calories, may be somewhat smaller than the true uncertainty in the heat of fusion.

Heat of Formation of Solid Manganous Nitrate Hexahydrate.—The heat of formation of the solid salt may be found by adding the heat of formation of the liquid and the heat of solidification. The skeleton equations for this calculation are shown in Table III.

TABLE III

HEAT OF FORMATION OF $Mn(NO_3)_2 \cdot 6H_2O(c)$

Reaction	$\Delta H_{298.16}$	Uncertainty
(12) $Mn + N_2 + 6O_2 + 6H_2 \longrightarrow Mn(N_3O)_2 \cdot 6H_2O(l)$	−557,070	310
(13) $Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	+9,610	10
(14) $Mn + N_2 + 6O_2 + 6H_2 \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(c)$	−566,680	310

$$\Delta H_{14} = \Delta H_{12} - \Delta H_{13}$$

Reactions (12) and (13) were discussed above as reactions (5) and (11), respectively. The value of the heat of formation of solid manganous nitrate, −566,680 ± 310 calories, is subject to the same lack of correction to 25° as the heat of fusion discussed under equation (9). By comparison with the uncertainty of 310 calories, however, this correction probably is not significant.

Discussion.—The results of this investigation are summarized in Table IV. In the reactions involving liquid water, Rossini's[12] value of the heat of formation of water is used.

The previous values for the reactions in Table IV, as summarized in the compilation of Bichowsky and Rossini,[14] are not in good agreement with the present results and emphasize the necessity of being critical of the older heat of formation data of nitrates. They tabulate −564.2 kilocalories for the heat of formation of solid manganous nitrate hexahydrate based upon Thomsen's data for the heat of formation of manganous hydroxide, the heat of solution of manganous nitrate hexahydrate in water, for which Thomsen reported +6.15 kilocalories, and the heat of reaction of manganous hydroxide with nitric acid. Combining the above value for the solid with the heat of fusion, 8.26 kilocalories, from the data of Riesenfeld and Milchsack,[15] Bichowsky and Rossini give −555.9 kilocalories for the heat of formation of the liquid nitrate from the elements. These older data, except for the heat of fusion, are reported at 291.16°K.

TABLE IV

HEATS OF REACTION (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
$Mn + N_2 + 6O_2 + 6H_2 \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	−557,070	310
$Mn + N_2 + 6O_2 + 6H_2(l) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(c)$	−566,680	310
$Mn + N_2 + 3O_2 + 6H_2O(l) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	−147,160	310
$Mn + N_2 + 3O_2 + 6H_2O(l) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(c)$	−156,770	310
$Mn(NO_3)_2 \cdot 6H_2O(c) \longrightarrow Mn(NO_3)_2 \cdot 6H_2O(l)$	+9,610	10

Summary

The heats of formation from the elements of liquid and solid manganous nitrate hexahydrate and the heat of fusion of this compound have been determined at room temperature by measuring the heats of solution in 1 *N* sulfuric acid. The results are, respectively, $\Delta H_{298.16} = -557{,}070 \pm 310$, $-566{,}680 \pm 310$, and $+9{,}610 \pm 10$ calories per mole.

BERKELEY, CALIF. RECEIVED FEBRUARY 7, 1944

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

[15] Riesenfeld and Milchsack, *Z. anorg. allgem. Chem.*, **85**, 401 (1914).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR, BERKELEY, CALIFORNIA]

Heats of Formation of $Mg(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Ba(NO_3)_2$[1]

BY FRANK E. YOUNG[2]

Thermal calculations pertaining to the nitrogen dioxide cyclic process for the hydrometallurgical extraction of manganese from ores require accurate values of the heats of formation of the nitrates of several constituents, particularly manganese, barium, calcium, and magnesium. No value of the heat of formation of anhydrous magnesium nitrate is available, and the existing heats of formation of the other nitrates are based largely on older data of uncertain reliability. New values of the heats of formation of solid and liquid manganous nitrate hexahydrate were reported in a previous paper.[3] The present paper records new determinations of the heats of formation of anhydrous magnesium, calcium, and barium nitrates, magnesium nitrate hexahydrate and calcium nitrate tetrahydrate.

