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Heat capacity and enthalpy of formation of synthetic alunite<sup>1</sup>

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## Abstract

The heat capacities of synthetic alunite have been measured between 16 and 375 K by quasi-adiabatic low-temperature calorimetry. Our best estimate for the entropy of stoichiometric alunite  $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$  is  $321.0 \pm 5.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  at 298.15 K. We have revised the reaction scheme and recalculated the enthalpy of formation of alunite as  $-5176.5 \pm 2.4 \text{ kJ}\cdot\text{mol}^{-1}$ . The experimental data from which both of these results were derived are based on measurements of the properties of synthetic alunite that most likely were not stoichiometric. Corrections have been applied, but significant assumptions have been necessary. Therefore, the values given here, although the best currently available, must be considered to be preliminary.

## Introduction

Alunite provides a characteristic adsorption signature that may be detected by remote sensing and can be used in surveys that seek to recognize and map mineralized areas (e.g., Podwysocki et al., 1983). For example, in the Marysvale, Utah, area, remote sensing has shown alunite cores surrounded by kaolinite in a mineralized area. It may also be used to date rock altered by hypogene and supergene hydrothermal alteration as it occurs in both environments, commonly in association with kaolinite. Alunites occur as low-temperature alteration products of sulfide-containing rock and as alteration products in the upper and sulfate portion of geothermal systems (including volcanic crater lakes). In the latter setting, alunites may have been formed in the upper boiling portion of a geothermal system and may be an indicator of gold formation. Therefore, alunites are useful as an exploration and resource assessment guide and in modelling the evolution of hydrothermal systems and associated ore genesis.

The thermodynamic data for alunite that are needed for modelling of geologic processes are based on heat capacity and enthalpy of formation measurements made in the mid-1940's (Kelley et al., 1946). These values need to be examined and verified or updated.

## Experimental data

Synthetic alunite was prepared by Richard W. Henley using the method of Parker (1962). Fisher certified ACS reagent  $\text{Al}_2(\text{SO}_4)_3\cdot n\text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4$  were mixed in the ratio 4:1, dissolved in 150 ml of water, and boiled under reflux conditions in pyrex glassware for 1 to 3 days. Batches of 30 g of reactant yielded about 4 g of sodium-free alunite (no sodium was detected in the product alunite).

The cell dimensions for the synthetic alunite were determined by our Survey colleague Howard Evans using a Guinier camera. The trimolecular cell referred to the hexagonal axes is  $a = 7.0149(2) \text{ \AA}$ ,  $c = 17.123(2) \text{ \AA}$ , and  $V = 729.7(1) \text{ \AA}^3$ . The standard deviation in  $2\theta = 0.019$  and 25 reflections were used. No other phases were found in optical and X-ray examination of the sample.

The cell parameters for our synthetic alunite deviate from those of natural alunite and those given by Parker (1962) for heat treated synthetic alunite. The values for our unheated sample are in good agreement with those given by Parker (1962) for his unheated synthetic samples. Parker (1962) concluded that excess water was removed by heating the synthetic alunite at 300° C, but some water remained and probably replaced the alkali as hydronium. Our heat capacity sample was heated in a platinum crucible at 300° C for 1 hour before it was loaded into the calorimeter. The sample lost 5.64% of the original weight during heating. Our heated sample showed a <sup>1</sup>H spectral band (Henley, written communication, 1985) which was attributed to hydronium and was not seen in natural alunites, but X-ray analysis of this sample was not performed.

The presence of hydronium in our heat capacity sample was found after the measurements had been completed. Our sample has similar cell dimensions to Parker's (1962) sample S-1. Based on that comparison and assuming that the hydronium ion is about the same size as the sodium ion, we estimate the hydronium and potassium to be (H<sub>3</sub>O<sub>0.09</sub>K<sub>0.91</sub>). This is in good agreement with the findings of Stoffregen and Cygan (1990) who note that alunite prepared by the Parker (1962) method was low in alkalis by 10 to 20 mol %. The molar mass of our sample is 412.407 g (using the 1985 atomic weights) as compared to 414.214 g for stoichiometric alunite, KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>.

