

Report of Investigations 8164

**Enthalpy of Formation
and Low-Temperature Heat
Capacities of Basic Aluminum Sulfite
($\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$)**

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CONTENTS

| | <u>Page</u> |
|---|-------------|
| Abstract..... | 1 |
| Introduction..... | 1 |
| Materials..... | 2 |
| Low-temperature thermal properties..... | 5 |
| Experimental..... | 5 |
| Results..... | 5 |
| Enthalpy of formation at 298 K..... | 7 |
| Experimental..... | 7 |
| Aluminum sulfate hydrate..... | 7 |
| Basic aluminum sulfite..... | 9 |
| Summary of results..... | 10 |
| References..... | 12 |

ILLUSTRATION

| | |
|--|---|
| 1. Low-temperature heat capacity of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ | 4 |
|--|---|

TABLES

| | |
|---|----|
| 1. Powder X-ray diffraction data of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ | 3 |
| 2. Experimental low-temperature heat capacities of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ | 6 |
| 3. Low-temperature thermodynamic properties of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ | 6 |
| 4. Reaction scheme for $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ at 298 K..... | 8 |
| 5. Experimental heats of solution at 298 K..... | 8 |
| 6. Reaction scheme for $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ at 298 K..... | 9 |
| 7. Experimental heats of solution at 298 K..... | 10 |
| 8. Thermodynamic data for $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ at 298.15 K..... | 11 |

ENTHALPY OF FORMATION AND LOW-TEMPERATURE HEAT CAPACITIES OF BASIC ALUMINUM SULFITE ($\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$)

by

H. C. Ko,¹ J. M. Stuve,¹ and R. R. Brown¹

ABSTRACT

Calorimetric determinations of low-temperature heat capacities and standard enthalpy of formation were made by the Federal Bureau of Mines for basic aluminum sulfite, $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$. The standard values of entropy (S°), enthalpy of formation (ΔH_f°), and calculated Gibbs energy of formation (ΔG_f°) at 298.15 K are 85.2 ± 0.1 cal/deg-mole, -943.1 ± 1.2 kcal/mole, and -820.7 ± 1.2 kcal/mole, respectively.

INTRODUCTION

The Bureau of Mines is engaged in a program to investigate processes for recovering alumina from domestic resources. An important part of such process planning and evaluation is the use of basic thermodynamic data to determine energy requirements and efficiencies.

In recognition of the desirability of having such data available when needed, the Bureau of Mines some years ago instituted a program for the determination of various thermodynamic properties (low-temperature heat capacities, high-temperature enthalpies, and enthalpies of formation) of aluminum-bearing minerals. Data have been published for alumina (Al_2O_3) (9),² diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) (11, 15), gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) (2, 15), kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (2, 11), halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (2, 11), dickite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (2, 11), anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) (1, 10, 12), and alunite ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$) (9).

The Bureau, in cooperation with several aluminum producers, has constructed a small pilot plant for the purpose of intercomparing different processing techniques which yield alumina from four domestic raw materials--clay, anorthosite, alunite, and dawsonite. Thermodynamic data relating to the first three were mentioned previously. Additional data on dawsonite have been published by the Bureau (7).

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²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The present investigation provides low-temperature heat capacities and the enthalpy of formation of monobasic aluminum sulfite, which is an intermediate compound precipitated during the sulfurous acid-caustic purification process for treating clay. The process is described in a Bureau publication by Peters (14).

Heat capacities from 11 to 311 K were determined by adiabatic calorimetry, and the standard enthalpy of formation at 298 K was determined by solution calorimetry. The results of the experimental investigations were combined with other pertinent entropy data to yield the standard Gibbs energy of formation.

No previous similar thermodynamic data have been reported in the literature for basic aluminum sulfite.

MATERIALS

The reference substances used in determining the enthalpy of formation of basic aluminum sulfite were Al(s) , $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O(l)}$, $\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O(l)}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O(s)}$, and $\text{H}_2\text{O(l)}$.

The aluminum metal was in the form of fine filings which were obtained from a 99.998-pct-pure ingot.

Aluminum sulfate dodecahydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, was prepared by first recrystallizing reagent-grade $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, which was then slowly dehydrated for several days over the temperature range 65° to 90° C. Care was taken in adjusting the composition to 12 H_2O of hydration. Analysis by direct ignition showed 18.25 pct Al_2O_3 , compared with the theoretical value of 18.26 pct. No significant impurities were detected spectrographically.

