

THERMODYNAMIC PROPERTIES OF CREEDITE $\text{Ca}_3\text{Al}_2(\text{F},\text{OH})_{10}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$

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Creedite – complicated fluoride – $\text{Ca}_3\text{Al}_2(\text{F},\text{OH})_{10}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$, was first found out in Colorado (USA), and subsequently repeatedly described in oxidized zones and ore formations of Mo-W deposits of Central Kazakhstan [1, 2]. Creedite was investigated by chemical, X-ray diffraction, optical and thermal methods [1-3]. There are no data on thermodynamic properties of creedite. The present work uses the different calorimetric methods to measure the heat capacity, the enthalpies of formation of mineral. The first data on standard thermodynamic properties of natural creedite, such as heat capacity, enthalpy of formation, entropy and free Gibbs energy are given.

We chose for investigation well crystallized transparent crystals of creedite (Akchatau, Kazakhstan) from aggregation and druses of late stages of hydrothermal process. Creedite was chemically analyzed by microchemical method. The composition of creedite is very close to the theoretical one. Crystallochemical formula of creedite was calculated for 5 cations: $-\text{Ca}_3\text{Al}_2\text{F}_{8.25}(\text{OH})_{1.75}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$. The relation F/OH in the mineral is higher, than in all compositions investigated earlier. X-ray study of creedite confirmed the monoclinic symmetry. Lattice parameters of creedite studied agree well with previous literature data [3].

High-temperature thermal behavior was studied using methods of differential thermal (DTA) and thermogravimetric (TG, DTG) analyses and differential scanning calorimetry (DSC). It is characterized by two legibly expressed endothermic processes. First of them occurs at 430-450°C and corresponds to losses of water and hydroxyl group (about 11 %). As have shown DSC measurement process of dehydration is accompanied by endothermic effect 220.3 ± 4.1 kJ/mol. The second endoeffect with a maximum at 815°C is produced by the reversible phase transition of decomposition products of creedite. Exoeffects at temperatures about 540°C and 730°C are minor. The composition of products of heating up to 1400°C is very multiphase, losses of mass reach 32 %.

The thermochemical investigations were performed in differential scanning calorimeter DSC «Mettler TA-2000B» and high-temperature heat-flux Calvet microcalorimeter «Setaram».

The heat capacity of creedite was measured by DSC method in the interval of 280-610 K in flowing nitrogen with a heating rate of 5-10 K/min. The molar enthalpy and melting temperature of indium reference substance (99.9999 % purity) were used to calibrate the DSC. The DSC measurements results in the interval of 280-610 K were fitted by least-squares

yielding with respective average deviation of approximation presented in brackets:

$$C^{\text{op}} = 423.80 + 379.45 \cdot 10^{-3}T - 88.70 \cdot 10^{-5}T^2 \text{ J/mol}\cdot\text{K} (\pm 1.3\%) \text{ at } 298.15\text{-}610 \text{ K}$$

Enthalpy of formation of creedite was determined by a set of thermochemical cycles using decomposition at 717 K (temperature of dehydration) and subsequent dissolution of decomposition products in molten lead borate, both reactions taking place in a Calvet calorimeter. The transposed temperature drop calorimetry method (sample was dropped into a calorimeter at 717 K) was used to obtain enthalpies of reaction of dehydration. When sample was dropped into a calorimeter at 717 K the heat effect measured was thus the sum of the heat content and the enthalpy of dehydrated at 717 K of creedite $-(H_{717}^{\text{op}} - H_{298.15}^{\text{op}}) + \Delta H_{\text{dehyd-717}}^{\text{op}}$. When the dehydrated creedite was dropped into the calorimeter and only heated from $T=298.15$ to $T=717$ K, the heat effect $(H_{717}^{\text{op}} - H_{298.15}^{\text{op}})$ was measured. The heat of dehydration was calculated from the experimental data.

The transposed temperature drop solution calorimetry method was used to obtain the enthalpy of solution of the dehydrated creedite. Samples of dehydrated creedite were dropped into molten $2\text{PBO}\cdot\text{B}_2\text{O}_3$ held at $T=973$ K. The heat effect measured was the sum of the heat content and the enthalpy of solution of the dehydrated creedite $-(H_{973}^{\text{op}} - H_{298.15}^{\text{op}}) + \Delta H_{\text{sol-973}}^{\text{op}}$.

Calibration was performed by the Pt and $\alpha\text{-Al}_2\text{O}_3$ drop method. A precision of weighing the samples was $\pm 2 \cdot 10^{-3}$ mg.

The standard enthalpy of formation of creedite from elements were calculated using the experimental values of table 1 as a sum of the enthalpy of dehydration and the enthalpy of formation of dehydrated creedite from the constituent substances such as CaO, CaSO_4 , CaF_2 and AlF_3 .

The entropy of creedite was estimated by addition of the entropies of the constituent cations and anions using Latimer method. By combining our enthalpy of formation data with the enthalpy values we estimated the standard molar Gibbs free energy of formation of creedite at 298.15 K (table 2). The thermodynamic data produced by this study can be useful in understanding creedite stability in low-temperature complex natural systems.

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Table 1

Results of calorimetric study of creedite (F.W.=492.787)

Mineral	Observed values	kJ/mol
Creedite	$[(H_{717}^{\circ} - H_{298.15}^{\circ}) + \Delta H_{\text{dehyd-717}}^{\circ}]$	458.8 ± 3.7 (7)
Dehydrated creedite	$(H_{717}^{\circ} - H_{298.15}^{\circ})$	185.4 ± 0.8 (12)
Dehydrated creedite	$[(H_{973}^{\circ} - H_{298.15}^{\circ}) + \Delta H_{\text{sol.973}}^{\circ}]$	498.8 ± 5.2 (10)

Table 2

 Thermodynamic properties of creedite $\text{Ca}_3\text{Al}_2\text{F}_{8.25}(\text{OH})_{1.75}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$
 (F.W.=492.787) at 298.15 K

V° cm^3	S° $\text{J/mol}\cdot\text{K}$	ΔH_f° kJ/mol	ΔG_f° kJ/mol	C_p° $\text{J/mol}\cdot\text{K}$
178,0	501 ¹	-7379.6 ± 1.2	-6866	437.2

¹ – estimation by Latimer method