loss resulted from so doing, and they would soon learn, as so many others have learned, that cheap work is usually bad work.

In the foregoing, I have endeavored to outline the present situation with its existing complications and some of the suggested remedies, in so far as concerns the future of our Society considered by itself. It may be permitted me, however, to look still further into the future, and to see therein the possibility of a yet wider affiliation than that already discussed, that of the several grand divisions of natural science, on a basis somewhat different from that now obtaining in the American Association for the Advancement of Science, an affiliation in which the American Chemical Society, by reason of its numbers and the importance of its field, shall occupy a most prominent position. Whether or not this vision is ever to come true, we should all work in harmony to the end of the formation of a grand organization of chemists that shall be a power for the greatest good to the profession and to mankind.

HYDRONITRIC ACID, V.

By L. M. Dennis and Helen Isham.

The following paper contains:

I. The Preparation of Some New Salts of Hydronitric Acid, with the analyses and properties of these compounds.

II. The Determination of Hydronitric Acid.

III. The Preparation of Alcoholic Hydronitric Acid.

IV. The Reduction of Hydronitric Acid and its Salts.

V. The Reaction between Hydronitric Acid and Sulphuric Acid.

VI. The Reaction between Hydronitric Acid and Hydrochloric Acid.

The hydronitric acid used in these investigations was prepared by the Wislicenus method[1], as modified by Dennis and Browne[2]. The yields of the acid were quite satisfactory, and in no case did the product show the presence of hydrocyanic acid.

I. The Preparation of Some New Salts of Hydronitric Acid, with the Analyses and the Properties of these Compounds.

In the analyses of the salts described below, copper was determined by the electrolysis of a nitric acid solution, and nickel and cobalt by the electrolysis of ammonium hydroxide solutions. Zinc was determined by titration with potassium ferrocyanide, using uranyl acetate as indicator. Pure zinc was prepared by dissolving 144 grams of $ZnSO_4.7H_2O$ in water, adding 1.2 cc. of concentrated sulphuric acid, diluting with water to one liter and electrolyzing with a current of 8 amperes per

[1] Ber. 25, 2084 (1892).
[2] This Journal, 26, 577 (1904).

square decimeter, using electrodes of commercial zinc. The zinc is deposited on the cathode in large crystals which are free from iron.

In the analyses of the salts containing pyridine, the sample was mixed with a large amount of dry powdered copper oxide and was poured directly into the combustion tube. The use of porcelain boats in these analyses was abandoned after one or two trials, because the boat was invariably broken by local explosions, even when the salt was mixed with copper oxide in the boat.

Copper.—Curtius describes[1] a copper trinitride, but on account of the explosive character of the substance, he was unable to analyze a dry sample. He obtained results that agreed fairly well with the formula, $CuN_6.\frac{1}{2}H_2O$, the copper and the nitrogen being in the ratio of $1 : 5.94$.

From the analogy between copper and silver it seemed probable that the crystalline salt of copper might be obtained from solution in ammonium hydroxide. For this reason copper hydroxide was precipitated by potassium hydroxide from a solution of copper sulphate. The precipitate was washed by decantation, filtered off, and while still moist, it was shaken with an excess of a solution of hydronitric acid that in the different preparations varied from two to six per cent. in strength. The granular black precipitate changed at once upon this treatment into a dark green flocculent substance. This was separated by filtration, washed, and dissolved on the filter with strong ammonium hydroxide. It dissolved readily, forming a clear, deep blue solution, and upon standing there separated out transparent green crystals so dark in color as to appear black by reflected light. These crystals explode with a loud report upon heating or upon percussion, but at ordinary temperatures they can be handled without danger. They are insoluble in water, but are easily soluble in dilute acids. Analysis showed this compound to be a normal copper trinitride with two molecules of ammonia of crystallization.

Theory for $CuN_6 . 2NH_3$ per cent.	Found per cent.	
NH_3	18.73	18.77	18.74
Cu	34.95	34.93	34.83
N_3	46.30	46.06	46.36

If the green product that is obtained by treating the precipitated copper hydroxide with hydronitric acid is treated on the filter with pyridine, instead of with ammonium hydroxide, it dissolves, yielding a dark-green solution, from which upon standing very fine brown needles crystallize out. These crystals are insoluble in water, but are readily soluble in dilute acids. They are not as explosive as $CuN_6.2NH_3$. They were dried upon a porous plate and then analyzed.