Sulfuric acid of the composition $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, sulfurous acid of the composition $\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O}$, and the two solvent media, $\text{HCl} \cdot 12.731\text{H}_2\text{O}$ (4.360 molal) and $\text{H}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 0.01\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 15\text{H}_2\text{O}$ (3.70 molal H_2SO_4 and H_3PO_4 , and 0.037 molal $\text{Na}_2\text{Cr}_2\text{O}_7$), were all prepared from reagent-grade materials. Analyses confirmed the compositions as given.

Basic aluminum sulfite, $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$, was prepared by slightly modifying the procedure described by E. Rosenkranz as summarized in the Handbook of Preparative Inorganic Chemistry (3). Aluminum hydroxide was first precipitated from a solution of 400 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 3.2 liters of water. The Al(OH)_3 was filtered, washed, and slurried with 2.5 liters of water. Sulfur dioxide gas was then bubbled into the mixture until solution of the Al(OH)_3 was complete. The solution was heated to 80° C for 4 hours while stirring constantly. At this point a homogeneous-type precipitation of the basic sulfite occurred and considerable SO_2 was evolved. A plastic bag was used to nearly seal the beaker, thereby maintaining a slight positive pressure of SO_2 during the heating and precipitation step. The basic sulfite was vacuum-filtered, washed, and spread on trays to air-dry for 16 hours. A final treatment consisted of resuspending the basic sulfite in 1 liter of SO_2 -saturated

water. The mixture was again heated to 80° C for 4 hours. An SO₂ atmosphere was maintained above the solution during heating and cooling to room temperature, and also during the final filtering. The filter cake was then vacuum-dried at room temperature, first by water aspiration, and then by mechanical pump evacuation for several days until the pressure was reduced to 15 micrometers. Analysis of the basic sulfite showed 31.33 pct Al₂O₃, 39.23 pct SO₂, and 29.44 pct H₂O. These values correspond to a formula of Al₂O₃ · 2.0SO₂ · 5.3H₂O. No significant impurities were detected spectrographically. X-ray diffraction analysis showed the material to be well crystallized with a pattern similar to that observed by Rosenkranz, but with more lines and a slight shift in the observed d values. The pattern was indexed³ on a hexagonal lattice with a₀ = 12.820 Å and C₀ = 7.015 Å. The relative line intensity (I) and the observed and calculated d values are presented in table 1.

TABLE 1. - Powder X-ray diffraction data of Al₂O₃ · 2.0SO₂ · 5.3H₂O

| Observed | | Calculated, d, Å | hkl | Observed | | Calculated, d, Å | hkl |
|----------|--------|---------------------|-----|----------|--------|---------------------|-----|
| I | d, Å | | | I | d, Å | | |
| 100..... | 5.581 | 5.556 | 200 | 2..... | 2.1971 | 2.1970 | 113 |
| 20..... | 4.715 | 4.734 | 111 | 2..... | 2.1739 | 2.1776 | 402 |
| 72..... | 4.366 | 4.355 | 201 | 4..... | 2.1560 | 2.1553 | 203 |
| 8..... | 4.199 | 4.200 | 210 | 8..... | 2.1015 | 2.0998 | 420 |
| 7..... | 3.601 | 3.603 | 211 | 4..... | 2.0149 | 2.0116 | 421 |
| 1..... | 3.505 | 3.508 | 002 | 1..... | 1.9922 | 1.9945 | 412 |
| 5..... | 3.212 | 3.208 | 220 | 3..... | 1.8934 | 1.8896 | 223 |
| 10..... | 3.063 | { 3.082 | 310 | 8..... | 1.8614 | 1.8628 | 313 |
| | | { 3.078 | 112 | 8..... | 1.8476 | 1.8519 | 600 |
| 55..... | 2.9631 | 2.9659 | 202 | 6..... | 1.8039 | 1.8016 | 422 |
| 12..... | 2.9233 | 2.9171 | 221 | 7..... | 1.7887 | 1.7889 | 403 |
| 27..... | 2.8087 | 2.8214 | 311 | 9..... | 1.7543 | 1.7538 | 004 |
| 1..... | 2.7681 | 2.7778 | 400 | 5..... | 1.7313 | 1.7323 | 104 |
| 11..... | 2.6936 | 2.6921 | 212 | 2..... | 1.6831 | 1.6832 | 413 |
| 2..... | 2.5945 | 2.5827 | 401 | 3..... | 1.6737 | 1.6724 | 204 |
| 34..... | 2.5579 | { 2.5491 | 320 | 2..... | 1.6455 | 1.6471 | 611 |
| | | { 2.5467 | 302 | 2..... | 1.6340 | 1.6376 | 602 |
| 3..... | 2.4219 | 2.4246 | 410 | 4..... | 1.6237 | 1.6201 | 432 |
| 2..... | 2.4044 | 2.3958 | 321 | 3..... | 1.6078 | { 1.6109 | 503 |
| 4..... | 2.3607 | 2.3670 | 222 | | | { 1.6038 | 440 |
| 2..... | 2.3088 | 2.3151 | 312 | | | | |
| 7..... | 2.2897 | { 2.2916 | 411 | | | | |
| | | { 2.2883 | 103 | | | | |

