identity of three of the fluorination products, hexafluoro-, tetrafluorodichloro- and trichlorotrifluoro-disiloxane was established. The formation of small amounts of what appears to be octafluorotrisiloxane, and pentafluoromonochloro-disiloxane, was indicated. None of these compounds has been reported previously. The boiling points freezing points, vapor pressures, gaseous and liquid densities of these compounds have been determined and are recorded along with a few of their chemical properties.

CLEVELAND, OHIO RECEIVED MARCH 3, 1945

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

# Specific Heats at Low Temperatures of $(NH_4)_2SO_4$, $NH_4Al(SO_4)_2$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$[1]

BY C. HOWARD SHOMATE[2]

The Pacific Experiment Station of the Bureau of Mines has undertaken a study of the thermochemical properties of compounds encountered in certain methods of extracting alumina from clays and alunite. One phase of this program concerns the measurement of low-temperature specific heats and entropies. This paper presents such data for ammonium sulfate, ammonium aluminum sulfate, and ammonium aluminum sulfate dodecahydrate. Similar data for anhydrous aluminum sulfate, aluminum sulfate hexahydrate, anhydrous potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate were reported in a recent paper.[3]

## Materials

Reagent grade ammonium sulfate was heated at 75° for several days. Analysis gave 72.67% $SO_4$ (theoretical 72.70%). No corrections were made in the specific heat measurements for impurities. The sample used in the measurements weighed 122.87 g.

Ammonium aluminum sulfate was prepared from reagent-grade ammonium aluminum sulfate dodecahydrate by gradually heating the latter to 210° over a period of several days. The final heating was done in vacuum. Analysis showed 21.20% $Al_2O_3$ (theoretical 21.50%); 79.63% $SO_4$ (theoretical 81.02%); 7.31% $NH_4$ (theoretical 7.61%), and 0.39% alkali salts. For the purpose of correcting the specific heat results, it was assumed that the sample used in the measurements was 98.1% $NH_4Al(SO_4)_2$ and 1.9% $H_2O$. The data of Giauque and Stout[4] were used in correcting for the water impurity. The measurements were made on a 134.87-g. sample.

Analysis of the reagent grade ammonium aluminum sulfate dodecahydrate used in the measurements gave 11.22% $Al_2O_3$ (theoretical 11.24%). No corrections for impurities were made in the results. A 123.54-g. sample was used in the measurements.

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(3) Shomate, THIS JOURNAL, **67**, 765 (1945).

(4) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

## Specific Heats

The method and apparatus used in the low-temperature specific heat measurements have been described previously.[5,6] The experimental results, expressed in defined calories (1 calorie =