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

Materials[4]

Magnesium nitrate hexahydrate was prepared from Merck C. P. product, containing a maximum of 0.07% impurities, by allowing it to stand for fifteen hours over potassium hydroxide to remove excess water and nitric acid. Analysis showed 9.50% Mg (theoretical, 9.48%). The average sample weight used in the present experiments was 6.0357 g.

Anhydrous magnesium nitrate was prepared by heating Merck C. P. magnesium nitrate hexahydrate *in vacuo*, beginning at 65° and raising the temperature gradually to 129° over a period of eleven hours, followed by fifteen hours at 129°. The flask then was opened and the solid cake broken up and pulverized, after which the heating at 129° was continued for six more hours. The temperature then was allowed to rise over a period of thirteen hours to 150°, and the heating was completed by a final half-hour at 150°. Analysis of the product showed 16.43% Mg (theoretical 16.40%) and 0.170% MgO (by titration). Correction was made in the thermal results for the presence of this oxide. The average sample size was 3.5024 g.

Calcium nitrate tetrahydrate was prepared by drying Mallinckrodt reagent-quality product over 78% sulfuric acid for twenty-two hours. Analysis showed 17.00% Ca (theoretical, 16.97%). No detectable amount of CaO was present. The average sample size was 5.2219 g.

Anhydrous calcium nitrate was prepared by melting Mallinckrodt reagent-quality calcium nitrate tetrahydrate and boiling off most of the water under reduced pressure. The material was then broken up and heated at 300° for twenty-four hours in an electric furnace. The product contained 24.43% Ca (theoretical, 24.42%) and 0.043% CaO. A correction was made for the presence of this calcium oxide. The average sample weight was 3.1962 g.

Calcium oxide was prepared by heating Mallinckrodt reagent-quality calcium carbonate to 900° for ninety hours in platinum, using an electric furnace. When the heating was completed, the calcium oxide was stored over dehydrite until the sample bulbs for the heats of solution were filled. These bulbs were filled allowing as little exposure to air as possible during filling and were sealed immediately after weighing. Analysis as sulfate showed 71.23% Ca, corresponding to 99.67% CaO. Titration gave 99.68% CaO. Samples of an average weight of 1.1156 g. were used.

Anhydrous barium chloride was prepared from Baker analyzed barium chloride dihydrate by drying at 135° for nineteen hours. Analyses by precipitation as barium sulfate gave an average of 65.90% Ba, corresponding to 99.92% $BaCl_2$. No oxide could be detected. The average sample weight was 8.3310 g. This size of sample was necessary because of the small heat of solution of barium chloride, the temperature rise being only 53.57 μv. with the sample used, corresponding to 0.04870°.

Anhydrous barium nitrate was prepared by grinding and drying Mallinckrodt analytical reagent barium nitrate at 115°. Analysis showed 99.89% $Ba(NO_3)_2$. The product was ground to pass an 80-mesh screen in order to decrease the time of solution. The average sample weight, 10.4550 g., corresponds to the weight of barium chloride used.

The 1.000 *N* hydrochloric acid used in the heat of solution measurements was prepared by dilution of reagent quality hydrochloric acid and standardization against sodium carbonate.

Method

The heats of formation were determined by measuring the heats of solution of the compounds in 1.000 *N* hydrochloric acid in the calorimeter previously described by Southard[5] and later by Shomate and Young.[3]

The results are expressed in defined calories (1 cal. = 4.1833 int. joules) and all formula weights were calculated from the 1941 International Atomic Weights. Corrections of weights to vacuum basis were made using the following densities: anhydrous magnesium nitrate, 2.2; magnesium nitrate hexahydrate, 1.46; calcium oxide, 3.40; calcium nitrate, 2.36; calcium nitrate tetrahydrate, 1.82; anhydrous barium chloride, 3.86; and anhydrous barium nitrate, 3.24. As the final temperature in each measurement was within a few hundredths of a degree of 25°, no correction of the results to 25° is necessary.

