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DEHYDROXYLATION HEAT OF ALUNITE

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ABSTRACT

The heat of dehydroxylation of two kinds of alunite has been obtained by differential thermal analysis (DTA) and differential dynamic calorimetry (DDC). As the values obtained differed for the two kinds of alunite, the influence of silica as a contaminant on the decrease of the heat of dehydroxylation and the temperature of decomposition has been studied. The equations of Claussius-Clapeyron or Van't Hoff should be avoided when deriving the heat of dehydroxylation of alunite because experiments have proved the dehydroxylation to be irreversible.

INTRODUCTION

The bibliography on the heat of dehydroxylation (usually known as dehydration) presents a large difference between the value given by Asada (1938), 8.5 cal/g, and that given by Kelley *et al.* (1946), calculated from thermochemical data, 210 cal/g at 477°C.

In the structure of alunite (Hendricks, 1967; Kulp and Adler, 1950) the aluminum is surrounded octahedrally by four hydroxyl groups and two oxygen atoms of sulfate groups, and potassium is surrounded by twelve oxygen and hydroxyl groups. The linkage is such that a loss of OH would cause complete decomposition of the structure, and considerable rearrangement must take place to form Al_2O_3 and $AlK(SO_4)_2$.

The dehydroxylation heat of alunite has been determined by two methods, DTA and DDC, in which a comparison is made with well-known heats of reaction.

DIFFERENTIAL THERMAL ANALYSIS (DTA) AND DIFFERENTIAL DYNAMIC CALORIMETRY (DDC)

Differential thermal analysis measures the difference between the heating curves of the sample powder and of an inert substance exhibiting no inversions or chemical changes. According to Boersma (1955), quantitative DTA has some defects because the thermal effects indicated by thermocouples embedded in the powders are: (1) limited by the small amount of powder immediately surrounding the couple junction and (2) influenced by the heat exchange factor between the couple and the powder, which changes as the powder sinters and shrinks. Also material is lost in reactions where volatile products are formed, so that the sample weight does not remain constant. For these reasons, Boersma (1955) and Schwiete and Ziegler (1958) suggested that DTA cannot give

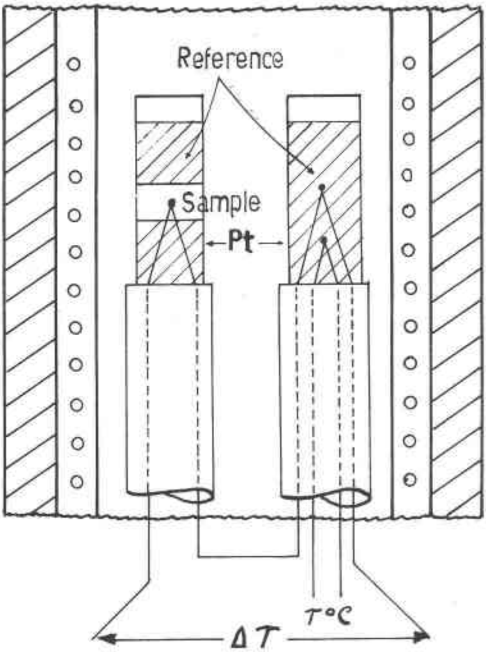

FIG. 1. Measuring head for DTA.

an accurate indication of characteristic thermal effects, and they developed a new method, "the differential dynamic calorimetry." In this method the powders are contained in separate, identical, substantially closed, metal crucibles, through the walls of which all the heat exchange occurs. The junctions of the thermocouples are in the thickened bases of the crucibles (not in the powder itself as in DTA). Figures 1 and 2 show the difference in the arrangement for DTA and DDC respectively; these figures are taken from the Netzch equipment used in this work. Platinum holders in DTA and platinum cups in DDC were used because of their low thermal capacity.

In order to obtain the greatest sensitivity in DTA, the sample centered with the differential thermocouple between two levels of inert material equal to the reference (α-Al_2O_3) like a sandwich; Figure 1 shows the sample set in the Pt holder. In DDC the centering of the sample is not necessary because the heat exchange occurs through the wall of the Pt cups.