[1] J. pr. Chem., **58**, 295.

Theory fo $CuN_6 \cdot 2C_5H_5N$ per cent.	Found per cent.	
Cu	20.78	20.76	20.62
N_3	27.53	27.9	27.67
C	39.2	39.56	
H	3.29	3.06	

Zinc.—Curtius obtained a basic trinitride of zinc by dissolving the metal in dilute hydronitric acid and allowing the water solution to evaporate in the open air. A scum formed. This was insoluble in water, and upon analysis, showed approximately the composition, $ZnOHN_3$.

If the solution of zinc in hydronitric acid is treated with an excess of ammonium hydroxide and allowed to crystallize in the open air, a white powder soon separates. If the solution is evaporated apparently to dryness, this powder begins to assume a definite crystalline form and in about three days crystals that are several millimeters in length appear. It was found to be impracticable to separate these crystals from the white powder upon which they grew, and consequently no extended examination of them was made.

To avoid hydrolysis an alcoholic solution of zinc trinitride was next employed. This was prepared by pouring upon an excess of zinc a six per cent. solution of hydronitric acid in methyl alcohol. The solution of the zinc was hastened by using the alcoholic hydronitric acid as the electrolyte with the zinc as anode and platinum as cathode. The solution of zinc trinitride in methyl alcohol was then filtered off from the excess of zinc, and dry ammonia gas was passed through it. A white crystalline precipitate appeared, which redissolved in an excess of ammonia: upon allowing this solution to evaporate, large white crystals separated in the form of long, branching needles. These were insoluble in water, but upon standing in contact with water, they changed in appearance, becoming opaque. Zinc hydroxide is probably formed in this change, for the water gives the ferric chloride reaction for hydronitric acid. When heated, the crystals decompose without explosion. If any free hydronitric acid is present in the alcoholic solution of the zinc trinitride, it will form ammonium trinitride when the compound is treated with ammonia. This ammonium trinitride is insoluble in methyl alcohol, but dissolves in an excess of ammonia. The ammonium trinitride is, however, less soluble than the zinc compound, and consequently separates first upon crystallization, thus rendering it easily possible to free the zinc compound from it by fractional crystallization. Analysis of the zinc salt gave the following results:

Theory for $ZnN_6 \cdot 2NH_3$ per cent.	Found per cent.	
Zn	35.60	35.53	35.70
N_3	45.85	45.88	45.77
NH_3	18.55	18.38	18.71

If metallic zinc is dissolved in a six per cent. aqueous solution of hydronitric acid and pyridine is then added to the clear solution, a crystalline white precipitate results. This precipitate showed varying composition, but if redissolved in an excess of pyridine and allowed to stand, white crystals of constant composition were formed. These crystals are insoluble in water, but are soluble in dilute acids. They do not explode upon percussion, but when thrown upon a hot plate they decompose with a sharp report and a bright flame. Analysis gave the following results:

	Theory for $ZnN_6 . 2C_5H_2N$, per cent.	Found per cent.
Zn	21.25	21.24
N_3	27.37	27.25
C	38.97	39.01
H	3.27	3.17

Nickel.—When freshly precipitated nickel carbonate is dissolved in hydronitric acid of a strength of about six per cent. and pyridine is then added, a green precipitate first forms, and this then dissolves in an excess of pyridine. Upon allowing this solution to stand, large prismatic, transparent, green crystals were obtained. These were insoluble in water, but when moistened with water and allowed to stand in the air they became opaque and gradually decomposed. When, however, they were removed from the solution, freed from the mother liquor by pressing them between filter papers and rapidly drying them upon a porous plate, they gave upon immediate analysis the following results:

	Theory for $NiN_6 . 4C_5H_6N$ per cent.	Found per cent.	
Ni	12.78	12.5	12.67
N_3	18.34	17.96	
C	52.27	52.08	52.3
H	4.35	4.49	4.59

