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.

BERKELEY, CALIFORNIA RECEIVED FEBRUARY 14, 1944

[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).

was then immersed in a bath of solid carbon dioxide, carbon tetrachloride and chloroform, which maintained a temperature of −78°, and dry ammonia was passed through the tube.[9] The quantity of ammonia condensed under these conditions could be readily controlled by maintenance of a constant rate of flow and regulation of the time of absorption, which varied, in different samples, from thirty seconds to three minutes. After a little practice, it was found possible to attain any desired composition by this means. Then, with the bend of the U-tube still in the cold bath, both ends of the tube were sealed in the blast-lamp, and it was allowed to come to room temperature and weighed. After the mixture had completely liquefied, it was again cooled until solidification occurred; the equilibrium temperature was then determined as that at which the last trace of crystals disappeared, while the tube was being slowly heated. Each f. p. was determined at least twice; the temperatures reported are believed to be correct to within 0.5°, except in the range from 67 to 75 mole % of ammonia, where, because of the extremely high rate of change of equilibrium temperature with concentration, the values are accurate only to ±2°.

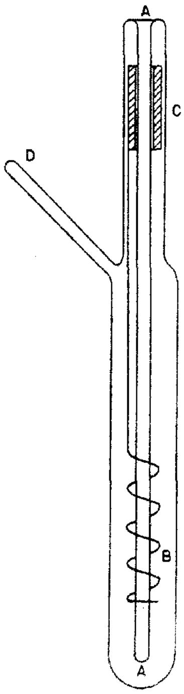

Fig. 1.—Freezing point cell.

At temperatures much below 0°, the mixtures became so viscous and equilibrium was attained so slowly that the procedure just described was no longer satisfactory. The method adopted for solutions of f. p. below −10° was similar to that described by Cady and Jones,[10] except that equilibrium temperatures were determined by means of cooling curves instead of by visual observation. The cells used were as pictured in Fig. 1; their outer dimensions were 35 by 2.5 cm., with a thermocouple well, AA, about 5 mm. in diameter. The stirrer, B, was of stainless steel wire, the upper end of which was attached to a short piece of iron pipe, C, which had been coated with stainless steel. The stirrer was operated by means of a solenoid, which was wired through a motor-driven interrupter making contact approximately 120 times per minute.

Mixtures of the desired composition were made by the following procedure. The weighed cell, surrounded by a weighed test-tube of slightly larger diameter which served as an air jacket, was one-third immersed in liquid air. About 20 cc. of ammonia was introduced by distillation through the side arm D, which was then closed by means of a rubber cap. After the ammonia had solidified, the jacketed cell was removed from the bath, the outer tube was warmed to room temperature, and the weight of the ammonia was determined. The air jacket provided sufficient insulation so that but little of the ammonia melted, and no appreciable amount vaporized, during the weighing. The desired quantity of acetic acid was introduced through the side arm, the end of which was then sealed. The jacket was removed, and the cell was warmed to room temperature and again weighed.

For the determination of equilibrium temperatures, the well, AA, was filled with a mixture of carbon tetrachloride and chloroform, in order to minimize convection effects. A copper–constantan thermocouple was introduced, and the cell was surrounded by several concentric tubes to provide air jackets. It was then immersed in a bath of solid carbon dioxide, or of liquid air, in a Dewar flask, so that cooling took place at a rate not exceeding one degree per minute. The rate of cooling in the neighborhood of the f. p. was kept approximately the same for all the determinations by the expedient of decreasing the number of jackets for mixtures of lower f. p.

The temperature–time curves were recorded directly by means of a Leeds and Northrup Micromax recorder, which had been calibrated at the b. p. of ammonia, the f. p. of pyridine, the sublimation point of carbon dioxide, and the b. p. of oxygen. The level to which the temperature rose immediately after the first break in the cooling curve was taken as the equilibrium temperature.[11] Data so obtained are believed to be correct to ±1.5°.

