Table I records the data for sodium methylate catalysis; Table II those for amine catalysis. In Table II the first three columns give the composition of the solution; the fourth gives the value of the logarithmic dissociation constant of the amine appropriate to the ionic strength of the solution at equilibrium[14]; the fifth, the concentration of methylate ion as calculated from the values in columns 2, 3, and 4; and the sixth column, the value of the observed velocity constant.

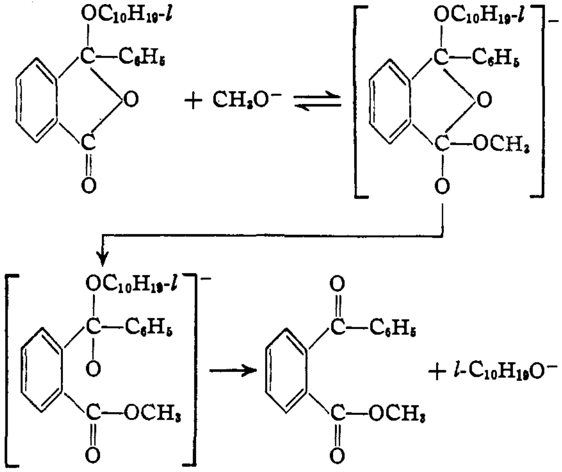
The data of the second and third columns of Table I, and of the fifth and sixth columns of Table II are plotted in Figs. 1 and 2. These figures show that the rate of the reaction at zero base concentration approximates zero. The linearity of the curves points to specific catalysis by the methylate ion, but the proportionality constants in the equation $k = k'(\mathrm{CH_3O^-})$ are different for the two sets of data, the values being 5.27 (25°) and 9.59 (35°) for Fig. 1, and 2.63 (25°) and 4.72 (35°) for Fig. 2. No satisfactory explanation for this discrepancy can be obtained from the data. The deviation of the first-order curves from linearity in the case of butylamine is not great enough to account for it. The data show that there is no retardation of the reaction due to the presence of free amine, and that there is no definite trend in the values of k' with change in the ionic strength.

Using the values of k' obtained from the slopes of the lines in Figs. 1 and 2, the energy of activation is calculated to be 11,100 cal. for the data of Fig. 1 and 10,800 cal. for the data of Fig. 2.

The average rotation at the end of the reaction is that of pure *l*-menthol at the same concentration. Therefore, in the ester interchange, no change in the configuration at the asymmetric carbon atom attached to the alcoholic oxygen has taken place, and it may be concluded that fission of the pseudo-ester takes place at the bond between the alcoholic oxygen and the carbonyl carbon of the acid.[15]

The following mechanism is postulated for the reaction, equation (1) being rate determining:

1



2 $l\text{-}\mathrm{C_{10}H_{19}O^-} + \mathrm{CH_3OH} \longrightarrow l\text{-}\mathrm{C_{10}H_{19}OH} + \mathrm{CH_3O^-}$

Summary

The reaction of pseudo *l*-menthyl *l*-*o*-benzoylbenzoate with methanol in the presence of methylate ion to form normal methyl *o*-benzoylbenzoate has been shown to be a pseudo first-order reaction, specifically catalyzed by methylate ion. The activation energy is 11,000 cal. There is no detectable primary salt effect. Fission of the pseudo-ester takes place at the bond between the alcoholic oxygen and the carbonyl carbon of the acid. A mechanism consistent with the facts has been postulated.

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[14] Schaefgen, Newman and Verhoek, THIS JOURNAL, 66, 1847 (1944).

[15] *Cf.* Holmberg, *Ber.*, 45, 2997 (1912).