³The X-ray diffraction analysis was made by Marion P. Krug, research physicist, Albany Metallurgy Research Center.

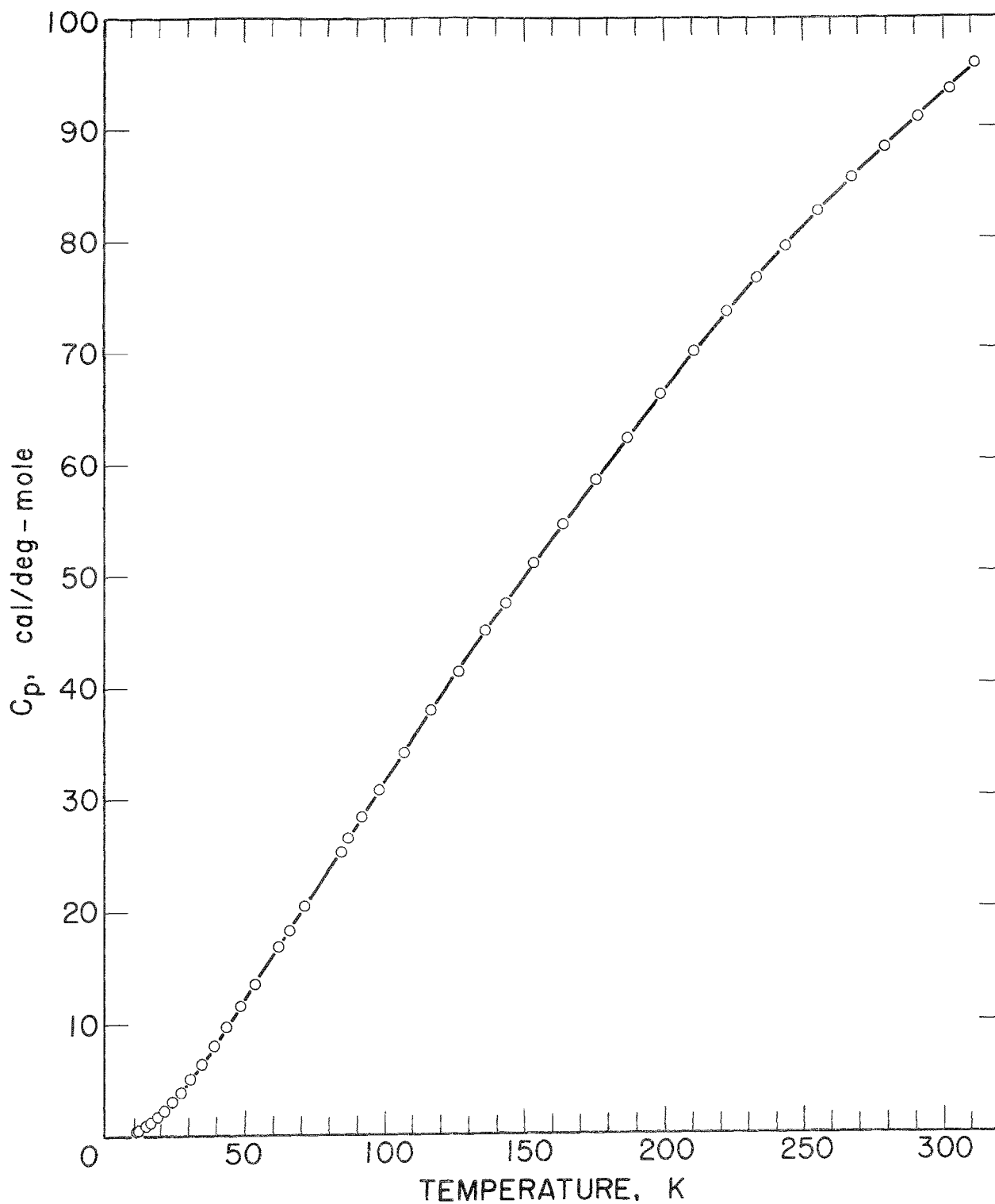


FIGURE 1. - Low-temperature heat capacity of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$.

LOW-TEMPERATURE THERMAL PROPERTIES

Experimental

Low-temperature heat capacity measurements were determined by means of a precision adiabatic calorimeter. Detailed descriptions of the apparatus and operating procedure were given elsewhere (16). The experimental determinations were made from 11 to 311 K in three ranges as follows: liquid nitrogen range, 80 to 311 K; solid nitrogen range, 47 to 80 K; and liquid helium range, 11 to 50 K.

A nominal bulk volume of 90 ml of sample was used for the measurements. The sample weighed 64.090 g in vacuum. Temperatures reported are based on the International Practical Temperature Scale of 1968 (IPTS-68) (4). Energy units given in this paper refer to the thermochemical calorie (1 cal = 4.1840 joules). Atomic weights are taken from the 1973 Table of Atomic Weights (8).

Temperatures below 15 K were determined with a National Bureau of Standards (NBS) calibrated germanium resistance thermometer. A high-precision platinum resistance thermometer was used from 15 to 311 K. Accurate potentiometric measurements in conjunction with these thermometers permitted a temperature resolution of ± 0.001 K or better.

The sample was loaded into a gold-plated copper calorimeter (sample container) in an argon-filled dry box. The argon was subsequently pumped out of the filled calorimeter and replaced with 0.0024 mole of helium gas to improve thermal conductivity within the sample mass.

Results

