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POTASSIUM AMMONO-ALUMINATE, POTASSIUM AMMONOMANGANITE AND MANGANOUS AMIDE

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The present investigation was undertaken to further our knowledge of reactions in liquid ammonia leading to the formation of amides, imides, nitrides and ammono salts. This, then, is a continuation of the previous researches of Franklin and his co-workers along similar lines. The preparation of the substances named in the title of this article has been accomplished.[2]

Manipulation

The general details of the special manipulations required in working with liquid ammonia solutions are to be found in previous articles.[3] A brief description will be given of any additional or improved procedure since developed in this Laboratory and not described elsewhere.

Collection and Analysis of Gases.—During evacuation to remove ammonia from a preparation it sometimes happened that nitrogen and hydrogen were also given off. To facilitate the collection of gases evolved in such cases, the apparatus shown in Fig. 1a was designed to be attached to the delivery tube of a Töpler pump.

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[1] From a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University. A portion of the subject matter was read before a meeting of the California section and at the Birmingham meeting of the American Chemical Society.

[2] For an explanation of the ammonia system of acids, bases and salts, and of the nomenclature used in this article, see *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912).

[3] (a) THIS JOURNAL, **27**, 832 (1905); (b) **29**, 1694 (1907); (c) **35**, 1460 (1913); (d) *J. Phys. Chem.*, **15**, 915 (1911); (e) **16**, 694 (1912).

Before a gas sample was collected, bulb B was squeezed until mercury was forced up in D to the stopcock S, and the latter was then closed. To remove gases from D, the following procedure was adopted.

A bent tube F of the form shown (Fig. 1a) was filled with water by applying suction to the rubber tube G, after which this latter was attached to the stopcock S. A pressure was produced inside the bottle by squeezing the rubber bulb and S opened. The gases collected in D were then expelled through F into the tube H by the rising mercury. Ammonia of course was absorbed by the water. When all gases had thus been expelled from D, G was closed with a pinchcock, P, and disconnected. The end of a short pipet filled with water was next inserted in the open end of G, and by releasing the pinchcock the gases contained in F were driven over into H. The sample was then transferred to a combined measuring and explosion buret containing very dilute sulfuric acid by means of the tube shown at F′, Fig. 1b. The rubber connection was attached to the buret and the adjustment tube M raised to displace the air inside both buret and Tube F′ with acidulated water. By placing the test-tube H containing the collected gases over F as indicated and lowering M, these could be drawn completely into the apparatus. Hydrogen was determined by the contraction of the volume resulting from explosion with air; the remainder was assumed to be nitrogen.

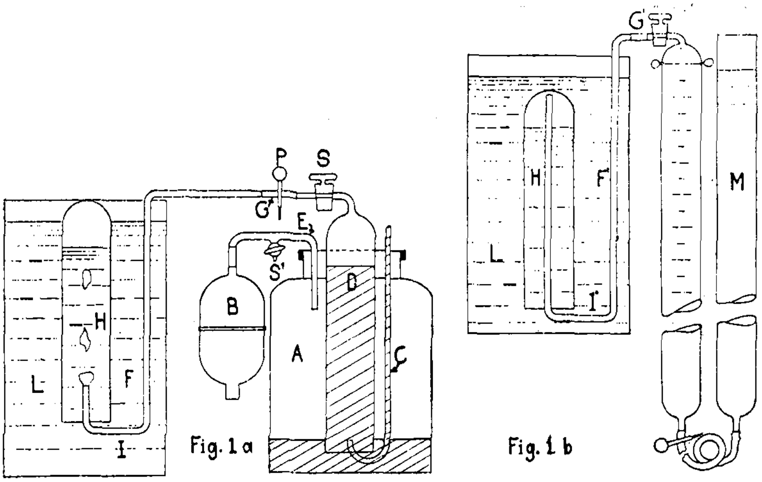

Fig. 1a

Fig. 1b

Fig. 1.

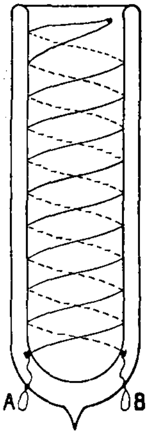

Fig. 2.

Heating in a Vacuum.—The heater shown in Fig. 2 was designed by Dr. Franklin in order to permit the operator to see the contents of the specimen tube at all times.

A helix of platinum or Nichrome wire was wound on the outside of a large tube, which was closed at the bottom and vacuum-jacketed in the same manner as are the familiar Dewar containers. The method of winding the coil is apparent from the figure, the direction of the winding being reversed near the top of the tube by passing the wire around a small glass knob. The ends of the coil were then tied to two other small glass knobs near the bottom of the tube, the terminals being joined to platinum wires sealed through the outer glass wall at A and B. The specimen tube was attached to the mercury pump in the customary manner and the heater then properly adjusted in position by means of a suitable clamp. Current was obtained from a 110-volt circuit and regulated by means of a convenient resistance.