[CONTRIBUTION FROM THE BUREAU OF MINES, PACIFIC EXPERIMENT STATION, U. S. DEPARTMENT OF THE INTERIOR]

Heats of Formation of $\mathrm{Al_2(SO_4)_3{\cdot}6H_2O}$, $\mathrm{Al_2(SO_4)_3}$, $\mathrm{KAl(SO_4)_2{\cdot}12H_2O}$, and $\mathrm{KAl(SO_4)_2}$[1]

BY FRANK E. YOUNG[2]

The heats of formation of several metallurgically important compounds of aluminum are being determined at the Pacific Experiment Station of the Bureau of Mines. A previous paper[3] described determinations of the heats of formation of aluminum nitrate hexahydrate and enneahydrate. New determinations of the heats of formation of anhydrous and hexahydrated aluminum sulfate and anhydrous and dodecahydrated potassium aluminum sulfate are reported in the present paper. The only previously available value of the heat of formation of anhydrous aluminum sulfate is an estimate, and those of the other compounds are based upon data antedating modern thermochemical methods. Such data frequently are found to be unreliable.

Materials

Aluminum sulfate hexahydrate was prepared by heating recrystallized J. T. Baker aluminum sulfate octodecahydrate (containing a maximum of 0.20% alkali salts before recrystallization) in a stream of dry air to 100° in five and one-half hours, followed by twenty-one hours at 120° Analysis showed a composition corresponding to $\mathrm{Al_2(SO_4)_3{\cdot}4.54H_2O}$. The water content was adjusted by

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

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

[3] Young, THIS JOURNAL, 66, 777 (1944).

adding the required amount of water to the substance contained in a flask, then rapidly removing most of the air and sealing, and finally heating for thirty hours at 60°, sixteen hours at 80° and thirty-four hours at 110°. Analysis by direct ignition in a gas–oxygen blast lamp gave 22.66% aluminum oxide (theoretical, 22.64%) as the mean of three determinations.

Anhydrous aluminum sulfate[4] was prepared from recrystallized Baker aluminum sulfate octodecahydrate originally containing less than 0.20% alkali salts, by heating the hydrated salt slowly to 325° and allowing it to stand between 325° and 340° for fourteen hours. It was then heated in a stream of dry air for thirty-three hours at 450°, followed by thirty-two hours at 320°. Analysis by direct ignition in a gas–oxygen blast lamp gave an average of 29.89% aluminum oxide (corresponding to the composition 99.42% aluminum sulfate, 0.27% aluminum oxide, and 0.31% water). Further removal of water was found to be impractical as it was accompanied by increasing decomposition. The thermal results were corrected for the presence of these impurities.

Potassium sulfate was prepared by drying Mallinckrodt analytical reagent material at 120° for two hours. Analysis for sulfate gave a purity of 99.70% potassium sulfate. The thermal results were corrected for impurities on the assumption that they were sodium sulfate (0.17%), calcium sulfate (0.12%), and insoluble material (0.01%). The ratio of sodium to calcium was that given by the manufacturer's analysis.

Mallinckrodt analytical reagent potassium aluminum sulfate dodecahydrate, containing less than 0.02% impurities, was used without drying or other treatment. Analysis for alumina gave an average of 10.74% aluminum oxide (theoretical, 10.74%).

Anhydrous potassium aluminum sulfate[5] was prepared by heating Mallinckrodt analytical reagent potassium aluminum sulfate dodecahydrate at 76 to 82° for forty-four hours, followed by twenty-nine hours at 195°, during which about 98% of the water was removed. Finally, the product was heated at 240° for one hundred and twenty-one hours; during the last thirty hours the heating chamber was evacuated. Analyses gave an average of 99.54% $KAl(SO_4)_2$, by precipitation of aluminum with 8-hydroxyquinoline, 0.28% water, by the Penfield method, and 0.22% insoluble material (Al_2O_3). Further dehydration was found to be disadvantageous because of the accompanying decomposition. Corrections were made for these impurities.

The heats of formation of the hydrated compounds were determined by measuring the heats of solution in 4.000 *N* hydrochloric acid ($HCl \cdot 12.68H_2O$), prepared by diluting reagent-quality hydrochloric acid and standardizing against sodium carbonate.

The heats of formation of the anhydrous compounds were determined by measuring the heats of solution in 0.2000 *N* potassium hydroxide ($KOH \cdot 277.3H_2O$), prepared from Mallinckrodt analytical reagent material and standardized against sulfuric acid which, in turn, had been standardized against sodium carbonate. It was necessary to use potassium hydroxide in determining the heats of solution of the anhydrous compounds because of their low rate of solution in acid.

