[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of Aluminum Oxide, Aluminum Sulfate, Potassium Sulfate, Ammonium Sulfate and Ammonium Bisulfate[1]

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A study of the thermodynamic properties of many of the compounds involved in the preparation of alumina from clays and alunite has been undertaken at the Pacific Experiment Station of the Bureau of Mines. High-temperature heat-content data are especially necessary for the accurate calculation of equilibria and heat balances for metallurgical processes at elevated temperatures. Data of this type are lacking in a large number of instances; accordingly this paper presents such data for aluminum oxide, anhydrous aluminum sulfate, potassium sulfate, ammonium sulfate and ammonium bisulfate.

Method and Materials

The high-temperature heat contents were determined by the "drop" method in a previously described apparatus.[3] The calorimeter was electrically calibrated, using the defined calorie (1 cal. = 4.1833 Int. joules). Each sample was enclosed in a platinum–rhodium alloy capsule whose heat content had been determined previously. For the aluminum oxide, aluminum sulfate, and potassium sulfate an unsealed capsule was used, while a gold-sealed capsule was employed for the ammonium sulfate and ammonium bisulfate measurements.

The aluminum oxide sample consisted of natural, almost colorless sapphires selected from a sample previously used by Parks and Kelley[4] for low-temperature specific-heat measurements. They were crushed and screened before using. Within the limits of experimental error, the sample analyzed 100.0% Al_2O_3.

Recrystallized reagent grade aluminum sulfate octodecahydrate was used to prepare anhydrous aluminum sulfate. The water of crystallization was removed by drying at 200° under reduced pressure for eight hours and then, at gradually increasing temperatures up to 450°, in a stream of dry air for approximately two hundred hours. Analysis showed 29.78% Al_2O_3 (theoretical 29.80%) and 0.2% H_2O.

The potassium sulfate was a portion of the sample which had been previously used by Moore and Kelley[5] for low-temperature specific heat measurements and carefully preserved. Previous analysis for sulfate had shown the material to be at least 99.7% pure.

Reagent grade ammonium sulfate was heated at 75° for several days. Analysis for sulfate gave 72.6% SO_4 (theoretical 72.73%).

The ammonium bisulfate was reagent grade material which was dried at 130° for several days. Titration with standard alkali gave 0.877% acid H (theoretical 0.876%) and analysis for sulfate, 83.5% SO_4 (theoretical 83.45%).

Results

The experimentally determined heat contents above 298.16°K. of aluminum oxide, aluminum sulfate, potassium sulfate, ammonium sulfate and ammonium bisulfate are given in Tables I, II, III, IV and V. The heat content values for aluminum sulfate have been corrected for the water impur-

TABLE I

HIGH-TEMPERATURE HEAT CONTENTS OF Al_2O_3

Mol. wt. = 101.94

Temp., °K.	$H_T - H_{298.16}$, cal./mole	Temp., °K.	$H_T - H_{298.16}$ cal./mole
462.6	3,670	1129.6	22,630
508.6	4,820	1318.1	28,370
651.8	8,660	1346.8	29,250
657.3	8,800	1510.0	34,300
725.1	10,680	1562.9	35,930
896.6	15,660	1660.2	38,880
920.5	16,350	1787.4	42,780
1119.8	22,330		

TABLE II

HIGH-TEMPERATURE HEAT CONTENTS OF $Al_2(SO_4)_3$

Mol. wt. = 342.12

Temp., °K.	$H_T - H_{298.16}$, cal./mole	Temp., °K.	$H_T - H_{298.16}$, cal./mole
475.7	13,020	936.8	56,130
568.5	21,390	978.1	59,840
661.2	29,270	1025.4	64,540
747.9	37,490	1072.5	69,110
812.9	43,990	1106.5	72,420
882.7	50,960		

