or two cases where 1 mg. of strontium was present, the tests were faint, but conclusive.

Summary.

The previous work of the authors[1] has shown that the systematic qualitative detection of barium is distinctly unreliable. They have devised a scheme of analysis by which small amounts of the alkalin earth metals may be detected. The method consists in the precipitation of the alkalin earth metals together with part of the lead as sulfates, with dilute sulfuric acid and alcohol, from a solution of definit acidity. After extracting the lead sulfate with ammonium acetate, the alkalin earth sulfates are converted to carbonates by boiling with sodium carbonate solution. The carbonates are then dissolved in acetic acid and the resulting solution analyzed in the usual manner. Numerous test analyses prove the method to be trustworthy.

POTASSIUM AMMONOTITANATE—$N \equiv Ti\text{-}NHK$.[2]

By Edward C. Franklin and Thomas B. Hine.

Received August 30, 1912.

In a paper on the ammonia system of acids, bases and salts,[3] the senior author has shown that the amides and imides and the nitrides of the non-metallic elements are to be looked upon respectively as ammono acids and acid ammonides, which may be expected to react with ammono bases in liquid ammonia solution to form ammono salts in a manner analogous to the action of aqueous potassium hydroxide on the hydroxides and oxides of the non-metallic elements.

In order to test this view experimentally, one of us (F.) prepared silicon amide[4] by the ammonolysis of silicon tetrabromide and subjected it to agitation in contact with excess of potassium amide in liquid ammonium solution, with the result that a product was obtained roughly approximating the composition represented by the formula $N \equiv Si\text{–}NHK$. The unsatisfactory results of this experiment, but more especially the prospect

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[1] *Loc. cit.*

[2] The experimental work here described was carried out by the junior author in the chemical laboratories of the Leland Stanford Junior University during the academic year 1910–11 and was incorporated in a thesis submitted in partial fulfilment of the requirements for the degree of Master of Arts. The publication of the rather unsatisfactory results obtained has been delayed in the hope that the opportunity would present itself for a continuation of the investigation. The appearance of a recent paper by Ruff and Treidel [*Ber.*, 45, 1364 (1912)] in which certain of Hine's results are anticipated [cf., however, *Am. Chem. J.*, 47, 306 (1912)] renders further delay in publication inadvisable.

[3] *Am. Chem. J.*, 47, 298 (1912).

[4] Lengfeld, *Ibid.*, 21, 531 (1899); Vigouroux and Hugot, *Compt. rend.*, 136, 1670 (1903).

that an ammonotitanate of potassium might be more easily prepared, led to the investigation of the action of potassium amide on titanium tetrabromide or rather upon an ammonolytic product of the bromide of the formula $N \equiv Ti\text{-}Br$.

Ruff and Eisner[1] have shown that liquid ammonia acts upon the chloride and the bromide of titanium to form compounds of the respective formulas $N \equiv Ti\text{-}Cl$ and $N \equiv Ti\text{-}Br$ which, in terms of Franklin's theory, may be interpreted either as ammonobasic salts or as acid nitride halides[2] resulting from the ammonolytic action of liquid ammonia on the respective halides. In view, however, of the distinctly acid forming properties of titanium, the compounds of Ruff and Eisner are to be looked upon rather as acid nitride halides than as ammonobasic salts, and in consequence would be expected to react with an ammono base, such as potassium amide, to form a salt of ammonotitanic acid just as acid oxides or acid oxyhalides react with potassium hydroxide to form aquo salts.

The experimental work described below shows that, as a matter of fact, such an ammono salt may be prepared.

Potassium Ammonotitanate, $N \equiv Ti\text{-}NHK$ or $KN = Ti = NH$. — The preparation of a number of impure specimens of this salt was conducted as follows:

The familiar reaction tube[3] is first attached to a cylinder of liquid ammonia by means of a small lead tube in the manner first practiced by Joannis.[4] Then, with a current of pure hydrogen passing through the apparatus, a cylinder is cut from a glass tube filled with titanium bromide[5] and introduced into one leg of the reaction tube, which is then closed before the blowpipe. Metallic potassium in quantity sufficient to furnish an excess of potassium amide is introduced into the second leg, which in turn is closed before the blowpipe. When now ammonia gas is cautiously run into the apparatus, its action on the titanium bromide, otherwise rather violent, is moderated by the presence of hydrogen. The acid bromide swells and crumbles to a powder under the action of gaseous ammonia. After the completion of this slaking process, liquid ammonia is condensed in the desired quantity into the two legs of the reaction tube, and the potassium amide formed by the interaction[6] of ammonia and

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[1] *Ber.*, **31**, 2250 (1908).

