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.

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[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).

temperature changes accompanying solution of these samples were: aluminum, 1.67155°; aluminum nitrate enneahydrate, 0.13869°; and aluminum nitrate hexahydrate, 0.01310°.

The Heat of Formation of Aluminum Nitrate Enneahydrate.—Table I gives the skeleton equations of the reactions used in obtaining the heat of formation of aluminum nitrate enneahydrate.

TABLE I

THE HEAT OF FORMATION OF $Al(NO_3)_3 \cdot 9H_2O$ (CAL. PER MOLE)

Reactions	$\Delta H_{298.16}$	Uncertainty
(1) $Al + 3H^+ \longrightarrow Al^{+++} + {}^3/_2H_2$	−126,834	62
(2) ${}^3/_2H_2 + {}^3/_2N_2 + {}^9/_2O_2 \longrightarrow 3H^+ + 3NO_3^-$	−144,695	456
(3) $Al(NO_3)_3 \cdot 9H_2O \longrightarrow Al^{+++} + 3NO_3^- + 9H_2O$	+11,194	11
(4) $9H_2 + {}^9/_2O_2 \longrightarrow 9H_2O$	−614,862	90
(5) $Al + {}^3/_2N_2 + 9H_2 + 9O_2 \longrightarrow Al(NO_3)_3 \cdot 9H_2O$	−897,590	470
$\Delta H_5 = \Delta H_1 + \Delta H_2 - \Delta H_3 + \Delta H_4$		

The heat of solution of aluminum in 4 N hydrochloric acid, ΔH_1, is the mean of six results: −126,810, −126,824, −126,727, −126,868, −126,884, and −126,875 cal. A correction of −143 cal. has been applied to these results for the presence of the impurities discussed above. It was also necessary to correct for the heat absorbed in the vaporization of water by the escaping hydrogen. This correction was made on the assumption that none of the hydrogen was left in the solution by the time thermal equilibrium was attained and that the hydrogen was completely saturated with water vapor when it left the solution. The partial pressure of water vapor over the solution was taken as 18.1 mm. and the heat of vaporization as 10,500 cal. per gram formula mass at 25°. Allowing an uncertainty of 10%, this correction was −376 ± 38 cal. for the 1.5 moles of hydrogen involved. The correction for vaporization of hydrogen chloride was nearly negligible, being only 1 cal. The total vaporization correction of −377 cal. has already been applied to the above results. The heat evolved in the reduction of the chloroplatinic acid used to increase the rate of solution of the aluminum made an additional correction of +16 cal. necessary. In making this correction, it was assumed that all of the chloroplatinic acid was reduced to the metal. Data for this correction were obtained from the compilation of Bichowsky and Rossini.[7]

Equation (2) represents the heat of formation of nitric acid in $AlCl_3 \cdot 358.6HCl \cdot 4585H_2O$. This heat of formation may be obtained from the reactions

(6) ${}^3/_2H_2 + {}^3/_2N_2 + {}^9/_2O_2 + 37.11H_2O \longrightarrow 3HNO_3 \cdot 37.11H_2O$

(7) $3HNO_3 \cdot 37.11H_2O + AlCl_3 \cdot 358.6HCl \cdot 4585H_2O \longrightarrow Al(NO_3)_3 \cdot 361.6HCl \cdot 4622.11H_2O$

(8) $Al(NO_3)_3 \cdot 361.6HCl \cdot 4585H_2O + 37.11H_2O \longrightarrow Al(NO_3)_3 \cdot 361.6HCl \cdot 4622.11H_2O$

The value for the heat of formation of nitric acid in 0.05 M solution, −49,234 ± 152 cal., was obtained from the data of Becker and Roth,[8] as explained in a previous paper.[3] The correction for the difference in acid strengths from 0.05 M to the present concentration of $3HNO_3 \cdot 37.11H_2O$ was obtained from the heats of dilution given by Becker and Roth.[9] This correction amounted to 56 cal., making $\Delta H_6 = 3(-49{,}178 \pm 152)$ or $-147{,}534 \pm 456$ cal. The heats of solution of nitric acid, ΔH_7, and the corresponding amount of water, ΔH_8, in the aluminum chloride solution were measured directly as $\Delta H_7 = +53 \pm 5$ cal. and $\Delta H_8 = -2786 \pm 2$ cal. The required ΔH_2 is $\Delta H_6 + \Delta H_7 - \Delta H_8$ or $-144{,}695 \pm 456$ cal.