TABLE III

HIGH-TEMPERATURE HEAT CONTENTS OF K_2SO_4

Mol. wt. = 174.252

Temp., °K.	$H_T - H_{298.16}$, cal./mole	Temp., °K.	$H_T - H_{298.16}$, cal./mole
462.4	5,700	1078.5	35,230
563.4	9,650	1143.1	38,360
669.9	14,060	1258.8	44,350
741.8	17,300	1316.3	47,710 (premelt.)
808.7	20,580	1337.3	49,240 (premelt.)
853.1	23,670 (pretran.)	1358.6	58,230
872.4	25,620	1461.9	63,250
889.6	26,420	1475.2	63,780
932.4	28,500	1578.8	68,840
1020.4	32,560	1698.0	74,240

TABLE IV

HIGH-TEMPERATURE HEAT CONTENTS OF $(NH_4)_2SO_4$

Mol. wt. = 132.14

Temp., °K.	$H_T - H_{298.16}$, cal./mole
402.1	5,080
441.2	7,090
482.8	9,350
551.5	13,490
594.3	16,180
639.6	19,560 (dec.)

TABLE V

HIGH-TEMPERATURE HEAT CONTENTS OF NH_4HSO_4

Mol. wt. = 115.108

Temp., °K.	$H_T - H_{298.16}$, cal./mole
354.6	2,050
373.0	2,840
380.9	3,080
397.7	3,840
420.7	8,210
451.0	9,690
505.4	12,500
569.5	16,110
632.2	19,520 (dec.)

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[2] Chemist, Pacific Experiment Station, Bureau of Mines.

[3] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

[4] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[5] G. E. Moore and K. K. Kelley, THIS JOURNAL, **64**, 2949 (1942).

TABLE VI

HEAT CONTENTS, ENTROPIES, AND FREE ENERGIES ABOVE 298.16°K.

	Al_2O_3			$Al_2(SO_4)_3$			K_2SO_4		
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$F_T - F_{298.16}$, cal./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$F_T - F_{298.16}$, cal./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$F_T - F_{298.16}$, cal./mole
400	2,175	6.27	− 1,610	7,160	20.55	− 6,880	3,400	9.79	− 4,790
500	4,600	11.67	− 3,760	15,220	38.76	−15,700	7,110	18.17	− 10,450
600	7,200	16.41	− 6,420	23,820	54.41	−26,090	11,130	25.49	− 16,840
700	10,000	20.72	− 9,530	32,880	68.36	−37,960	15,390	32.05	− 23,920
800	13,030	24.76	−13,050	42,690	81.45	−51,180	20,100	38.33	− 31,640
856							22,860(α)	41.67	− 36,240
856							24,800(β)	43.93	− 36,240
900	16,050	28.33	−16,970	52,650	93.19	−65,650	26,950	46.39	− 40,080
1000	18,890	31.32	−21,200	62,020	103.06	−81,180	31,630	51.32	− 49,170
1100	21,760	34.05	−25,720	71,790	112.37	−97,680	36,250	55.72	− 58,720
1200	24,740	36.64	−30,500				41,210	60.04	− 68,720
1300	27,800	39.09	−35,540				46,390	64.18	− 79,120
1342							48,660(β)	65.90	− 83,620
1342							57,420(l)	72.43	− 83,620
1400	30,890	41.38	−40,820				60,210	74.46	− 90,310
1500	33,980	43.51	−46,310				65,070	77.82	−102,140
1600	37,070	45.51	−52,020				69,840	80.89	−114,260
1700	40,110	47.35	−57,910				74,330	83.62	−126,700
1800	43,120	49.07	−63,980						

ity previously mentioned. The values marked "(pretran.)" or "(premelt.)" are considered to involve pretransition or premelting effects. Evidence of decomposition was observed for those runs marked "(dec.)" and measurements were then discontinued. All molecular weights accord with the 1941 International Atomic Weights.

