possible saturated solutions was investigated as the rest has been done by Meerburg. The following results were obtained. The work was carried out by Mr. E. H. Norton.

TABLE III.—SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND CUPRIC CHLORIDE IN WATER AT 25°.

No.	Per cent NH_4Cl in solution.	Per cent $CuCl_2$ in solution.	Per cent $CuCl_2$ in residue.	Residue contains.
1	28.13	0.83	1.08	Mixed crystals
2	27.90	1.41	1.35	
3	27.83	1.63	1.66	
4	27.74	1.79	14.50	Mixed crystals and double salt
5	27.70	1.87	37.39	

The solutions in Nos. 1–3 vary somewhat in composition and deposited only mixed crystals, while in Nos. 4 and 5, with constant solubility and variable residue, mixed crystals were present together with the well known double salt $2NH_4Cl.CuCl_2.2H_2O$. All residues were examined under the microscope where the different solids were easily detected. The mixed crystals have only a faint tinge of blue. They become yellow when heated in the oven, so the dihydrate is evidently present as in the other cases. The mixed crystals in equilibrium with double salt contain only about 1.8% of cupric chloride.

Whether any of the substituted ammonium chlorides form mixed crystals similar to those of ammonium chloride is a matter of some interest. It has been shown by Retgers[1] that methylamine hydrochloride forms no such crystals with ferric chloride. Similar experiments have been tried in this investigation with aniline hydrochloride. A strong solution of nickel chloride was heated with enough of the hydrochloride so that the latter crystallized on cooling. The crystals formed in thin plates almost impossible to free completely from solution. They had a slight greenish—not yellow—tinge and contained 1.46% $NiCl_2$. Some of this was undoubtedly due to contamination from the solution. It is safe to conclude, therefore, that little or no mixing occurs between these salts.

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BEHAVIOR OF POTASSIUM TRINITRIDE TOWARD MANGANESE DIOXIDE AT HIGH TEMPERATURES.

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In view of the analogy existing between nitrogen and oxygen, between ammonia and water,[2] and, therefore, perhaps also between the pernitrides

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[1] *Z. physik. Chem.*, 9, 393 (1892).

[2] Franklin, THIS JOURNAL, 27, 820–51 (1905); *Am. Chem. J.*, 47, 285–317 (1912).

and the peroxides,[1] it has been deemed advizable to study the behavior at high temperatures of a typical salt of hydronitric acid, such as potassium trinitride, toward certain elements of variable valence or toward compounds of such elements, in order to ascertain whether or not the process of nitridation, analogous to ordinary oxidation processes, might be observed to take place. The recent work of Turrentine,[2] in which attention has been called to the remarkable analogy between hydronitric acid and nitric acid, greatly enhances the probability that the pernitrides should behave similarly in many respects to the peroxides.

Potassium trinitride was first described by Dennis and Benedict[3] and in the same year was also prepared by Curtius and Rissom.[4] It is a white crystallin solid which is stable under ordinary conditions, but which explodes with a mild puff when heated to temperatures much above its melting point, with evolution of nitrogen and with formation of a residue of metallic potassium.

The potassium trinitride employed in the preliminary experiments to be described in the present article was prepared by partly[5] neutralizing with potassium hydroxide the hydronitric acid obtained from commercial sodium trinitride (Raschig) by distillation with sulfuric acid. The distinctly acid aqueous solution of the potassium salt was evaporated on the water bath until crystallization took place, when it was allowed to cool. The supernatant liquid was removed from the crystals, which were then dried at room temperature in a desiccator over calcium chloride, and were finally heated to 110° in an air bath. The product was shown by analysis to be of a high degree of purity.

When mixtures of potassium trinitride and manganese dioxide are heated in the Bunsen flame the former substance in each case soon decomposes with the usual explosive puff, while the manganese dioxide is oxidized with formation of potassium manganate in considerable quantity. When the experiments are conducted in an atmosphere of air it is invariably found that the reaction appears to take place in several stages: the first apparently consisting chiefly in the decomposition of the trinitride, with subsequent oxidation of the products of the first stage by the oxygen of the air. In fact, after the explosion has occurred, the residual mass may be observed to glow distinctly as it comes into contact with air at the high temperature of the experiment. Upon cooling, the mass assumes the dark green manganate color. In an atmosphere of nitrogen the trinitride explodes as before, yielding a mass which if allowed to cool out of contact with air shows a light gray color occasion-

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[1] Browne and Welsh, THIS JOURNAL, **33**, 1728 (1911).

[2] THIS JOURNAL, **34**, 385 (1912).

[3] *Ibid.*, 20, 225–32 (1898); *Z. anorg. Chem.*, **17**, 18–25 (1898).

[4] *J. prakt. Chem.*, [2] **58**, 261–309 (1898), p. 279.

[5] Dennis and Benedict, *loc. cit.*, p. 20.

ally tinged with yellow and with green. This substance when heated for a few moments in air glows, undoubtedly as the result of its rapid union with oxygen, and yields considerable quantities of potassium manganate.

After a number of preliminary qualitative experiments had been performed, the following series of mixtures were heated in air or in nitrogen respectively as indicated below. In Experiments 1, 2, 3 and 4, 0.5 gram of manganese dioxide was treated respectively with 0.467, 0.934, 1.401 and 2.335 grams of potassium trinitride or with one, two, three and five molecules of the trinitride to one molecule of manganese dioxide. The two substances were finely powdered and were thoroughly mixed together in each case. The mixture was placed in a No. 3 (Meissen) porcelain crucible over which, in order to minimize loss of the solid products of the reaction, a No. 1 crucible was inverted. To bring about the reaction a medium sized Bunsen flame was employed, which was extinguished as soon as the explosion had occurred. The time of heating was usually about half a minute. In Experiments 2 and 4, the rush of gas attendant on the explosion blew out the flame. The residual mass was in each case allowed to cool without uncovering the crucible and was therefore found in general to have undergone only the first stage of the process. The crucible was consequently heated again for a few moments in order to permit the manganate formation to take place. The dark green mass thus obtained was finally treated with water. In every case a deep green solution was obtained, the color of which changed to that of a permanganate solution, rather slowly when the solution was allowed to stand without treatment but rapidly upon acidification with sulfuric acid. In Experiment 4, for example, the residue imparted a deep green color to six liters of water.

