3. That hydrazine monosulfate when treated with ammonia gas at room temperature undergoes ammonolysis to some extent, and that a liquid consisting essentially of a solution of hydrazine monosulfate in free hydrazine may be separated from the mixture by centrifugal action.

These facts may serve as the basis for a new method for the preparation of free hydrazine from its salts. Further work upon this phase of the investigation is projected.

CORNELL UNIVERSITY, ITHACA, N. Y.

BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. III. ACTION OF AMMONIUM TRINITRIDE UPON CERTAIN METALS.

BY A. W. BROWNE AND A. E. HOULEHAN.

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In his epoch-making work upon reactions in liquid ammonia, E. C. Franklin[1] makes the statement that "many acids, both oxygen acids and halogen acids, as a matter of course in the form of their ammonium salts, dissolve freely in ammonia to form solutions which exhibit certain truly acid properties, as follows: First, they discharge the color of an ammonia solution of phenolphthalein, which has been rendered alkaline by the addition of a small quantity of a base. Second, solutions of ammonium salts in ammonia dissolve sodium, potassium, calcium and magnesium with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation,

$$M + NH_4X = MX + NH_3 + H.$$

Third, many metallic oxides and certain basic salts, all members of both classes of compounds being insoluble in ammonia, dissolve in solutions of ammonium salts."

The present investigation has been undertaken with a view to ascertaining whether or not ammonium trinitride behaves in liquid ammonia solution toward metals in accordance with the generalization made by Franklin. In the prosecution of this work an incidental study of the following topics has been found necessary: (1) Methods of preparing pure ammonium trinitride, (2) method for conveniently carrying out at —33° the reaction between weighed amounts of a metal and of ammonium trinitride in liquid ammonia, and under such conditions that the gas evolved may be collected, measured, and analyzed without difficulty, and that the solid reaction product may be readily weighed and analyzed.

Preparation of Ammonium Trinitride.—Ammonium trinitride was first prepared by Curtius,[2] who saturated an alcoholic solution of diazohippuramide with gaseous ammonia, and precipitated the pure ammonium

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[1] THIS JOURNAL, 27, 820-51 (1905), page 822.

[2] *Ber.*, 23, 3023-33 (1890), page 3033.

trinitride from the alcoholic filtrate by the addition of ether.[1] Curtius also prepared the compound by the action of hot alcoholic ammonia upon certain acid azides.[2] Certain of the properties of ammonium trinitride have been studied by Curtius,[3] by Berthelot and Matignon,[4] by Hittorf,[5] by Bach,[6] and by Berthelot and Vieille.[7]

The method employed in this laboratory for the preparation of comparatively large amounts of ammonium trinitride involves three operations: (1) preparation of an anhydrous ethereal solution of hydronitric acid, (2) precipitation of ammonium trinitride from this solution by the action of a current of pure dry ammonia gas, and (3) evaporation of the ether from the filtered ammonium trinitride.

The first of these operations was carried out by extracting with ether in three successive portions, either (*a*) an aqueous solution of hydronitric acid prepared by distilling the acid from Raschig sodium trinitride which had been acidified with dilute sulfuric acid, or (*b*) an aqueous solution of sodium trinitride to which had just been added in the cold the theoretical quantity of dilute sulfuric acid. The ethereal solution was in either case dried by prolonged shaking with dehydrated copper sulfate, which was finally removed by filtration.

The second step was, in general, carried out in a large Erlenmeyer flask. Pure, dry ammonia gas was slowly bubbled through the ethereal solution until precipitation was complete, and finally the precipitated ammonium trinitride was filtered out and was stored in a vacuum desiccator which from time to time was alternately evacuated and filled with dry air, until the ether had completely evaporated. The product was analyzed as follows: a sample weighing 1.2445 grams was dissolved in water, and the solution was diluted to exactly 100 cc. Thirty cc. of this solution were found to contain 0.1045 gram of ammonia, which corresponds to 28.2 per cent. NH_3. The hydronitric acid in two 10 cc. samples was precipitated and weighed as silver trinitride,[8] yielding 0.3086 and 0.3084 gram of that substance. These results correspond to 71.43 and 71.48 per cent. Theory for NH_3 in NH_4N_3, 28.4 per cent.; for HN_3, 71.6 per cent.