Preparation of the Anhydrous Halides of Molybdenum, Tungsten and Iron.[3f]—In the present work it was necessary to use halides of these three metals free from oxygen, moisture, or aquobasic material. The preparations were therefore carried out by passing dried chlorine or bromine diluted with carbon dioxide over the heated metal which was placed in one end of a long tube constricted in a number of places to form compartments for the reception of the volatilized products of the reaction (Fig. 3a). The desired temperature was maintained by a combustion furnace.

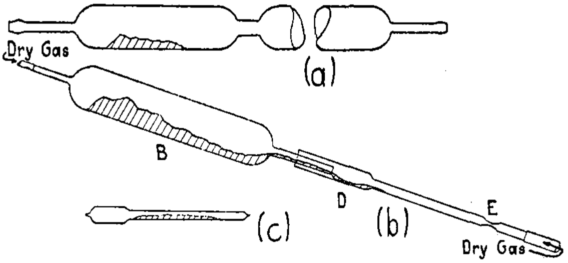

Fig. 3.

It was found desirable with hygroscopic preparations to seal in smaller specimen tubes quantities sufficient for use in one experiment. The following method was used in transferring the halide from the original container.

A stream of dry inert gas was passed through the large tube B which contained the bulk of the product and at the same time through the small specimen tube D. The end C of the large container was inserted in the open end of D, and the desired quantity of material transferred by tapping B. This specimen was then shaken into the smaller tube E and D was sealed off with a hand blast lamp. The constriction at E was sealed after removal of the rubber connection tube. When ready to be used, the end of the small container was broken off in a stream of ammonia and then rapidly introduced into the reaction tube and the contents shaken out. The weight of material was found by subtracting the weight of the empty tube plus the end broken from the initial weight of the sealed container and its contents.

Analyses.—Unless otherwise noted the preparations were all dried in a vacuum at decomposition pressures under five millimeters of mercury. The analyses were made upon aliquot portions of the acid solutions of the specimens. "Subs. (20°), 0.2345" signifies that the weight of the specimen dried in a vacuum at 20° was 0.2345 g.; "($\frac{1}{4}$) 0.1243 K_2SO_4" signifies that one-quarter of the specimen dried in a vacuum at the highest temperature indicated gave 0.1243 g. of potassium sulfate.

[3f] The work on molybdenum and tungsten will be described in a forthcoming article.

Potassium Ammono-aluminate[4]

$Al(NH_2)_2NHK.NH_3$ and $Al(NH_2)_2NHK$

In view of the fact that aluminum and zinc dissolve in aqueous solutions of alkalies, and that zinc is acted upon by a liquid ammonia solution of potassium amide,[5] it was thought that a potassium ammono-aluminate might be prepared by the analogous action of potassium amide on aluminum.

1. Preparation of Potassium Ammono-aluminate by the Action of Potassium Amide Solution on Metallic Aluminum.—A solution of potassium amide has no appreciable action on aluminum, either in the form of thin sheet or powder. A qualitative test made on a solution of potassium amide which had been in contact with aluminum powder for ten and one-half months failed to show that more than a trace of the metal had been dissolved. Amalgamated aluminum, on the other hand, was found to react readily with a solution of potassium amide, converting 0.4 or 0.5 g. of this ammono base completely to potassium ammono-aluminate within two or three days. As in the case of the reaction between magnesium and potassium amide[6] an intermediate blue solution was formed and a visible evolution of gas was obtained.

2. Preparation of Potassium Ammono-aluminate by the Action of a Solution of Potassium on Aluminum.—A solution of metallic potassium in liquid ammonia is slowly converted by the catalytic action of unamalgamated aluminum into potassium amide, but no further action takes place. Amalgamated aluminum and potassium solution react within a few days to give the same potassium ammono-aluminate described under (1) above, with the important advantage of greater convenience of preparation. It is probable that potassium amide is first formed by the action of the solvent upon the dissolved potassium, subsequent action being the same as described in the preceding section. It should be remembered that aluminum and mercury catalyze the reaction between potassium and liquid ammonia.

A Periodic Reaction between Potassium Amide and Aluminum.—In general, the blue solution resulting from the action of potassium amide on well amalgamated aluminum became opaque rather rapidly and so remained almost until the end of the reaction, when the color gradually faded, yielding finally a colorless solution of potassium ammono-aluminate. In one instance, an aluminum strip was superficially amalgamated in a few spots by contact with metallic mercury. The development of the blue color was retarded, of course, because of this imperfect amalgamation but the solution after the lapse of a few days became an opaque blue,

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[4] Previously announced in *Science*, **53**, 578 (1922).