Method

The heats of formation were determined by measuring heats of solution in the appropriate solvent in a calorimeter similar to that described by Southard.[6] The thermometer in the present work had a sensitivity of 1170 μv. per degree. At the beginning of each heat of solution measurement, the calorimeter was calibrated electrically. Both the thermometer and heater currents were measured on a White, 10,000 μv., double potentiometer and were estimated to 0.01 μv. by galvanometer deflections.

The results are expressed in defined calories (1 cal. = 4.1833 Int. joules). All formula weights were calculated in accordance with the 1941 International Atomic Weights and corrected to vacuum by the following densities: anhydrous aluminum sulfate, 2.71; aluminum sulfate hexahydrate, 2.14; potassium sulfate, 2.66; anhydrous potassium aluminum sulfate, 2.55; and potassium aluminum sulfate dodecahydrate, 1.75.[7]

Measurements and Results

Each heat of formation has been obtained from the heats of the reactions represented by skeleton equations in the pertinent table below. The uncertainties given in the last column of each table are twice the standard deviations from the means of the experimental results concerned. When a series of reactions is involved, the uncertainty has been taken as the square root of the sum of the squares of the uncertainties of the individual reactions. Rossini and Deming[8] have discussed this method of calculating uncertainties. The final values of the heats of formation and the corresponding uncertainties have been rounded to the nearest 10 calories. As the final temperatures of the heat-of-solution measurements were always within a few hundredths degree of 25°, no correction to the standard temperature was needed. The average sample weights used in the heat of solution measurements correspond to final concentrations of $Al_2(SO_4)_3 \cdot 723.2HCl \cdot 9170H_2O$ for the samples dissolved in hydrochloric acid and $2KAlO_2 \cdot 3K_2SO_4 \cdot 136.4KOH \cdot 40{,}048H_2O$ for the samples dissolved in potassium hydroxide after making necessary minor corrections. The temperature changes during solution ranged from 9.19 μv. (0.00785°) for the solution of potassium sulfate in potassium hydroxide to 286.38 μv. (0.24477°) for the solution of potassium aluminum sulfate dodecahydrate in hydrochloric acid. The time required for complete solution of the sample varied from one minute for potassium sulfate to thirty minutes for aluminum sulfate hexahydrate in hydrochloric acid.

Heat of Formation of Aluminum Sulfate Hexahydrate.—The skeleton equations representing the reactions from which the heat of formation of aluminum sulfate hexahydrate was obtained are shown in Table I.

TABLE I

HEAT OF FORMATION OF $Al_2(SO_4)_3 \cdot 6H_2O$ (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$	Uncertainty
(1)	$2Al + 6H^+ \longrightarrow 2Al^{+++} + 3H_2$	−253,668	124
(2)	$3H_2 + 3S + 6O_2 \longrightarrow 6H^+ + 3SO_4^{=}$	−627,660	330
(3)	$Al_2(SO_4)_3 \cdot 6H_2O \longrightarrow 2Al^{+++} + 3SO_4^{=} + 6H_2O$	−23,084	31
(4)	$6H_2 + 3O_2 \longrightarrow 6H_2O$	−409,908	60
(5)	$2Al + 3S + 9O_2 + 6H_2 \rightarrow Al_2(SO_4)_3 \cdot 6H_2O$	−1,268,150	360

$$\Delta H_5 = \Delta H_1 + \Delta H_2 - \Delta H_3 + \Delta H_4$$

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(4) This substance was prepared by Dr. E. H. Huffman, formerly chemist, Pacific Experiment Station, Bureau of Mines.

(5) This substance was prepared by A. E. Salo, metallurgist, Pacific Experiment Station, Bureau of Mines.

(6) Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

(7) The densities of $Al_2(SO_4)_3 \cdot 6H_2O$ and $KAl(SO_4)_2$ were measured by A. E. Salo, metallurgist, Pacific Experiment Station, Bureau of Mines.