CALIBRATION OF THE THERMAL ANALYSIS APPARATUS

For the calibration of the peak areas in terms of cal/cm^2, the following substances of pro-analysis purity have been used: $CuSO_4 \cdot 5H_2O$, $BaCl_2$

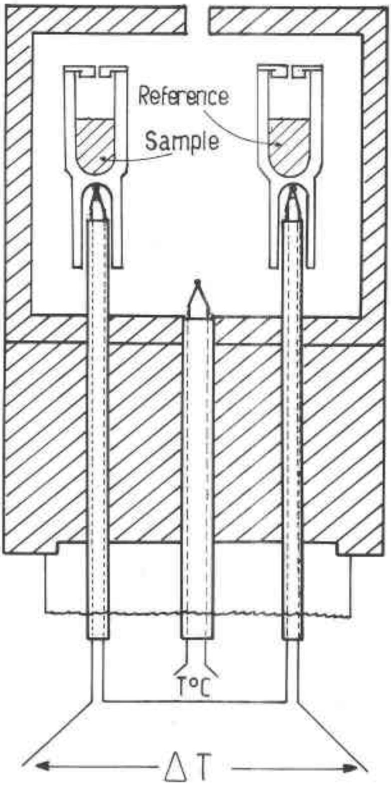

FIG. 2. Measuring head for DDC.

$\cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, $CdCO_3$, and $CaCO_3$. $Na_2WO_4 \cdot 2H_2O$ was also used to check the calibration of the DDC at 588°C.

Table 1 gives the heats of reaction of the calibration substances.

TABLE 1. HEATS OF REACTION OF SUBSTANCES USED FOR CALIBRATION.

Substance	Temperature of reaction (°C)	Type of reaction	Heat of reaction (cal/g)
$BaCl_2 \cdot 2H_2O$	130	$-2H_2O$	116.6
$CaSO_4 \cdot 2H_2O$	180	$-2H_2O$	157.2
$CuSO_4 \cdot 5H_2O$	150	$-4H_2O$	228.5
$CdCO_3$	350	$-CO_2$	134.5
$CaCO_3$	850	$-CO_2$	427.1
Na_2WO_4	588.8	$\text{c, III} \longrightarrow \text{c, I}$	28.57

TABLE 2. CHEMICAL ANALYSES OF THE ALUNITE SAMPLES.

	Alunite "K"	Alunite "C"
SiO_2	2.86%	27.4%
Al_2O_3	35.86	26.5
Fe_2O_3	0.61	1.36
TiO_2	0.26	0.02
MgO	0.05	0.15
CaO	0.15	0.17
K_2O	8.45	5.35
Na_2O	1.70	2.0
SO_3	36.26	25.62
P_2O_5	0.37	0.29
Loss up to 560°C	13.24	11.92
Loss from 0°C to 160°C	0.14	2.05
Loss from 160°C to 560°C	13.10	9.87
Loss from 0°C to 1000°C	41.97	32.06

These heats have been calculated at the corresponding temperatures of decomposition following the methods of Lewis and Randall (1923) and of Glasstone (1947).

For each of these substances the corresponding differential curves have been obtained either by DTA or DDC, varying the sample and reference quantities used in each case as follows: 25, 50, 100, 150, and 200 mg; and for each sample weight three differential curves have been obtained. With these differential curves the calibration curves have been determined. The values obtained from these curves have been of 4 percent precision for both methods. All measurements were made at a heating rate of 10°C./min.

THERMAL DECOMPOSITION OF ALUNITE

Two alunites have been used: one from Camarones (Chubut Province Argentina), named C alunite, and the other from the west side of the Province of Chubut, named *K* alunite. Their chemical analyses are given in Table 2; the probable compositions, excluding the SiO_2 and other impurities, are given in Tables 3 and 4 respectively. The theoretical formula for alunite being $K_2Al_6(SO_4)_4(OH)_{12}$ or $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$, Tables 3 and 4 show that, on a mole basis, both alunites agree well with the ideal composition.

The differential curves corresponding to alunites *K* and *C*, either by DTA or DDC, have been obtained. The heats of dehydroxylation were obtained by using the calibration curves. The results are given in Table 5.

TABLE 3. PROBABLE COMPOSITION OF ALUNITE K.

	Wt.%	Relative moles	Scaled to total of 6 moles	
K_2SO_4	15.63	8.97	0.759	0.990
Na_2SO_4	3.89	2.74	0.231	
$Al_2(SO_4)_3$	38.30	11.19	0.945	
$Al(OH)_3$	37.42	48.00	4.063	
		Total	5.998	

The value of 13.1 percent for hydroxyl water in alunite *K* (Table 2) is within the theoretical value corresponding to a pure alunite with an error of 0.38 percent. That is why, in spite of having been working with an alunite of approximately 97 percent purity (considering Na_2O in its equivalent in K_2O), we have taken alunite *K* as a pure alunite for the calculation of the dehydroxylation heat. For alunite *C*, with a hydroxyl water content of 9.87 percent, the experimental results have been multiplied by 13.1/9.87 to obtain the values corresponding to alunite with 13.1 percent H_2O.