TABLE I

SPECIFIC HEATS

| $(NH_4)_2SO_4$ Mol. wt. = 132.14 | | $NH_4Al(SO_4)_2$ Mol. wt. = 237.13 | | $NH_4Al(SO_4)_2 \cdot 12H_2O$ Mol. wt. = 453.32 | |
|---|---|---|---|---|---|
| $T$, °K. | $C_p$, cal./mole | $T$, °K. | $C_p$, cal./mole | $T$, °K. | $C_p$, cal./mole |
| 52.8 | 8.900 | 54.5 | 7.984 | 54.0 | 31.38 |
| 56.6 | 9.719 | 58.2 | 9.002 | 54.9 | 32.02 |
| 60.4 | 10.57 | 62.6 | 10.23 | 57.8 | 34.18 |
| 64.3 | 11.45 | 67.1 | 11.48 | 59.1 | 35.09 |
| 68.3 | 12.36 | 71.5 | 12.72 | 63.1 | 38.00 |
| 72.5 | 13.28 | 75.8 | 13.93 | 65.8 | 39.94 |
| 80.6 | 15.01 | 81.5 | 15.47 | 68.1 | 41.61 |
| 84.8 | 15.88 | 86.3 | 16.70 | 75.5 | 47.61 |
| 94.8 | 17.92 | 95.0 | 18.95 | 75.8 | 48.07 |
| 104.4 | 19.88 | 104.5 | 21.36 | 81.0 | 51.03 |
| 115.4 | 22.12 | 115.1 | 23.91 | 85.9 | 54.01 |
| 125.1 | 24.06 | 124.4 | 26.07 | 90.1 | 56.56 |
| 134.8 | 26.09 | 134.9 | 28.42 | 94.6 | 59.33 |
| 145.4 | 28.23 | 145.8 | 30.76 | 104.3 | 65.15 |
| 155.5 | 30.42 | 155.6 | 32.81 | 115.2 | 71.49 |
| 165.3 | 32.69 | 165.6 | 34.72 | 124.2 | 76.72 |
| 175.5 | 35.38 | 175.8 | 36.75 | 134.9 | 82.89 |
| 185.3 | 38.19 | 185.6 | 38.48 | 145.3 | 88.53 |
| 196.0 | 42.19 | 196.0 | 40.32 | 155.6 | 94.22 |
| 205.4 | 46.78 | 206.0 | 41.97 | 165.5 | 99.62 |
| 208.6 | 48.87 | 215.6 | 43.54 | 175.7 | 105.2 |
| 211.5 | 50.55 | 226.4 | 45.10 | 185.5 | 110.2 |
| 214.3 | 53.17 | 236.0 | 46.40 | 196.4 | 115.8 |
| 216.8 | 55.90 | 246.2 | 47.75 | 205.8 | 120.5 |
| 219.3 | 59.29 | 256.0 | 49.22 | 210.1 | 122.9 |
| 221.5 | 64.34 | 266.3 | 50.53 | 214.4 | 125.0 |
| 223.0 | 201.3 | 276.3 | 51.64 | 218.4 | 127.0 |
| 223.4 | 1324 | 286.0 | 52.74 | 222.4 | 128.8 |
| 224.5 | 78.75 | 296.2 | 53.90 | 226.3 | 131.0 |
| 227.1 | 39.66 | (298.16) | 54.12 | 235.7 | 135.0 |
| 230.2 | 39.77 | | | 246.0 | 139.8 |
| 233.3 | 39.90 | | | 256.1 | 144.7 |
| 237.0 | 40.19 | | | 266.0 | 149.2 |
| 246.7 | 41.00 | | | 276.5 | 153.8 |
| 256.7 | 41.98 | | | 285.9 | 157.8 |
| 266.0 | 42.48 | | | 296.1 | 162.0 |
| 276.4 | 43.25 | | | (298.16) | 163.3 |
| 286.0 | 43.96 | | | | |
| 296.1 | 44.80 | | | | |
| 305.7 | 45.35 | | | | |
| 310.6 | 45.58 | | | | |
| (298.16) | 44.81 | | | | |

(5) Kelley, *ibid.*, **63**, 1137 (1941).

(6) Shomate and Kelley, *ibid.*, **66**, 1490 (1944).

4.1833 int. joules),[7] are listed in Table I and shown graphically in Fig. 1. The values of the specific heats at 298.16° K., obtained by extrapolation of a smooth curve through the experimental points, also are included in Table. I. The molecular weights are in accordance with the 1941 International Atomic Weights. All weights were corrected to vacuum, using the following densities: ammonium sulfate, 1.77; ammonium aluminum sulfate, 2.04; and ammonium aluminum sulfate dodecahydrate, 1.65. Density determinations were made in this Laboratory by A. E. Salo.[8]

Ammonium aluminum sulfate exhibited normal behavior in the temperature range studied. Ammonium sulfate, however, showed a marked "hump" in its specific heat curve extending over a temperature range of about 100°, the maximum occurring at 223.4° K. This "hump" is similar in appearance to those found in the specific heat curves of the ammonium halides.[9] Ammonium aluminum sulfate dodecahydrate showed a sharp transition at 71.0° K., analogous to the transition found in the corresponding potassium compound at 59.7°.[3]

## Entropies

The evaluation of the entropy at 298.16° K. is obtained by graphical integration of a plot of $C_p$ against log $T$. This necessitates extrapolation of the specific heat curve from the temperature of the lowest measurement down to the absolute zero of temperature. The transition at 71.0° K. in ammonium aluminum sulfate dodecahydrate makes extrapolation of the specific heat curve difficult by any method. The extrapolation method adopted here is that used in a previous paper[3] for extrapolating the specific heat curve of potassium aluminum sulfate dodecahydrate. Essentially it is the method of Kelley, Parks and Huffman,[10] using for the "standard substance" in their method the sum of the specific heats of ice[4] and anhydrous ammonium aluminum sulfate, and assuming that their constant "B" is zero. Effectively, this extrapolation may be summed as follows: $C_{p\,NH_4Al(SO_4)_2\cdot 12H_2O} = 0.960\ (C_{p\,NH_4Al(SO_4)_2} + 12C_{p\,H_2O})$ for the range 0 to 53° K.