(8) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

The heat of solution of aluminum in 4 *N* hydrochloric acid reported in a previous paper,[3] $-126{,}834 \pm 62$ cal. per mole, has been adopted here as it was measured under identical conditions of concentration and temperature. ΔH_1 represents twice this value or $-253{,}668 \pm 124$ cal. per mole.

Reaction (2) represents the heat of formation of 3 moles of sulfuric acid in the final solution of reaction (1), or $2(AlCl_3{\cdot}358.6HCl{\cdot}4{,}585H_2O)$. This value was obtained from the following set of reactions

(6) $3H_2 + 3S + 6O_2 + 79.11H_2O \longrightarrow 3H_2SO_4{\cdot}79.11H_2O$

(7) $3H_2SO_4{\cdot}79.11H_2O + 2(AlCl_3{\cdot}358.6HCl{\cdot}4585H_2O) \longrightarrow Al_2(SO_4)_3{\cdot}2(361.6HCl{\cdot}4624.56H_2O)$

(8) $Al_2(SO_4)_3{\cdot}2(361.6HCl{\cdot}4585H_2O) + 79.11H_2O \longrightarrow Al_2(SO_4)_3{\cdot}2(361.6HCl{\cdot}4624.56H_2O)$

The required heat of formation, ΔH_2, is equal to $\Delta H_6 + \Delta H_7 - \Delta H_8$. The value for ΔH_6 was obtained from the work of Roth, Grau, and Meichsner,[9] who reported $\Delta H_{293.16} = -194{,}150 \pm 100$ for the reaction, $S(\text{rh}) + 2O_2 + H_2 \rightarrow H_2SO_4(\text{l})$. Using the data of Becker and Roth,[10] $\Delta H_{293.16}$ may be calculated for the reaction $H_2SO_4(\text{l}) + 26.37H_2O \rightarrow H_2SO_4{\cdot}26.37H_2O$ as $-17{,}035$ cal. Addition of these two reactions gives the reaction $S(\text{rh}) + 2O_2 + H_2 + 26.37H_2O \rightarrow H_2SO_4{\cdot}26.37H_2O$, for which $\Delta H_{293.16}$ is found to be $-211{,}185 \pm 110$ cal. per mole or, correcting to 25°, $\Delta H_{298.16} = -211{,}220 \pm 110$ cal. The desired heat, ΔH_6, is three times this value or $-633{,}660 \pm 330$ cal. The heats of reactions (7) and (8) were found to be $+54 \pm 14$ and $-5{,}946 \pm 18$ cal., respectively, by direct measurement in the present work. Subtracting ΔH_8 from the sum of $\Delta H_6 + \Delta H_7$ gives $-627{,}660 \pm 330$ cal. for ΔH_2.

Five measurements were made of the heat of solution of aluminum sulfate hexahydrate, giving $-23{,}507 \pm 8$ as the mean of $-23{,}505$, $-23{,}505$, $-23{,}523$, $-23{,}502$, and $-23{,}502$ cal. per mole. A directly determined correction of $+423 \pm 30$ cal. for the heat of solution of the water of hydration ($\Delta H = -423 \pm 30$ cal.) gives $-23{,}084 \pm 31$ for ΔH_3.

The value of ΔH_4 was obtained by multiplying the result of Rossini[11] for the heat of formation of water, $-68{,}318 \pm 10$ cal. per mole, by six, giving $-409{,}908 \pm 60$ cal.

The heat of formation of aluminum sulfate hexahydrate from the elements, found by subtracting ΔH_3 from $\Delta H_1 + \Delta H_2 + \Delta H_4$, is $-1{,}268{,}150 \pm 360$ cal. per mole.

Heat of Formation of Anhydrous Aluminum Sulfate.—The skeleton equations, representing the reactions by which the heat of formation of anhydrous aluminum sulfate was determined, are shown in Table II. Because of the difficulty in dissolving the anhydrous compound in acid, reactions (9), (10) and (11) were carried out in 0.2000 *N* potassium hydroxide.

