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

High-temperature Heat Contents of Magnesium Nitrate, Calcium Nitrate and Barium Nitrate[1]

BY C. HOWARD SHOMATE[2]

Thermal properties of several nitrates are of interest in connection with the hydrometallurgy of manganese, and the Pacific Experiment Station of the Bureau of Mines has undertaken studies of their low- and high-temperature specific heats and their heats of formation. The present paper reports high-temperature heat-content data of magnesium nitrate, calcium nitrate, and barium nitrate, in the anhydrous crystalline state. No previous reliable data for these substances exist.

Materials and Method

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

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 a furnace at 300° for twenty-four hours. Analysis gave 24.43% Ca (calcd. 24.42%) and 0.04% CaO.

The sample of barium nitrate used was a reagent-grade material dried at 115°. Analysis gave 52.50% Ba (calcd. 52.55%).

All formula weights are in accord with the 1941 International Atomic Weights. Sample weights were corrected to vacuum, using the following densities: magnesium nitrate, 2.2; calcium nitrate, 2.36; and barium nitrate, 3.24, g./cc.

The heat content determinations of magnesium nitrate and calcium nitrate were corrected for the oxide impurities indicated above. These corrections averaged 0.15 and 0.03%, respectively.

The high temperature heat contents were determined in an apparatus previously described.[3] The calorimeter was calibrated electrically, using the defined calorie (1 cal. = 4.1833 int. joules). Each sample was enclosed in a gold-sealed platinum–rhodium alloy capsule during the measurements. The heat content of the capsule was determined in a separate series of experiments.

Results

The experimentally determined heat contents above 298.16°K. of magnesium nitrate, calcium nitrate, and barium nitrate are given in Tables I, II, and III. Determinations were made starting at about 100°, and extending up to the point where dissociation was detected. No discontinuities were found in the temperature ranges studied.

Heat content equations, given below, of the form $H_T - H_{298.16} = aT + bT^2 + c/T + d$ were derived for each of the three substances. The coefficients a, b, c and d were determined by plotting the function

$$\frac{T[(H_T - H_{298.16}) - C_{p_{298.16}}(T - 298.16)]}{(T - 298.16)^2}$$

of the experimental values against T, and drawing the best straight line through the points. The slope of this straight line is the coefficient b in the above general equation. The value of the y-intercept is $c/(298.16)^2$. The coefficient $a = c/(298.16)^2 - 596.32\ b + C_{p_{298.16}}$ and $d = (298.16)^2\ b - 2c/298.16 - 298.16C_{p_{298.16}}$.

$$\text{Mg(NO}_3)_2\text{: } H_T - H_{298.16} = 10.68T + 0.03560T^2 - 179{,}000/T - 5{,}749 \quad (1)$$

$$\text{Ca(NO}_3)_2\text{: } H_T - H_{298.16} = 29.37T + 0.01840T^2 + 413{,}000/T - 11{,}778 \quad (2)$$

$$\text{Ba(NO}_3)_2\text{: } H_T - H_{298.16} = 30.05T + 0.01785T^2 + 401{,}000/T - 11{,}891 \quad (3)$$

Differentiating the above equations gives the following specific heat relationships

$$\text{Mg(NO}_3)_2\text{: } C_p = 10.68 + 0.07120T + 179{,}000/T^2 \quad (4)$$

$$\text{Ca(NO}_3)_2\text{: } C_p = 29.37 + 0.03680T - 413{,}000/T^2 \quad (5)$$

$$\text{Ba(NO}_3)_2\text{: } C_p = 30.05 + 0.03570T - 401{,}000/T^2 \quad (6)$$

The coefficients in these equations were chosen so that the equations would give the specific heats at 298.16°K. recently determined by Shomate and Kelley.[4] These values for $C_{p_{298.16}}$ are as follows: magnesium nitrate, 33.92; calcium nitrate, 35.69; and barium nitrate, 36.18 calories per mole, respectively. The agreement of the above heat content equations with the experimental data is shown in Tables I, II and III.

TABLE I

HIGH-TEMPERATURE HEAT CONTENT OF $Mg(NO_3)_2$ (CAL. PER MOLE)

T, °K.	$H_T - H_{298.16}$ Exptl.	$H_T - H_{298.16}$ Eqn. 1	Deviation	% Deviation
398.6	3,707	3,715	+ 8	+0.2
435.8	5,251	5,255	+ 4	+ .1
476.9	7,072	7,066	− 6	− .1
535.9	9,877	9,864	−13	− .1
573.6	11,757	11,778	+21	+ .2
622.5	15,328	(decomposition)		

TABLE II

HIGH-TEMPERATURE HEAT CONTENT OF $Ca(NO_3)_2$ (CAL. PER MOLE)

T, °K.	$H_T - H_{298.16}$ Exptl.	$H_T - H_{298.16}$ Eqn. 2	Deviation	% Deviation
402.8	4,073	4,063	−10	−0.2
456.3	6,336	6,360	+24	+ .4
499.2	8,302	8,296	− 6	− .1
560.4	11,168	11,196	+28	+ .2
621.9	14,263	14,267	+ 4	.0
677.9	17,230	17,197	−33	− .2
726.4	19,835	19,834	− 1	.0
775.1	22,556	22,574	+18	+ .1
815.0	25,190	(decomposition)		

---

[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Chemist, Western Region, Bureau of Mines.