A nickel trinitride with six molecules of pyridine was made by precipitating nickel trinitride from water solution by the addition of an amount of pyridine that was not sufficient to redissolve the salt, filtering, washing the precipitate with a small amount of pyridine, then redissolving the substance in an excess of pyridine, and rapidly evaporating the resulting solution in a vacuum desiccator. Small transparent green crystals separated. These decompose in the air much more rapidly than the crystals of nickel trinitride with four molecules of pyridine. When thrown upon a hot plate they decompose without explosion. Dried and analyzed as quickly as possible they gave the following results:

	Theory for $NiN_6 . 6C_5H_5N$ per cent.	Found per cent.	
Ni	9.57	9.66	9.60
N_3	13.64	13.64	
C	58.3	58.34	
H	4.89	4.81	

Cobalt.—Upon adding pyridine to an aqueous solution of cobalt trinitride a pink precipitate is formed. This dissolves partially in an excess of pyridine and leaves behind a green, insoluble substance. Evaporation of the pyridine solution in the open air yielded a green crystalline precipitate that was insoluble in water. This was not further examined. Another portion of the pink precipitate that results when pyridine is added to the aqueous solution of cobalt trinitride was filtered, washed with a small amount of pyridine and then redissolved in an excess of pyridine. A dark-red solution was obtained. Upon evaporation in a vacuum desiccator, small red transparent crystals, similar in appearance to those of the $NiN_6.6C_5H_5N$ appeared. These crystals were insoluble in water, but became opaque when allowed to stand in contact with water or when exposed to the air. Analysis gave the following results:

	Theory for $CoN_6 . 6C_2H_5N$ per cent.	Found per cent.
Co	9.55	9.64
N_3	13.63	13.81
C	58.28	57.9
H	4.89	4.77

Silver.—Silver trinitride is soluble in ammonium hydroxide, from which solution it crystallizes in large colorless crystals which explode more readily than the precipitated silver trinitride. To ascertain whether the compound contains ammonia of crystallization, a sample of it was prepared and the silver was determined by decomposing the compound in a weighed crucible with hydrochloric acid, fuming down to dryness, and weighing the resulting silver chloride. The results show that silver trinitride crystallizes as such from ammonium hydroxide.

	Theory for AgN_3 per cent.	Found per cent.
Silver,	71.93	71.99

Hydroxyl-ammonium Trinitride.—Dihydroxyl-ammonium chloride, $(NH_2OH)_2.HCl$, hydroxyl-ammonium chloride, $NH_2OH.HCl$, trihydroxyl-ammonium iodide, $(NH_2OH)_3.HI$, dihydroxyl-ammonium iodide, $(NH_2OH)_2.HI$, and hydroxyl-ammonium iodide, $NH_2OH.HI$, have been prepared by different investigators[1]. The normal hydroxyl-ammonium iodide is less stable than the normal chloride, but hydroxylamine forms basic salts more readily with hydriodic acid than it does with hydrochloric acid. Since hydronitric acid closely resembles the halogen acids in chemical behavior, and since it is a very much weaker acid than is hydrochloric acid, it was to be expected that if a hydroxylamine salt of hydronitric acid could be prepared it would probably be basic. The only compound that we have thus far obtained is dihydroxyl-ammonium trinitride,

[1] Lossen, Ann. **160**, 242 ; Dunstan and Goulding, J. Chem. Soc. (London), **69**, 839 ; Wolffenstein and Groll, Ber. **34**, 2417.

$(NH_2OH)_2.HN_3$. This compound resulted upon evaporating a mixture of a solution of hydroxylamine in methyl alcohol and of hydronitric acid in methyl alcohol. The same salt appeared whether the components were present in the proportion of $1:1$ or $2:1$. A solution of free hydroxylamine in methyl alcohol was prepared by the method of Lobry de Bruyn[1], which consists in treating a solution of hydroxyl-ammonium chloride in methyl alcohol with sodium methylate, and filtering off the sodium chloride. It later was found, however, that an appreciable amount of sodium chloride remained in solution in the methyl alcohol. The greater part of this was removed by adding to the methyl alcohol solution of the free hydroxylamine an equal volume of anhydrous ether.

A solution of hydronitric acid in methyl alcohol was prepared by the method described in Part III. of the present article.