Six measurements of the heat of solution of aluminum nitrate enneahydrate, ΔH_3, were made to obtain +11,194 ± 11 cal., the mean of +11,192, +11,173, +11,216, +11,186, +11,196, and +11,201 cal., after application of a +676 ± 1 cal. correction for the measured heat of dilution by the water of hydration.

The heat of formation of 9 moles of water, ΔH_4, was obtained by multiplying Rossini's[10] heat of formation of water by 9: $9(-68{,}318 \pm 10) = -614{,}862 \pm 90$ cal. The heat of formation of aluminum nitrate enneahydrate from the elements, ΔH_5, is $-897{,}590 \pm 470$ cal. per mole. The heat of formation of this compound from the elements and liquid water, $\Delta H_1 + \Delta H_2 - \Delta H_3$, is $-282{,}720 \pm 260$ cal. per mole.

The Heat of Formation of Aluminum Nitrate Hexahydrate.—Table II summarizes the reactions used in this work in obtaining the heat of formation of aluminum nitrate hexahydrate.

TABLE II

THE HEAT OF FORMATION OF $Al(NO_3)_3 \cdot 6H_2O$ (CAL. PER MOLE)

Reaction	$\Delta H_{298.16}$	Uncertainty
(9) $Al + 3H^+ \longrightarrow Al^{+++} + {}^3/_2H_2$	−126,834	62
(10) ${}^3/_2H_2 + {}^3/_2N_2 + {}^9/_2O_2 \longrightarrow 3H^+ + 3NO_3^-$	−144,695	456
(11) $Al(NO_3)_3 \cdot 6H_2O \longrightarrow Al^{+++} + 3NO_3^- + 6H_2O$	−543	6
(12) $6H_2 + 3O_2 \longrightarrow 6H_2O$	−409.908	60
(13) $Al + {}^3/_2N_2 + {}^{15}/_2O_2 + 6H_2 \longrightarrow Al(NO_3)_3 \cdot 6H_2O$	−680.890	460
$\Delta H_{13} = \Delta H_9 + \Delta H_{10} - \Delta H_{11} + \Delta H_{12}$		

Reactions (9) and (10) have been discussed already as reactions (1) and (2), respectively.

Six measurements of the heat of solution of aluminum nitrate hexahydrate in 4 N hydro-

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

[8] Becker and Roth, *Z. Elektrochem.*, **40**, 842 (1934).

[9] Becker and Roth, *Z. physik. Chem.*, **A174**, 104 (1935).

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

chloric acid gave −543, −531, −550, −539, −550, and −546, with a mean of −543 ± 6 cal. per mole after application of a measured 450 ± 1 cal. correction for the heat of dilution by the water of hydration.

Reaction (12) again involves Rossini's heat of formation of water, −409,908 ± 60 cal. for 6 moles.

The heat of formation of aluminum nitrate hexahydrate from the elements, ΔH_{13}, is −680,890 ± 460 cal. per mole. The heat of formation of this hydrate from the elements and liquid water, $\Delta H_9 + \Delta H_{10} - \Delta H_{11}$, is −270,990 ± 460 cal. per mole.

Whenever a better heat of formation of nitric acid becomes available, the present measurements may be corrected accordingly.