Determinations were made from temperatures as low as 354°K. in the case of ammonium bisulfate to as high as 1773°K. for aluminum oxide. With all samples, except aluminum oxide, measurements were extended to the point where decomposition occurred, as evidenced by loss in weight of the capsule and contents.

The heat contents are represented graphically in Fig. 1. Aluminum oxide, aluminum sulfate and ammonium sulfate yield smooth curves with no discernible discontinuities. Both potassium sulfate and ammonium bisulfate exhibit sharp melting points, the premelting being only slight for the former and negligible at 20° below the melting point of the latter. The heats of fusion calculated from the heat content data were found to be 8,760 calories at 1,342°K. and 3,420 calories at 417°K., respectively. Potassium sulfate has a transition with a heat effect of 1,940 calories at 856°K. This transition has been observed by Roberts[6] and by Hüttner and Tammann.[7] The data of some other investigators, to be discussed below, have also been plotted in the case of aluminum oxide.

In Table VI the heat contents read at 100° intervals from the smooth curves through the data for aluminum oxide, aluminum sulfate and potassium sulfate have been listed. The corresponding graphically computed entropy increments and the free energy changes above 298.16° K. also are included. Table VII is a similar compilation for ammonium sulfate and ammonium bisulfate, except that the data have been listed at 50° intervals. For calculating the free energy values the following molal entropies at 298.16° K. were used: aluminum oxide, 12.5[8]; aluminum

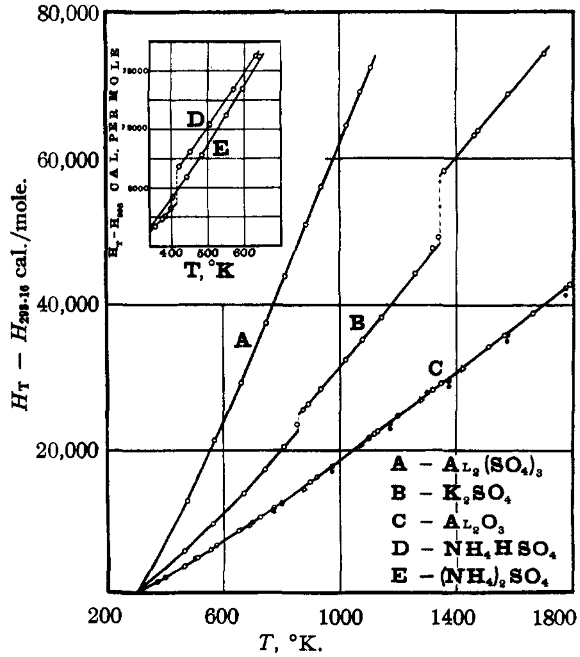

Fig. 1.—Heat contents above 298.16°K.: this work, ○; Auzhbikovich, △; Gronow and Schwiete, ⊖; Newman and Brown, ⊕; Wilkes ●.

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(6) H. S. Roberts, *Am. J. Sci.*, **35A**, 273 (1938).

(7) K. Hüttner and G. Tammann, *Z. anorg. Chem.*, **43**, 215 (1904–1905).

(8) K. K. Kelley, Bureau of Mines Bulletin 434, 1941, 115 pp.

sulfate, 57.2[9]; potassium sulfate, 42.0[5]; and ammonium sulfate, 52.6.[9] No entropy value has been reported for ammonium bisulfate.

TABLE VII

HEAT CONTENTS, ENTROPIES, AND FREE ENERGIES ABOVE 298.16°K.