[2] That is, compounds of the ammonia system analogous to the acid oxyhalides of the water system.

[3] THIS JOURNAL, **27**, 831 (1905).

[4] Mémoire de la Société des Sciences physiques et naturelles de Bordeaux t. V. (4e Série).

[5] Prepared by the method recommended by Thorpe [*J. Chem. Soc.*, **47**, 126 (1885)] and preserved for use in accordance with the directions of Fitzgerald [THIS JOURNAL, **29**, 1694 (1907)].

[6] This interaction is very slow unless accelerated by the presence of platinum black.

metallic potassium is poured upon the insoluble ammonolytic product and, with occasional shaking, is left in contact with it for several days. The yellow color of the ammonated ammonobasic titanium bromide formed by the ammonolysis of titanium bromide in accordance with the equation,

$$TiBr_4 + (4 + n)NH_3 = N \equiv Ti\text{-}Br.nNH_3 + 3NH_4Br,$$

changes to a brick red as the result of more or less complete conversion of the ammonobasic salt into potassium ammonotitanate. After thoroughly washing the product by the familiar decantation method, the reaction tube is sealed apart at the bend, thus leaving the salt in a container from which it is removed for analysis after the manner elsewhere described.[1]

Six experiments were carried to completion in the manner just indicated and the products analyzed with the following results:

Preparation I. One-half of 0.1435 gram of the substance gave 0.0490 gram TiO_2 and 0.0485 gram K_2SO_4. The other half gave 0.0147 gram N. Preparation II. One-half of 0.2881 gram of the substance gave 0.1070 gram TiO_2 and 0.0895 gram K_2SO_4. The other half gave 0.0357 gram N. Preparation III. One-half of 0.1957 gram of the substance gave 0.0662 gram TiO_2 and 0.0570 gram K_2SO_4. The other half gave 0.0218 gram N. Preparation IV. One-half of 0.1523 gram of the substance gave 0.0508 gram TiO_2 and 0.0515 gram K_2SO_4. The other half gave 0.0170 gram N. Preparation V. One-half of 0.2535 gram substance gave 0.0902 gram TiO_2 and 0.0763 gram K_2SO_4. The other half gave 0.0306 gram N. Preparation VI. One-half of 0.2590 gram substance gave 0.0849 gram TiO_2 and 0.0834 gram K_2SO_4. The other half gave 0.0298 gram N.

The percentage composition of these preparations calculated from the above analytical data, together with an analysis by Ruff and Treidel, are given herewith:

Calculated for $N \equiv Ti\text{-}NHK$.		Found.						
		I.	II.	III.	IV.	V.	VI.	R. & T.
Ti	41.3	41.0	44.5	40.7	40.0	42.6	39.4	43.0
N	24.1	20.4	24.7	22.2	22.4	24.1	23.0	25.7
K	33.6	30.3	27.9	26.5	30.3	27.0	28.9	28.1
H	0.9	..	..	..	..	..	..	..

Obviously the products analyzed were far from being pure compounds, although the analytical results obtained point with a fair degree of certainty to the existence of a potassium ammonotitanate of the formula $N \equiv Ti\text{-}NHK$ or $NH = Ti = NK$, which is formed from Ruff and Eisner's nitride bromide in accordance with the equation:

$$N \equiv Ti\text{-}Br + 2KNH_2 = N \equiv Ti\text{-}NHK + KBr + NH_3.$$

It is worth while to consider the nature and extent of the impurities present in these preparations for the reason that a satisfactory explanation of the unduly divergent analytical results will lend considerable support to the conclusion stated in the preceding paragraph.

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[1] *J. Physic. Chem.*, 15, 516 (1911).

In the first place, it is to be noted that titanium nitride bromide and the brick red product of the action of potassium amide thereon are both quite insoluble in liquid ammonia, and that the latter product was always obtained in the form of a dense powder of varying degrees of fineness. These are conditions which may have interfered with the complete transformation of titanium nitride bromide, and, such being the case, it certainly would not be surprising if some of the particles of the nitride bromide should have failed of complete conversion into the potassium salt. This contingency was recognized and the attempt was made to eliminate the effects feared, as far as possible, by floating off the finer portions of the product for analysis. In view, therefore, of the fact that Ruff and Eisner[1] have prepared titanium nitride bromide by the action of liquid ammonia on titanium bromide and that Ruff and Treidel[2] have shown that this compound is more or less completely converted into titanium nitride by the action of potassium amide, it seems reasonable to suppose that our preparations were contaminated with either the one or both of these compounds.