Experimental heat capacity data are listed in table 2. A plot of these data as a function of temperature is given in figure 1. Polynomial functions were fitted to the experimental data with a digital computer. The functions were used to calculate heat capacities at regular temperature intervals. Calculated heat capacities as well as the related functions S° and $H^\circ - H_0^\circ$ are given in table 3. Values of S° and $H^\circ - H_0^\circ$ at 10 K were determined by extrapolation to be 0.12 cal/deg-mole and 0.89 cal/mole, respectively.

TABLE 2. - Experimental low-temperature heat capacities of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$

| T, K | Cp, cal/deg-mole | T, K | Cp, cal/deg-mole |
|------------|------------------|-------------|------------------|
| 11.49..... | 0.502 | 106.81..... | 34.046 |
| 12.03..... | .568 | 116.75..... | 37.854 |
| 14.86..... | .998 | 126.48..... | 41.296 |
| 16.64..... | 1.329 | 136.17..... | 44.942 |
| 18.85..... | 1.795 | 143.66..... | 47.328 |
| 21.19..... | 2.331 | 153.31..... | 50.940 |
| 24.27..... | 3.113 | 164.04..... | 54.400 |
| 27.20..... | 3.972 | 175.64..... | 58.360 |
| 30.65..... | 5.095 | 186.86..... | 62.121 |
| 34.75..... | 6.463 | 198.67..... | 65.966 |
| 39.14..... | 8.047 | 210.70..... | 69.803 |
| 43.63..... | 9.695 | 222.54..... | 73.365 |
| 48.42..... | 11.525 | 233.26..... | 76.395 |
| 53.66..... | 13.510 | 243.67..... | 79.230 |
| 62.07..... | 16.813 | 255.58..... | 82.382 |
| 65.85..... | 18.288 | 267.67..... | 85.448 |
| 71.27..... | 20.414 | 279.47..... | 88.211 |
| 84.34..... | 25.281 | 291.04..... | 90.891 |
| 86.88..... | 26.481 | 302.40..... | 93.442 |
| 91.58..... | 28.328 | 311.43..... | 95.745 |
| 97.91..... | 30.755 | | |