	$(NH_4)_2SO_4$			NH_4HSO_4	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$F_T - F_{298.16}$, cal./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
350	2,510	7.78	− 2,940	1,880	5.81
400	4,970	14.35	− 6,130	3,900	11.20
417				4,620(s)	12.96
417				8,040(l)	21.16
450	7,570	20.46	− 9,620	9,650	24.88
500	10,340	26.30	−13,430	12,220	30.29
550	13,380	32.09	−17,520	15,000	35.58
600	16,590	37.67	−21,890	17,940	40.70

Heat content equations have been derived from the experimental data and the following specific heat values at 298.16°K.: aluminum oxide, 18.81[4]; aluminum sulfate, 62.00[9]; potassium sulfate, 31.08[5]; and ammonium sulfate, 44.81[9] cal. per deg. per mole, respectively. The appropriate temperature range and the mean percentage deviation of the heat content equation from the experimental data are indicated after each equation.

$Al_2O_3(s)$: $H_T - H_{298.16} = 27.43T + 0.00153T^2 + 847{,}000/T - 11{,}155$ (298°–1800°K.; 0.4%)

$Al_2(SO_4)_3(s)$: $H_T - H_{298.16} = 88.09T + 0.00740T^2 + 2{,}712{,}000/T - 36{,}020$ (298°–1100°K.; 0.7%)

$K_2SO_4(\alpha)$: $H_T - H_{298.16} = 27.43T + 0.01276T^2 + 352{,}000/T - 10{,}494$ (298°–856°K.; 0.4%)

$K_2SO_4(\beta)$: $H_T - H_{295.16} = 26.80T + 0.01005T^2 - 5{,}335$ (856°–1342°K.; 0.2%)

$K_2SO_4(l)$: $H_T - H_{298.16} = 47.28T - 5{,}938$ (1342°–1700°K.; 0.1%)

$(NH_4)_2SO_4(s)$: $H_T - H_{298.16} = 24.77T + 0.0336T^2 - 10{,}372$ (298°–600°K.; 0.8%)

$NH_4HSO_4(s)$: $H_T - H_{298.16} = 10.00T + 0.0405T^2 - 6{,}582$ (298°–417°K.; 1.0%)

$NH_4HSO_4(l)$: $H_T - \mathrm{H}_{298.16} = 16.06T + 0.0374T^2 - 5{,}160$ (417°–600°K.; 0.4%)

Differentiating the above heat content equations gives the following specific heat relationships

$Al_2O_3(s)$: $C_p = 27.43 + 0.00306T - 847{,}000/T^2$
$Al_2(SO_4)_3(s)$: $C_p = 88.09 + 0.01480T - 2{,}712{,}000/T^2$
$K_2SO_4(\alpha)$: $C_p = 27.43 + 0.02552T - 352{,}000/T^2$
$K_2SO_4(\beta)$: $C_p = 26.80 + 0.02010T$
$K_2SO_4(l)$: $C_p = 47.28$
$(NH_4)_2SO_4(s)$: $C_p = 24.77 + 0.0672T$
$NH_4HSO_4(s)$: $C_p = 10.00 + 0.0810T$
$NH_4HSO(l)$: $C_p = 16.06 + 0.0748T$

Discussion

In the present study the maximum error involved in measuring the temperature of the capsule and its contents in the furnace has been estimated as varying from 0.5° at 400°K. to 3° at 1800°K., corresponding to errors of 0.5 and 0.2%, respectively, in the heat content values at these temperatures. Frequent calibrations of the thermocouple were made at the gold and palladium points in the manner described by Southard.[3]

Of the five compounds investigated, there appear to be pertinent heat content data only for aluminum oxide. Gronow and Schwiete,[10] Wilkes,[11] and Miehr, Immke and Kratzert,[12] have made measurements to temperatures as high as those reached in this study. The results of Gronow and Schwiete check the present work very well; those of Wilkes are lower by approximately 3%, while those of Miehr and co-workers (not plotted) are erratic and higher by about 1%. Also Newman and Brown[13] and Auzhbikovich[14] have reported measurements to 1300°K. and 1400°K., respectively. The results of the former differ from the present work on the average by 0.5%, while those of the latter deviate by about 1% in the lower temperature range and are in excellent agreement at higher temperatures.