Analysis of Solid Phases.—Two of the three new compounds encountered in this work exist only under such conditions of temperature and pressure that the obtaining of samples for analysis would have been extremely difficult, if not impossible. Fortunately, however, both of these compounds melt congruently, so that the composition of each is clearly indicated by the position of the corresponding maximum in the f. p. curve. In the case of the third compound, the probable composition is indicated by the course of the curve, but an attempt was made to confirm this by direct analysis. A solution of appropriate composi-

TABLE I

ACETIC ACID–AMMONIA

S	*T*
(a) Solid phase $NH_3 \cdot 2HC_2H_3O_2$	
23.7	50.1
26.3	59.5
30.2	66.0
31.3	66.5
32.6	67.0
(b) Solid phase $NH_3 \cdot HC_2H_3O_2$	
34.0	69.0
34.9	73.5
35.9	79.5
39.6	96.5
40.8	100.5
43.3	106.5
45.6	112.0
46.7	114.0
48.0	115.5
50.0	117.0
51.0	117.0
51.6	117.0
(c) Solid phase $5NH_3 \cdot 4HC_2H_3O_2$	
53.1	119.0
54.5	120.0
55.2	119.5
55.7	119.5
56.0	119.5
59.0	118.0
61.4	116.4
63.9	113.0
66.0	109.5
67.8	104.5
(c) Solid phase $5NH_3 \cdot 4HC_2H_3O_2$ (cont.)	
69.2	100.0
71.2	91.0
71.9	87.0
72.2	85.0
72.7	81.0
73.2	78.0
73.7	68.5
74.2	40.0
(d) Solid phase $2NH_3 \cdot HC_2H_3O_2$ (?)	
74.4	6.5
75.7	4.5
76.2	3.0
78.0	−1.0
78.6	−3.0
80.2	−7.0
81.2	−9.0
84.6	−20.5
87.3	−29.5
(e) Solid phase $9NH_3 \cdot HC_2H_3O_2$	
88.8	−35.5
89.6	−34.0
90.9	−34.5
92.6	−40.5
97.6	−61.5
98.0	−64.0
98.9	−77.5
(f) Solid phase NH_3	
99.3	−78.5
100.0	−77.5

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(9) It was attempted, at first, to carry out the absorption of ammonia in an ice–salt bath; under these conditions, however, condensation occurred so extremely slowly that the method proved to be impracticable.

(10) Cady and Jones, *J. Phys. Chem.*, **37**, 303 (1933).

(11) The difference in the rates of cooling above and below the equilibrium point was usually not sufficiently great to make it possible to fix this point by extrapolation of the lower portion of the curve.

tion was made up in the lower end of a cell consisting of two bulbs, about 8 by 2 cm. each, connected by a vertical tube 10 cm. long and 8 mm. in diameter. The upper end of the cell was then sealed. After equilibrium had been reached at the desired temperature, the cell was inverted and the mother liquor allowed to drain into the lower bulb, both bulbs being maintained at the same temperature throughout the process. After two days, the narrow portion of the cell was sealed and the bulbs separated. The one containing the crystalline solid was weighed, broken under dilute acid, washed out, and weighed again; the amount of ammonium salt formed in the solution was then determined in the usual manner.

Results

In the preceding table, *S* denotes the mole percentage of ammonia, and *T* the corresponding equilibrium temperature. These data, together with those of Davidson and McAllister, are presented graphically in Fig. 2, in which, however, a few of the points have been omitted in order to avoid crowding.

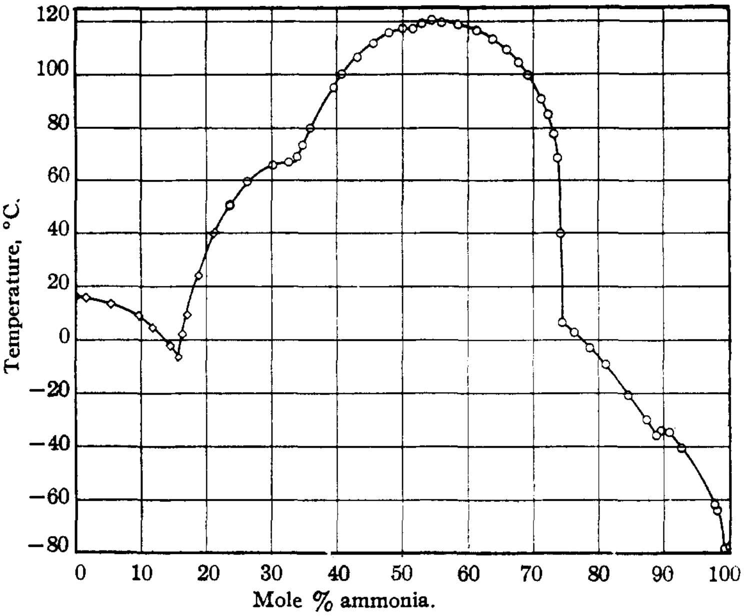

Fig. 2.—System acetic acid–ammonia; the data of Davidson and McAllister (recalculated) are indicated by squares, those of the present work by circles.