To some of the methyl alcohol solution of hydroxylamine, prepared as above described, a little more than one-half of the molecular equivalent of the methyl alcohol solution of hydronitric acid was added and the solution was then evaporated in a vacuum desiccator over calcium chloride. Transparent, colorless crystals appeared, but since these were found to contain small amounts of sodium, they were dissolved in a mixture of one part of methyl alcohol and twenty parts of ether. The solution was filtered and was then rapidly evaporated in a vacuum desiccator. Colorless, transparent, leaf-like crystals were deposited. These were completely soluble in water and gradually volatilized at ordinary temperatures. The salt melts at 66°.

In the analysis of the compound, hydrogen was determined by combustion in the usual manner, the dried salt being weighed as rapidly as possible because of its hygroscopic character.

The volatility of the compound made it impossible to determine nitrogen by placing the substance directly in a combustion tube and then displacing the air with carbon dioxide. To overcome this difficulty the following device was used.
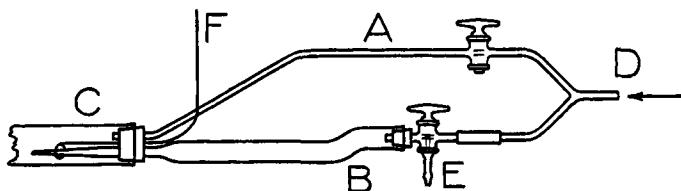

Fig. 1

A combustion tube was filled as usual with copper oxide and contained also a piece of reduced copper gauze about 16 cm. long. Into the end of the combustion tube there was inserted the device shown in Fig. 1. The tube A is provided with a one-way stopcock and is connected on the one

[1] Rec. trav. chim.. 11, 18.

side with a carbon dioxide generator (heated magnesite) and on the other side with the combustion tube C. The tube B is bent into bayonet shape and is drawn out at one end to a thin-walled tube which is sealed. The open end of B is fitted with a rubber stopper, through which passes a glass tube carrying the tail stopper E, and is connected beyond the stopcock by a Y-tube with the carbon dioxide generator. The tube B is weighed with the stopper and stopcock E attached. The salt to be analyzed is then introduced and the glass tube is weighed again. It is then connected as shown in the figure, the tip of the tube passing through a loop of stout steel wire F. The stopper C is then inserted in the combustion tube and the current of carbon dioxide is passed through A. After all air has been removed from the combustion tube, the tail stopper E is turned so that the air as far as that stopper is displaced by carbon dioxide.

The further end of the combustion tube is connected with a Schiff nitrometer that is filled with a solution of potassium hydroxide. The combustion tube is now heated, and when hot the tip of B is broken, the stopcock E is opened and A is closed, and the salt in B is driven over into the combustion tube by heating B with the flame of a Bunsen burner. When the combustion is complete, the volume of the nitrogen in the nitrometer is read. The volume of the tube, B, is then ascertained and 79.1 per cent. of it is subtracted from the volume of the nitrogen in the nitrometer. The remaining volume of nitrogen is then corrected to standard conditions and its weight calculated. The results of the analyses are as follows:

	Theory for $(NH_2OH)_2 . HN_3$ per cent.	Found per cent.	
N	64.24	64.13	63.45
H	6.45	6.77	6.49

II. The Determination of Hydronitric Acid.

Curtius[1] recommends the absolute Dumas method for the determination of nitrogen in those salts of hydronitric acid which are not dangerously explosive, such as the salts of the alkalies and the alkaline earths. He also used the distillation of hydronitric acid from dilute sulphuric acid, followed by the titration of the distillate with a standardized solution of potassium hydroxide, using phenolphthalein as indicator. West[2] varied this method by decomposing the salt with an excess of decinormal sulphuric acid, boiling off the hydronitric acid and titrating the excess of sulphuric acid. In the case of hydrazine trinitride, N_5H_5, the explosive and volatile character of the compound prevented the employment of the com-

[1] J. pr. Chem., **58**, 269.
[2] J. Chem. Soc. (London), **77**, 705.

bustion method in the determination of its hydrogen and nitrogen, and consequently Curtius precipitated silver trinitride from a solution made slightly acid with nitric acid, washed the precipitate and dried it at 100°. The result that he obtained was 0.4 per cent. below the theoretical amount of nitrogen. The error in his determination was probably due to the presence of free nitric acid.