The heat content of a sample of aluminum oxide prepared by ignition of aluminum sulfate also was determined at several temperatures during the course of the present work. However, the weight of sample used was limited by the small apparent density and corrections for the moisture impurity were uncertain, especially at high temperatures; hence the results were somewhat erratic and not as reliable as those for the sapphires. In general, a slightly higher heat content was indicated.

The transition temperature and melting point of potassium sulfate, 856°K. and 1,342°K., respectively, used in this paper are those reported by Roberts.[6] The melting point of the ammonium bisulfate sample was found experimentally by cooling rates to be 417 ± 0.5°K. Kendall and Davidson[15] have reported 420.1 ± 0.5°K. for the melting point.

Summary

The high-temperature heat contents, above 298.16°K., of aluminum oxide (sapphire), anhydrous aluminum sulfate, potassium sulfate, ammonium sulfate and ammonium bisulfate were determined from about 473°K. to temperatures between 623 to 1773°K., depending on the thermal stability of the substance. The heats of fusion of potassium sulfate and ammonium bisulfate and the heat of the transition in potassium sulfate have been obtained from these data.

Heat content and specific heat equations, adequately representing the experimental data, have been derived for each substance. The data also

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(9) C. H. Shomate, unpublished data.

(10) H. E. v. Gronow and H. E. Schwiete, *Z. anorg. allgem. Chem.*, **216**, 185 (1933).

(11) G. B. Wilkes, *J. Am. Ceram. Soc.*, **15**, 72 (1932).

(12) W. Miehr, H. Immke and I. Kratzert, *Tonind.-Ztg.*, **50**, 1791 (1926).

(13) A. B. Newman and G. G. Brown, *Ind. Eng. Chem.*, **22**, 995 (1930).

(14) A. E. Auzhbikovich, *Legkie Metal.*, **5**, No. 11, 23 (1936).

(15) J. Kendall and A. Davidson, *Ind. Eng. Chem.*, **13**, 303 (1921).

have been summarized by giving the heat content, entropy and free energy increments above 298.16°K. at even temperature intervals.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Properties of Vanadium Tetrachloride

BY J. H. SIMONS AND M. G. POWELL

Vanadium tetrachloride is an inorganic compound of interesting properties. It is a dark red liquid which hydrolyzes readily, which decomposes slowly at ordinary temperatures to chlorine and the trichloride, and which reacts as a chlorinating agent. It is non-salt-like in character, has a low dielectric constant, is soluble in carbon tetrachloride, has a liquid range from −26 to +152° at atmospheric pressure and has a relatively low boiling point. Its valence is unexpected in view of the existence of the tri- and penta-fluorides, and the non-existence of a tetrafluoride. It is an odd molecule, if the formula VCl_4 is correct; and its intense color may be used as supporting evidence of the free radical assumption.

Vanadium tetrachloride was prepared by Roscoe[1] by the reaction of chlorine on vanadium or vanadium nitride at red heat. From the analysis of his product and the determined vapor density, he assigned the formula VCl_4 to the compound. He found the liquid density to be 1.8584 g./cc. at 0°, 1.8363 at 8°, and 1.8159 at 30°. He was unable to obtain the pentachloride by the reaction of the tetrachloride with chlorine. He found its boiling point to be 154° at 760 mm. pressure. Biltz and Kuenecke[2] found the boiling point to be 148.5° at 755 mm. pressure, and Ruff and Lickfett[3] report 153.7° at 768 mm. pressure. The freezing point was found by Biltz and Kuenecke[2] to be −109°, but Morette[4] obtained the value of $-28 \pm 2°$. Voigt and Biltz[5] found the electrical conductivity to be too small to measure. Loomis and Schlundt[6] determined the dielectric constant at room temperature. Their average value was 3.05.