TABLE 3. - Low-temperature thermodynamic properties of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}(\text{s})$

| T, K | Cal/deg-mole | | Cal/mole, $\text{H}^\circ - \text{H}_0^\circ$ | T, K | Cal/deg-mole | | Cal/mole, $\text{H}^\circ - \text{H}_0^\circ$ |
|----------|-------------------|------------------|--|------------|-------------------|------------------|--|
| | Cp° | S° | | | Cp° | S° | |
| 10..... | 0.329 | 0.120 | 0.890 | 160..... | 53.11 | 40.21 | 3857 |
| 15..... | .995 | .366 | 4.031 | 170..... | 56.52 | 43.54 | 4405 |
| 20..... | 2.042 | .787 | 11.48 | 180..... | 59.87 | 46.86 | 4987 |
| 25..... | 3.369 | 1.381 | 24.92 | 190..... | 63.16 | 50.19 | 5602 |
| 30..... | 4.872 | 2.126 | 45.46 | 200..... | 66.38 | 53.51 | 6250 |
| 35..... | 6.526 | 2.999 | 73.89 | 210..... | 69.52 | 56.83 | 6930 |
| 40..... | 8.347 | 3.988 | 111.0 | 220..... | 72.56 | 60.13 | 7640 |
| 45..... | 10.26 | 5.081 | 157.5 | 230..... | 75.49 | 63.42 | 8380 |
| 50..... | 12.10 | 6.257 | 213.4 | 240..... | 78.30 | 66.69 | 9149 |
| 60..... | 15.98 | 8.806 | 353.8 | 250..... | 80.98 | 69.94 | 9946 |
| 70..... | 19.90 | 11.56 | 533.2 | 260..... | 83.53 | 73.17 | 10770 |
| 80..... | 23.83 | 14.48 | 751.9 | 270..... | 85.97 | 76.37 | 11615 |
| 90..... | 27.72 | 17.51 | 1010 | 273.15.... | 86.72 | 77.37 | 11890 |
| 100..... | 31.55 | 20.63 | 1306 | 280..... | 88.32 | 79.54 | 12490 |
| 110..... | 35.30 | 23.81 | 1640 | 290..... | 90.62 | 82.68 | 13380 |
| 120..... | 38.99 | 27.04 | 2012 | 298.15.... | 92.50 | 85.21 | 14130 |
| 130..... | 42.60 | 30.31 | 2420 | 300..... | 92.93 | 85.79 | 14300 |
| 140..... | 46.16 | 33.59 | 2864 | 310..... | 95.36 | 88.87 | 15240 |
| 150..... | 49.66 | 36.90 | 3343 | | | | |

ENTHALPY OF FORMATION AT 298 K

Experimental

The enthalpy of formation was determined by solution calorimetry. The calorimeter employed and the method of operation were described by Ko (13). A few changes were made as follows:

1. The Hallikainen Thermotrol⁴ temperature controller was replaced by a Precision temperature controller (Bayley Instrument Co., Danville, Calif.). With this controller the temperature of the water bath was maintained to $\pm 0.002^\circ \text{C}$.

2. The stirring mechanism for the calorimeter formerly used a rubber O-ring. This was replaced by a geared-type pulley system employing a no-slip drive belt to give a more uniform stirring speed.

3. The FORTRAN computer program for calculating results from calorimetric experiments was replaced by a new program developed for a Wang 600 calculator system (Wang Laboratories, Inc.).

The calorimeter was calibrated by measuring the heats of solution of THAM [Tris (hydroxymethyl) aminomethane] in 0.10-N HCl and of ZnO in 4.360 molal HCl at 298 K. The results, -7.100 ± 0.005 and -15.811 ± 0.007 kcal/mole, respectively, were in good agreement with accepted values.

The solution media used in this study were 2.131.1 g of $\text{HCl} \cdot 12.731\text{H}_2\text{O}$ and 2,592.9 g of $\text{H}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 0.01\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 15\text{H}_2\text{O}$. The temperature of operation was 298.15 K. Weights were corrected to vacuum.

The assignment of precision uncertainties was based on the following criteria: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as twice the standard deviation of the mean; (2) when the heats of two or more reactions were combined, the uncertainty of the resulting reaction was taken as the square root of the sum of the squares of the individual uncertainties.