[5] Fitzgerald, *Am. Chem. J.*, **47**, 307 (1912).

[6] Ref. 3 c, p. 1463.

which changed within a few more days to yellow, showing that potassium amide was still present but that free potassium was absent. At this point it was noticed that the amalgamated spots of the metal were covered with a dirty white deposit, which for the most part was readily removed by shaking the containing tube. The reaction then started almost immediately with the formation of a blue solution. The entire cycle was repeated five times during the next two weeks before the potassium amide had been completely converted to potassium ammono-aluminate, although the reaction tube was not shaken during this time.

Discussion.—It was shown during a subsequent investigation of sodium ammono-aluminate[7] that the formation of potassium ammono-aluminate may be represented by the equations: $Al + 3KNH_2 \rightleftharpoons Al(NH_2)_3 + 3K$; $Al(NH_2)_3 + KNH_2 = Al(NH_2)_2NHK.NH_3$; $3K + 3NH_3 = 3KNH_2 + \frac{3}{2}H_2$.

Inasmuch as dilute solutions of the alkali metals in liquid ammonia possess salt-like properties[8] and aluminum must have a very slight solubility in liquid ammonia, such a solution by analogy possessing salt-like properties, the first equation above represents a simple case of an equilibrium involving four different ions: Al^{+++}, K^+, NH_2^-, and e^-, the solvated negative electron which behaves as an anion in the solutions of metallic potassium and aluminum. The second and third equations represent subsequent reactions which cause the initial equilibrium to shift continually toward the right.

The periodic reaction between potassium amide and aluminum discussed above affords good evidence of the intermediate existence of aluminum amide. When only a very limited area of aluminum is amalgamated, it is readily conceivable that the aluminum amide formed might under proper conditions completely cover the active amalgamated spots, temporarily stopping the reaction. When this protective coating is removed, either by shaking or by solution in potassium amide, the amalgamated spots come in contact with the solution and the reaction starts again.

Properties of Potassium Ammono-aluminate.—Potassium ammono-aluminate is very soluble in liquid ammonia at room temperatures, but may be obtained in the form of small colorless needles by cooling a concentrated solution to —40°. The first crop of crystals, after being freed from its mother liquor and dissolved in fresh solvent, frequently suffers a slight ammonolysis with the deposition of a white ammonobasic precipitate. Occasionally, fairly concentrated solutions deposit this same material on standing. This slow ammonolysis may be prevented by the addition of a small quantity of potassium amide.

When the salt is dried in a vacuum at —40° the composition of the

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[7] This Journal, **45**, 2788 (1923).

[8] Kraus, *ibid.*, **44**, 1224 (1922).

crystals corresponds to the formula $Al(NH_2)_3.KNH_2$, $Al(NH_2)_2NHK.NH_3$ or, following Werner, $K[Al(NH_2)_4]$. A small but unimportant quantity of ammonia is lost on heating in a vacuum at room temperature. At 50–65° and at a pressure around 6 cm. of mercury the salt melts in its own solvent of crystallization and gives off in a vacuum one molecule of ammonia, forming $Al(NH_2)_2NHK$ or $Al(NH_2)(NH).KNH_2$, which is white and non-crystalline. Both of these compounds react very vigorously with water with the development of a great deal of heat. In spite of the vigor of the action, however, no appreciable amounts of free hydrogen or nitrogen are formed. Earlier attempts[9] to isolate this salt by the action of potassium amide on aluminum iodide resulted in failure because potassium ammono-aluminate is extremely soluble and so could not be separated from the reaction mixtures that contained in addition potassium iodide and amide, substances of the same order of solubility.

Experimental Work

The preparation of potassium ammono-aluminate was most readily accomplished by the action of a solution of potassium in liquid ammonia upon amalgamated aluminum.[10] The desired quantity of potassium, contained in a short length of glass tubing, was placed in one leg of a two-legged reaction tube together with a piece of amalgamated sheet aluminum, the other leg being shortened for more convenient crystallization of the product of the reaction. The clear, colorless solution of potassium ammono-aluminate, which was formed within two or three days, was decanted into the clean leg of the reaction tube, concentrated and cooled to —40° in a bath of liquid ammonia. The resulting crop of colorless needles was freed from its mother liquor, dried in a vacuum and analyzed according to the customary procedure. In Expt. 4, the solution of the aluminate was simply evaporated to dryness and analyzed because of the appearance of an ammonobasic precipitate. In spite of the fact that this preparation was not crystallized, the analyses are close to the calculated values.