The heat capacity of our alunite sample was measured between about 16 and 375 K by quasi-adiabatic low-temperature calorimetry. The method and equipment have been described elsewhere (e.g., Robie and Hemingway, 1984, and references there in). The experimental values are listed in Table 1, and smoothed values of the thermodynamic properties are listed at integral temperatures in Table 2. The entropy at 298.15 K, estimated from our measurements, is 329.2 ± 1.0 J·mol<sup>-1</sup>·K<sup>-1</sup> for alunite of the composition (H<sub>3</sub>O<sub>0.09</sub>K<sub>0.91</sub>)Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>. This value is in good agreement with the value (328.0 ± 3.8 J·mol<sup>-1</sup>·K<sup>-1</sup>) reported by Kelley et al. (1946) for their synthetic alunite sample reported as the composition KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>.

Kelley et al. (1946) report a value of -10339.3 ± 3.9 kJ·mol<sup>-1</sup> for the enthalpy of formation of a synthetic alunite (as twice the mole used above) from the elements at 298.15 K. The accepted values for some of the reference phases have changed or have been improved in the intervening years since Kelley et al. (1946) completed their study. A modified version of their reaction scheme is listed in Table 3. Reactions 82-84 (Table 52, page 51) of the reaction scheme used by Kelley et al. (1946) essentially provide the enthalpy of formation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O. These reactions are omitted, reactions 91 and 92 are modified because reactions 82-84 are omitted, and current accepted values for the formation properties of the reference phases are used. The enthalpy of formation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O is taken from the study of DeKock (1986), the remaining reference values are taken from Robie et al. (1978). Recalculation of the modified reaction scheme yields -10353.0 ± 4.7 kJ·mol<sup>-1</sup> for the enthalpy of formation of alunite as 2[KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>].

## Discussion

Synthetic alunites commonly are low in alkalis when compared to the stoichiometric formula and to natural alunites. Parker (1962) concluded that  $K^+$  and  $Na^+$  are replaced by  $H_3O^+$  based on chemical analyses. Ripmeester et al. (1986) used  $^1H$  nuclear magnetic resonance technique to confirm the existence of hydronium ion in synthetic alunites. Fielding (1980) has synthesized and studied a series of compositions along the oxonium (hydronium) alunite-potassium alunite join. He notes that synthetic alunites are commonly nonstoichiometric in aluminum and sulfur.

Kelley et al. (1946) provide chemical analyses for their alunite samples, but did not provide optical or other information that would establish that their sample was a single phase as they assumed. Both their natural and synthetic alunite samples show an apparent excess of potassium and water. They corrected their heat capacity and enthalpy of formation data by assuming that the natural and synthetic alunites contained excess  $K_2SO_4$  and water, and were deficient in  $Al_2(SO_4)_3$ . It is difficult to do anything further with their data because we lack the necessary information to make a better set of corrections. It should be noted that Kelley et al. (1946) used a method to synthesize alunite that is similar to that developed by Parker (1962). Further, Kelley et al. (1946) "re-autoclaved" their synthetic alunites in water for 16 hours, a process that could lead to additional replacement of potassium by hydronium (see for example the process used by Stoffregen and Cygan, 1990). We suspect that the synthetic alunite measured by Kelley et al. (1946) had significant replacement of potassium by hydronium, and that, not crystallinity as assumed by Kelley et al. (1946), was the cause of the difference in the heat capacities of the natural and synthetic alunite they reported.

Correction of our heat capacity and entropy data for the hydronium will be difficult because we lack information on the change in these properties with hydronium content. If our sample were assumed to be stoichiometric alunite (molar mass of 414.214 g) then the entropy at 298.15 K would be  $330.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Kelley et al. (1946) report heat capacities for a natural (from Marysvale, Utah) and a synthetic sample of alunite. Larger values were found for the heat capacities of the synthetic alunite as compared to the natural sample. Kelley et al. (1946) reported that the entropy of the natural alunite sample was  $318.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . These results and the observation that the entropy (and consequently, the heat capacities) of  $KH_2AsO_4$  ( $155.02 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) is larger than that of  $K_3AsO_4$  ( $144.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) suggests that the heat capacities and entropies of stoichiometric alunite will be significantly smaller than the values listed in Table 2. We estimate that the entropy of stoichiometric alunite at 298.15 K is  $321.0 \pm 5.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . This estimate is based on the difference in entropy observed by Kelley et al. (1946) for their natural and synthetic alunite, the assumption that the synthetic alunite measured by Kelley et al. (1946) contained hydronium in about the same amount as our sample, and the fictive entropy value ( $330.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) calculated from our heat capacity data.