It was found that the following summations adequately represent the specific heat data (within 0.5%) in the temperature ranges indicated:

$$(NH_4)_2SO_4\text{: } D\left(\frac{121.7}{T}\right) + 2E\left(\frac{201}{T}\right) + 4E\left(\frac{472}{T}\right) + 8E\left(\frac{1090}{T}\right) \quad (50\text{–}150^\circ\text{ K.})$$

$$NH_4Al(SO_4)_2\text{: } D\left(\frac{165.2}{T}\right) + 3E\left(\frac{248}{T}\right) + 5E\left(\frac{538}{T}\right) + 5E\left(\frac{1216}{T}\right) \quad (50\text{–}298^\circ\text{ K.})$$

$$NH_4Al(SO_4)_2\cdot 12H_2O\text{: } D\left(\frac{75.5}{T}\right) + 4E\left(\frac{109}{T}\right) + 10E\left(\frac{283}{T}\right) \quad (50\text{–}71^\circ\text{ K.})$$

The symbols $D$ and $E$ denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the specific heat curves to 0° K. The summation for ammonium aluminum sulfate dodecahydrate identically fits the above-mentioned extrapolation for that substance.

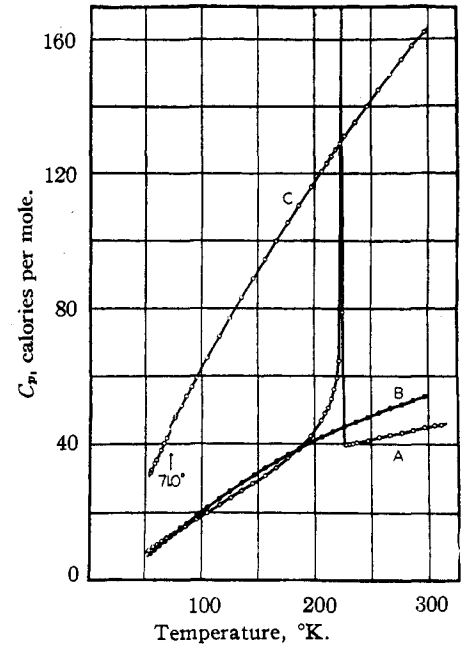


Fig. 1.—Specific heats: A, $(NH_4)_2SO_4$; B, $NH_4Al(SO_4)_2$; C, $NH_4Al(SO_4)_2\cdot 12H_2O$.

The total heat absorption in the region of the "hump" in ammonium sulfate was determined by separate runs to be 2222 and 2216 cal./mole, respectively, between 190.00 and 230.00° K. The mean of these values checks very well the value of 2219 cal./mole obtained by summing the energies of thirteen successive specific heat determinations over this same temperature range in the manner described by Shomate.[11] The total entropy increase from 190.00 to 230.00° K. is 10.47 E.U./mole. If a smooth curve is drawn, joining the specific heat values above the "hump" with those below 100° K., the excess entropy in the "hump," above this "normal" curve, is computed to be 4.0 E.U./mole; since the interpolation of the so-called "normal" curve between such wide temperature limits is rather uncertain, this value may be in error by 0.4 E.U./mole.

Two determinations of the total heat absorp-

(7) Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

(8) Metallurgist, Pacific Experiment Station, Bureau of Mines.

(9) Simon, *Ann. Physik.*, [4] **68**, 241 (1922); Simon, Simson and Ruhemann, *Z. physik. Chem.*, **129**, 344 (1927); Zlunitsyn, *J. Exp. Theoret. Phys.* (U. S. S. R.), **8**, 724 (1938); *ibid.*, **9**, 72 (1939); Lawson, *Phys. Rev.*, **57**, 417 (1940).

(10) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(11) Shomate, *Ind. Eng. Chem.*, **36**, 910 (1944).

TABLE II

ENTROPIES AT 298.16° K. (E.U./MOLE)

| | |
|---|---|
| $(NH_4)_2SO_4$ | |
| 0–50.12° K. (extrap.) | 4.55 |
| 50.12–298.16° K. (graph.) | 48.10 |
| $S^0_{298.16}$ | 52.6 ± 0.3 |
| $NH_4Al(SO_4)_2$ | |
| 0–53.09° K. (extrap.) | 3.37 |
| 53.09–298.16° K. (graph.) | 48.33 |
| $S^0_{298.16}$ | 51.7 ± 0.3 |
| $NH_4Al(SO_4)_2 \cdot 12H_2O$ | |
| 0–53.09° K. (extrap.) | 18.44 |
| 53.09–71.0° K. (graph.) | 10.73 |
| 71.0° K. (Transition) | 2.72 |
| 71.0–298.16° K. (graph.) | 134.72 |
| $S^0_{298.16}$ | 166.6 ± 1.0 |

tion in the region of the transition at 71.0° K. in ammonium aluminum sulfate dodecahydrate gave 511.5 and 511.3 cal./mole, respectively, for the temperature range 69.00 to 76.00° K. Subtracting the heat content associated with the "normal" curves below and above the transition temperature leaves 193.5 cal./mole for the heat of transition, or 2.725 E.U./mole for the entropy of transition.