Apparatus Employed in the Experiments.—The apparatus consisted essentially of the modified Schiff nitrometer *A*, provided with the three-way stopcock *K* through which communication may be established,

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[1] *Ber.*, **24**, 3341–9 (1891), page 3342.

[2] *Ibid.*, **29**, 759–83 (1896), page 771..

[3] *Loc cit.*, and *J. prakt. Chem.*, [2] **58**, 261–309 (1898), page 271.

[4] *Compt. rend.*, **113**, 673 (1891).

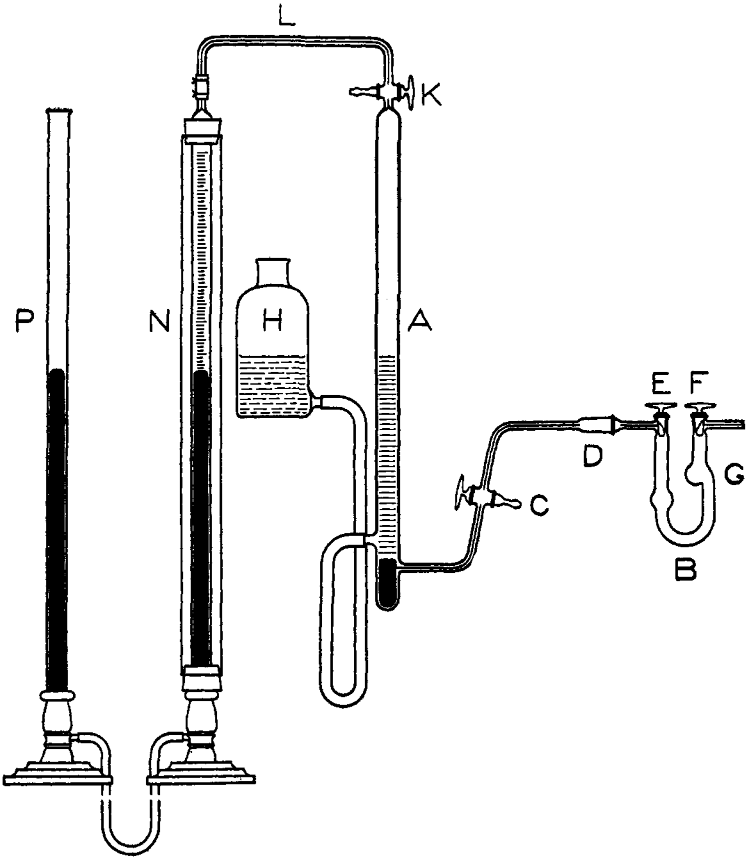
[5] *Z. physik. Chem.*, **10**, 593–620 (1892).

[6] *Ibid.*, **9**, 241–263 (1892).

[7] *Ann. chim. phys.*, [7] **2**, 339–351 (1894).

[8] THIS JOURNAL, **33**, 1569–76 (1911).

by means of the capillary tube *L* with the jacketed Hempel buret *NP*. The U-tube *B*, which was prepared from an ordinary glass stoppered U-tube by blowing a small bulb on one arm and the pocket *G* on the other, was connected with the nitrometer tube by means of the ground glass joint *D*. Communication between *B* and *A* or between either of these tubes and the outer air could be established through the three-way stopcock *C*. The stopcocks *E* and *F*, which were originally hollow, were filled with paraffin in such a way as to prevent the trapping of gas during the aspiration of ammonia through the apparatus.