TABLE II

HEAT OF FORMATION OF $Al_2(SO_4)_3$ (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$	Uncertainty
(9)	$2Al + 3S + 9O_2 + 6H_2 \longrightarrow Al_2(SO_4)_3{\cdot}6H_2O$	−1,268,150	360
(10)	$Al_2(SO_4)_3{\cdot}6H_2O + 8OH^- \longrightarrow 2AlO_2^- + 3SO_4^{=} + 10H_2O$	−65,616	51
(11)	$Al_2(SO_4)_3 + 8OH^- \longrightarrow 2AlO_2^- + 3SO_4^{=} + 4H_2O$	−102,869	216
(12)	$6H_2 + 3O_2 \longrightarrow 6H_2O$	−409,908	60
(13)	$2Al + 3S + 6O_2 \longrightarrow Al_2(SO_4)_3$	−820,990	430

$\Delta H_{13} = \Delta H_9 + \Delta H_{10} - \Delta H_{11} - \Delta H_{12}$

Reactions (9) and (12) already have been discussed as reactions (5) and (4), respectively.

Seven measurements of ΔH_{10} were made, yielding $-65{,}616 \pm 51$ cal. per mole as the mean of $-65{,}620$, $-65{,}680$, $-65{,}595$, $-65{,}515$, $-65{,}639$, $-65{,}546$, and $-65{,}700$. These individual results and their mean include a directly measured correction of -10 cal. for the heat of solution of the water of hydration ($\Delta H = +10$ cal.).

Eight measurements of ΔH_{11} were made to obtain $-103{,}139$, $-102{,}582$, $-102{,}431$, $-102{,}474$, $-103{,}052$, $-102{,}990$, $-103{,}248$, and $-103{,}036$. These have a mean of $-102{,}869 \pm 210$ cal. per mole, after applying a -958-cal. correction for impurities, of which -682 cal. was attributable to water. This correction was made by treating the Al_2O_3-impurity as insoluble and correcting for the water-impurity on the basis of the heat of hydration obtained from heats of solution of the hexahydrate and nearly anhydrous materials.

The heat of formation of anhydrous aluminum sulfate, $\Delta H_{13} = \Delta H_9 + \Delta H_{10} - \Delta H_{11} - \Delta H_{12}$, is $-820{,}990 \pm 430$ cal. per mole.

Heat of Formation of Potassium Aluminum Sulfate Dodecahydrate.—The skeleton equations, representing the reactions to determine the heat of formation of potassium aluminum sulfate

TABLE III

HEAT OF FORMATION OF $KAl(SO_4)_2{\cdot}12H_2O$ (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$	Uncertainty
(14)	$K + \frac{1}{2}S + O_2 \longrightarrow \frac{1}{2}K_2SO_4$	−171,335	150
(15)	$Al + \frac{3}{2}S + 3H_2 + \frac{9}{2}O_2 \longrightarrow \frac{1}{2}[Al_2(SO_4)_3{\cdot}6H_2O]$	−634,075	180
(16)	$\frac{1}{2}\left[Al_2(SO_4)_3{\cdot}6H_2O\right] \longrightarrow Al^{+++} + \frac{3}{2}SO_4^{=} + 3H_2O$	−11,542	16
(17)	$\frac{1}{2}K_2SO_4 \longrightarrow K^+ + \frac{1}{2}SO_4^{=}$	+4,767	9
(18)	$KAl(SO_4)_2{\cdot}12H_2O \longrightarrow K^+ + Al^{+++} + 2SO_4^{=} + 12H_2O$	+20,654	61
(19)	$9H_2 + \frac{9}{2}O_2 \longrightarrow 9H_2O(\text{l})$	−614,862	90
(20)	$K + Al + 2S + 10O_2 + 12H_2 \longrightarrow KAl(SO_4)_2{\cdot}12H_2O$	−1,447,700	260

$\Delta H_{20} = \Delta H_{14} + \Delta H_{15} + \Delta H_{16} + \Delta H_{17} - \Delta H_{18} + \Delta H_{19}$

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(9) Roth, Grau, and Meichsner, *Z. anorg. Chem.*, **193**, 161 (1930).

(10) Becker and Roth, *Z. physik. Chem.*, **A169**, 287 (1934).

(11) Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

dodecahydrate are shown in Table III. These reactions, except (14), were carried out in 4.000 *N* hydrochloric acid.