Preparation 1 was made by the action of a solution of potassium amide upon amalgamated aluminum. The potassium amide was separately prepared by the action of a solution of potassium, contained in one leg of the reaction tube, upon the solvent in the presence of a small quantity of platinum black to act as a catalyst. After decanting the potassium amide solution upon the amalgamated aluminum in the other leg of the tube, the latter was cooled to —40° and the first leg opened, cleaned and sealed again in the manner outlined by Franklin in the articles referred to. This was done in order to have one leg of the tube clean for the crystal-

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[9] Franklin, Ref. 3 a, p. 849.

[10] The methods for preparation of substances in liquid ammonia solution and their analysis have been discussed under the section dealing with Manipulation near the beginning of this article, and in the articles there referred to.

lization of the potassium ammono-aluminate. Subsequent procedure was the same as that described by Franklin. The products of the reaction of water with the specimen were dissolved in dil. hydrochloric acid, and analyses made on aliquot portions of the resulting solution. Aluminum was precipitated as hydroxide. Potassium was weighed as sulfate. Nitrogen was determined as ammonia by distillation with sodium hydroxide in the customary manner. The method of reporting analyses is that described on p. 1547.

Preparation 1. Subs., (—40°) 1.8830, (19°) 1.8679, (102°) 1.6304: ($\frac{1}{4}$) 0.1489 N; ($\frac{1}{8}$) 0.07432 N; ($\frac{1}{4}$) 0.1876 Al_2O_3 and 0.3159 K_2SO_4; ($\frac{1}{8}$) 0.0921 Al_2O_3.

Preparation 2. Subs., (19°) 1.2584, (104°) 1.1201: ($\frac{1}{5}$) 0.1058 Al_2O_3 and 0.1725 K_2SO_4; ($\frac{1}{5}$) 0.1042 Al_2O_3; ($\frac{1}{5}$) 0.08305 N.

Preparation 3. Subs., (—40°) 0.8454, (20°) 0.8347: ($\frac{1}{5}$) 0.0659 Al_2O_3 and 0.1162 K_2SO_4; ($\frac{1}{5}$) 0.0669 Al_2O_3; ($\frac{1}{5}$) 0.07029 N.

Preparation 4. Subs., (115°) 1.1253, (20°) 1.3157, (—40°) 1.3244: ($\frac{1}{4}$) 0.1314 Al_2O_3 and 0.2268 K_2SO_4; ($\frac{1}{4}$) 0.1013 N.

SUMMARY OF ANALYSES

Preparations dried in a vacuum at —40°

Calc. for $Al(NH_2)_2NHK.NH_3$		Found			Average of Nos. 1, 2, 3, 4 (20°)
		1	3	4	
Al	20.8	20.9	20.8	21.0	21.4
N	43.1	42.7	42.6	43.0	42.3
K	30.1	30.1	30.9	30.8	30.8

Preparations dried in a vacuum at 80–115°

Calc. for $Al(NH_2)_2NHK$		Found		
		1	2	4
Al	23.9	24.2	24.8	24.8
N	37.1	36.5	37.1	36.0
K	34.6	34.8	34.6	36.2

The analyses of the preparations dried in a vacuum at —40° are the most satisfactory. It is probable that too much ammonia was removed from the heated specimens in endeavoring to solidify fully the last traces of the viscous aluminate sirup. Sodium ammono-aluminate[11] resembles potassium ammonoaluminate closely in regard to both physical and chemical properties. It is interesting to note that the specimens of the former salt dried in a vacuum at room temperatures differ very little in composition from those dried in a vacuum at —40°. The differences observed in the case of the potassium salt are more noticeable.

Action of Ammonia on Amalgamated Aluminum.—Beyond the possible formation of a thin film of amide over the amalgamated portions, liquid ammonia has no detectable action on amalgamated aluminum, nor did solution take place with the development of a visible blue color after the surface had been cleaned with potassium amide and then washed with the pure solvent.

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[11] Ref. 7, p. 2792.

Potassium Ammonomanganite

$Mn(NHK)_2.2NH_3$[4]

Aluminum and magnesium have been shown to react with potassium amide initially with the replacement of potassium by the less electropositive metal and eventually with the formation of the ammono salts, potassium ammono-aluminate and ammonomagnesiate. It was of interest to try the action of a solution of potassium amide on manganese, an element which occurs immediately below aluminum in the electropotential series, to see whether a reaction of a similar nature would take place. It was desired in this connection also to effect the preparation of an ammono salt by the action of potassium amide on a solution of a manganous salt.