In Experiments 5, 6, 7, and 8, the same weights of material were used as in the four experiments just described. The method of procedure was also the same except that the air was displaced from the crucible by means of nitrogen before heat was applied. In each case a part or all of the gray residue was treated with water. The presence of small particles of metallic potassium was made manifest by a hissing sound and by the appearance of occasional sparks when the water was first added. Tests for ammonia gave positive results in each case. In Experiment 5, a portion of the mass left after the explosion was heated for a few moments in air with the result that it immediately began to glow and on cooling was found to have assumed the manganate color.

In an attempt to throw light upon the nature of the first stage of the reaction, which seems to consist chiefly in the decomposition of the potassium trinitride, several samples of this compound weighing 0.5 gram each were heated in air under conditions similar to those of the first four experiments. The residual product contained metallic potassium and some unchanged potassium trinitride. The solution obtained by treatment of portions of the residue with dilute sulfuric acid was found to contain no detectable quantity of hydrogen peroxide. Appreciable amounts of ammonia were liberated on treatment of the residue with water. When a sample of potassium trinitride is heated in an ordinary test tube, the compound decomposes with a mild explosion producing a beautiful mirror of metallic potassium upon the walls of the tube.

Since the decomposition of potassium trinitride results in the liberation of metallic potassium, it was considered advizable to perform a series of experiments in which the action of metallic potassium upon manganese dioxide in an atmosphere of air or of nitrogen could be investigated. After some preliminary experimentation a sample of metallic potassium weighing 0.86 gram was covered over with a sample of manganese dioxide weighing 0.5 gram and heat was applied as in the preceding experiments. A vigorous but not explosive reaction ensued with formation of a mass which on cooling showed a dark gray color and which on further heating for a few moments in an open crucible with free access of air glowed quietly and assumed on cooling a dark green manganate color. On treatment with water a solution was obtained which imparted a deep green color to three liters and a distinctly recognizable green to six liters of water. In a second experiment 0.79 gram of metallic potassium was heated with 0.5 gram of manganese dioxide in an atmosphere of nitrogen, and a portion of the grayish mass left after the vigorous reaction had gone to completion and the crucible had been allowed to cool to room temperature, was treated with water. The presence of an excess of metallic potassium was demonstrated but ammonia was found only in traces. Another portion of the residue was heated for a few moments in air with the result that a considerable amount of potassium manganate was formed as before.

In view of the behavior of potassium toward manganese dioxide, it would appear that the action of potassium trinitride may be most reasonably attributed to initial liberation of metallic potassium and subsequent action of the potassium upon the manganese dioxide. The resulting product is then oxidized in air to potassium manganate.

The formation of ammonia on treatment with water of the product of the first stage may of course be ascribed to the decomposition of the excess of potassium trinitride. It is conceivable, however, that the ammonia, which substance, it will be remembered, is not obtained in appreciable amounts by the action of potassium upon manganese dioxide in an atmosphere of nitrogen, may have been liberated by hydrolysis of some compound akin to potassium ammono manganate. If this be the case, a part of the nitrogen of the potassium trinitride probably enters into combination with the manganese, and the reaction might be regarded in a sense as one of nitridation. Before this matter can be decided one way or the other, it will be necessary to perform a series of quantitative experiments upon the decomposition of the potassium trinitride, and upon the behavior of the substance toward manganese dioxide, in which the deportment of the nitrogen is studied gasometrically. The author is now engaged in this investigation and hopes to be able to present a definit solution of the problem in the near future.

Preliminary experiments have been performed in connection with the action of potassium trinitride and certain other trinitrides at high temperatures upon a number of other substances. When potassium trinitride is heated in air for a few moments with chromic oxide, for example, a considerable quantity of potassium chromate is obtained.

Summary.

In the preliminary experiments described in the preceding paragraphs, it has been shown that:

(1) Mixtures of potassium trinitride and manganese dioxide containing one, two, three and five molecules of the trinitride respectively to one of the dioxide yield when heated with free access of air considerable amounts of potassium manganate.

(2) The reaction apparently takes place in several stages. First, decomposition of the trinitride with liberation of metallic potassium; second, action of the potassium upon the manganese dioxide; third, oxidation of the product by means of atmospheric oxygen to potassium manganate. The precise nature of the reaction can not, however, be stated with certainty until the completion of a series of gasometric determinations which are now in progress.

The work was undertaken at the suggestion of Professor A. W. Browne, and has been carried out under his supervision.

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THE ACTION OF THIONYL CHLORIDE ON METALS AND METALLOIDS.

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Although thionyl chloride has long been employed as a reagent in organic chemistry, its reaction on metals and metalloids has been but little studied. Apparently the first research along this line was carried out in 1883 by Heumann and Köchlin[1] who investigated the action of thionyl chloride on antimony. During the following year the reaction with selenium was studied by Prinz,[2] and this work was repeated by Lenher and North[3] in

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[1] *Ber.*, 16, 1625 (1883).

[2] *Ann.*, 223, 355 (1884).

[3] THIS JOURNAL, 29, 33 (1907).