The value adopted for ΔH_{14} was one-half the value given by Bichowsky and Rossini[12] as the heat of formation of potassium sulfate. This value, after correction to 25°, is −342,670, making $H_{14} = -171,335$, to which an uncertainty of 150 cal. was assigned. ΔH_{15} and ΔH_{16} are one-half the values of ΔH_5 and ΔH_3, respectively.

Six measurements were made of the heat of solution of potassium sulfate with +9,534 ± 18 cal. per mole as the mean of +9,506, 9,562, 9,549, 9,542, 9,523, and 9,513. These values include a +31-cal. correction for impurities. One-half of the mean molal heat of solution was used for ΔH_{17}.

Six determinations of the heat of solution of potassium aluminum sulfate dodecahydrate gave +19,810, 19,797, 19,821, 19,817, 19,819, and 19,786, with a mean of 19,808 ± 11 cal. per mole. $\Delta H_{18} = +20,654 \pm 61$ cal. is obtained by adding a directly determined correction of +846 ± 60 cal. for the heat of solution of the 12 moles of water of hydration ($\Delta H = -846 \pm 60$ cal.) to the above mean of +19,808 ± 11 cal. per mole.

ΔH_{19} is nine times Rossini's heat of formation of water, $9(-68,318 \pm 10) = -614,862 \pm 90$ cal. The heat of formation of potassium aluminum sulfate dodecahydrate from the elements is found to be −1,447,700 ± 260 cal. per mole by subtracting ΔH_{18} from the sum $\Delta H_{14} + \Delta H_{15} + \Delta H_{16} + \Delta H_{17} + \Delta H_{19}$.

Heat of Formation of Potassium Aluminum Sulfate.—Table IV shows the skeleton equations of reactions used to determine the heat of formation of anhydrous potassium-aluminum sulfate. It was necessary to make the measurements in 0.2000 *N* potassium hydroxide because of the difficulty in dissolving the anhydrous compound in acid.

TABLE IV

HEAT OF FORMATION OF $KAl(SO_4)_2$ (CAL. PER MOLE)

	Reaction	$\Delta H_{298.16}$	Uncertainty
(21)	$K + \frac{1}{2}S + O_2 \longrightarrow \frac{1}{2}K_2SO_4$	−171,335	150
(22)	$Al + \frac{3}{2}S + \frac{9}{2}O_2 + 3H_2 \longrightarrow \frac{1}{2}[Al_2(SO_4)_3 \cdot 6H_2O]$	−634,075	180
(23)	$\frac{1}{2}[Al_2(SO_4)_3 \cdot 6H_2O] + 4OH^- \longrightarrow AlO_2^- + \frac{3}{2}SO_4^{=} + 5H_2O$	−32,808	26
(24)	$\frac{1}{2}K_2SO_4 \longrightarrow K^+ + \frac{1}{2}SO_4^{=}$	+2,974	14
(25)	$KAl(SO_4)_2 + 4OH^- \longrightarrow K^+ + AlO_2^- + 2SO_4^{=} + 2H_2O$	−41,120	200
(26)	$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$	−204,954	30
(27)	$K + Al + 2S + 4O_2 \longrightarrow KAl(SO_4)_2$	−589,170	310

$\Delta H_{27} = \Delta H_{21} + \Delta H_{22} + \Delta H_{23} + \Delta H_{24} - \Delta H_{25} - \Delta H_{26}$

Reactions (21), (22) and (23) have been discussed as reactions (14), (5), and (10), respectively, one-half of each molal heat of reaction being used.

Seven measurements of the heat of solution of potassium sulfate in 0.2000 *N* potassium hydroxide were made, yielding +5,911, 5,882, 5,978, 5,965, 5,966, 5,979 and 5,957, with a mean of 5,948 ± 27 cal. per mole. One-half this value was assigned for ΔH_{24}. The values include a correction of +29 cal. per mole of potassium sulfate for impurities. It was observed that variations in sample size had a marked effect on the heat of solution, making a correction necessary. This correction, which averaged 26 cal. per mole, also is included in the above heats of solution.