Preparation of Potassium Ammonomanganite by the Action of a Solution of Potassium Amide on Manganese.—Although manganese is not attacked by aqueous potassium hydroxide it was found to react very slowly with a liquid ammonia solution of the ammono base, potassium amide, to give a sparingly soluble crystalline compound of the formula $Mn(NHK)_2.2NH_3$. Manganese, then, in this behavior resembles zinc, aluminum and magnesium. Manganese metal converts a liquid ammonia solution of potassium to potassium amide, which in turn reacts in the manner described. The light yellow crystals of potassium ammonomanganite first deposited are very small, but grow on standing for some time into well-defined needles.

The action of potassium amide on manganese may be represented by the equation, $Mn + 2KNH_2 + 2NH_3 = Mn(NHK)_2.2NH_3 + H_2$. The initial stage of this reaction, which is undoubtedly the same as for the reactions between potassium amide and magnesium and aluminum, results probably in the formation of manganous amide and a solution containing metallic potassium, in accordance with the following equation: $Mn + 2KNH_2 \rightleftharpoons Mn(NH_2)_2 + 2K$. When the reaction is carried out in the presence of mercury, the latter is found to contain large quantities of potassium. In view of the slowness of formation of potassium ammonomanganite by this method, potassium can never exist in sufficiently high concentration in solution to yield a good blue color, for manganese catalyzes the reaction between potassium and the solvent resulting in the formation of potassium amide.

Preparation of Potassium Ammonomanganite by the Action of Potassium Amide on Manganous Thiocyanate.—Manganous thiocyanate was prepared by adding barium thiocyanate to an equivalent quantity of manganous sulfate in aqueous solution. The salt, recovered by evaporating the solution to dryness, was thoroughly dehydrated at 150° in a current of dry coal gas and preserved in small sealed tubes, such as described in the first part of this article. The salt was abundantly soluble in liquid ammonia, leaving a fairly voluminous white residue composed of hydroxide or aquo-basic thiocyanates of manganese. The solution was separated from this impurity by decantation before use in any of the following experiments.

Potassium ammonomanganite is readily obtained as a light yellow microcrystalline precipitate by pouring a solution of manganous thiocyanate into an excess of a solution of potassium amide, the reaction proceeding according to the equation, $Mn(SCN)_2 + 4KNH_2 = Mn(NHK)_2.2NH_3 + 2KSCN$. The precipitate, although fairly bulky at first, after a time settles well and to a smaller volume, leaving the supernatant liquid colored a bright golden-yellow. A loosely coherent mass of cream-colored crystals was obtained after the precipitate was dried in a vacuum at —40° or at room temperature. These were vigorously hydrolyzed by water and converted into nearly white manganous hydroxide, ammonia and potassium hydroxide.

Potassium ammonomanganite decomposes in a vacuum above 110–120°, giving off $1^1/_5$ to $1^1/_3$ molecules of ammonia per atom of manganese and turning black. In addition, nitrogen and hydrogen are given off, the latter comprising by far the greater proportion of the mixed gases. It is probable that potassium ammonomanganite when heated breaks up into potassium amide and a mangano-manganic nitride or a mixture of manganous and manganic nitrides, perhaps in accordance with the following equation: $4Mn(NHK)_2.2NH_3 = Mn_3N_2.MnN + 8KNH_2 + 5NH_3 + {}^1/_2H_2$. Water reacts with the heated mixtures so obtained initially with the development of a small amount of heat, but the appearance and color of the precipitate remain unchanged. A simple de-ammonation product of potassium ammonomanganite should not differ greatly from the latter in its behavior towards water.

Calculated from the above equation, 51 cc. of hydrogen under standard conditions would be liberated when a quantity of potassium ammonomanganite containing 1.000 g. of metallic manganese is decomposed by heat. Preparations 4, 5, 6 and A (analysis of latter is omitted from this article) gave, respectively, 56, 66, 54 and 67 cc. of hydrogen and 4, 8, 12 and 8 cc. of nitrogen per g. of manganese in the specimen. The volumes of nitrogen may be high, as they were determined by difference. In addition, it should be remembered that these volumes were multiplied by a factor of approximately ten to obtain the figures given, as the various preparations contained only about 0.1 g. of manganese. The nitrogen may possibly have been produced by a catalytic decomposition of the ammonia.

Valence of the Manganese.—Preparations of potassium ammonomanganite in the solid state, as well as in solution in liquid ammonia rapidly absorb oxygen on exposure to the air, becoming brown-black. A trace of air entering a reaction tube is sufficient to cause some color. When dry the compound is pyrophoric. These facts, coupled with the observation that some of the more concentrated acid solutions possessed the pink color characteristic of solutions of manganous salts, and that the insoluble product of the hydrolysis of potassium ammonomanganite had the same appearance of manganous hydroxide, indicate the bivalence of the manganese.