From a series of thermochemical reactions Ruff and Friedrich[7] concluded the heats of formation of the chlorides of vanadium to be

$$V(s) + Cl_2(g) = VCl_2(s) + 147 \pm 4 \text{ kcal.}$$
$$V(s) + 3/2\ Cl_2(g) = VCl_3(s) + 187 \pm 8 \text{ kcal.}$$
$$V(s) + 2Cl_2(g) = VCl_4(l) + 165 \pm 4 \text{ kcal.}$$

From this the following equation for the decomposition of vanadium chloride results

$$2VCl_4(l) \longrightarrow 2VCl_3(s) + Cl_2(g) + 44 \pm 20 \text{ kcal.}$$

Preparation.—Vanadium tetrachloride was prepared by a modification of the method given by Mentes.[8] Dry chlorine was passed over ferro-vanadium contained in a glass combustion tube in an electric furnace. One-quarter-inch mesh ferro-vanadium containing 90% vanadium was used. The entering chlorine passed through a pair of sulfuric acid bubblers for the purpose of drying. The product from the exit side of the combustion tube was received in a 500-cc. flask. This was the part of an all-glass fractionating column which contained no stopcock and its attendant grease.[9] On the take-off of the fractionating column was sealed a small condenser and a fraction cutter. This fraction cutter had a number of 50-cc. flasks sealed onto it to receive the fractions. Each of these receivers was provided with a side arm containing an internal capillary for breaking off purposes. Rotation of the fraction cutter on a ground joint provided a means of directing the liquid stream into the different receivers. The entire apparatus was sealed together so that the product came in contact only with glass.

The temperature of the reaction tube was adjusted to 200°. This is a lower temperature than has been previously used but was employed to reduce the amount of ferric chloride in the product.

At the end of the reaction, the connection between the reaction tube and receiver was sealed, and the product was distilled. The receivers were sealed off from the fraction cutter after they were filled.

The samples collected boiled at 149.7° at a pressure of 731 mm. These samples were found to remain in a satisfactory condition for several months without appreciable decomposition, if kept in the dark.

Vanadium trichloride was prepared from vanadium tetrachloride by heating it at 140° for one week, while passing dry carbon dioxide over it. The vanadium trichloride was dried by heating it at 160° for three days. It was analyzed for vanadium by titrating with potassium permanganate and found to contain 32.30%. The theoretical is 32.39%. A gravimetric analysis for chlorine gave 67.10%, while the theoretical is 67.61%.

The Equilibrium Constant for the Reaction $2VCl_3(s) + Cl_2(g) \rightleftharpoons 2VCl_4(g)$.—The equilibrium constant for this reaction was determined by subjecting a sample of vanadium trichloride to a known volume of chlorine and determining the increase in pressure when equilibrium was attained.

A diagram of the apparatus used is shown in Fig. 1. This consisted essentially of a reaction vessel containing a boat of vanadium trichloride in an electric furnace. This was connected with capillary tubing to a U-tube of sulfuric acid which in turn was connected to an adjustable mercury manometer. The sulfuric acid U-tube was calibrated in cubic centimeters.

As the apparatus was originally sealed together, the reaction vessel was open at the end opposite the capillary tubing. A stream of dry nitrogen was passed through the apparatus. A sample of vanadium trichloride was transferred to a small porcelain boat, the operation being performed in a dry box. It was placed in a glass tube and transported in an atmosphere of dry nitrogen. After introduction of the porcelain boat, the end of the reaction tube was drawn out to form a capillary, using care to pre-

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[1] Roscoe, *Ann. Chem.*, Supplement **7**, 70 (1869).

[2] Biltz and Kuenecke, *Z. anorg. allgem. Chem.*, **147**, 171.(1925).

[3] Ruff and Lickfett, *Ber.*, **44**, 506 (1911).

[4] Morette, *Compt. rend.*, **202**, 1846 (1936).

[5] Voigt and Biltz, *Z. anorg. allgem. Chem.*, **133**, 277 (1924).

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[9] Simons, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 29 (1938).