Measurements and Results

Each of the heats 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 of the means of the experimental results involved. This method of calculating uncertainties has been discussed more fully by Rossini and Deming.[6] The final values for the heats of formation and the uncertainties have been rounded to the nearest 10 calories.

The Heat of Formation of Anhydrous Magnesium Nitrate.—The skeleton equations for the present method of obtaining the heat of formation of anhydrous magnesium nitrate are shown in Table I.

TABLE I

THE HEAT OF FORMATION OF $Mg(NO_3)_2$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(1) $Mg + 2H^+ \longrightarrow Mg^{++} + H_2$	−111.322	41
(2) $H_2 + N_2 + 3O_2 \longrightarrow 2H^+ + 2NO_3^-$	−98,087	304
(3) $Mg(NO_3)_2 \longrightarrow Mg^{++} + 2NO_3^-$	−20,636	14
(4) $Mg + N_2 + 3O_2 \longrightarrow Mg(NO_3)_2$	−188,770	310

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

The value for ΔH_1 was taken directly from the work of Shomate and Huffman,[7] who determined the heat of solution of magnesium metal under the same conditions as in the present measurements.

Reaction (2) represents the heat of formation of nitric acid in the final solution of reaction (1) or $MgCl_2 \cdot 75.2\ HCl \cdot 4190\ H_2O$. This value may be obtained by the use of the following equations:

$$H_2 + N_2 + 3O_2 + 26.5\ H_2O \longrightarrow 2\ HNO_3 \cdot 26.5\ H_2O \quad (5)$$

$$2HNO_3 \cdot 26.5\ H_2O + MgCl_2 \cdot 75.2\ HCl \cdot 4190\ H_2O \longrightarrow Mg(NO_3)_2 \cdot 77.2\ HCl \cdot 4216.5\ H_2O \quad (6)$$

$$Mg(NO_3)_2 \cdot 77.2\ HCl \cdot 4190\ H_2O + 26.5\ H_2O \longrightarrow Mg(NO_3)_2 \cdot 77.2\ HCl \cdot 4216.5\ H_2O \quad (7)$$

The required heat of formation, ΔH_2, is equal to $\Delta H_5 + \Delta H_6 - \Delta H_7$. The value −98,398 ± 304 was adopted for ΔH_5. This value was obtained from the heat-of-formation and dilution data of Becker and Roth[8] as explained in the previous paper.[3] The values for ΔH_6 and ΔH_7 were determined in the present work by direct experiment as +198 ± 4 and −113 ± 4 calories, respectively.

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(4) The materials used in this research were prepared by Dr. E. H. Huffman, formerly chemist in this laboratory.

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

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

(7) Shomate and Huffman, THIS JOURNAL, **65**, 1625 (1943).

(8) Becker and Roth, *Z. Elektrochem.*, **40**, 842 (1934); *Z. physik. Chem.*, **A174**, 104 (1935).

Six determinations of ΔH_3 were made, giving $-20{,}619$, $-20{,}621$, $-20{,}639$, $-20{,}647$, $-20{,}627$, and $-20{,}664$, with a mean of $-20{,}636 \pm 14$. These results have been corrected by $+189$ calories for the presence of 0.170% magnesium oxide and for variations in sample size which had a noticeable effect on the heats of solution, the average correction being 12 calories.

The heat of formation of anhydrous magnesium nitrate, ΔH_4, obtained by subtracting ΔH_3 from the sum of $\Delta H_1 + \Delta H_2$ is $-188{,}770 \pm 310$ calories.

The Heat of Formation of Magnesium Nitrate Hexahydrate.—Table II summarizes the data necessary for obtaining the heat of formation of magnesium nitrate hexahydrate.

TABLE II

THE HEAT OF FORMATION OF $Mg(NO_3)_2\cdot 6H_2O$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(8) $Mg + 2H^+ \longrightarrow Mg^{++} + H_2$	$-111{,}322$	41
(9) $H_2 + N_2 + 3O_2 \longrightarrow 2H^+ + 2NO_3^-$	$-98{,}087$	304
(10) $Mg(NO_3)_2\cdot 6H_2O \longrightarrow Mg^{++} + 2NO_3^- + 6H_2O$	$+5{,}095$	2
(11) $6H_2 + 3O_2 \longrightarrow 6H_2O$	$-409{,}908$	60
(12) $Mg + N_2 + 6O_2 + 6H_2 \longrightarrow Mg(NO_3)_2\cdot 6H_2O$	$-624{,}410$	310

$$\Delta H_{12} = \Delta H_8 + \Delta H_9 - \Delta H_{10} + \Delta H_{11}$$

Reactions (8) and (9) are identical with reactions (1) and (2) which have been discussed previously.