Dennis[1] precipitated hydronitric acid from aqueous solution by silver nitrate, washed the silver trinitride with cold water until the filtrate was free from silver, dissolved the precipitate with nitric acid and determined the silver as silver chloride.

Dennis and Doan[2] dissolved the thallium salts of hydronitric acid in water, precipitated with silver nitrate, washed thoroughly, collected the precipitate in a weighed crucible, fumed down with hydrochloric acid and weighed the silver chloride.

Dennis and Benedict[3], in their analyses of a number of inorganic trinitrides, used the method employed by Dennis[4].

In order to determine the relative merits of some of these methods, analyses were made as tabulated below, the hydronitric acid being determined by precipitation of silver trinitride under varying conditions. The weight of silver chloride was obtained by washing the precipitated silver trinitride with water, decanting the water with as little of the precipitate as possible upon a hardened filter, and continuing this washing until the filtrate was entirely free from silver salts. The silver trinitride was then dissolved in hot nitric acid (1:4) by pouring the acid first upon the filter paper and then into the flask containing the greater part of the silver trinitride. Occasionally, complete solution of the precipitate could not be accomplished by this treatment. In such case, the insoluble portion, which was always dark brown in color, was collected on a hardened filter and the paper was boiled with concentrated nitric acid. The solution was diluted and was then filtered into the flask containing the remainder of the solution of the precipitate. This nitric acid solution was boiled to free it from hydronitric acid, hydrochloric acid was added in excess and the silver chloride was washed, collected on a Gooch crucible, dried at 110°, and weighed. When sodium acetate was first added, the solution containing the silver trinitride frothed a good deal, but otherwise behaved like the other solutions.

In Table I. the strength of the solution of hydronitric acid is taken as 0.0481 gram hydronitric acid in 10 cc. of solution, two exactly agreeing results having been obtained by adding to 10 cc. of the solution an excess

[1] This Journal **18,** 947.

[2] Ibid, **18,** 970.

[3] Ibid, **20,** 225.

[4] Loc. cit.

of potassium hydroxide, exactly neutralizing the solution with nitric acid, using litmus as indicator, then adding one drop of nitric acid (1 : 4) and precipitating as silver trinitride with silver nitrate.

TABLE I.

	HN_3 taken	HN_3 found	Method
I.	0.0481	0.0474	HN_3 solution added directly to an excess of $AgNO_3$.
2.	0.0481	0.0473	AgN_3 washed, filtered, etc.
3.	0.0481	0.0479	HN_3 added to a little less $\frac{N}{20}$ KOH than necessary to neutralize it, then exactly neutralized with the same re-
4.	0.0481	0.0480	agent, with phenolphthalein as indicator. One drop of HNO_3 (1 : 100) added and AgN_3 precipitated.

A different solution of hydronitric acid was employed in Table II. The strength of this solution was ascertained by the method used in determinations Nos. 3 and 4 in Table I, since the results of that method agreed quite closely with those of the procedure employed in ascertaining the strength of the first solution.

TABLE II.

	HN_3 taken	HN_3 found	Method
5.	0.0309	0.03088	0.3 gram $NaC_2H_3O_2$ dissolved in water, 10 cc.
6.	0.0309	0.03094	$\frac{N}{4}$ $AgNO_3$ added, then water added until silver acetate is completely dissolved. HN_3 then added and the precipitated AgN_3 washed, filtered, etc.
	0.0309	0.0310	HN_3 added to somewhat less $\frac{N}{20}$ KOH than would fully neutralize the acid. AgN_3 then precipitated.

To ascertain the accuracy of the determination of nitrogen by the precipitation of silver trinitride from a solution of a soluble salt of hydronitric acid, the following determinations were made:

TABLE III.

	Gram KN_3 taken	Gram AgCl obtained	Gram HN_3 calculated from AgCl	Gram HN_3 calculated from weight KN_3	Method
8.	0.0946	0.1670	0.0502	0.0502	KN_3 dissolved in 50 cc. water, precipitated by $AgNO_3$. AgN_3 converted into
9.	0.1168	0.2062	0.0620	0.0620	AgCl by method before described.

From the above results the following conclusions may be drawn:

1. Silver trinitride is soluble in free nitric acid even when the latter is present in very small amounts (Determinations 1 and 2).