In the second place, the above supposition as to the nature of the impurites contained in the analyzed specimens of potassium ammonotitanate becomes a practical certainty in the light of the fact that the sum of the weights of titanium, nitrogen and potassium are short from two to ten per cent of the weights of the specimens analyzed, and that bromine was shown qualitatively to be present in some of the specimens.

Finally, on the assumption that the preparations obtained by Hine were contaminated with titanium nitride bromide, or with both titanium nitride bromide and titanium nitride, the following schemes have been calculated to show their composition:

I. $TiN_2HK + 0.10\ TiNBr - 0.20\ NH_3$.
I. $TiN_2HK + 0.04\ TiNBr + 0.20\ TiN_{1.33} + 0.09NH_3$.
III. $TiN_2HK + 0.12\ TiNBr + 0.07\ TiN_{1.33} + 0.06NH_3$.
IV. $TiN_2HK + 0.10\ TiNBr$.
V. $TiN_2HK + 0.10\ TiNBr + 0.18\ TiN_{1.33} + 0.41NH_3$.
VI. $TiN_2HK + 0.14\ TiNBr + 0.06\ NH_3$.
VII.[3] $TiN_2HK + 0.04\ TiNBr + 0.21\ TiN_{1.33} + 0.25NH_3$.

Hine's impure potassium ammonotitanate was obtained as a rather dense, brick red powder, insoluble in liquid ammonia solutions of either potassium amide or ammonium bromide. Although not soluble in ammonium bromide, this acid[4] changes the color of the precipitate from red to yellow as the result, probably, of its more or less complete con-

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[1] *Ber.*, 41, 2250 (1908).

[2] *Ibid.*, 45, 1364 (1912).

[3] Calculated from Ruff and Treidel's data on the assumption that bromine was present in their preparation.

[4] The fact is recalled that ammonium salts in liquid ammonia solutions exhibit acid properties.

version into titanium nitride or imide or titanium nitride bromide. Titanium seems to be too weak a base forming element to permit the formation of titanium bromide in the presence of an excess of ammoniacal hydrobromide acid.[1] The salt is vigorously hydrolyzed in the presence of water; with a limited supply of water the temperature of the reacting mass may rise to incandescence. It is not explosive, as are many of the heavy metal derivatives of ammonia.

Summary.

In this investigation it has been shown that potassium amide in liquid ammonia solution reacts with titanium nitride bromide to form potassium ammonotitanate in accordance with the equation,

$$N \equiv Ti\text{–}Br + 2KNH_2 = N \equiv Ti\text{–}NHK + KBr + NH_3,$$

thus adding another representative to the rather small group of ammono salts of inorganic ammono acids.

Hygienic Laboratory,
United States Public Health and Marine Hospital Service,
Washington, July, 1912.

THE ACTION OF POTASSIUM AMIDE ON CUPRIC NITRATE IN LIQUID AMMONIA SOLUTION.

(CUPROUS IMIDE, CUPROUS NITRIDE AND POTASSIUM AMMONOCUPRITE.)

By Edward C. Franklin.

Received August 30, 1912.

Introduction.

In a paper published some years ago, Fitzgerald[2] made note of the fact that the precipitate formed by the action of potassium amide on cupric nitrate in liquid ammonia solution readily goes into solution again upon the addition of an excess of potassium amide. This behavior suggests the formation of a copper compound related to ammonia as the familiar alkali zincates are related to water. The experimental proof of the existence of such a compound would be a matter of considerable interest; and such interest is considerably enhanced when the fact is recalled that cuprous hydroxide (oxide), the water analogue of cuprous amide, is apparently devoid of amphoteric properties, that is to say, it is incapable of forming a salt with potassium hydroxide. It was for the purpose of isolating and determining the composition and some of the more obvious properties of the compound formed by the solution of cuprous amide[3] in potassium amide solution that the investigation described in this paper was undertaken. Incidentally some observations

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[1] Ammonium bromide in solution in liquid ammonia.

[2] This Journal, 29, 657 (1907).

[3] The precipitate is assumed to be cuprous amide. When dried under conditions described elsewhere in this paper, cuprous imide and cuprous nitride, respectively, are obtained.