Six determinations of ΔH_{10} were made, giving $+5096$, $+5092$, $+5094$, $+5096$, $+5096$, $+5095$, with a mean of $+5095 \pm 1$ calories after applying a correction of $+26 \pm 1$ calories for the heat of dilution by the water of hydration. The mean value for ΔH_{10} corresponds to a temperature drop of 76.34 μv. or 0.06940° in the calorimeter.

Rossini's[9] value for the heat of formation of water, $-68{,}318 \pm 10$ calories per mole, was multiplied by six to obtain ΔH_{11}, giving $-409{,}908 \pm 60$ calories.

$\Delta H_8 + \Delta H_9 - \Delta H_{10} + \Delta H_{11}$ gives the heat of formation of magnesium nitrate hexahydrate from the elements as $\Delta H_{12} = -624{,}410 \pm 310$ calories.

Anhydrous Calcium Nitrate.—Table III outlines the reactions for determining the heat of formation of anhydrous calcium nitrate.

The heat of reaction (13) was taken from the compilation of Bichowsky and Rossini,[10] the correction of 25° being negligible.

Six determinations were made of ΔH_{14}, giving $-46{,}220 \pm 14$ as the mean of: $-46{,}216$, $-46{,}235$, $-46{,}230$, $-46{,}204$, $-46{,}197$, $-46{,}240$. These values include a correction of -151 calories for the presence of impurities and a correction of $+4$ calories for the heat of dilution by the water formed in the reaction.

TABLE III

THE HEAT OF FORMATION OF $Ca(NO_3)_2$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(13) $Ca + \frac{1}{2}O_2 \longrightarrow CaO$	$-151{,}800$	200
(14) $CaO + 2H^+ \longrightarrow Ca^{++} + H_2O$	$-46{,}220$	14
(15) $H_2 + N_2 + 3O_2 \longrightarrow 2H^+ + 2NO_3^-$	$-98{,}087$	304
(16) $Ca(NO_3)_2 \longrightarrow Ca^{++} + 2NO_3^-$	$-3{,}740$	9
(17) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$	$-68{,}318$	10
(18) $Ca + N_2 + 3O_2 \longrightarrow Ca(NO_3)_2$	$-224{,}050$	360

$$\Delta H_{18} = \Delta H_{13} + \Delta H_{14} + \Delta H_{15} - \Delta H_{16} - \Delta H_{17}$$

The heat of formation of nitric acid in $CaCl_2\cdot 85.25\ HCl\cdot 4775\ H_2O$ is found in the same way as ΔH_2, discussed previously. The heats of solution of nitric acid and water in the calcium chloride solution were determined by direct experiment and were found to have the same values as corresponding heats of solution in the magnesium chloride solution discussed before, namely, $+194 \pm 4$ and -113 ± 4 calories, respectively.

The heat of solution of anhydrous calcium nitrate, ΔH_{16}, is the mean of seven results: -3742, -3759, -3736, -3742, -3749, -3725, and -3725 calories, after application of a $+57$-calorie correction for calcium oxide content. It was thought that the abnormally large spread in these results might be attributed to the effects of a transition of small thermal magnitude near room temperature. In order to test this the fifth sample (-3749 cal.) was heated to 110° for forty hours immediately before measuring its heat of solution; the sixth result (-3725) was obtained using a sample that had been kept at 0° for sixty-four hours and the seventh result (-3725) using a sample that had been cooled in a carbon dioxide–ethyl alcohol mixture and allowed to warm up over a period of twenty-four hours to 10° before it was put into the calorimeter. After completion of these heat of solution measurements, a minor transition actually was found in the heat capacity of anhydrous calcium nitrate at 288°K.[11] It thus appears that the larger heats of solution correspond to the high-temperature form and the smaller values to the low-temperature form, as might be expected.