Summary

The heats of formation of aluminum nitrate enneahydrate and aluminum nitrate hexahydrate have been determined by measuring the heats of solution of these compounds and aluminum in 4.000 *N* hydrochloric acid. The heats of formation from the elements are −897,590 ± 470 cal. per mole for aluminum nitrate enneahydrate and −680,890 ± 460 cal. per mole for aluminum nitrate hexahydrate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The System Acetic Acid–Ammonia

BY ARTHUR W. DAVIDSON, HARRY H. SISLER AND RAYMOND STOENNER

The familiar salt ammonium acetate, $NH_4C_2H_3O_2$, as well as solutions of this salt in acetic acid, may readily be prepared by the direct combination of dry ammonia and anhydrous acetic acid. It is obvious, then, that the entire system acetic acid–ammonium acetate, freezing point data for which have previously been presented,[1] may be regarded as constituting only one-half of the more comprehensive binary system acetic acid–ammonia, in which ammonium acetate assumes the role merely of an especially stable addition compound.[2] Although ammonium acetate has long been known to be readily soluble in liquid ammonia,[3] and a determination of its solubility at a single temperature has indeed been reported,[4] no attempt has thus far been made to study the system throughout the entire range of concentrations.

It will readily be appreciated that the investigation of liquid solutions consisting of ammonium acetate and excess ammonia presents experimental difficulties which are not encountered with solutions of ammonium acetate in acetic acid. Especially is this true at room temperatures and above, since the lowering of the vapor pressure of liquid ammonia produced by ammonium acetate is not nearly so great as might be expected.[5] Other similar systems, consisting of ammonia and ammonium nitrate,[6] ammonium thiocyanate,[7] and the ammonium halides,[8] have been successfully studied, although only in the first two instances was it found possible to cover the entire range of concentrations from ammonia to pure ammonium salt.

The present work consisted mainly of a study of the ammonium acetate–ammonia portion of the system. A part of the earlier work[1] was repeated, also, and somewhat more accurate data were obtained for temperatures above 60°. Three new addition compounds of ammonia and acetic acid, two of them stable at their melting points, have been discovered.

Method

Preparation of Materials.—Anhydrous acetic acid was prepared as described in previous papers from this Laboratory.[1] No sample used had a freezing point of less than 16.60°.

Commercial synthetic anhydrous ammonia, which was stated to be at least 99.95% pure, was found to have a freezing point of −77.5 ± 0.4°, in good agreement with the values of −77.7 to −77.8° found in the literature. Distillation over metallic sodium was found to bring about no change in freezing point; hence this product was used without further purification.

Ammonium acetate was obtained, as described previously,[1] by the passage of dry ammonia over anhydrous acetic acid in a desiccator over calcium oxide. The preparation of pure ammonium acetate (50 mole % of ammonia) by this process is very slow, and requires the use of a large excess of ammonia; furthermore, there is no advantage to be gained by the use of a salt of exactly this composition. Hence, various solid products containing from 38 to 43 mole % of ammonia were used as starting materials, after determination of their compositions by treatment with sodium hydroxide solution and distillation of the ammonia into standard hydrochloric acid.

Determination of Equilibrium.—A few mixtures, containing from 23 to 43 mole % of ammonia, were made up by the addition of acetic acid to the solid starting material, and their freezing points were determined in sealed tubes, as previously described,[1] as a check on the earlier results. For all other mixtures of f. p. higher than −10° (45 to 82 mole % of ammonia), the method used was essentially that of Bradley and Alexander.[7] A small quantity (0.5 to 0.6 g.) of a solid mixture of known composition was introduced into the bend of a U-shaped glass tube of 8 mm. internal diameter and a total length of about 30 cm., and its weight was determined by difference. The lower part of the tube

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(1) Davidson and McAllister, THIS JOURNAL, **52**, 507 (1930).

(2) Davidson, *Chem. Rev.*, **8**, 175 (1931).

(3) Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898).

(4) Hunt and Boncyk, THIS JOURNAL, **55**, 3528 (1933).

(5) Shatenshtein and Uskova, *Acta Physicochim.*, *U. R. S. S.*, **2**, 337 (1935); *C. A.*, **29**, 6489 (1935).

(6) Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).

(7) Bradley and Alexander, THIS JOURNAL, **34**, 15 (1912).

(8) Kendall and J. G. Davidson, *ibid.*, **42**, 1141 (1920).