To obtain the heat of solution of completely dehydrated potassium aluminum sulfate, ΔH_{25}, heats of solution of samples with several different amounts of water were measured and the heat of solution of the anhydrous compound obtained by extrapolation. These samples were prepared by adding small weighed amounts of water to the original material, which contained 0.28% water. The water was added as droplets to the upper surface of the walls of the containing flask, which then was evacuated quickly and heated at 80° for about 24 hours to assure uniform distribution. Adding the water in this manner allowed it to vaporize completely before contacting the potassium aluminum sulfate, thus preventing formation of lumps.

Seven measurements were made of the heat of solution of the original material containing 0.28% water, giving −39,986, −39,989, −39,958, −39,966, −39,870, −39,966, and −39,782. No explanation can be given for the two low results, −39,870 and −39,782, which were considerably outside the usual limits of error and were excluded in computing the average of −39,973 ± 12 cal. per mole. It was necessary to make correction for the marked differences in heats of solution accompanying variations in sample weight. This correction, averaging 222 cal., was made graphically and is included in the above results.

Three measurements were made of the heat of solution of potassium aluminum sulfate containing 0.39% water. The results, corrected for variations in sample weight (average correction, 75 cal.), were −39,527, −39,483, and −39,516, with a mean of −39,509 ± 26 cal. per mole.

Four values were obtained for the heat of solution of potassium aluminum sulfate containing 0.46% water: −39,253, −39,263, −39,243 and −39,253, with a mean of −39,253 ± 8 cal. per mole. These results include a correction averaging 8 cal. for differences in sample weight.

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[12] Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

Heats of solution of two other samples were measured; one, with 0.57% water, gave −39,134 cal. per mole, and one, with 0.67% water, gave −38,892, −38,881, and −38,886, with a mean of −38,887 ± 6 cal. per mole.

The mean heats of the solution of the samples containing 0.28, 0.39, and 0.46% water fall on a straight line when plotted against water content. The results for the two remaining samples, with 0.57 and 0.67% water, respectively, lie considerably above this line and indicate that the water is held differently when the amount is 0.57% or more. The line obtained from the three less-hydrated samples was extrapolated to zero water content and used for correcting the results. The corrected values are: −41,133, −41,135, −41,104, −41,112, (−41,017), −41,112 and (−40,929) for the sample with 0.28% water; −41,122, −41,079 and −41,112 for the sample containing 0.39% water; and −41,133, −41,143, −41,122 and −41,133 for the sample with 0.46% water. The mean value is −41,120 ± 10. In all these results, a correction of −82 cal. has been made for the aluminum oxide impurity. Because of the difficulty in determining the water content accurately, the actual uncertainty in the above mean value probably is much larger than the empirically calculated 10 cal. For this reason, the uncertainty in the heat of solution has been increased to 200 cal. as indicated by the spread in the water analyses (0.06%). The value used for ΔH_{25} is −41,120 ± 200 cal. per mole.

Three times Rossini's[11] heat of formation of water, −204,954 ± 30 cal., was used for ΔH_{26}.

The heat of formation of anhydrous potassium aluminum sulfate, $\Delta H_{27} = \Delta H_{21} + \Delta H_{22} + \Delta H_{23} + \Delta H_{24} - \Delta H_{25} - \Delta H_{26}$, is −589,170 ± 310 cal. per mole.

Discussion

The heats of formation from the elements involve results from the literature for sulfuric acid, potassium sulfate and water, as indicated above. However, several heat-of-reaction values of less general applicability may be obtained from the present work without recourse to any values from the literature. These reactions, their heats, and methods of calculation are indicated below

(28) $2Al + 3H_2SO_4\ (aq., 26.37H_2O) + 6H_2O(l) \longrightarrow Al_2(SO_4)_3{\cdot}6H_2O(c) + 3H_2$
$\Delta H_{28} = \Delta H_1 - \Delta H_3 + \Delta H_7 - \Delta H_8 = -224{,}580 \pm 130$ cal.

