temperature range of 650–780 K (10.8%) and desulfation of the substance over the temperature range of 960–1110 K (22.6%). The first stage is present on curve DTA as a sharp endothermic peak with the maximum at 760 K. The substance mass loss at the second stage also occurs at a high rate; and it is characterized by a pronounced endothermic effect with the maximum at 1100 K. The obtained results agree with the preceding data [1–4] throughout the studied temperature range. The values of T_{max} of dehydroxylation process according to [1–4] are in the range of approximately 720–770 K, the values of T_{max} of desulfation process according to abovementioned works are in the range of about 1000–1100 K. The exothermic effect detected in [2, 3] on DTA curve at about 820 K, corresponding to crystallization of intermediate phases of dolerophanite Cu_2OSO_4 and tenorite CuO is not found in our research, as well as in [1, 4].

To confirm the interpretation of the results of thermal analysis, the IR spectroscopic study of the products of antlerite ignition at temperatures of 870 and 1200 K (points A and B in Fig. 2, respectively) has been carried out. The IR spectrum of antlerite heated up to 870 K (Fig. 1b), revealed the disappearance of the absorption bands in the area of 3400–3600 cm^{-1}, corresponding to absorption of the two types of hydroxyl groups that reflects the complete dehydroxylation of the substance in comparison with the initial specimen. At the same time, the change of the absorption spectrum in the region of 400–1200 cm^{-1} is noted as appearance of features of a new anhydrous phase different from the initial mineral. In the spectrum of the specimen heated up to 1200 K (Fig. 2c), a new tenorite-like phase has been registered.

A value of standard formation enthalpy of a natural antlerite from the elements has been obtained by the reaction (1) using the calorimetric data on its solution obtained in this study.

Table 1 Wavenumbers of IR-absorption bands of antlerite and their assignment

No.	Absorption wavenumbers of antlerite/cm^{-1}	Type of vibration of a free ion $(SO_4)^{2-}$	Description of the form of vibrations
1	420		
2	459	ν_2 (E)	Symmetric deformation vibrations O–S–O
3	491		
4	517		
5	600		
6	614	ν_4 (F_2)	Asymmetric deformation vibrations O–S–O
7	638		
8	668		
9	750		Angle Cu–O–H change, when group OH is not bound by a hydrogen bond
10	790		
11	851		Angle Cu–O–H change, when group OH is bound by a hydrogen bond
12	879		
13	988	ν_1 (A_1)	Symmetric stretching vibrations of S–O bonds
14	1074		
15	1103	ν_3 (F_2)	Asymmetric stretching vibrations of S–O bonds
16	1123		
17	1154		

$$3CuO + CaSO_4 + 2H_2O = Cu_3SO_4(OH)_4 + CaO \tag{1}$$

The calculations have been done according to the formulae:

$$\begin{aligned}\Delta_{\mathrm{react.(1)}}H^{\mathrm{o}}\ (298.15\mathrm{K}) = {} & 3\Delta H\mathrm{CuO} + \Delta H\mathrm{CaSO_4} \\ & + 2\Delta H\mathrm{H_2O} - \Delta\mathrm{Hantlerite} \\ & - \Delta H\mathrm{CaO}\end{aligned} \tag{2}$$

$$\begin{aligned}\Delta_f H^{\mathrm{o}}_{\mathrm{m}}\ (298.15\mathrm{K})\ \mathrm{antlerite} = {} & \Delta_{\mathrm{react.(1)}}H^{\mathrm{o}}\ (298.15\mathrm{K}) \\ & + 3\Delta_f H^{\mathrm{o}}_{\mathrm{m}}\ (298.15\mathrm{K})\ \mathrm{CuO} \\ & + \Delta_f H^{\mathrm{o}}_{\mathrm{m}}\ (298.15\mathrm{K})\ \mathrm{CaSO_4} \\ & + 2\Delta_f H^{\mathrm{o}}_{\mathrm{m}}\ (298.15\mathrm{K})\ \mathrm{H_2O} \\ & - \Delta_f H^{\mathrm{o}}_{\mathrm{m}}\ (298.15\mathrm{K})\ \mathrm{CaO},\end{aligned} \tag{3}$$

