

HIGH-TEMPERATURE HEAT CAPACITY OF NATURAL ANNITE

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Annite, trioctahedral mica with idealized composition $\text{KFe}^{+2}_3[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$ is the end member of the phlogopite – annite isomorphic range. The thermochemical investigation of natural annite (Katuginsky deposit, Sev.Zabaikalje, Russia) was performed. The chemical formula calculated on the basis of 22 charges is: $(\text{K}_{0.87}\text{Na}_{0.03}\text{Rb}_{0.02})_{0.92}(\text{Li}_{0.18}\text{Fe}^{2+}_{2.25}\text{Mg}_{0.02}\text{Mn}_{0.06}\text{Fe}^{3+}_{0.26}\text{Ti}_{0.13})_{2.90}[\text{Si}_{2.97}\text{Al}_{0.98}\text{Fe}^{3+}_{0.05}\text{O}_{10}](\text{F}_{0.89}(\text{OH})_{1.11})$, m. m. = 496.279 g/mole. The polytype of the annite studied is 1M. The lattice parameters are $a=5.34 \text{ \AA}$, $b=9.24 \text{ \AA}$, $c=10.10 \text{ \AA}$, $\beta=100^\circ$; density – 3.27 g/cm^3 .

High-temperature heat contents of natural annite were determined on the heat flux Tian-Calvet microcalorimeter (“Setaram”, France) using the drop method. The annite sample weighing 3-10 ($\pm 2 \cdot 10^{-3}$) mg was dropped directly from room temperature into the calorimeter at experiment temperature from 444 to 781 K and the enthalpy increment $[H^\circ(T)-H^\circ(298.15 \text{ K})]$ (Table 1) was measured. Calibration was performed by dropping standard substance corundum $\alpha\text{-Al}_2\text{O}_3$, the required thermochemical data were taken from [1].

Table 1.

$T, \text{ K}$	444	507	567	636	734	781
$[H^\circ(T)-H^\circ(298.15 \text{ K})]$, J/g	139.8 ± 12.8 (6)*	183.3 ± 15.2 (6)	229.6 ± 8.2 (6)	296.4 ± 14.6 (8)	424.2 ± 16.1 (8)	454.5 ± 17.2 (6)

*- Errors are expressed by interval for $P=95\%$, in brackets the number of determinations is given

The experimental results for natural annite were combined with value of standard heat capacity C_p° (298.15 K) = 360.78 J/K·mol, determined by I.Paukov (private communication) from low temperature calorimetry data, and fitted by least-squares method yielding:

$$C_p^\circ = 373.4 + 245.4 T \cdot 10^{-3} - 76.3 T^2 \cdot 10^{-5}, \text{ J/K mol};$$

$$H^\circ(T)-H^\circ(298.15 \text{ K}) = 373.4 T + 122.7 T^2 \cdot 10^{-3} + 76.3 T^3 \cdot 10^{-5} - 147806, \text{ J/mol}.$$

Thermodynamic function of natural annite at high temperature is presented in Table 2.

Table 2.

$T, \text{ K}$	$H^\circ(T) - H^\circ(298.15 \text{ K})$, J/mol	C_p°	$S^\circ(T)$	$-[G^\circ(T)-H^\circ(298.15 \text{ K})]/T$
		J/K mol		
298	0	360.78	391.54	391.54
400	40243	423.90	507.20	406.59
500	84814	465.61	606.48	436.86
600	133111	499.48	694.45	472.59
700	184589	529.65	773.74	510.04
800	238976	557.84	846.32	547.60
900	296120	584.89	913.60	584.57
1000	355931	611.23	976.59	620.66

Reference

1. Robie R.A., Hemingway B.S. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures // U.S. Geol. Surv. Bull. 1995. N 2131. 461 p.

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