A specimen of potassium ammonomanganite was prepared by the action of a solution of potassium amide on metallic manganese. One half of the solution of this specimen in dil. sulfuric acid gave 0.0593 g. of manganese pyrophosphate, $Mn_2P_2O_7$, and hence contained 0.0230 g. of manganese. The remaining half required 13.80 cc. of a solution of potassium permanganate for oxidation to Mn^{IV} according to the Volhard method, this value corresponding to 0.0233 g. of manganese, as 1 cc. of potassium permanganate was equivalent to 0.00169 g. of manganese.

Experimental Work

Potassium ammonomanganite is precipitated by slowly pouring a solution of manganous thiocyanate into a solution containing 4.5 to 5 equivalents of potassium amide, the reaction taking place in the familiar two-legged reaction tube. The washings of the salt should preferably be begun within five or ten minutes after completion of the precipitation, for the reason that on standing more potassium amide is slowly taken up by the precipitate, rendering the analyses of the specimens high with respect to potassium. Unfortunately, this fact was not recognized until after the preparations, from (2) to (5) inclusive, had been carried out, so that these analyses are not in general as satisfactory as desirable. The preparations were dried in a vacuum at pressures of 1 to 3 mm., hydrolyzed by water and then dissolved in dil. sulfuric acid prior to analysis. Small quantities of nitrogen and hydrogen obtained as a result of solution of some of the specimens in acid may partly have been caused by a too rapid hydrolysis. Manganese was always separated from potassium as manganese carbonate.

Preparation 1. A solution containing 0.41 g. of potassium as potassium amide had at the end of a year reacted with a small lump of manganese with the formation of a little over 0.5 g. of potassium ammonomanganite. This latter was then transferred to the other leg of the reaction tube by repeated extractions with the solvent, leaving the unused manganese behind. The solubility of the salt, estimated from the volume of ammonia used in the extractions, is approximately 0.8 g. per liter at room temperatures.

Subs., (—40°) 0.5479, (20°) 0.5472: ($\frac{1}{4}$) 0.0974 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.03756 N; ($\frac{1}{4}$) 0.1235 K_2SO_4.

($\frac{1}{1}$) material not dissolved by dil. sulfuric acid ignited to 0.0020 g. of Mn_3O_4. The entire specimen gave on treatment with acid 0.0016 g. of nitrogen.

Preparation 2. Subs., (18°) 0.4455: ($\frac{1}{5}$) 0.0601 $Mn_2P_2O_7$; ($\frac{1}{5}$) 0.0326 Mn_3O_4 and 0.0817 K_2SO_4; ($\frac{1}{5}$) 0.0014 AgSCN.

Preparation 3. Subs., (20°) 0.3796: ($\frac{1}{4}$) 0.02500 N; ($\frac{1}{1}$) 0.0009 g. of N_2 was obtained when the specimen was dissolved in acid; ($\frac{1}{4}$) 0.0639 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.0900 K_2SO_4.

Preparation 4. Subs., (—40°) 0.4162, (22°) 0.4154, (155°) 0.3715: ($\frac{1}{5}$) 0.0596 $Mn_2P_2O_7$; ($\frac{1}{5}$) 0.0746 K_2SO_4; ($\frac{1}{3}$) 0.01547 N; ($\frac{1}{1}$) 0.3 cc. of H_2 and 1.3 cc. of N_2 were given off on treatment of the specimen with acid; 6.5 cc. of H_2 and 0.5 cc. of N_2 were obtained during evacuation at 155°; the residue insoluble in dil. sulfuric acid was ignited, and gave 0.0007 g. of Mn_3O_4.

Preparation 5. Subs., (24°) 0.4079, (160°) 0.3643: ($\frac{1}{5}$) 0.0572 $Mn_2P_2O_7$; ($\frac{1}{5}$) 0.0747 K_2SO_4; ($\frac{1}{5}$) 0.01484 N; ($\frac{1}{1}$) 0.0 cc. of H_2 and 2.5 cc. of N_2 were given off on treatment of the specimen with acid; 7.3 cc. of H_2 and 0.9 cc. of N_2 were given off during the evacuation at 160°.

Preparation 6. Subs., (22°) 0.3344, (160°) 0.2972: ($\frac{1}{4}$) 0.0589 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.0741 K_2SO_4; ($\frac{1}{4}$) 0.01569 N; ($\frac{1}{1}$) 0.0 cc. of H_2 and 2.5 cc. of N_2 were given off when the specimen was treated with acid; 4.9 cc. of H_2 and 1.1 cc. of N_2 were obtained on evacuation at 160°.