Aluminum Sulfate Hydrate

No relevant thermodynamic data were available for the reference compound, $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s})$. Consequently, it was necessary to first determine the enthalpy of formation of this compound. The solution medium used was 2,131.1 g of $\text{HCl} \cdot 12.731\text{H}_2\text{O}$. The details of the reaction scheme for determining the enthalpy of formation of $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ are given in table 4. The symbols s, l, g, and sol denote substances that are crystalline, liquid, gaseous, and in solution. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained. Also listed in table 4 are the average measured heat values and uncertainties for the individual reactions. A quantity of 0.005 g-mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ was used as the weight basis for this scheme, and other substances conformed stoichiometrically with this quantity.

⁴Reference to specific manufacturers and brands of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 4. - Reaction scheme for $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ at 298 K

| | ΔH , kcal | Uncertainty, kcal |
|---|----------------------|----------------------|
| (1) $2\text{Al}(\text{s}) + 6\text{H}^+(\text{sol}) = 2\text{Al}^{+3}(\text{sol}) + 3\text{H}_2(\text{g})$ | -254.10 | 0.24 |
| (2) $3[\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}](1) = 6\text{H}^+(\text{sol}) + 3\text{SO}_4^{2-}(\text{sol})$ + $18\text{H}_2\text{O}(\text{sol})$ | -3.64 | .02 |
| (3) $6\text{H}_2\text{O}(1) = 6\text{H}_2\text{O}(\text{sol})$ | -0.46 | .001 |
| (4) $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s}) = 2\text{Al}^{+3}(\text{sol}) + 3\text{SO}_4^{2-}(\text{sol})$ + $12\text{H}_2\text{O}(\text{sol})$ | -2.38 | .03 |
| (5) $2\text{Al}(\text{s}) + [3 \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}](1) = \text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s})$ + $6\text{H}_2\text{O}(1) + 3\text{H}_2(\text{g})$ | -254.90 | .25 |

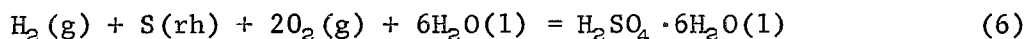
Reactions 1-2 were measured consecutively in 2,131.1 g of solvent. Reactions 3-4 were measured consecutively in a fresh portion of 2,131.1 g of solvent. Reactions 1 and 3 were both measured previously in this laboratory. Coughlin (5) reported a heat of solution value of -127.050 ± 0.120 kcal/mole for reaction 1. Ko (13) determined the heat for reaction 3 to be -0.0761 ± 0.0001 kcal/mole. These values are adopted here in the reaction scheme. The experimental heats of solution for reactions 2 and 4 are given in table 5 along with their mean values and uncertainties.

TABLE 5. - Experimental heats of solution
at 298 K, kcal/mole

| $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(1)$, reaction 2 | $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s})$, reaction 4 |
|--|---|
| -1.211 | -2.434 |
| -1.222 | -2.360 |
| -1.218 | -2.355 |
| -1.223 | -2.393 |
| -1.214 | -2.331 |
| -1.196 | -2.343 |
| -1.213 | -2.329 |
| ¹ -1.214 \pm 0.007 | ¹ -2.377 \pm 0.034 |

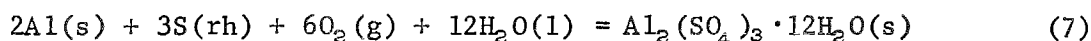
¹Mean.

Reactions 1-4 and their heats can be combined to give the overall calorimetric reaction 5 and a heat value of -254.90 ± 0.25 kcal for ΔH_5 at 298.15 K. Combination of ΔH_5 with ΔH_8 , the enthalpy of formation of $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at 298.15 K, gives the formation reaction 7 for $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$.



$$\Delta H_8 = -208.944 \pm 0.100 \text{ kcal/mole.}$$

The enthalpy change for reaction 6 was from Wagman (17).



$$\Delta H_7 = \Delta H_5 + 3\Delta H_8$$

$$\Delta H_f^\circ(298.15 \text{ K}) = \Delta H_7 = -881.73 \pm 0.39 \text{ kcal/mole.}$$