General Procedure.—The Hempel buret *NP* was first filled with the proper amount of clean, dry mercury, and the nitrometer tube *A* was provided with such an amount of mercury that there was no danger of drawing acid into *B* when the pressure in the U-tube was for any reason temporarily lowered. A 5 per cent. solution of sulfuric acid was introduced into *A* and into the level bottle *H*. The U-tube was thoroughly cleaned and dried and was weighed, first empty and then with a convenient sample of ammonium trinitride. By passing a current of pure, dry ammonia[1] through the U-tube all air was displaced and the stopcocks *E* and *F* were then closed.

A weighed sample of the metal under investigation was introduced into the pocket *G*, and the stopcock *F*, which had been removed for a moment, was replaced. During the handling of metals that were easily corroded by moist air, care was taken to protect the samples from exposure. By working very rapidly and by warming the weighing bottles, it was found possible to prepare weighed samples of the alkali metals sufficiently free from the oxide for the purpose of present experiments.

A current of pure, dry ammonia was now passed through the U-tube for some time, in order to displace the air that had entered during the introduction of the metallic sample. This current entered the apparatus through the side-arm of the stopcock *F* and left it at *C*. After the tube *A* had been filled with acid by raising *H* and suitably manipulating *K*, the stopcock *C* was so turned as to divert the current of ammonia into the nitrometer. In case the bubbles of gas were immediately absorbed by the acid solution, all air was considered to have been displaced from *B*. If, however, residual bubbles of appreciable size rose through the acid after the ammonia had been absorbed, the passage of the current was continued for a sufficient length of time to insure complete displacement of the air. A vacuum beaker containing solid carbon dioxide and alcohol was now cautiously raised about *B* until a sufficient quantity of ammonia had condensed to dissolve the ammonium trinitride. In certain cases it was found expedient to bring the metal into contact with the dry ammonium trinitride immediately after the air had been displaced and before the ammonia was liquefied. During these operations care was taken, either by regulating the speed of the flow of the ammonia gas or by varying the depth of immersion of the U-tube in the refrigerant, to keep the U-tube under a pressure as nearly as possible equal to that of the atmosphere. It is obvious that if condensation were so rapidly effected as to produce a partial vacuum in *B*, mercury, and ultimately acid, might easily be drawn over from the nitrometer.

The current of ammonia was finally interrupted by closing stopcock *F*, and the sample of metal was brought into contact with the solution of ammonium trinitride by gently tapping the U-tube. The gas evolved

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[1] In connection with this operation a question concerning the possible formation of a compound of ammonia with ammonium trinitride naturally arizes. In an investigation completed some months ago the authors have found, by exploration of the pressure-concentration diagram, that ammonium trinitride forms a diammonate at —33°, which however decomposes at ordinary temperatures, and even at 0°. This compound, which has the formula $NH_4N_3.2NH_3$, or N_6H_{10}, and which is obviously a new hydronitrogen, will be described in the near future.

during the reaction escaped through the stopcocks *E* and *C* into *A*. During the course of the reaction the temperature was so regulated as to permit slow evaporation of the solution. After the reaction had gone to completion, the evolved gas was completely transferred from *B* into *A* by means of a current of ammonia. The entire sample of gas was drawn from the nitrometer into the Hempel buret, and was then passed successively into pipets containing 5 per cent. sulfuric acid, and alkaline pyrogallol. The hydrogen in each sample was directly determined by passing the gas over palladium sponge. Throughout this analytical work care was taken to saturate with hydrogen all reagents that were brought into contact with the gas. The solution of sulfuric acid in the nitrometer tube was also saturated with hydrogen, and the gas was prevented from diffusing out of the liquid by passing a slow current of hydrogen through the level bottle so as to maintain an atmosphere of the gas above the liquid.

After the liquid ammonia in the U-tube had completely evaporated, and the gaseous ammonia had been completely expelled by means of a current of dry air, the U-tube was removed, externally dried, and was weighed. The solid contents of the tube were then removed and were subjected to analysis.