SUMMARY OF ANALYSES

Substance dried in a vacuum at room temperatures

	Calc. for $Mn(NHK)_2.2NH_3$	Found 1	2	3	4	5	9
Mn	27.9	27.8	26.1	26.0	27.9	27.1	27.3
N	28.4	27.7	..	26.6	27.6	27.7	28.8
K	39.6	40.5	41.2	42.6	40.3	41.1	39.8

Substance heated in a vacuum at 140–160°

	Calc. for $Mn_3N_2.MnN + 8KNH_2$	Found 4	5	6
Mn	31.3	31.2	30.4	30.7
N	21.9	21.2	21.2	22.1
K	44.5	45.1	46.0	44.8

Potassium ammonomanganite may be formulated additionally as $Mn(NH_2)_2.2KNH_2$ or, following Werner, as $[Mn(NH_2)_4]K_2$. No higher ammonates were obtained by drying the preparations in a vacuum at —40°. Inasmuch as the manganites of the water system are derivatives of tetravalent manganese, the salt prepared in liquid ammonia solution perhaps should be called a hypomanganite rather than a manganite. The simpler name has been adopted, as it was not thought probable that stable derivatives of the higher valences of manganese will be prepared in liquid ammonia.

It was found possible to prepare a salt containing approximately four atoms of potassium per atom of manganese by evaporating crystals of dipotassium ammonomanganite to dryness several times with an excess of potassium amide. The resulting product was washed with small quantities of solvent and submitted to analysis. Two experiments failed to yield a tetrapotassium ammonomanganite of definite composition.

Manganous Amide and Deammonation Products

$Mn(NH_2)_2$

Light yellow manganous amide in not altogether pure condition may be prepared by the addition of potassium amide to a solution of manganous thiocyanate. On heating the material so precipitated rather indefinite black deammonation products are obtained. The reactions may be represented by the equations, $Mn(SCN)_2 + 2KNH_2 = Mn(NH_2)_2 + 2KSCN$ and $x\ Mn(NH_2)_2 = y\ Mn_3N_2.(x-3y)MnNH + (x + y)NH_3$. The very bulky and sometimes gelatinous precipitate first formed was easily broken up by shaking the reaction tube. Within a few days most of the clots so formed had further disintegrated and the resulting fine material settled more rapidly and to a smaller volume than when initially precipitated. Occasionally this change had not taken place at the end of a week, a fact which made the thorough washing of the amide a tedious process. On too rapid addition of potassium amide to a solution of manganous thiocyanate it frequently happened that the manganous amide precipitate was colored a bright yellow, possibly due to adsorbed potassium ammonomanganite.

When manganous amide is heated in a vacuum to a little above 120° it blackens and gives off quantities of ammonia, but practically no nitrogen or hydrogen, differing in this respect from potassium ammonomanganite. Accordingly, the valence of the manganese does not change. The resulting products are empirically mixtures of manganous imide and nitride in varying proportions and are very indefinite in composition. Preparations of the amide invariably contained potassium as an impurity and the nitrogen was consistently low, although manganese was not far from the calculated value for $Mn(NH_2)_2$.

Manganous amide and water react with the evolution of heat to form manganous hydroxide and ammonia, occasionally accompanied by small quantities of nitrogen and hydrogen. The preparations heated in a vacuum above 100° are on the other hand scarcely affected by water, a slight initial action probably being due to the small quantity of potassium in the product. Dil. sulfuric acid dissolves this black material slowly. In the air manganous amide is converted to a brownish-black substance, presumably manganomanganic oxide, Mn_3O_4, with the evolution of heat.

Experimental Work

It was convenient to use a three-legged reaction tube for the preparation of manganous amide in order to have one clean tube into which the clear solution of manganous thiocyanate could be decanted to separate it from the aquobasic residue insoluble in ammonia. The precipitation of manganous amide was effected then by slowly pouring a solution of potassium amide, prepared in one leg of the reaction tube, into the solution of manganous thiocyanate. In the belief that the inclusion of potassium in the precipitates was due to the use of too small an excess of manganous thiocyanate, Expts. 5 and 6 were carried out with double the quantity of this salt necessary to react with the potassium amide. The precipitates still contained potassium, as well as some new impurity whose nature was not ascertained. The analyses on this account are low. After several days, the clumpy precipitates generally had broken up to a large extent, enabling the washings to be accomplished more readily and efficiently. In many cases the washings were continued until long after the precipitate had begun to form a fine suspension or colloidal solution, without removing the potassium present as an impurity. After drying in a vacuum, the preparations were dissolved in dil. sulfuric acid, following an initial hydrolysis by means of water alone and analyses were then made on aliquot portions of these solutions.

Preparation 1. Subs., (—40°) 0.1474, (18°) 0.1457: ($\frac{1}{4}$) 0.0597 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.01033 N; ($\frac{1}{4}$) SCN a trace.