Table II summarizes the entropy calculations of the three substances.

## Free Energies

The heats, entropies, and free energies of formation from the elements are listed in Table III, together with the thermal data for other pertinent reactions. The heats of reaction are those recently reported by Young.[12] The entropies of reaction combine the values in Table II with the entropies of the elements,[13] liquid water,[4] anhydrous aluminum sulfate,[3] and aluminum sulfate hexahydrate.[3] Free energies of reaction are computed from the relationship $\Delta F^0_{298.16} = \Delta H^0_{298.16} - 298.16\ \Delta S^0_{298.16}$.

## Summary

Specific heats of ammonium sulfate, ammonium aluminum sulfate, and ammonium aluminum sulfate dodecahydrate were measured in the temperature range 52 to 298° K. Ammonium sulfate has a marked "hump" in its specific-heat curve, the maximum being at 223.4° K. There are approximately 4.0 units of excess entropy in the "hump" above the "normal" curve. Ammonium aluminum sulfate dodecahydrate has a sharp transition at 71.0° K., with a heat of transition of 193.5 cal./mole.

TABLE III

THERMAL DATA AT 298.16° K.

| | $\Delta H^0_{298.16}$, cal./mole | $\Delta S^0_{298.16}$, E.U./mole | $\Delta F^0_{298.16}$, cal./mole |
|---|---|---|---|
| $N_2 + 4H_2 + S(rh.) + 2O_2 \longrightarrow (NH_4)_2SO_4$ | −281,740 ± 480 | −223.8 ± 0.3 | −215,010 ± 490 |
| $\frac{1}{2}N_2 + 2H_2 + Al + 2S(rh.) + 4O_2 \longrightarrow NH_4Al(SO_4)_2$ | −561,190 ± 480 | −215.8 ± 0.3 | −486,110 ± 490 |
| $\frac{1}{2}N_2 + 14H_2 + Al + 2S(rh.) + 10O_2 \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O$ | −1,419,360 ± 300 | −805.8 ± 1.0 | −1,179,100 ± 420 |
| $NH_4Al(SO_4)_2 + 12H_2O(liq.) \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O$ | −38,350 ± 410 | −86.1 ± 1.1 | −12,680 ± 530 |
| $\frac{1}{2}Al_2(SO_4)_3 + \frac{1}{2}(NH_4)_2SO_4 \longrightarrow NH_4Al(SO_4)_2$ | −9,820 ± 410 | −3.2 ± 0.4 | −8,870 ± 430 |
| $\frac{1}{2}Al_2(SO_4)_3 + \frac{1}{2}(NH_4)_2SO_4 + 12H_2O(liq.) \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O$ | −48,170 ± 110 | −89.3 ± 1.1 | −21,540 ± 350 |
| $\frac{1}{2}Al_2(SO_4)_3 \cdot 6H_2O + \frac{1}{2}(NH_4)_2SO_4 + 9H_2O(liq.) \longrightarrow NH_4Al(SO_4)_2 \cdot 12H_2O$ | −29,540 ± 25 | −66.5 ± 1.1 | −9,710 ± 330 |

The following molal entropies at 298.16° K. were computed: ammonium sulfate, 52.6 ± 0.3; ammonium aluminum sulfate, 51.7 ± 0.3; and ammonium aluminum sulfate dodecahydrate, 166.6 ± 1.0.

Combination of the above entropies with related thermal data yields the following free energies of formation from the elements at 298.16° K.: ammonium sulfate, −215,010 ± 490; ammonium aluminum sulfate, −486,110 ± 490; and ammonium aluminum sulfate dodecahydrate, −1,179,100 ± 420 cal./mole. Other pertinent thermal data have been calculated.

BERKELEY, CALIFORNIA RECEIVED MARCH 16, 1945

(12) Young, THIS JOURNAL, **67**, 851 (1945).

(13) Kelley, Bureau of Mines Bulletin 434 (1941).