It was in general found convenient to perform simultaneous, double experiments in each case, using two entirely independent pieces of apparatus. In one of the U-tubes a slight measured excess of metal was in general present, and in the other an excess of ammonium trinitride.

It should, perhaps, be stated that it was not in any way the purpose of the present investigation to prepare and analyze the pure trinitrides of the various metals studied, since these substances have already been prepared by more convenient means. The object has been merely to ascertain whether or not the reactions take place in the sense of the general equation given by Franklin.

It will be noted that in several cases the volume of hydrogen obtained shows a deviation from theory that can by no means be explained by ordinary experimental error. This deviation is undoubtedly to be accounted for by the influence of two opposing factors. The first of these, which tends to lower the volume of hydrogen, depends upon the ability of nascent hydrogen to reduce hydronitric acid.[1] The second, which tends to increase the volume of hydrogen, depends upon the possible action of the excess of certain metals upon the ammonia itself, with formation of a metallic amide and free hydrogen.

If the metal under consideration is appreciably acted upon by dry

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[1] Peratoner and Oddo, *Gazz. chim. ital.*, **25**, II, 13 (1895); 30, II, 95 (1900). Szarvasy, *J. Chem. Soc.* (*London*), **77**, 603 (1900). Cooke, *Proc. Chem. Soc.*, **19**, 213 (1903). Dennis and Isham, THIS JOURNAL, **29**, 18–31 (1907), page 28. Browne and Lundell, THIS JOURNAL, **31**, 435–48 (1909).

ammonia gas, it is quite possible that small amounts of hydrogen might be lost during the displacement of air by ammonia after the introduction of the metal into the U-tube.

It will also be noted that the weight of N_3 as determined in the residue is almost invariably appreciably smaller than the weight of N_3 in the ammonium trinitride used. This can by no means be explained as a result of experimental error, but is probably due in part to the reduction of hydronitric acid by nascent hydrogen, as noted in a preceding paragraph, and, in cases where an excess of the trinitride was used, in part to the volatilization of the ammonium trinitride[1] in the current of ammonia used to displace the air from the U-tube at the beginning, and in the current of dry air used to remove the free ammonia at the end of the experiment. This volatilization of ammonium trinitride may also help to explain in some cases the deficit in the volume of hydrogen evolved, as well as the repeated failure to detect ammonia in the residual solid even when an excess of ammonium trinitride was used at the outset.

Details of Individual Experiments. Action of Ammonium Trinitride upon Lithium.[2]—In each of the two experiments performed in connection with the present research an excess of metallic lithium was employed. In the first case 0.2077 gram of ammonium trinitride was caused to react with 0.0309 gram of lithium. The volume of hydrogen collected in the nitrometer tube, when reduced to standard conditions, amounted to 46.3 cc. Theory for hydrogen liberated from the ammonium trinitride used, 38.7 cc.; on the basis of the amount of lithium used, 49.9 cc. The residue in the U-tube weighed 0.1648 gram. After this had been dissolved in water and diluted to exactly 100 cc., two 20 cc. samples were analyzed for hydronitric acid, and were found to yield respectively 0.1025 and 0.1023 gram of AgN_3, corresponding to 87.1 per cent. N_3. The entire residue therefore contained 0.1435 gram N_3, while the ammonium trinitride taken at the outset contained 0.1453 gram N_3. No ammonia was found in the solid residue.

In the second experiment 0.3591 gram of ammonium trinitride was brought into contact with 0.0800 gram of lithium. The volume of hydrogen, reduced to standard conditions, was 52.0 cc. Theory for hydrogen on the basis of the ammonium trinitride used, 67.0 cc. Owing to an accident that resulted in the breaking of the U-tube at the conclusion of the

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[1] Curtius and Rissom, *J. prakt. Chem.*, [2] **58**, 261–309 (1898), page 272.