ΔH_{17} is Rossini's[9] value of the heat of formation of water.

The heat of formation of anhydrous calcium nitrate from the elements, ΔH_{18}, is $-224{,}050 \pm 360$ calories per mole.

The Heat of Formation of Calcium Nitrate Tetrahydrate.—The skeleton equations representing the reactions necessary to obtain the heat of formation of calcium nitrate tetrahydrate are shown in Table IV.

The first three reactions, ΔH_{19}, ΔH_{20} and

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[9] Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

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

[11] Shomate and Kelley, unpublished measurements.

TABLE IV

THE HEAT OF FORMATION OF $Ca(NO_3)_2 \cdot 4H_2O$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(19) $Ca + {}^1/_2O_2 \longrightarrow CaO$	−151,800	200
(20) $CaO + 2H^+ \longrightarrow Ca^{++} + H_2O$	−46,220	14
(21) $H_2 + N_2 + 3O_2 \longrightarrow$ $2H^+ + 2NO_3^-$	−98,087	304
(22) $Ca(NO_3)_2 \cdot 4H_2O \longrightarrow$ $Ca^{++} + 2NO_3^- + 4H_2O$	+8,360	3
(23) $3H_2 + {}^3/_2O_2 \longrightarrow 3H_2O$	−204,954	30
(24) $Ca + N_2 + 5O_2 + 4H_2 \longrightarrow$ $Ca(NO_3)_2 \cdot 4H_2O$	−509,420	370

$$\Delta H_{24} = \Delta H_{19} + \Delta H_{20} + \Delta H_{21} - \Delta H_{22} + \Delta H_{23}$$

ΔH_{21}, were discussed above as ΔH_{13}, ΔH_{14} and ΔH_{15}, respectively.

ΔH_{22} is the mean of six results after applying a correction of +17 ± 1 calories for the heat of dilution by the water of hydration. These corrected heats of solution are +8353, 8361, 8360, 8358, 8363, and 8365, with a mean of 8360 ± 3 calories.

ΔH_{23} represents the heat of formation of 3 molecules of water or three times Rossini's[9] value for the heat of formation of water.

The heat of formation of calcium nitrate tetrahydrate, ΔH_{24}, is −509,420 ± 370.

The Heat of Formation of Anhydrous Barium Nitrate.—Table V summarizes the reactions used to obtain the heat of formation of anhydrous barium nitrate.

TABLE V

THE HEAT OF FORMATION OF $Ba(NO_3)_2$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.1}$	Uncertainty
(25) $Ba + Cl_2 \longrightarrow BaCl_2$	−205,260	210
(26) $BaCl_2 \longrightarrow Ba^{++} + 2Cl^-$	−2,086	4
(27) $H_2 + Cl_2 \longrightarrow 2H^+ + 2Cl^-$	−78,466	100
(28) $H_2 + N_2 + 3O_2 \longrightarrow 2H^+ +$ $2NO_3^-$	−98,164	304
(29) $Ba(NO_3)_2 \longrightarrow Ba^{++} + 2NO_3^-$	+9,944	8
(30) $Ba + N_2 + 3O_2 \longrightarrow Ba(NO_3)_2$	−236,990	380

$$\Delta H_{30} = \Delta H_{25} + \Delta H_{26} - \Delta H_{27} + \Delta H_{28} - \Delta H_{29}$$

The heat of formation of barium chloride given by Bichowsky and Rossini,[10] corrected to 25°, was adopted for reaction (25).

Six determinations were made of the heat of solution of barium chloride in 1.000 *N* hydrochloric acid, reaction (26), giving −2088, −2080, −2086, −2090, −2084 and −2095 calories, with a mean of −2086 ± 4 calories per mole. It was necessary to correct these heats of solution for variations in sample size. The average correction was 5 calories.