The equilibrium temperatures in the range from 25 to 50 mole % of ammonia were found to be a little higher than those previously reported, the difference increasing with increasing ammonia content. Thus, the melting point of the compound $NH_3 \cdot 2HC_2H_3O_2$ (or $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$) was found to be 67.0° instead of 66.5°, and that of ammonium acetate ($NH_3 \cdot HC_2H_3O_2$ or $NH_4C_2H_3O_2$) to be 117° instead of 113°.

Because of the decidedly unexpected course of the curve just beyond the mid-point, this region was studied with special care; the data reported above are representative of a much larger number of determinations. The evidence for the existence of a eutectic point at about 52 mole % of ammonia, and of a surprisingly stable compound of ammonia content but slightly higher than that of ammonium acetate, is unmistakable. The composition of this compound (55.6 mole % of ammonia) corresponds to the formula $5NH_3 \cdot 4HC_2H_3O_2$ (or $4NH_4C_2H_3O_2 \cdot NH_3$), and its melting point is 119.5 ± 0.5°. Its saturated solution in liquid ammonia at 25° is found to contain 25.7 mole % of acetic acid. This figure agrees fairly well with that of 26.4% calculated from the data of Hunt and Boncyk,[4] who, however, do not mention the solvation of ammonium acetate under these conditions.

At about 6.5° this compound undergoes transition to solid phase (d), which is stable in contact with solutions containing from 74.4 to 88.8 mole % of ammonia. Because of the impossibility of freeing the crystals completely from the rather viscous mother liquor, especially since suction could not be applied, accuracy in direct analysis was unattainable; the proportion of ammonia found would inevitably be too high. Three analyses of samples obtained from solutions of different initial concentration gave fairly concordant results averaging 71.9 mole % NH_3. This figure, together with the course of the curve in this region, indicates that the compound is probably $2NH_3 \cdot HC_2H_3O_2$, although the possibility of its having the composition $5NH_3 \cdot 2HC_2H_3O_2$ is not altogether exluded. If the first supposition is correct, the m. p. of the compound, by extrapolation, would appear to be about 16°.

A marked halt in the cooling curves for solutions in the concentration range just mentioned clearly indicated a eutectic point at −35.5°. Beyond 88.8 mole % of ammonia, the stable solid phase is a compound $9NH_3 \cdot HC_2H_3O_2$ (or $NH_4C_2H_3O_2 \cdot 8NH_3$), which melts congruently at −34°. A saturated solution of this compound in liquid ammonia at the f. p. of the latter contains little more than 1 mole % of acetic acid, and the last eutectic temperature is no more than 1° below the f. p. of ammonia.

Discussion

It is of interest to compare the freezing point curve just described with that for the system water–ammonia, first investigated in its entirety by Rupert.[12] Such comparison clearly brings out the enormous difference in stability of the addition compounds in the two cases, which is undoubtedly a consequence of the much greater tendency of acetic acid than of water to act as a proton donor. There are two solid compounds of water and ammonia, $NH_3 \cdot H_2O$ (ammonium hydroxide) and $2NH_3 \cdot H_2O$ ($NH_4OH \cdot NH_3$, or am-

(12) Rupert, THIS JOURNAL, **32**, 748 (1910); *cf.* Postma, *Rec. trav. chim.*, **39**, 515 (1920); and Elliott, *J. Phys. Chem.*, **28**, 887 (1924).

monium oxide), each of which melts congruently—although with considerable dissociation—at −79°. The corresponding compounds in the acetic acid–ammonia system, $NH_3 \cdot HC_2H_3O_2$ (ammonium acetate) and $2NH_3 \cdot HC_2H_3O_2$, have melting points, respectively, 196° and 95° higher than their ammonia–water analogs. The other three acetic acid–ammonia compounds have no analogs in the water–ammonia system. The light thrown by this contrast on the question of the weakness of aqueous "ammonium hydroxide" as a base at ordinary temperatures, has been discussed previously.[2]

Summary

1. The temperature–concentration curve for the system acetic acid–ammonia has been completed throughout the entire concentration range.

2. The melting point of pure anhydrous ammonium acetate has been found to be 117°.

3. The existence of the new solid compounds $5NH_3 \cdot 4HC_2H_3O_2$ and $9NH_3 \cdot HC_2H_3O_2$, and of a third having the probable composition $2NH_3 \cdot HC_2H_3O_2$, has been demonstrated.