[2] The action of lithium upon ammonia itself has been studied by a number of investigators. See for example, Weyl, *Ann. Physik*, **121**, 601 (1864). Seeley, *Chem. News*, **23**, 169–170 (1871). Titherley, *J. Chem. Soc. (London)*, **65**, 504–22 (1894). Moissan, *Compt. rend.*, **127**, 685–93 (1898); **128**, 26 (1899); *Bull. soc. chim.*, [3] **21**, 904 (1899); *Compt. rend.*, **133**, 715 (1901). Lebeau, *Bull. soc. chim.*, [3] **27**, 163 (1902). Ruff and Geisel, *Ber.*, **39**, 828–43 (1906). Kraus, THIS JOURNAL, 30, 653–68 (1908). Ruff and Zedner, *Ber.*, **41**, 1948–60 (1908).

experiment, a satisfactory analysis of the solid residue could not be obtained. A sample was, however, tested for ammonia, with negative results. This indicates that the residue, aside from the excess of lithium, consisted of nothing but lithium trinitride.

The foregoing facts indicate that metallic lithium reacts with ammonium trinitride in liquid ammonia in the sense of the following equation:

$$Li + NH_4N_3 = LiN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Sodium.[1]—In the first experiment 0.5034 gram of ammonium trinitride and 0.1725 gram of sodium were used. An excess of 0.0529 gram of the salt was therefore present. The characteristic blue color formed when the sodium was first brought into contact with the liquid ammonia solution very quickly disappeared, and a rather brisk evolution of gas took place. Under standard conditions the hydrogen occupied a volume of 79.7 cc. Theory for hydrogen, as calculated from the sodium used, 84.1 cc. This deficit in the amount of hydrogen is undoubtedly to be explained, in part at least, by the fact that in this particular experiment the nitrometer solution was not saturated with hydrogen and that the sample of gas was permitted to stand in the nitrometer for several hours before it was analyzed. In all other experiments error from this source was entirely eliminated. The solid residue, which weighed 0.5409 gram, was found to contain 0.3474 gram N_3. The ammonium trinitride used in the experiment contained 0.3522 gram N_3. No ammonia was present in the solid residue.

A sample of ammonium trinitride, weighing 0.1502 gram, was next brought into contact with an excess of sodium weighing 0.0942 gram. In this experiment, as was to have been expected, the color of the sodium solution persisted to the end of the experiment. The volume of hydrogen under standard conditions was 29.1 cc. Theory for hydrogen, on the basis of the ammonium trinitride taken, 28.0 cc.

An excess of ammonium trinitride weighing 0.2885 gram was caused to react with 0.0942 gram of sodium. The volume of hydrogen obtained,

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[1] For information concerning the action of sodium upon ammonia reference should be made to the work of the following investigators: Wehl, *Pogg. Ann.*, **121**, 601 (1864). Seeley, *Chem. News*, **22**, 217 (1870); and **23**, 169 (1870). Gore, *Proc. Roy. Soc.*, 20, 441 (1872). Joannis, *Compt. rend.*, **109**, 900, 965 (1898); **110**, 238 (1890); **112**, 392–94 (1891); **113**, 795 (1891); **114**, 585–87 (1892); **115**, 820–23 (1892); **116**, 1370–73, 1518–21 (1893); **119**, 557–59 (1894). Titherley, *J. Chem. Soc. (London)*, **65**, 504–22 (1894), page 504. Cady, *J. Physic. Chem.*, **1**, 707–13 (1897). Hugot, *Compt. rend.*, **126**, 1719–22 (1898); **127**, 553 (1898); **129**, 299, 388–90 (1899); *Ann. chim. phys.*, [7] **21**, 5 (1900). Franklin and Kraus, *Am. Chem. J.*, **23**, 277–313 (1900); **24**, 83–93 (1900). Rengade, *Compt. rend.*, **138**, 629–31 (1904). Chablay, *Compt. rend.*, 140, 1262–63, 1343–44, 1396–98 (1905). Lebeau, *Compt. rend.*, 140, 1042–44 (1905). Joannis, *Ann. chim. phys.*, [8] **7**, 5–118 (1906). Ruff and Geisel, *Ber.*, **39**, 828–43 (1906). Joannis, *Ann. chim. phys.*, **11**, 101–10 (1907). Kraus, THIS JOURNAL, **29**, 1557–71 (1907); **30**, 653–68, 1197–1219, 1323–44 (1908). Ruff and Zedner, *Ber.*, **41**, 1948–60 (1908).