2. Silver trinitride can be precipitated quantitatively from neutral solutions (Determinations 3, 4, 8 and 9), or from a solution containing free acetic acid (Determinations 5 and 6).

3. The presence of phenophthalein in no way interferes with the precipitation of silver trinitride (Determinations 3 and 4).

It was further found during this work that hydrochloric acid and hydro-

nitric acid can be satisfactorily separated by precipitating both with silver nitrate and treating the precipitate with hot nitric acid ($1:4$), the silver trinitride dissolving and the silver chloride remaining unaffected.

III. The Preparation of Alcoholic Hydronitric Acid.

In the preparation of the hydroxylamine salt of hydronitric acid already described, it became necessary to prepare a solution of the acid in some solvent other than water. Lobry de Bruyn has described a method for preparing a solution of hydroxylamine in methyl alcohol, and consequently methyl alcohol was used as a solvent for the hydronitric acid because it seemed undesirable to employ two different solvents in the preparation of the hydroxylamine salt.

Potassium trinitride was made by neutralizing with an aqueous solution of hydronitric acid an aqueous solution of potassium hydroxide purified from alcohol, and evaporating on a water bath until crystallization ensued. Hydronitric acid was then added to the solution until it again showed acid reaction, and the solution was placed under a bell jar together with sticks of sodium hydroxide to keep the atmosphere free from carbon dioxide. The crystals of potassium trinitride that formed were removed from the mother liquor and placed in a desiccator over calcium chloride and sodium hydroxide. Analysis of one sample showed the following composition:

	Found per cent.	Theory per cent.
N	51.83	51.83

In other preparations of this substance the purity of the salt was assumed.

The solution of hydronitric acid in methyl alcohol was prepared as follows: The crystalline trinitride was placed in a 300 cc. distilling flask, and through a two-hole rubber stopper in the neck of the flask were inserted a dropping funnel and a glass tube reaching nearly to the surface of the salt. The delivery tube of the flask was connected with a five-inch U-tube containing calcium chloride, and this was joined to a bent glass tube dipping under the surface of methyl alcohol contained in a small Erlenmeyer flask. The exit tube of this Erlenmeyer flask was provided with another calcium chloride tube. The distilling flask was placed in a water bath which was gradually raised in temperature while sulphuric acid was slowly dropped in through the funnel. During this procedure a current of dry air free from carbon dioxide was introduced through the glass tube and passed through the apparatus. It was found that a solution of sulphuric acid containing 2 parts of sulphuric acid to one part of water by volume, worked more satisfactorily than concentrated sulphuric acid or a $1:1$ solution of sulphuric acid.

When concentrated sulphuric acid was employed the yield was low, probably because of secondary reactions that are described under Part

V. With a 1:1 solution of sulphuric acid the evolution of hydronitric acid was very slow, due to the solubility of the hydronitric acid in this reagent. The 2:1 solution of sulphuric acid acts rather slowly upon the potassium trinitride until the temperature has risen to about 60°, when the evolution of hydronitric acid gas becomes fairly rapid. The sulphuric acid was added until an excess was present, two hours usually being consumed in the slow addition of sufficient sulphuric acid to react with the amounts of potassium trinitride given in the table below. The heating of the contents of the flask and the passing of air through the apparatus were continued for from three to five hours longer to drive over into the methyl alcohol as much hydronitric acid as possible. The variation in the yields of hydronitric acid by this method when 2:1 sulphuric acid was employed shows that even under the above conditions some hydronitric acid is probably held back in the generating flask and some is probably decomposed through its reaction with sulphuric acid. The residue in the flask invariably showed the presence of hydronitric acid and of a volatile alkaline substance. It also contained a reducing agent which set free iodine from a solution of potassium iodate. Moreover, after adding an excess of potassium iodate and driving off the freed iodine by boiling the acid solution, there still can be obtained from the residue a gas of alkaline reaction upon heating the solution with potassium hydroxide. This indicates that the decomposition of hydronitric acid by a strong acid solution forms not only ammonia as Curtius[1] supposed, but also other hydrides of nitrogen that possess a reducing action.