INFLUENCE OF SILICA

The corrected dehydroxylation heats obtained for alunite *C* are lower than those deduced by Kelley (1946) and those determined by us for alunite *K* (considering all analyzed water as due to hydroxyl groups). This difference is attributed to the effect of contaminants, in this case mainly SiO_2.

Silica in alunite *C*, as seen by microscopy, is mostly in the form of opal and constitutes a sort of "cellular" mesh with the voids occupied by alunite crystals either singly or as aggregates; alunite crystals measure

TABLE 4. PROBABLE COMPOSITION OF ALUNITE C.

	Wt.%	Relative moles	Scaled to total of 6 moles	
K_2SO_4	9.90	5.68	0.652	1.022
Na_2SO_4	4.58	3.22	0.370	
$Al_2(SO_4)_3$	26.34	7.70	0.884	
$Al(OH)_3$	28.53	35.68	4.094	
		Total	6.000	

TABLE 5. HEATS OF DEHYDROXYLATION FOR ALUNITES K AND C.

Sample	Test method	Heat of dehydroxylation		
		Experimental		Given by Kelley (1946)
		cal/g	cal/g	cal/g
		sample	alunite (13,1% H_2O)	alunite (13,1% H_2O)
Alunite *K*	DTA	203±8	203±8	210
	DDC	206±8	206±8	210
Alunite *C*	DTA	125.2±5	165.4±6	210
	DDC	136.0±5	180.5±7	210

2–4 μm as a rule; opal partitions have an average width of 1 μm; quartz is rare and found only in large crystals. Figure 3 is a picture of alunite C as seen by microscopy.

Alunite *K* has a fine-grained mosaic, partly equi-dimensional, but mostly columnar; grain size is about 12 μm for well developed tabular crystals; silica is rare and mostly in the form of quartz. Figure 4 is a picture of alunite *K* as seen by microscopy.

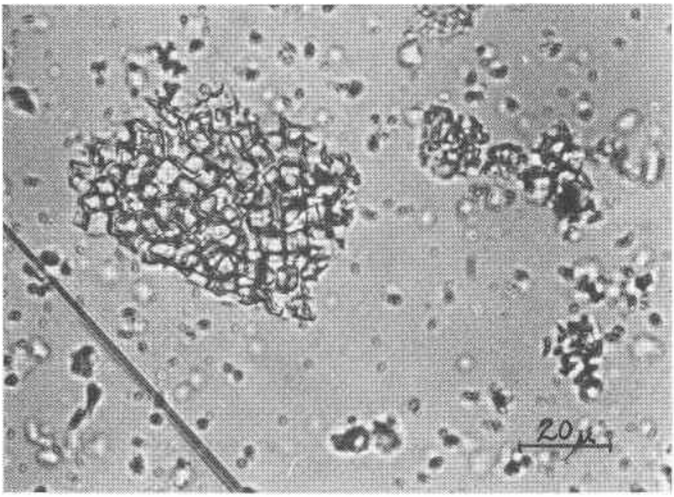

FIG. 3. Alunite C. Stubby microcrystals of alunite make up the fragments and are separated by thin opal partitions. Parallel nicols.

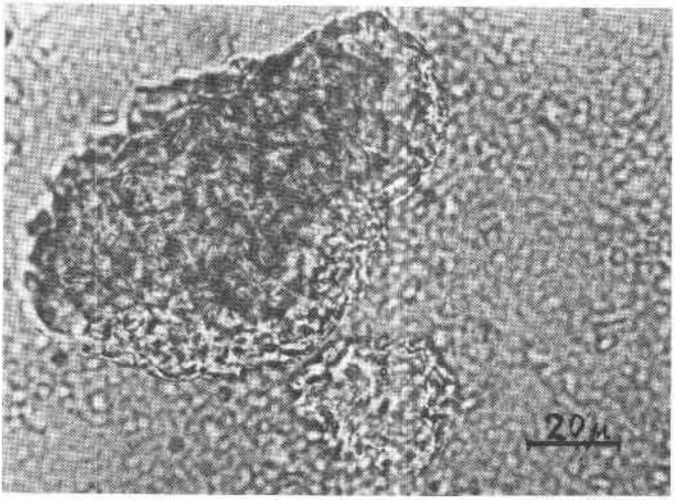

FIG. 4. Alunite K. Fragments made up of earthy alunite without opal partitions. Parallel nicols.