under standard conditions, was 44.4 cc. Theory as calculated from weight of sodium, 45.9 cc. The residue weighed 0.3157 gram and was found to contain 0.2007 gram N_3. Weight of N_3 taken, 0.2019 gram. Tests for ammonia in the residue yielded negative results.

From these facts it appears that metallic sodium reacts with ammonium trinitride in liquid ammonia in accordance with the equation:

$$Na + NH_4N_3 = NaN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Potassium.[1]—The samples of ammonium trinitride and potassium used in the first experiment weighed respectively 0.3422 and 0.2351 gram. The potassium was therefore in excess. Volume of hydrogen under standard conditions, 64.5 cc.; theory, as calculated from the weight of ammonium trinitride, 63.8 cc. The residue weighed 0.4655 gram, and was found to contain 0.2220 gram N_3. Weight of N_3 taken, 0.2394 gram. The deficit in this case points toward a relatively large amount of reduction. It seems only fair to state, therefore, that the comparatively close agreement between the volume of hydrogen found and the theory for hydrogen is probably due to a balancing of the two sources of error mentioned in an earlier paragraph. The residue was tested for ammonia with negative results.

In another experiment an excess of ammonium trinitride weighing 0.2212 gram was caused to react with 0.1185 gram of potassium. Volume of hydrogen under standard conditions, 31.5 cc.; theory, as calculated from potassium used, 34.0 cc. The residue, which weighed 0.2528 gram, was found to contain 0.1466 gram N_3. Weight of N_3 taken, 0.1548 gram. No ammonia was found in the residue.

It is apparent from the foregoing results that metallic potassium reacts with ammonium trinitride in liquid ammonia as indicated by the equation:

$$K + NH_4N_3 = KN_3 + NH_3 + H.$$

Action of Ammonium Trinitride upon Calcium.[2]—In the first experiment 0.3150 gram of ammonium trinitride was brought into contact with an

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[1] The behavior of potassium toward ammonia has been studied by the following investigators: Wehl, *Pogg. Ann.*, **121**, 601 (1864); **123**, 350 (1864). Seeley, *Chem. News*, **23**, 169 (1870). Gore, *Proc. Roy. Soc.*, 20, 441 (1872). Joannis, *Compt. rend.*, **109**, 900, 965 (1889); **110**, 238 (1890); **113**, 795–98 (1891); **114**, 585–87 (1892); **115**, 820–23 (1892); **116**, 1370–73, 1518–21 (1893); **118**, 713–16 (1894); **119**, 557–59 (1894). Titherley, *J. Chem. Soc.* (*London*), **65**, 504–22 (1894), page 511. Hugot, *Compt. rend.*, **129**, 299–302 (1899); **129**, 388–90, 603–5 (1899); *Ann. chim. phys.*, [7] **21**, 5 (1900). Franklin and Kraus, *Am. Chem. J.*, **23**, 277–313 (1900); **24**, 83–93 (1900). Rengade, *Compt. rend.*, **138**, 529–31 (1904). Joannis, *Compt. rend.*, **140**, 1243–1245 (1905). Chablay, *Compt. rend.*, **140**, 1396–98 (1905). Joannis, *Ann.*, [8] **7**, 5–118 (1906). Ruff and Geisel, *Ber.*, **39**, 828–43 (1906). Joannis, *Ann. chim. phys.*, **11**, 101–10 (1907). Kraus, THIS JOURNAL, **29**, 1557–71 (1907); **30**, 653–68, 1323–44 (1908). Ruff and Zedner, *Ber.*, **41**, 1948–60 (1908).

