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

The Specific Heats at Low Temperatures of Nitrates of Magnesium, Calcium, Barium and Aluminum[1]

BY C. HOWARD SHOMATE[2] AND K. K. KELLEY[3]

Thermal data for certain inorganic nitrates are of special interest in connection with the Bureau of Mines nitrogen dioxide process[4] for extraction of manganese from low-grade ores. Previous papers from this station have dealt with heats of formation[5,6] and high-temperature heat contents[7] of several nitrates.

This paper presents low-temperature specific heat and entropy data for the anhydrous nitrates of magnesium, calcium and barium, and for aluminum nitrate hexahydrate. Previous data exist for barium nitrate[8] only.

Materials

Anhydrous magnesium nitrate was prepared from reagent-quality magnesium nitrate hexahydrate. The latter was heated *in vacuo*, the temperature being raised gradually from 65 to 150° over a period of forty hours. Analysis gave 16.43% Mg (calcd., 16.40%) and 0.17% MgO. The specific-heat measurements were made on a 133.37-g. sample.

Reagent-grade calcium nitrate tetrahydrate was used for the preparation of anhydrous calcium nitrate. The tetrahydrate was melted and most of the water removed under reduced pressure. The material then was broken up and heated in an electric furnace at 300° for twenty-four hours. Analysis gave 24.43% Ca (calcd., 24.42%) and 0.04% CaO. The measurements were made on a 119.01-g. sample.

The sample of anhydrous barium nitrate was a reagent-grade material, which was dried at 115°. Analysis gave 52.50% Ba (calcd. 52.55%). A 229.66-g. sample was used in the measurements.

Aluminum nitrate hexahydrate was prepared from reagent-grade aluminum nitrate enneahydrate by storing the latter *in vacuo* over Dehydrite for five days. Analysis showed 15.86% Al_2O_3 (calcd. 15.87%). The sample used in the measurements weighed 105.71 g.

Specific Heats

The method and apparatus used in the measurements of the specific heats of the anhydrous nitrates have been previously described.[9] A new calorimeter of essentially the same design was installed for the measurements on aluminum nitrate hexahydrate. The measurements of the low-temperature specific heats of some forty substances had been made with the older calorimeter, the last being on barium nitrate.

The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[10] are given in Table I and shown graphically in Fig. 1. The

TABLE I

T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
SPECIFIC HEAT OF $Mg(NO_3)_2$ (MOL. WT., 148.34)					
54.2	7.747	114.7	18.90	216.3	28.42
57.4	8.484	124.0	20.14	226.0	29.16
61.2	9.326	134.6	21.38	235.9	29.79
65.4	10.30	145.2	22.47	245.8	30.52
69.3	11.16	155.6	23.49	255.6	31.17
76.4	12.62	165.5	24.42	265.9	31.99
80.8	13.46	175.8	25.30	276.1	32.72
85.3	14.30	185.6	26.10	285.9	33.24
94.9	15.99	196.2	26.99	296.3	33.84
104.2	17.43	206.0	27.68		
SPECIFIC HEAT OF $Ca(NO_3)_2$ (MOL. WT., 164.10)					
53.1	10.20	114.5	22.04	261.9	34.59
56.2	11.00	124.3	23.25	266.4	35.06
59.9	11.94	135.0	24.44	276.4	35.98
64.0	13.02	145.6	25.42	281.6	36.56
67.8	14.00	155.8	26.40	283.1	36.84
74.1	15.50	165.6	27.24	286.2	37.32
81.0	16.91	175.4	27.98	286.3	37.16
83.3	17.46	185.8	28.82	289.4	36.19
85.5	18.09	195.9	29.66	291.5	35.72
86.3	18.55	206.2	30.37	292.6	35.68
86.4	18.08	213.5	30.90	296.7	35.68
89.4	18.43	216.0	31.08	299.1	35.70
92.1	18.84	226.2	31.91	307.8	36.18
94.7	19.24	236.2	32.60	312.3	36.32
94.9	19.28	246.3	33.45		
104.6	20.72	255.9	34.19		
SPECIFIC HEAT OF $Ba(NO_3)_2$ (MOL. WT., 261.38)					
54.5	13.64	134.9	26.20	256.1	33.78
58.2	14.62	145.5	26.98	261.3	34.02
61.9	15.64	155.4	27.67	266.0	34.52
69.2	17.49	165.3	28.34	267.1	34.46
73.2	18.37	175.7	28.93	271.9	34.70
77.2	19.15	185.5	29.55	276.4	35.27
80.6	19.79	196.2	30.25	276.7	35.00
84.8	20.49	205.8	30.77	281.5	35.22
94.9	22.04	216.1	31.36	286.5	35.56
104.4	23.22	226.1	32.01	296.1	36.00
114.8	24.34	236.2	32.51		
124.5	25.32	246.5	33.22		
SPECIFIC HEAT OF $Al(NO_3)_3 \cdot 6H_2O$ (MOL. WT., 321.09)					
53.6	25.11	115.0	48.66	215.8	78.05
56.7	26.64	124.2	51.37	225.8	81.00
60.3	28.34	134.8	54.57	235.7	83.82
67.8	31.81	145.4	57.62	245.9	86.79
72.3	33.77	155.3	60.44	255.9	90.15
76.6	35.57	165.7	63.43	265.9	93.13
80.7	37.15	175.6	66.34	276.4	96.35
85.3	38.82	185.6	69.20	286.3	99.60
94.7	42.12	195.8	72.11	296.4	102.90
104.4	45.33	205.5	74.99		