The effect of silica is seen in two ways:

a) We have observed that the dehydroxylation heat obtained by DTA for alunite C is lower than the one obtained by DDC; this is due to the fact that the dilution effect of SiO_2 produces differences in the centering of the minute alunite crystals with the position of the differential thermocouple in DTA. The effect, on DTA curves, of a sample placed at different positions with respect to the thermocouple was studied by Barshad (1952). This difference does not occur in DDC where the thermocouple is out of contact with the sample. In order to prove the effect of dilution (through simple mixing) by SiO_2 (as quartz), tests have been made by DTA, using mixtures of alunite *K* with various quantities of SiO_2 from 5 to 40 percent. A decrease of the peak area per gram of pure alunite is observed as the content of SiO_2 is increased; the decrease for a 30 percent SiO_2 dilution was about 5 percent. However, it does not correspond to the difference between 203 cal/g (in DTA) obtained for pure alunite and the one of 165.4 cal/g calculated from silicified alunite. That is why this anomaly is also attributed to the following:

b) The SiO_2 diluting alunite *C*, mainly opal, does not occur as a simple mixture but is closely interwoven with alunite in a three dimensional network, the alunite crystals being even smaller than in alunite *K*. This fact has been observed by microscopy and less crystallinity has been observed by X-ray diffraction. The combined result makes the value obtained from alunite *C* lower than the corresponding one for alunite *K*.

Besides the decrease of the thermal effect, a decrease occurs also in the decomposition temperatures of alunite *C*; this also is attributed to the effect of the opal interwoven with the alunite, which produces decrease of the energy of association of crystals with its consequent decrease in the heat and temperature of decomposition. Similar considerations were made by Kelley *et al.* (1946, p. 18) where they said that the values of the specific heat for synthetic alunite are greater than those of natural alunite because the synthetic product is poorly crystallized.

TESTS OF ALUNITE *K* BY DTA UNDER REDUCED PRESSURE

In order to confirm the character of the reaction of dehydroxylation of alunite, which does not follow Van't Hoff equation for the equilibrium, several tests have been made with alunite *K* by DTA under reduced pressure. In these tests no variation in the temperature of the dehydroxylation peak ($-6H_2O$) has been observed, but, on the other hand, a noticeable decrease in the temperature of the desulfation peak ($-3SO_3$) was obtained.

If the reactions of dehydroxylation and desulfation were reversible, the application of Van't Hoff equation (1) showed that in case of dehydroxylation we would have to obtain a decrease in peak temperature of 45°C (working at 300 mm of Hg) and in case of desulfation (also at 300 mm of Hg) a decrease of 34°C.

$$\frac{\mathrm{d}\ln K_p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{1}$$

From experiments made under reduced pressure we have seen that in case of dehydroxylation there were no noticeable changes in peak temperatures. The dehydroxylation peak temperature was 580°C ± 2°C, at an atmospheric pressure of 760 mm Hg, and also under reduced pressure of 300 mm Hg. In the case of desulfation, a temperature of 817°C ± 2°C was obtained at 760 mm Hg and of 780°C ± 2°C at 300 mm. The decrease of 33°C ± 2°C in peak temperature was practically the fall theoretically calculated.

CONCLUSIONS

1) The temperatures of decomposition found are:
   Reaction of dehydroxylation ($-6H_2O$):
      Alunite K: initial 480°C and final 590°C. Peak temperature 566°C.
      Alunite C: initial 430°C and final 560°C. Peak temperature 540°C.

The temperatures of decomposition for alunite C with an equivalent content in pure alunite of 73.3% are lower than those obtained for alunite K with an equivalent content in alunite of 97 percent.

2) The heat of dehydroxylation for alunite K, either by DTA or DDC, agree with the value calculated by Kelley (1946).

3) The values for alunite C, calculated as a 100 percent of equivalent alunite, are less than those obtained for alunite K and as given by Kelley (1946), presumably due to the effect of contaminants, mainly opal, closely interwoven with the alunite in a three-dimensional network.

4) The tests of dehydroxylation and desulfation made under reduced pressure show that the first reaction occurs irreversibly and the second is a reaction that occurs in equilibrium. Under these circumstances neither the Clausius-Clapeyron equation nor the Van't Hoff equation is applicable for the dehydroxylation of alunite.

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