[2] In connection with the action of calcium upon ammonia the following articles

excess of metallic calcium weighing 0.1249 gram. Volume of hydrogen under standard conditions, 55.7 cc. Theory, on the basis of the ammonium trinitride used, 58.8 cc. The residue, which weighed 0.3684 gram, was found to contain 0.2162 gram N_3. Weight of N_3 used, 0.2204 gram. Although a current of dry air had been passed through the U-tube for half an hour after the liquid ammonia had completely evaporated and the tube had warmed up to room temperature, the residue was still found to give off ammonia. Analysis showed that the total residue contained 0.0540 gram, or 14.7 per cent. of ammonia.

In a second experiment a slight excess of ammonium trinitride weighing 0.2071 gram was treated with a sample of calcium weighing 0.0690 gram. The total volume of gas obtained measured, after the absorption of ammonia with dilute sulfuric acid, and reduction to standard conditions, 38.0 cc. The residue weighed 0.2416 grams and was found to contain 0.1438 gram N_3. Weight of N_3 in ammonium trinitride taken, 0.1449. In this experiment a current of dry air was passed through the U-tube after the reaction had taken place, for seventy-five minutes, at the end of which period no ammonia could be detected with the aid of Nessler's solution in the air as it escaped from the tube. The residue was nevertheless found to contain 0.0266 gram, or 11.0 per cent. of ammonia.

From these results the conclusion may be drawn that metallic calcium reacts with ammonium trinitride in liquid ammonia in the sense of the equation

$$Ca + 2NH_4N_3 = Ca(N_3)_2 + 2NH_3 + 2H.$$

The calcium trinitride apparently unites with ammonia to form an ammonate, which, however, undergoes gradual deammonation in a current of dry air at ordinary temperatures.

Action of Ammonium Trinitride upon Magnesium.[1]—In the experiments with magnesium some difficulty was experienced in causing the reaction to proceed to completion. Because of the lightness of the metal, and because of its comparative insolubility in liquid ammonia, the sample was frequently carried upward by the brisk evolution of gas so as to adhere to the walls of the tube above the solution.

In the first experiment, 0.3986 gram of ammonium trinitride was treated with a sample of magnesium weighing 0.0471 gram. The volume of

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should be consulted: Moissan, *Compt. rend.*, **127**, 685–93 (1898); *Bull. soc. chim.*, [3] **19**, 947 (1898); *Ann. chim. phys.*, [7] **18**, 289–351 (1899); *Bull. soc. chim.*, [3] **21**, 904–11 (1899); *Compt. rend.*, **133**, 715–17 (1901); *Bull. soc. chim.*, [3] **27**, 423–25 (1902). Lebeau, *Compt. rend.*, 140, 1042–44 (1905). Kraus, THIS JOURNAL, 30, 653–68 (1908).

[1] For the behavior of magnesium toward ammonia, the following references may be consulted: Briegleb and Geuther, *Ann.*, **123**, 228–41 (1862). Warren, *Chem. News*, **58**, 297–98 (1888). Merz, *Ber.*, **24**, 3940–44 (1891). Kraus, THIS JOURNAL, **29**, 1557–71 (1907).

hydrogen under standard conditions was 45.6 cc. Theory, as calculated from weight of magnesium used, 43.4 cc. The residue was found to contain a large amount of ammonia.

In order to ascertain whether the magnesium trinitride formed undergoes ammonation under the conditions of these experiments, the residues obtained in two additional experiments were analyzed as follows: in the first case a residue weighing 0.2972 gram was found to contain 0.1513 gram or 50.9 per cent. N_3. Weight of N_3 in ammonium trinitride taken, 0.1512 gram. The percentage of magnesium was 9.68 and the percentage of ammonia, 38.76. In the second case, 0.2692 gram of residue was found to contain 0.1424 gram or 52.9 per cent. N_3. Weight of N_3 in ammonium trinitride used, 0.1434 gram. In this experiment 9.9 per cent. of magnesium and 34.9 per cent. of ammonia were found.