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Table 2. Thermodynamic properties for synthetic alunite.

Temp.	Heat Capacity	Entropy	Enthalpy function	Gibbs energy function
K	-----	J·mol <sup>-1</sup> ·K <sup>-1</sup>	-----	-----
5	0.184	0.089	0.059	0.030
10	0.814	0.378	0.255	0.123
15	2.070	0.918	0.627	0.291
20	4.369	1.794	1.246	0.549
25	8.123	3.144	2.219	0.925
30	13.21	5.053	3.607	1.446
35	19.30	7.527	5.396	2.132
40	26.36	10.56	7.570	2.994
45	33.09	14.06	10.04	4.022
50	39.92	17.89	12.67	5.217
60	55.99	26.56	18.53	8.035
70	74.16	36.52	25.15	11.37
80	91.30	47.57	32.37	15.20
90	108.0	59.29	39.85	19.45
100	124.0	71.51	47.47	24.04
110	139.2	84.03	55.12	28.91
120	154.5	96.81	62.77	34.04
130	169.6	109.7	70.40	39.32
140	184.4	122.9	78.02	44.84
150	198.8	136.1	85.60	50.51
160	212.6	149.3	93.10	56.25
170	226.0	162.7	100.6	62.13
180	239.3	175.9	107.8	68.10
190	252.1	189.3	115.1	74.18
200	264.7	202.5	122.3	80.25
210	276.9	215.8	129.3	86.42
220	288.6	228.9	136.3	92.60
230	300.1	241.9	143.2	98.77
240	311.4	255.0	149.9	105.0
250	322.5	267.9	156.6	111.3
260	333.6	280.8	163.3	117.5
270	344.6	293.5	169.8	123.8
280	355.4	306.3	176.2	130.0
290	365.4	318.9	182.6	136.3
300	375.0	331.5	188.8	142.7
310	383.7	343.9	195.0	149.0
320	392.4	356.2	201.0	155.2
330	402.0	368.5	206.9	161.6
340	413.2	380.6	212.9	167.8
350	423.6	392.8	218.7	174.0
360	430.1	404.8	224.5	180.3
370	433.7	416.6	230.1	186.5
273.15	348.1	297.6	171.9	125.8
298.15	373.2	329.2	187.7	141.5
	±0.4	±1.0	±0.7	±1.0

Table 3. Reaction scheme for determining the enthalpy of formation of alunite,  $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$ .

Reaction	Enthalpy $\text{kJ}\cdot\text{mol}^{-1}$
$3[\text{Al}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}] + 24(\text{OH})^- \rightarrow$ $6\text{AlO}_2^- + 9\text{SO}_4^{2-} + 30\text{H}_2\text{O}$	-823.61 $\pm 0.65$
$2\text{K}^+ + 6\text{AlO}_2^- + 4\text{SO}_4^{2-} + 12\text{H}_2\text{O} \rightarrow$ $2[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6] + 12(\text{OH})^-$	69.96 $\pm 2.65$
$12\text{H}_2\text{O} \rightarrow 12(\text{OH})^- + 12\text{H}^+$	665.47 $\pm 1.38$
$12\text{H}^+ + 6\text{SO}_4^{2-} \rightarrow 6\text{H}_2\text{SO}_4(\text{l})$	487.39 $\pm 0.63$
$\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}$	24.89 $\pm 0.11$
$6\text{Al} + 9\text{S} + 18\text{H}_2 + 27\text{O}_2 \rightarrow 3[\text{Al}_2(\text{SO}_4)_3\cdot 6\text{H}_2\text{O}]$	-15938.2 $\pm 2.5$
$2\text{K} + \text{S} + 2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4$	-1437.7 $\pm 0.5$
$6\text{H}_2\text{SO}_4(\text{l}) \rightarrow 6\text{H}_2 + 6\text{S} + 12\text{O}_2$	4884.0 $\pm 2.4$
$6\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 3\text{O}_2$	1714.8 $\pm 0.6$
$2\text{K} + 6\text{Al} + 4\text{S} + 6\text{H}_2 + 14\text{O}_2 \rightarrow$ $2[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$	-10353.0 $\pm 4.7$