KN_3 used	Theoretical HN_3	CH_3OH used	Theoretical % solution	Actual % solution	% Yield	Remarks
8.978	4.766	100 cc.	4.765	4.26	89.3	H_2SO_4 2:1
12.9	6.8	100 cc.	6.8	5.5	80.8	" "
10.	5.3	75 cc.	7.06	6.31	89.3	" "
9.8	5.2	75 cc.	7.00	6.15	88.0	" "
5.186	2.751	70 cc.	3.93	3.22	81.9	" "
6.726	3.570	60 cc.	5.95	3.48	58.5	Conc. H_2SO_4

IV. The Reduction of Hydronitric Acid and its Salts.

Curtius and Rissom[2] observed that in distilling hydronitric acid from a mixture of lead trinitride and dilute sulphuric acid, the theoretical yield of hydronitric acid was never obtained, but partial decomposition took place and some ammonia was formed. As they obtained no indications of the formation of a reducing agent, they stated that neither hydrazine nor hydroxylamine is formed.

Curtius[3] also found that concentrated sulphuric acid acting upon a dry salt of hydronitric acid caused slow but complete decomposition with an

[1] J. pr. Chem., **58**, 261.
[2] J. pr. Chem., **58**, 263.
[3] Ber., **23**, 3023.

evolution of gas, so that this method could not be used for the preparation of the free acid. He did not study the decomposition products.

Peratoner and Oddo[1] found that on electrolysis of a water solution of hydronitric acid, part of the nascent hydrogen acts as a reducing agent and some ammonia is formed in the electrolyte. Szarvasy[2] found that on electrolyzing hydronitric acid or sodium trinitride, the amount of nitrogen given off was sometimes less than one-third the hydrogen. He would explain this by a polymer of nitrogen, N_3, being present. Peratoner and Oddo[3] have pointed out, however, that the true explanation is probably to be found in the reduction of the hydronitric acid at the cathode.

W. T. Cooke[4] found that hydronitric acid, when acted upon by zinc and hydrochloric acid or sulphuric acid, by sodium polysulphide or by ferrous hydroxide, was partially reduced, both ammonia and hydrazine being formed, although he obtained appreciable amounts of hydrazine only when this was removed from the solution during the reaction. He writes the equation in this way:—

$$HN.N_2 + 3H_2 = NH_3 + N_2H_4,$$
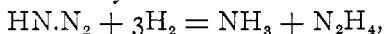
the hydrazine being then further reduced to ammonia.

No quantitative results are reported except in the case of the reaction between hydronitric acid and hydrochloric acid worked out by Curtius, who, from rather insufficient data, deduces the equation,

$$3HN_3 + HCl = 4N_2 + NH_4Cl.$$
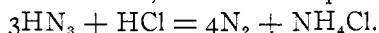
The reduction reactions first studied in this laboratory consisted in attempts to obtain quantitative reduction of hydronitric acid to ammonia by the Kjeldahl method: (a) in acid solution; (b) in alkaline solution. The reaction between hydronitric acid and sulphuric acid, and between hydronitric acid and hydrochloric acid will be discussed under Parts V and VI of this article.

Kjeldahl Method.

(a) *In Acid Solution.*—Asboth[5] recommends for azo and cyan bodies a modification of the Kjeldahl method in which he adds an amount of sugar equal to twice the weight of the substance taken and then proceeds with the sulphuric acid digestion as usual. This method was carried out with potassium trinitride. The dry salt was mixed with sugar, placed in a digestion flask, and 20 cc. of concentrated sulphuric acid and 10 grams of potassium sulphate were then added. Upon adding the sulphuric acid, there was a slight effervescence and faint odor of hydronitric acid, so that

---

[1] Chem. Centb. 1895, (2) 964.
[2] J. Chem. Soc., (London), 77, 603.
[3] Chem. Centb. 1900, (2), 660.
[4] Proc. Chem. Soc., 19, 213.
[5] Chem. Centr., 1886, 161.

it seems likely that one-third of the nitrogen of the hydronitric acid undergoes reduction under these circumstances, the low results being due to loss of hydronitric acid.