Basic Aluminum Sulfite

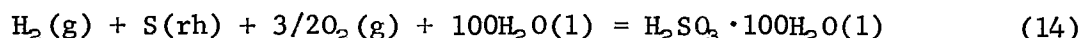
The details of the reaction scheme for $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ are given in table 6. The solution medium was 2,592.9 g of $\text{H}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 0.01\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 15\text{H}_2\text{O}$. The presence of $\text{Na}_2\text{Cr}_2\text{O}_7$ insured the oxidation of sulfur of +4 to sulfate. A test was made for complete oxidation by titrating the excess $\text{Na}_2\text{Cr}_2\text{O}_7$ with ferrous ammonium sulfate solution. The amount of $\text{Na}_2\text{Cr}_2\text{O}_7$ actually consumed in oxidation of SO_3^{2-} to SO_4^{2-} confirmed the theoretical calculation according to stoichiometry. Also listed in table 6 are the average measured heat values and uncertainties for the individual reactions. A quantity of 0.005 g-mole of $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ was used as the weight basis for this scheme. Other substances conformed stoichiometrically with this quantity.

TABLE 6. - Reaction scheme for $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$ at 298 K

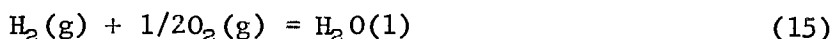
| Reaction | ΔH , kcal | Uncertainty, kcal |
|---|----------------------|----------------------|
| (8) $6[\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O}](\text{l}) + 2\text{Cr}_2\text{O}_7^{2-}(\text{sol}) + 4\text{H}^+(\text{sol}) = 4\text{Cr}^{+3}(\text{sol}) + 6\text{SO}_4^{2-}(\text{sol}) + 608\text{H}_2\text{O}(\text{sol}) \dots \dots \dots$ | -516.90 | 2.42 |
| (9) $3[\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}](\text{s}) = 6\text{Al}^{+3}(\text{sol}) + 9\text{SO}_4^{2-}(\text{sol}) + 36\text{H}_2\text{O}(\text{sol}) \dots \dots \dots$ | 8.75 | 0.11 |
| (10) $563.1\text{H}_2\text{O}(\text{l}) = 563.1\text{H}_2\text{O}(\text{sol}) \dots \dots \dots$ | -122.92 | .11 |
| (11) $3[\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}](\text{s}) + 2\text{Cr}_2\text{O}_7^{2-}(\text{sol}) + 22\text{H}^+(\text{sol}) = 6\text{Al}^{+3}(\text{sol}) + 6\text{SO}_4^{2-}(\text{sol}) + 4\text{Cr}^{+3}(\text{sol}) + 26.9\text{H}_2\text{O}(\text{sol}) \dots \dots \dots$ | -484.06 | .29 |
| (12) $9[\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}](\text{l}) = 18\text{H}^+(\text{sol}) + 9\text{SO}_4^{2-}(\text{sol}) + 54\text{H}_2\text{O}(\text{sol}) \dots \dots \dots$ | -5.99 | .06 |
| $\Delta H_{13} = 1/3(\Delta H_8 + \Delta H_9 - \Delta H_{10} - \Delta H_{11} - \Delta H_{12})$ | | |
| (13) $2[\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O}](\text{l}) + \text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s}) = 187.7\text{H}_2\text{O}(\text{l}) + \text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}(\text{s}) + 3[\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}](\text{l}) \dots \dots \dots$ | 34.94 | .82 |

Reactions 8-9 were measured consecutively in 2,592.9 g of solvent. Reactions 10-12 were measured consecutively in a fresh portion of 2,592.9 g of solvent. The experimental heats of solution for these reactions are given in table 7 along with their mean values and uncertainties. Reactions 8-12 and

their heats can be combined to give the overall calorimetric reaction 13 and a value of 34.94 ± 0.82 kcal for ΔH_{13} at 298.15 K. Combination of ΔH_{13} with the enthalpies of formation of $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, $\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and H_2O at 298.15 K gives the formation reaction 16 for $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2 \cdot 5.3\text{H}_2\text{O}$.