Equation (27) represents the heat of formation of hydrogen chloride in $Ba(NO_3)_2 \cdot 45.5HCl \cdot 2474H_2O$. This heat of formation was estimated by assuming it to be the same in the above solution as in a solution in which the barium nitrate had been replaced by enough hydrogen chloride to maintain the same ionic strength, giving the equation:

$$(31)\quad 48.5HCl \cdot 2474H_2O + H_2 + Cl_2 \longrightarrow 50.5HCl \cdot 2474H_2O$$

The heat of reaction (31) may be calculated from the difference of the two reactions

$$(32)\quad 24.25H_2 + 24.25Cl_2 + 2474H_2O \longrightarrow 48.5HCl \cdot 2474H_2O$$

$$(33)\quad 25.25H_2 + 25.25Cl_2 + 2474H_2O \longrightarrow 50.5HCl \cdot 2474H_2O$$

using the heat of formation of hydrochloric acid at infinite dilution given by Rossini[12] and the heats of dilution reported by Sturtevant.[13] The heat of reaction (27) calculated in this manner is −78,466 for 2 moles of hydrochloric acid, in which the uncertainty is estimated as ±100 calories.

ΔH_{28} is found in the same way as ΔH_2 and ΔH_{15}, using the directly determined values of +115 ± 10 and −113 ± 4 for the heats of solution of nitric acid and the corresponding amount of water in the barium chloride solution, respectively.

The value given for ΔH_{29} is the mean of six results, +9950, 9950, 9931, 9951, 9930 and 9951, or 9944 ± 8 calories. As with the barium chloride, it was necessary to make a small correction for variations in sample weights. In this instance, the average correction was 2 calories.

The heat of formation of barium nitrate, $\Delta H_{30} = \Delta H_{25} + \Delta H_{26} - \Delta H_{27} + \Delta H_{28} - \Delta H_{29}$, is −236,990 ± 380 calories per mole.

Discussion.—The results obtained in this research are compared in Table VI with previous values taken from the compilation of Bichowsky and Rossini.[10]

TABLE VI

HEATS OF FORMATION (CAL. PER MOLE)

	Heat of formation			
	From elements		From elements and $H_2O(1)$	
Substance	This research	Previous value	This research	Previous value
$Mg(NO_3)_2$	−188,770	...	...	...
$Mg(NO_3)_2 \cdot 6H_2O$	−624,410	−622,500	−214,500	−212,590
$Ca(NO_3)_2$	−224,050	−224,040	...	...
$Ca(NO_3)_2 \cdot 4H_2O$	−509,420	−509,590	−236,150	−236,320
$Ba(NO)_3$	−236,990	−236,900	...	...

The previous values are for a temperature of 18° and have not been corrected to the base temperature of the present work, 25°. They are based on heats of solution of metallic calcium and barium reported by Guntz and Benoit,[14] the heat of solution of calcium oxide determined by Gautier,[15] the heat of solution of calcium nitrate tetrahydrate determined by Ewing, Rogers, Miller and McGovern,[16] and various heats of solution and reaction measured by Thomsen. The agreement is satisfactory, except for the mag-

[12] Rossini, *Bur. Standards J. Research*, **9**, 679 (1932).

[13] Sturtevant, THIS JOURNAL, **62**, 584 and 3265 (1940).

[14] Guntz and Benoit, *Ann. chim.*, **20**, 5 (1923).

[15] Gautier, *Compt. rend.*, **128**, 939 (1899).

[16] Ewing, Rogers, Miller and McGovern, THIS JOURNAL, **54**, 1335 (1932).

nesium nitrate hexahydrate results. The difference between the values for this material again illustrates the necessity for redetermination of heats of formation which are based on data antedating modern methods, *i. e.*, the data of Thomsen in the present instance.

It will be noted that the part of the uncertainty in the heats of formation attributable to the heat of formation of the nitric acid alone ranges from 44 to 86% of the total uncertainty. Correction of the present results may be made readily whenever a better heat of formation of nitric acid becomes available.

Summary

The heats of formation of several nitrates of magnesium, calcium and barium have been determined at 25° by measuring heats of solution in 1.000 *N* hydrochloric acid. These heats of formation from the elements are: magnesium nitrate, −188,770 ± 310; magnesium nitrate hexahydrate, −624,410 ± 310; calcium nitrate, −224,050 ± 360; calcium nitrate tetrahydrate, −509,420 ± 370, and barium nitrate, −236,990 ± 380 calories per mole.