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

[4] Shomate and Kelley, unpublished measurements.

TABLE III

HIGH-TEMPERATURE HEAT CONTENT OF $Ba(NO_3)_2$ (CAL. PER MOLE)

T, °K.	$H_T - H_{298.16}$ Exptl.	$H_T - H_{298.16}$ Eqn. 3	Deviation	% Deviation
411.1	4,434	4,454	+20	+0.4
448.9	6,077	6,098	+21	+ .3
496.2	8,230	8,223	− 7	− .1
549.8	10,788	10,756	−32	− .3
626.1	14,549	14,560	+11	+ .1
693.5	18,101	18,112	+11	+ .1
769.9	22,339	22,346	+ 7	.0
820.8	25,299	25,289	−10	.0
862.1	28,363	(premelting)		

Table IV is a compilation, at 50° intervals, of the heat content and entropy above 298.16°K. of magnesium nitrate, calcium nitrate, and barium nitrate. These values have been derived from smoothed curves drawn through points representing the experimental data.

Summary

High-temperature heat content measurements of magnesium nitrate, calcium nitrate, and barium nitrate were made from about 100° up to as high a temperature as was permitted by the thermal stability of each substance.

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

The entropy increments above 298.16°K., at 50° intervals, have been tabulated along with smoothed values of the heat contents.

TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	$Mg(NO_3)_2$		$Ca(NO_3)_2$		$Ba(NO_3)_2$	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
350	1,821	5.63	1,962	6.07	1,947	6.00
400	3,782	10.81	3,958	11.40	3,963	11.39
450	5,866	15.77	6,053	16.32	6,132	16.49
500	8,153	20.58	8,340	21.14	8,410	21.29
550	10,569	25.19	10,687	25.61	10,799	25.84
600	13,118	29.62	13,151	29.90	13,234	30.08
650			15,738	34.04	15,780	34.15
700			18,409	38.00	18,453	38.11
750			21,139	41.76	21,218	41.93
800			23,974	45.42	24,070	45.61
850					27,007	49.17

BERKELEY, CALIF. RECEIVED FEBRUARY 19, 1944

[CONTRIBUTION FROM RESEARCH LABORATORIES, MUTUAL CHEMICAL COMPANY OF AMERICA]

Crystallized Basic Zinc Chromates

BY O. F. TARR, MARC DARRIN AND L. G. TUBBS

The yellow pigment which is ordinarily produced by the reaction of acidified zinc oxide and potassium bichromate is known as zinc yellow. For almost a century there has been controversy as to whether it is a definite chemical compound, an adsorption complex or a mixture. The great variation in analyses and impurities, the selective solution of CrO_3 and K_2O, and a lack of crystalline form, led Mellor[1] to consider the various suggested formulas as representing adsorption products rather than a pure chemical compound. Although recent investigators[2,3] have reported some analyses corresponding fairly closely to molecular proportions of the combined oxides, and the major evidence[2,4] indicates the probable existence of the compound, $K_2O{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$, no prior investigator has reported the preparation of a pure crystallized compound. The authors obtained well-defined crystals having analyses corresponding to simple molecular proportions by the following procedure.

Basic Potassium Zinc Chromate

Preparation.—Zinc yellow having an analysis corresponding to the formula $K_2O{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$ was prepared by the direct reaction between an aqueous suspension of zinc oxide and a solution of potassium tetrachromate,[5] thus

$$4ZnO + K_2Cr_4O_{13} + 3H_2O \longrightarrow K_2O{\cdot}4ZnO{\cdot}4CrO_3{\cdot}3H_2O$$

On separation and drying the zinc yellow appeared to be a non-crystalline powder. When suspended in water it slowly underwent partial decomposition, releasing into solution a mixture of K_2CrO_4 and $K_2Cr_2O_7$. Equilibrium was reached when the concentration of dissolved chromate and bichromate was equivalent to about 15 g. of $K_2Cr_2O_7$ per liter.

Ten grams of the above zinc yellow was suspended in a solution containing 22.5 g. of $K_2Cr_2O_7$ in 1500 ml. of water, and brought into solution at room temperature by the addition of a minimum amount of nitric acid. This solution was slowly neutralized at 80° without mechanical agitation, with a solution containing 5 g. of potassium hydroxide and 20 g. of potassium chromate per liter. Heat was applied at the edge of the beaker and the caustic solution was added dropwise to the rising convection current. After the addition of about 300 ml., which required from six to twenty-four hours, small crystals could be seen

---

(1) W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1931, Vol. 11, p. 279.

(2) A. A. Brizzolara, R. R. Denslow, and S. W. Rumbel, *Ind. Eng. Chem.*, **29**, 656–657 (1937).

(3) I. V. Riskin and G. Pugacheva, *J. Appl. Chem.* (U. S. S. R.), **12**, 1780–1785 (1939).

(4) M. Gröger, *Sitzber. Akad. Wien*, **113**, 155 (1904).

(5) O. F. Tarr and Marc Darrin, U. S. Patent Appl., Ser. 403,707 (1941).