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(4) Dean, Fox, and Back, Bureau of Mines Report of Investigation No. 3626, March, 1942.

(5) Shomate and Young, THIS JOURNAL, **66**, 771 (1944).

(6) Young, *ibid.*, **66**, 773, 777 (1944).

(7) Shomate, *ibid.*, **66**, 928 (1944).

(8) Latimer and Ahlberg, *Z. physik. Chem.*, **A148**, 466 (1930).

(9) Kelley, THIS JOURNAL, **63**, 1137 (1941).

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

molecular weights in Table I are in accordance with the 1941 International Atomic weights.

The specific-heat results for magnesium nitrate were corrected for the 0.17% magnesium oxide content. If, however, 100% purity had been assumed for the magnesium nitrate, an error ranging from only 0.14% at 50°K. to 0.00% at room temperature would have been made in the results in Table I. Likewise the calcium nitrate results were corrected for the 0.04% calcium oxide impurity. Neglecting this correction would have introduced errors of less than 0.03% in the results in Table I.

Magnesium nitrate, barium nitrate, and aluminum nitrate hexahydrate exhibit normal behavior throughout the temperature range studied. Calcium nitrate, however, has a marked "hump" in its specific-heat curve between 280° and 292°K., the maximum being at 287.8°K. A small "hump" appears at 88.5°K. also. Two sets of specific-heat measurements were made over the temperature ranges of each of these "humps," and the abnormal specific heats in these regions were found to be entirely reproducible. Evidence for the 287.8°-"hump" was mentioned previously by Young.[6]

The results of Latimer and Ahlberg[8] for barium nitrate, shown by black dots in Fig. 1, are in substantial agreement with the present work, as is shown in Table II by the comparison of smoothed values.

TABLE II

SPECIFIC HEAT OF $Ba(NO_3)_2$

T, °K.	C_p, cal./mole Latimer and Ahlberg	Shomate and Kelley	Dev	% Dev.
55	13.77	13.77	0.00	0.0%
75	18.81	18.74	+ .07	+ .4
100	22.73	22.70	+ .03	+ .1
150	27.37	27.32	+ .05	+ .2
200	30.50	30.41	+ .09	+ .3
250	33.50	33.40	+ .10	+ .3
298.16	36.30	36.18	+ .12	+ .3