where value $\Delta H = [(H^{\mathrm{o}}_{973} - H^{\mathrm{o}}_{298.15}) + \Delta_{\mathrm{sol}}H^{\mathrm{o}}_{973}]$ for antlerite is determined in the present work (Table 2); for other participants of the reaction (1) we obtained these values in previous studies; and they are presented in Table 3. Table 3 also shows the reference data [8] on enthalpies of formation of calcium and copper oxides, water and calcium sulfate (anhydrite) necessary for calculation. The obtained value of $\Delta_f H^{\mathrm{o}}_{\mathrm{m}}$ (298.15 K) antlerite is -1750 ± 10 kJ mol^{-1}.

Table 2 Calorimetric data for antlerite studied (molar mass = 354.73 g·mol^{-1})

Sample weight/mg	$\Delta H = H^{\mathrm{o}}_{973} - H^{\mathrm{o}}_{298.15} + \Delta_{\mathrm{sol}}H^{\mathrm{o}}_{973}$	
	J g^{-1}	kJ mol^{-1}
3.478	995.89	353.27
5.286	1006.29	356.96
3.316	1004.59	356.36
5.622	1004.23	356.23
3.872	993.19	352.31
2.867	1012.21	359.06
		Average: 355.7 ± 2.6*

* An uncertainty is expressed by a 95% confidence interval

Table 3 Thermochemical data used in calculations of enthalpy of formation of antlerite/kJ mol^{-1}

Substance	ΔH^{a}	$-\Delta_f H^{\mathrm{o}}_{\mathrm{m}}$ (298.15 K) [8]
CuO (tenorite)	70.1 ± 0.84$^{\mathrm{b}}$	156.1 ± 2.0
CaO (crystal)	−21.78 ± 0.29$^{\mathrm{c}}$	635.1 ± 0.9
$CaSO_4$ (anhydrite)	131.3 ± 1.6 [13]	1434.4 ± 4.2
H_2O (liquid)	40.9 ± 2.5$^{\mathrm{d}}$	285.8 ± 0.1

[a] The values of $\Delta H = H^{\mathrm{o}}_{973} - H^{\mathrm{o}}_{298.15} + \Delta_{\mathrm{sol}}H^{\mathrm{o}}_{973}$ were calculated using reference data for $(H^{\mathrm{o}}_{973} - H^{\mathrm{o}}_{298.15})$ [8] and experimental data for $\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{973}$

[b] [10]

[c] [8]

[d] The value is evaluated on the basis of experimental data on heats of solution [14] and the reference data [8] on the enthalpy of formation of hydroxyl-bearing minerals—brucite $Mg(OH)_2$ and talc $Mg_3Si_4O_{10}(OH)_2$ [12]

To calculate the Gibbs energy of the studied mineral formation from the elements, the value of the standard entropy of antlerite (263.46 ± 0.47) J K^{-1} mol^{-1} obtained by one of the authors of this work [15] from measurements of the low-temperature heat capacity by the method of adiabatic calorimetry, and reference data [8] on entropies of the corresponding elements have been taken. The calculated value of $\Delta_f G^{\mathrm{o}}_{\mathrm{m}}$ (298.15 K) of the studied mineral equal to (-1467 ± 10) kJ mol^{-1} agrees within the limits of uncertainties with the value of (-1445.0 ± 10) kJ mol^{-1} calculated in [5]. Slightly more negative value of the Gibbs energy for a natural mineral obtained by us reflects its greater thermodynamic stability explained by its more perfectly ordered crystalline structure having formed under the natural geological conditions.

New thermodynamic data for antlerite can be recommended for thermodynamic modeling of processes of natural mineral formation. They can also be used while elaborating theoretical and technological foundations for beneficiation of copper ores; while constructing phase state diagrams, while evaluating the probability of chemical reactions taking place in hydrometallurgy, chemical technology, while studying mineral equilibria in combination of experimental and thermodynamic approaches.

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