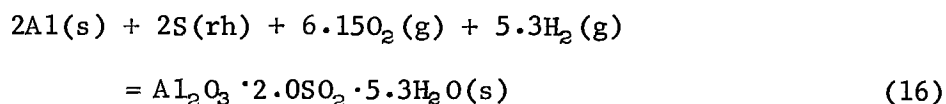


$$\Delta H_{14} = -146.369 \pm 0.100 \text{ kcal/mole};$$



$$\Delta H_{15} = -68.315 \pm 0.010 \text{ kcal/mole}.$$

The enthalpy changes for reactions 14-15 were from Wagman (17).



$$\Delta H_{16} = \Delta H_{13} + \Delta H_7 + 2\Delta H_{14} - 3\Delta H_8 + 6.3\Delta H_{15}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = \Delta H_{16} = -943.08 \pm 0.98 \text{ kcal/mole}.$$

TABLE 7. - Experimental heats of solution at 298 K, kcal/mole

| $\text{H}_2\text{SO}_3 \cdot 100\text{H}_2\text{O}(\text{l})$, reaction 8 | $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{s})$, reaction 9 | $\text{H}_2\text{O}(\text{l})$, reaction 10 | $\text{Al}_2\text{O}_3 \cdot 2.0\text{SO}_2$ $\cdot 5.3\text{H}_2\text{O}(\text{s})$, reaction 11 | $\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{l})$, reaction 12 |
|---|---|---|--|--|
| -85.531 | 2.865 | -0.2183 | -161.407 | -0.6830 |
| -86.436 | 2.988 | -.2185 | -161.169 | -.6623 |
| -86.459 | 2.955 | -.2183 | -161.174 | -.6667 |
| -86.837 | 2.863 | -.2183 | -161.427 | -.6495 |
| -85.450 | 2.922 | -.2184 | -161.315 | -.6670 |
| -86.473 | 2.887 | -.2183 | -161.313 | -.6661 |
| -85.863 | 2.937 | -.2187 | -161.489 | -.6737 |
| - | - | -.2179 | -161.541 | -.6589 |
| ¹ -86.150 | ¹ 2.917 | ¹ -0.2183 | ¹ -161.354 | ¹ -0.6659 |
| ± 0.404 | ± 0.036 | ± 0.0002 | ± 0.097 | ± 0.0070 |

¹Mean.

SUMMARY OF RESULTS

No anomalous behavior of the heat capacity was noted within the experimental data range. The values of standard entropy and $(H^\circ - H_0^\circ)$ at 298.15 K of basic aluminum sulfite are 85.2 ± 0.1 cal/deg mole and 14.13 kcal/mole, respectively. The precision uncertainty of heat capacity measurements was estimated as ± 0.1 pct at 50 to 311 K; ± 0.2 pct at 20 to 50 K; and about ± 5 pct at 11 K.

Owing to the lack of thermodynamic data on basic aluminum sulfite in the literature, no comparisons can be made with the results of this investigation.

Impurity corrections were not considered significant in deriving the formation enthalpy of basic aluminum sulfite. However, a larger uncertainty than the one calculated was assigned to the final value because of uncertainties associated with calibration measurements and auxiliary thermodynamic data. Based on the results of this investigation, the final value for the standard enthalpy of formation of basic aluminum sulfite at 298.15 K is -943.1 ± 1.2 kcal/mole.

Combination of the entropy of basic aluminum sulfite with entropies of Al(s), S(rh), O₂(g), and H₂(g) (6) gives a value of -410.4 ± 1.0 cal/deg-mole for the standard entropy of formation for reaction 16. The standard Gibbs energy of formation of basic aluminum sulfite is calculated to be -820.7 ± 1.2 kcal/mole by combining the enthalpy of formation and entropy of formation for reaction 16.

A summary of the thermodynamic data for Al₂O₃ · 2.0SO₂ · 5.3H₂O at 298.15 K is given in table 8.

TABLE 8. - Thermodynamic data for Al₂O₃ · 2.0SO₂ · 5.3H₂O
at 298.15 K

| | |
|----------------------------|--------------------------|
| ΔHf°..... | -943.1±1.2 kcal/mole. |
| ΔGf°..... | -820.7±1.2 kcal/mole. |
| S°..... | 85.2±0.1 cal/deg-mole. |
| ΔSf°..... | -410.4±1.0 cal/deg-mole. |
| (H°-H° ₀)..... | 14.13 kcal/mole. |

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⁵Title enclosed in parentheses is a translation from the language in which the item was originally published.

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