4. Attention has been directed to the contrast between this system and that of water–ammonia.

LAWRENCE, KANSAS RECEIVED FEBRUARY 14, 1944

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Analytical Procedures Employing Karl Fischer Reagent. XI. The Determination of Primary Plus Secondary Amines[1]

BY J. MITCHELL, JR., WALTER HAWKINS AND DONALD MILTON SMITH

The identification of amines by acylation techniques has been used to some extent,[2,3] but little has been done on their quantitative acetylation. Olson and Feldman[4] modified the acidimetric acetyl chloride procedure of Smith and Bryant[5] so that most amines reacted 90% or better. However, some amides also reacted so that this technique did not differentiate between these classes of compounds. Although acetic anhydride has been used in the determination of tertiary amines,[6,7] it apparently has not been used in the quantitative estimation of primary and secondary amines.

In the present research an acetylation method has been developed which is based on the selective reaction of acetic anhydride with the primary and secondary amines, according to the equations

$$RNH_2 + (CH_3CO)_2O = CH_3CONHR + CH_3COOH$$
$$RNHR' + (CH_3CO)_2O = CH_3CONRR' + CH_3COOH$$
$$(CH_3CO)_2O + H_2O = 2CH_3COOH$$

The new technique, independent of acid–base titrimetry, determines the excess acetic anhydride, after acetylation, by hydrolysis followed by titration of excess water with Karl Fischer reagent under conditions reported in an earlier publication for the determination of anhydrides.[8]

The new procedure is applicable to primary and secondary amines generally including aliphatic, alicyclic, heterocyclic and aromatic types. However, diaryl secondary amines and pyrrole fail to react. Since tertiary amines do not interfere, the method can be used indirectly for the determination of tertiary amine by correcting the total base titer for primary plus secondary amine.

In the presence of primary alcoholic hydroxyl the procedure is modified to effect quantitative acetylation of both the amine and alcohol.

Experimental

Reagents.—The acetylating reagent is prepared by mixing 1.5 moles (142 ml.) of pure acetic anhydride in sufficient dry pyridine to make one liter of solution.[9] The hydrolysis reagent consists of 100 g. of J. T. Baker C. P. or Merck A. R. grade dry sodium iodide and 22 ml. of water in 1 liter of pyridine solution. The preparation of the Karl Fischer reagent has been reported in a previous publication.[10]

Analytical Procedure.—In the absence of hydroxyl the sample, containing up to 10 milliequivalents of primary plus secondary amine, is transferred to a 250-ml. glass-stoppered volumetric flask.[11] To this is added exactly 20 ml. of the acetylating reagent. The flask together with a blank is then stoppered, shaken and allowed to stand for thirty minutes at room temperature.[12] At the end of this time 25 ml. (calibrated pipet) of the hydrolysis reagent is added. The flask is placed in a water-bath at 60 ± 1°, and after momentarily raising the stopper to allow for expansion of the included air, is firmly stoppered and maintained at that temperature for thirty minutes. After cooling spontaneously to room temperature, the contents are titrated directly for water with Karl Fischer reagent.

Ten ml. (calibrated pipet) of the hydrolysis reagent is titrated for water. Free water in the sample is determined by titration of a portion of the sample acidified with glacial acetic acid.

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(1) Presented in part before the Division of Analytical and Micro Chemistry at the Pittsburgh meeting of the American Chemical Society, Sept. 9, 1943.

(2) Alexander and McElvain, THIS JOURNAL, **60**, 2285 (1938).

(3) Billman and O'Mahony, *ibid.*, **61**, 2340 (1939).

(4) Olson and Feldman, *ibid.*, **59**, 2003 (1937).

(5) Smith and Bryant, *ibid.*, **57**, 61 (1935).

(6) Blumrich, *Angew. Chem.*, 374 (1941), used excess acetic anhydride to acetylate primary and secondary amines in order to titrate tertiary amine in glacial acetic acid solution.

(7) Haslam and Guthrie, *Analyst*, **68**, 328 (1943); acetylated ethylaniline quantitatively to determine diethylaniline.

(8) Smith, Bryant and Mitchell, THIS JOURNAL, **63**, 1700 (1941).

(9) Eastman Kodak Co. No. 4 acetic anhydride and J. T. Baker C. P. or Eastman Kodak Co. No. 214-H pyridine meet these requirements.

(10) Smith, Bryant and Mitchell, THIS JOURNAL, **61**, 2407 (1939).

(11) The sample may be weighed directly or added volumetrically in pyridine solution.

(12) In the presence of primary hydroxyl an additional thirty minutes at 60 ± 1° is required to effect complete esterification. In this case sample size is limited to 10 milliequivalents of amine plus hydroxyl.