Entropies

The measured specific heats, except those in the regions of the "humps" in the calcium nitrate curve, are represented adequately by the following combinations of Debye and Einstein functions:

$$Mg(NO_3)_2:\ D\left(\frac{133}{T}\right) + 2E\left(\frac{240}{T}\right) + 2E\left(\frac{391}{T}\right) + 2E\left(\frac{1027}{T}\right) + 2E\left(\frac{1540}{T}\right)$$

$$Ca(NO_3)_2:\ D\left(\frac{105}{T}\right) + 2E\left(\frac{209}{T}\right) + 2E\left(\frac{297}{T}\right) + 2E\left(\frac{875}{T}\right) + 2E\left(\frac{1480}{T}\right)$$

$$Ba(NO_3)_2:\ D\left(\frac{104}{T}\right) + 2E\left(\frac{167}{T}\right) + 2E\left(\frac{244}{T}\right) + 2E\left(\frac{860}{T}\right) + 2E\left(\frac{1795}{T}\right)$$

$$Al(NO_3)_3 \cdot 6H_2O:\ D\left(\frac{58.1}{T}\right) + 6E\left(\frac{153}{T}\right) + 6E\left(\frac{443}{T}\right) + 18E\left(\frac{1216}{T}\right)$$

Except in the instance of barium nitrate, these function sums were used in obtaining the extrapolated portions of the entropies, *i. e.*, the portions lying below 53.09°K. Since Latimer and Ahlberg's data are in good agreement with our own and extend down to 16°K., their results fix the entropy below 53.09°K. as $S^0_{53.09} = 7.82$ E. U. with an extrapolation of 0.56 E. U. below 15.8°K.

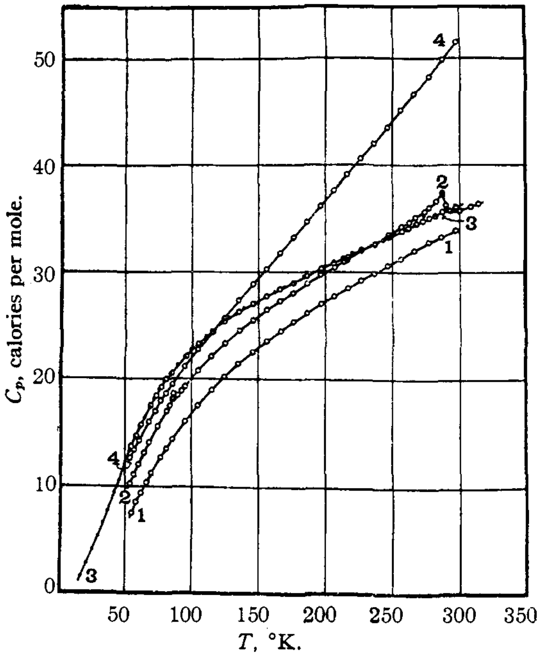

Fig. 1.—Specific heats: curve 1, $Mg(NO_3)_2$; curve 2, $Ca(NO_3)_2$; curve 3, $Ba(NO_3)_2$; curve 4, $Al(NO_3)_3 \cdot 6H_2O$ (C_p for 0.5 mole).

The portions of the entropies between 53.09 and 298.16°K. were obtained graphically from plots of C_p against log T. In the case of barium nitrate a mean value 43.23 E. U., between the present data and those of Latimer and Ahlberg is adopted, the individual results being 43.18 and 43.28, respectively. The value for barium nitrate, $S^0_{298.16} = 51.1 \pm 0.3$ E. U., is the same as the previously accepted value, but on the basis of the new measurements the assigned uncertainty has been reduced somewhat.

Table III summarizes the entropy calculations of the four nitrates.

TABLE III

ENTROPIES AT 298.16°K. (E. U./MOLE)

	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Ba(NO_3)_2$	$Al(NO_3)_3 \cdot 6H_2O$
0–53.09°K.	4.09	5.90	7.82	15.82
53.09–298.16°K.	35.06	40.27	43.23	95.94
$S^0_{298.16}$	39.2 ± 0.5	46.2 ± 0.7	51.1 ± 0.3	111.8 ± 1.9