These facts indicate that while magnesium reacts with ammonium trinitride in liquid ammonia in the manner expressed by the equation

$$Mg + 2NH_4N_3 = Mg(N_3)_2 + 2NH_3 + 2H$$

the magnesium trinitride formed probably unites with ammonia to form an ammonate.

Behavior of Ammonium Trinitride toward Zinc, Aluminium and Tin.

Zinc.—A sample of ammonium trinitride weighing 0.4605 gram was brought into contact with a sample of zinc weighing 0.2497 gram. During the progress of the treatment, which lasted for three hours, no evidence could be obtained that a reaction had taken place. No appreciable amount of gas was evolved, nor was the U-tube found to have undergone any significant change in weight after the liquid ammonia had been evaporated. After the removal of the sample of zinc, tests for that element were made upon the residual contents of the tube, with entirely negative results. A duplicate experiment was performed with the same results.

Two further experiments were now conducted under conditions similar to those of the foregoing except that a small piece of platinum foil was introduced into the U-tube in each case so as to be in contact with the sample of zinc. Small bubbles soon began to form upon the surfaces of the zinc, but the reaction proceeded so slowly that at the end of two and one-half hours only about 2 cc. of gas were collected in each case. The presence of zinc in the residues was established after the samples of the metal had been removed from the U-tubes.

Aluminium.—No action whatever was observed when weighed samples of aluminium were brought into contact with weighed amounts of ammonium trinitride dissolved in liquid ammonia. Even when active aluminium was used purely negative results were obtained. In order to be certain that the metal was really active the samples were removed from the U-tubes at the conclusion of the experiments and were immersed in water. In each case immediate evolution of hydrogen was observed.

Tin.—A weighed sample of tin was kept in contact with a solution of ammonium trinitride in liquid ammonia for four hours. No action was observed to take place, and the presence of tin in the residual solid after the metallic sample had been removed could not be detected.

Summary.

In the present investigation it has been shown that:

1. Metallic lithium, sodium, potassium, calcium, and magnesium react vigorously with a liquid ammonia solution of ammonium trinitride, with formation of the respective trinitrides and with liberation of ammonia and hydrogen in accordance with the general equation given by Franklin.

2. Zinc does not react perceptibly with ammonium trinitride in liquid ammonia. In contact with platinum, however, a very slow reaction takes place.

3. Aluminium (both ordinary and active) and tin undergo no perceptible reaction when brought into contact with a solution of ammonium trinitride in liquid ammonia.

In order to facilitate the gasometric study of such reactions as the foregoing, a modified Schiff nitrometer has been designed, in which (*a*) weighed amounts of two solids may be brought together in liquid ammonia in the absence of air and moisture, (*b*) the evolved gases may be collected, measured, and preserved for subsequent analysis, and (*c*) the residual solid may be weighed and preserved or prepared for analysis.

CORNELL UNIVERSITY, ITHACA, N. Y.

POTASSIUM: ITS TITRIMETRIC ESTIMATION IN SMALL AMOUNTS.

BY LEON T. BOWSER.

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There are in present use two colorimetric methods for the estimation of small quantities of potassium. One depends upon the red color developed by a potassium iodide solution to which potassium chloroplatinate is added, the other upon the yellow color developed by stannous chloride under the same conditions. Both are unduly sensitive to exterior conditions and even with the greatest of care it is very often impossible to obtain satisfactory results. The writer knew of a case where a set of determinations was spoiled by fumes from a fresh coat of paint in the room. While in some few laboratories no difficulties are encountered, in numerous others neither of these methods can be used; hence there is need of one indifferent to any but the most unusual of exterior conditions.

After the development of the qualitative method described in the pre-