Preparation 2. Subs., (22°) 0.2657, (175°) 0.2097: ($\frac{1}{1}$) 0.3 cc. of N_2 and 1.1 cc. of H_2 given off during evacuation at 175°; 1.7 cc. of H_2 and 3.6 cc. of N_2 given off on treatment with acid; ($\frac{1}{8}$) 0.00396 N; ($\frac{1}{8}$) 0.0012 K_2SO_4; ($\frac{1}{4}$) 0.1091 $Mn_2P_2O_7$.

Preparation 3. Subs., (20°) 0.1800, (150°) 0.1456: ($\frac{1}{4}$) 0.0749 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.00508 N; ($\frac{1}{1}$) 1.2 cc. of H_2 and 0.8 cc. of N_2 given off on treatment with acid; no N_2 or H_2 was obtained on heating in a vacuum at 150°; ($\frac{1}{4}$) 0.0025 K_2SO_4.

Preparation 4. Subs., (—40°) 0.3497, (20°) 0.3440: ($\frac{2}{5}$) 0.2245 $Mn_2P_2O_7$; ($\frac{2}{5}$) 0.03722 N; ($\frac{2}{25}$) 0.0030 K_2SO_4; ($\frac{1}{1}$) 0.1 cc. of H_2 and 1.9 cc. of N_2 given off on treatment with acid; material insoluble in dil. sulfuric acid when ignited gave 0.0006 g. of Mn_3O_4.

Preparation 5. Subs., (23°) 0.4471, (156°) 0.3639, (330°) 0.3533: ($\frac{1}{4}$) 0.1865 $Mn_2P_2O_7$; ($\frac{1}{4}$) 0.0029 K_2SO_4; ($\frac{1}{8}$) 0.00510 N; ($\frac{1}{1}$) 0.0 cc. of H_2 and 1.6 cc. of N_2 given off on treatment with acid.

Preparation 6. Subs., (—40°) 0.2327, (26°) 0.2300: ($\frac{1}{4}$) 0.01561 N, ($\frac{1}{4}$) 0.0936 $Mn_2P_2O_7$, ($\frac{1}{4}$) 0.0015 AgSCN; ($\frac{1}{1}$) 0.0 cc. of H_2 and 0.6 cc. of N_2 were given off on treatment with acid.

Summary of Analyses

	Dried in a vacuum at —40°				Dried in a vacuum at room temperatures					
	Calc. for $Mn(NH_2)_2$	1	4	6	1	2	3	4	5	6
Mn	63.2	62.7	62.2	62.2	63.5	63.6	64.4	63.2	64.6	63.0
N	32.2	29.0	28.8	28.1	28.4	31.0	27.7	27.8	26.9	27.5
K	..	..	4.8	..	..	1.6	2.5	4.9	1.2	..

Heated in a vacuum at 140–175°

	Calc. for MnNH	Calc. for Mn_3N_2	No. 2	No. 3	No. 5
Mn	78.5	85.5	80.5	79.6	79.3
N	20.1	14.5	17.3	14.7	14.2
K	..	..	2.0	3.1	1.4

The analytical results, while by no means satisfactory, indicate the existence of manganous amide, $Mn(NH_2)_2$, at room temperatures or —40°. The nature of the black de-ammonation products is unknown, but they undoubtedly are not Mn_3N_2, for preparation 5 lost a small additional quantity of ammonia when heated in a vacuum at 330°.

Iron

Professor Franklin and others working in this Laboratory some years ago found that potassium amide reacts with the white ammonia addition products of ferrous iodide and bromide and with a solution of ferric thiocyanate to form apparently amorphous black precipitates. The analytical results were discouraging, as no two sets were in agreement. The preparations contained 5 to 20% potassium, and 61 to 84% iron according to the iron salt initially used and to the conditions of precipitation. Although a few analyses did calculate roughly to a formula, the inability to reproduce them left the question as to the identity of the precipitate still open. The results obtained in the present work made a more complete investigation desirable and accordingly publication will be reserved for the future.

In conclusion the author wishes to express his sincerest gratitude to Prof. E. C. Franklin at whose suggestion and under whose direction this work was carried out.

Summary

The following compounds have been prepared in liquid ammonia solution: (1) potassium ammono-aluminate, $Al(NH_2)_2NHK.NH_3$, and its deammonation product, $Al(NH_2)_2NHK$; (2) potassium ammonomanganite $Mn(NHK)_2.2NH_3$, a derivative of divalent manganese, which decomposes on heating, yielding probably a mixture of potassium amide and manganese nitrides, $MnN + Mn_3N$; (3) manganous amide, which, however, has not been obtained in altogether pure condition, together with rather indefinite deammonation products. Potassium amide was found to react with metallic aluminum (amalgamated) and manganese initially with replacement of potassium by the less electropositive element.

Experiments having as an aim the preparation of ferrous nitride and potassium ammonoferrite have been mentioned in a preliminary manner.

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