The entropy associated with the "hump" at 287.8°K. in the specific heat curve of calcium nitrate was determined by actual summation, $\sum_{i=1}^{n} C_{pi}\Delta T/T$, of a series of short-interval specific-heat determinations with little or no intervening temperature gaps. Minor corrections were applied to bring the final temperature of each determination into exact coincidence with the initial temperature of the immediately following determination. The total entropy increase from 281.8 to 291.7°K is 1.267 E. U., and the total heat absorption in this interval, also obtained by summation $\sum_{i=1}^{n} C_{pi}\Delta T$, is 363.4 calories per mole. If a smooth curve is drawn, joining the results just above the "hump" with those below 200°K., the excess entropy in the "hump" is computed to be 0.24 E. U. No real significance should be attached to this figure, but it is of interest to compare it with a similarly obtained value, only 0.01 E. U., for the 88.5° "hump." The abnormal specific heat in both "humps" is too great to be attributed to effects of impurities.

Free Energies of Formation

The heats, entropies, and free energies of formation from the elements are listed in Table IV. The heats of formation are those recently determined by Young.[6] The entropies of formation combine the values in Table III with the entropies of the elements.[11] Free energies of formation are computed from the relationship, $\Delta F^0 = \Delta H^0 - 298.16\,\Delta S^0$.

(11) Kelley, Bureau of Mines Bulletin 434, 1941; estimate for barium, *ibid.*, 384, 1935.

TABLE IV

THERMAL DATA AT 298.16°K.

Substance	$\Delta H^0_{298.16}$, cal./mole	$\Delta S^0_{298.16}$, E. U./mole	$\Delta F^0_{298.16}$, cal./mole
$Mg(NO_3)_2$	−188,770 ± 310	−161.5 ± 0.5	−140,620 ± 340
$Ca(NO_3)_2$	−224,050 ± 360	−156.6 ± .7	−177,360 ± 420
$Ba(NO_3)_2$	−236,990 ± 380	−157.8 ± 1.1	−189,940 ± 500
$Al(NO_3)_3 \cdot 6H_2O$	−680,890 ± 460	−518.7 ± 1.9	−526,230 ± 730

Summary

Specific heats of the anhydrous nitrates of magnesium, calcium, and barium, and of aluminum nitrate hexahydrate, were measured throughout the temperature range 52 to 298°K. Anhydrous calcium nitrate has two anomalies in its specific-heat curve, one peak occurring at 287.8°K. and another small peak at 88.5°K.

The following molal entropies at 298.16°K. were computed: magnesium nitrate, 39.2 ± 0.5; calcium nitrate, 46.2 ± 0.7; barium nitrate, 51.1 ± 0.3; and aluminum nitrate hexahydrate, 111.8 ± 1.9.

Combination of the above entropies with related thermal data yields the following free energies of formation from the elements at 298.16°K.: magnesium nitrate, −140,620 ± 340; calcium nitrate, −177,360 ± 420; barium nitrate −189,940 ± 500; and aluminum nitrate hexahydrate, −526,230 ± 730 cal./mole.

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The Heats of Combustion of Some Substituted Eicosanes, Heneicosanes and Docosanes[1]

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Introduction

The Petroleum and Natural Gas Division of the Bureau of Mines has recently inaugurated a program of research to determine the thermodynamic properties of petroleum hydrocarbons and certain of their derivatives. As a part of this general program the authors have determined the heats of combustion of ten hydrocarbons that appear in the light-lube range of petroleum. These data have been utilized in conjunction with existing data to calculate the heats of formation of these compounds.

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Experimental

Calorimetric Method.—The calorimetric method has been described previously,[4] and the same apparatus was used in this investigation, with no significant changes. The combustion apparatus was loaned to the Bureau of Mines by the California Institute of Technology and was moved to and set up in Bartlesville, Okla. All combustions were carried out in a Parr dual-valve bomb having a volume of 0.358 liter, with an initial oxygen pressure of 30 atmospheres, and with 0.1 ml. of water in the bomb.

The energy equivalent of the calorimetric system was determined during the course of the investigation by frequent calibration with benzoic

(4) (a) Huffman and Ellis, THIS JOURNAL, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, *ibid.*, **60**, 1171 (1938).