(29) $Al_2(SO_4)_3 + 6H_2O(l) \longrightarrow Al_2(SO_4)_3{\cdot}6H_2O$;
$\Delta H_{29} = \Delta H_{11} - \Delta H_{10} = -37{,}250 \pm 220$ cal.

(30) $2Al + 3H_2SO_4\ (aq., 26.37H_2O) \longrightarrow Al_2(SO_4)_3\ (c) + 3H_2$
$\Delta H_{30} = \Delta H_{28} - \Delta H_{29} = -187{,}330 \pm 260$ cal.

(31) $\frac{1}{2}[Al_2(SO_4)_3{\cdot}6H_2O] + \frac{1}{2}K_2SO_4 + 9H_2O(l) \longrightarrow KAl(SO_4)_2{\cdot}12H_2O$;
$\Delta H_{31} = \Delta H_{16} + \Delta H_{17} - \Delta H_{18} = -27{,}430 \pm 50$ cal.

(32) $\frac{1}{2}Al_2(SO_4)_3 + \frac{1}{2}K_2SO_4 + 12H_2O \longrightarrow KAl(SO_4)_2{\cdot}12H_2O$;
$\Delta H_{32} = \Delta H_{31} + \frac{1}{2}\Delta H_{29} = -46{,}060 \pm 130$ cal.

(33) $\frac{1}{2}Al_2(SO_4)_3 + \frac{1}{2}K_2SO_4 \longrightarrow 2KAl(SO_4)_2$;
$\Delta H_{33} = \frac{1}{2}\Delta H_{11} + \Delta H_{24} - \Delta H_{25} = -7{,}340 \pm 230$ cal.

(34) $KAl(SO_4)_2 + 12H_2O(l) \longrightarrow KAl(SO_4)_2{\cdot}12H_2O$;
$\Delta H_{34} = \Delta H_{31} - \Delta H_{23} - \Delta H_{24} + \Delta H_{25} = -38{,}720 \pm 210$ cal.

The heat of formation values derived above are compared in Table V with previous results taken from the compilation of Bichowsky and Rossini.[12]

TABLE V

HEATS OF FORMATION (CAL. PER MOLE)

Substance	From elements This research	From elements Previous value	From elements and liquid water This research	From elements and liquid water Previous value
$Al_2(SO_4)_3{\cdot}6H_2O$	−1,268,150	−1,250,000	−858,240	−840,090
$Al_2(SO_4)_3$	−820,990	−770,000		
$KAl(SO_4)_2{\cdot}12H_2O$	−1,447,700	−1,448,100	−627,900	−628,280
$KAl(SO_4)_2$	−589,170	−569,000		

The previous values, cited in Table V, are for 18° and have not been corrected to the temperature of the present work, 25°. The heat of formation of aluminum sulfate hexahydrate was based on the work of Favre and Silbermann[13] and the result for anhydrous aluminum sulfate was estimated by Bichowsky and Rossini from the heat of formation of the hydrate. The heat of formation of potassium aluminum sulfate dodecahydrate was obtained from the determinations of Favre and Silbermann[13] and Thomsen. Combining this value with the heat of dehydration reported by Krauss, Fricke and Querengässer[14] from vapor-pressure studies and the heat of formation of 12 moles of water gives the heat of formation of anhydrous potassium aluminum sulfate cited in the table. The lack of agreement of the values emphasizes the necessity for redeterminations of the older thermochemical data.

Summary

Measurements have been made of the heats of solution of aluminum sulfate hexahydrate, potassium sulfate, and potassium aluminum sulfate dodecahydrate in $HCl{\cdot}12.68H_2O$ and of anhydrous and hexahydrated aluminum sulfate, potassium sulfate, and anhydrous potassium aluminum sulfate in $KOH{\cdot}277.3H_2O$.

Heats of formation from the elements were computed for aluminum sulfate, aluminum sulfate hexahydrate, potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate, based on the present results and values from the literature for sulfuric acid, potassium sulfate, and water.

Several heat-of-reaction values, based on the present work alone, have been derived and listed.

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[13] Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 406 (1853).

[14] Krauss, Fricke and Querengässer, *Z. anorg. allgem. Chem.*, **181**, 38 (1929).