BERKELEY, CALIF. RECEIVED FEBRUARY 14, 1944

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

The Heats of Formation of $Al(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$[1]

BY FRANK E. YOUNG[2]

The heats of formation of several metallurgically important nitrates have been determined recently at the Pacific Experiment Station of the Bureau of Mines. Previous papers have described determinations of the heats of formation of solid and liquid manganous nitrate hexahydrate[3] and the anhydrous nitrates of barium, calcium and magnesium, as well as calcium nitrate tetrahydrate and magnesium nitrate hexahydrate.[4] The present paper reports values of the heats of formation for two hydrated aluminum nitrates for which no previous results are available.

Materials and Method

The aluminum metal used in the measurements was cut from the center of a small ingot of 99.78% aluminum. The principal impurities were 0.10% magnesium and 0.10% iron. The only other impurity, except a negligible amount of surface oxide, was 0.02% copper. The magnesium and copper were determined chemically and the iron was determined both chemically and spectrographically. Titanium and manganese were shown to be absent by the spectrograph. After the aluminum was cut, it was washed several times with benzene, dried *in vacuo*, and weighed into bulbs which were sealed immediately. Corrections in the thermal measurements were made for the impurities.

Aluminum nitrate enneahydrate was prepared by Dr. E. H. Huffman, formerly of this Laboratory, by recrystallization of Mallinckrodt analytical reagent grade of aluminum nitrate from 4 *N* nitric acid. After air drying, the material was stored over 80% sulfuric acid for seventeen hours to remove excess water. Direct ignition to aluminum oxide, in platinum, over a gas-oxygen blast lamp, gave 13.58% Al_2O_3 (theoretical, 13.59%).

Aluminum nitrate hexahydrate was prepared by storing the enneahydrate over Dehydrite for five days. Analysis by direct ignition in platinum over the blast lamp gave 15.86% Al_2O_3 (theoretical, 15.87% Al_2O_3).

The heats of formation were determined by measuring the heats of solution in 4.000 *N* hydrochloric acid, which was prepared by diluting concentrated reagent quality hydrochloric acid and standardized against sodium carbonate.

To shorten the time required for taking the aluminum into solution, 1 ml. of chloroplatinic acid solution was added to the hydrochloric acid in the calorimeter before each determination. The chloroplatinic acid solution was prepared by dissolving 0.1002 g. of Mallinckrodt Analytical Reagent chloroplatinic acid hexahydrate in enough 4.000 *N* hydrochloric acid to make 100 ml. of solution. A correction was applied to the thermal results for the reduction of the chloroplatinic acid by the aluminum. The use of chloroplatinic acid reduced the solution time of the aluminum from several hours to twenty or thirty minutes.

The calorimetric measurements were made in the apparatus described by Southard[5] and later by Shomate and Young.[3] 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. Corrections of weights to vacuum were made using the following densities: aluminum metal, 2.70; aluminum nitrate enneahydrate, 1.4; aluminum nitrate hexahydrate, 1.7 (estimated).

Measurements and Results

The reactions by which the heats of formation of aluminum nitrate enneahydrate and aluminum nitrate hexahydrate were obtained are shown as skeleton equations in Tables I and II, respectively. The uncertainties in the last column of each table are twice the standard deviations of the means of the experimental results. This method of ascribing uncertainties has been discussed by Rossini and Deming.[6] The final values of the heats of formation and the corresponding uncertainties have been rounded to the nearest ten calories. The final temperatures in the solution measurements were always within a few hundredths of a degree of 25°, so that no correction was needed. The average sample weights, aluminum, 0.5394 g.; aluminum nitrate enneahydrate, 7.5028 g.; and aluminum nitrate hexahydrate, 6.4214 g., correspond to a dilution of 1 mole of anhydrous salt in $361.6HCl \cdot 4585H_2O$. The calorimetric

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(2) Chemist, Western Region, Bureau of Mines.

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

(4) Young, *ibid.*, **66**, 773 (1944).

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

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