Weight KN_3 taken	Weight sugar added	Weight N as NH_3	Per cent. Nitrogen	Theory 1/3 Nitrogen
0.1527	1. g.	0.0255	16.6	17.27
0.0682	1.5 g.	0.0115	16.8	

(*b*) *In Alkaline Solution.*—Thinking that an alkaline reduction would do away with the error due to the loss of hydronitric acid, the method of Bardoch[1] was tried. The potassium trinitride was dissolved in water, aluminum foil was added, and the flask was connected with a condenser and a receiver containing standardized acid. Caustic soda was then admitted through a separatory funnel. This mixture was allowed to react in the cold for twelve hours, and was then diluted and distilled.

	Weight KN_3 taken	Weight Al added	Weight N as NH_3	Per cent. N
	gram	gram		
1.	0.1136	0.5 foil	0.0215	18.9
2.	0.0976	1. powder	0.0017	1.74
3.	0.1108	1. foil	0.0214	19.31

The residue in No. 3 was found to still contain unchanged hydronitric acid.

The results from the acid reduction would seem to indicate that this could be made a quantitative method, if the loss of hydronitric acid could be avoided. It also points toward the structural formula already given for the acid, $H - N\diagdown_N^N$, since one-third of the nitrogen acts differently from the other two-thirds, which is probably evolved as nitrogen gas.

## V. The Reaction between Hydronitric Acid and Sulphuric Acid.

In the attempt to use concentrated sulphuric acid as a drying agent in the preparation of anhydrous hydronitric acid, it was noticed that the sulphuric acid effervesced violently, and in a short time crystals were deposited from it. These crystals proved to be a sulphate of a volatile alkali. A microscopic examination was made by Professor Gill, of Cornell University, who reported that the crystals which separated from the sulphur acid are monoclinic with double refraction, 0.017, but that when this substance is recrystallized from water, the resulting crystals show the orthorhombic form of hydrazine sulphate with double refraction, 0.008.

The crystals that separated from the sulphuric acid were studied in some detail, but we are not yet prepared to make a definite statement concerning their structure. The work will be continued in this laboratory.

[1] Z. anal. Chem., **36**, 776.

VI. The Reaction between Hydronitric Acid and Hydrochloric Acid.

Curtius has already described the reaction between dilute aqueous solutions of hydrochloric acid and hydronitric acid, ammonium chloride being formed and nitrogen given off. He writes the equation,

$$3HN_3 + HCl = NH_4Cl + 4N_2,$$
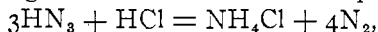
although he obtained only 130 cc. of nitrogen, instead of a theoretical 270 cc. He found no trace of a reducing substance, showing that no hydrazine nor hydroxylamine is formed.

To ascertain whether the concentration of the acid was a governing factor in the nature of the resulting reduction product, dry hydronitric acid, hydrochloric acid gas and air were passed through a glass tube cooled by ice and salt. There appeared a transparent crystalline deposit, closely adhering to the walls of the glass. The crystals were well formed icositetrahedrones, showing no reducing action with potassium iodate. Analyses for ammonia and hydrochloric acid gave

	Theory for NH$_4$Cl per cent.	Found per cent.
NH$_3$	31.85	31.11
HCl	68.15	68.24

showing that the salt is ammonium chloride.

The ratio of nitrogen evolved to nitrogen retained as ammonia was determined by passing hydrochloric acid through a U-tube filled with anhydrous hydronitric acid, then to a nitrometer filled with water. There was a very slight deposit of crystals on that part of the tube with which the hydronitric acid had been in actual contact. This was washed out and distilled into standardized hydrochloric acid and found to contain 0.00087 gram nitrogen as ammonia. 5.3 cc. of nitrogen under standard conditions was evolved, equivalent to 0.00665 gram nitrogen. The ratio of evolved nitrogen to nitrogen retained as ammonia was consequently 0.00665 : 0.00087 or 7.64 : 1. Inasmuch as very small quantities of material were used, the results may be regarded as within the limits of experimental error and the equation of Curtius which calls for a ratio of 8 : 1, may be accepted.

CORNELL UNIVERSITY,
October, 1906.

PENTAVALENT BISMUTH

By E. B. HUTCHINS, JR., AND VICTOR LENHER.

Peculiar interest has been attached to investigations of a higher state of valence than that of three with bismuth. Its many analogies to the other members of the fifth group of the periodic system have caused the pentavalent condition to be sought for repeatedly. Pentavalent arsenic