On the other hand Edgar[1] finds chlorine to be 35.461 referred to oxygen 16.000, whence silver is 107.893. Richards and Forbes[2] have found the per cent. of silver in silver nitrate to be 63.5005. Upon this basis, if the atomic weight of silver is assumed to be 107.850, the atomic weight of nitrogen is 13.991. The results of this research certainly confirm the belief that Stas's values for the atomic weights of silver and nitrogen are much too high.

We are very greatly indebted to the Carnegie Institution of Washington for pecuniary assistance which has done much to aid the progress of this research; also to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

The results of this research may be briefly summed up as follows:

1. The preparation of pure iodic acid is described.
2. The existence of the compound $I_2O_5 . HIO_3$ is confirmed.
3. It is shown that while iodic acid may be almost completely converted to pentoxide by heating at 240°, a small proportion of water remains, which is constant for definite conditions of heating.
4. It is shown that silver iodide occludes silver sulphate and that sulphur dioxide may not be used as a reducing agent if the iodine is to be precipitated by means of silver.
5. Hydrazine salts are found to be suitable reducing agents.
6. The specific gravity of iodine pentoxide at 25° referred to water at 4° is found to be 4.80.
7. It is shown that iodine pentoxide does not adsorb appreciable amounts of air.
8. The ratio of silver to iodine pentoxide is found to be 0.646230.
9. Upon this basis, if oxygen is assumed to be 16.000, the atomic weight of silver is 107.850 and that of iodine is 126.891.

CAMBRIDGE, MASS., November 24, 1908.

ON THE OXIDATION OF HYDRAZINE. III.

BY A. W. BROWNE AND F. F. SHETTERLY.

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The present article contains the description of a series of experiments upon the behavior of hydrazine sulphate in aqueous solution toward the following oxidizing agents: potassium persulphate, potassium permanganate, hydrogen peroxide, potassium perchlorate, sodium periodate, lead dioxide, red lead and manganese dioxide. The experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid and ammonia as products of the reaction between these oxidizing agents and hydrazine sulphate, and for the pur-

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[1] *Chem. News*, 98, 97 (1908).

[2] *Pub. Car. Inst.*, 69, 47 (1907).

pose of determining the yield of these products under certain specified conditions. Inasmuch as hydrazine has been employed by Pannain[1] and by Rimini[2] in the determination of persulphates, while potassium permanganate has been used (1) in acid solution by Petersen,[3] and by Roberto and Roncali,[4] and (2) in alkaline solution by Sabanejeff[5] for the determination of hydrazine, and since Roberto and Roncali[6] have suggested the use of hydrazine sulphate in the analysis of oxidizing agents in general, including peroxides and chlorates,[7] it has also been considered advisable to ascertain whether hydronitric acid is formed under conditions so far as possible corresponding to those recommended by these authors. The procedure followed throughout this work is in general similar to that described in the earlier articles of this series,[8] unless otherwise specified. The identity of the hydronitric acid was in each case established by means of the usual tests,[9] and the yield was determined either by the method of Dennis and Isham,[10] in case a fairly large amount of the acid was formed, or by means of an approximate colorimetric method[11] in case the amount formed was rather small.

Reaction between Hydrazine Sulphate and Potassium Persulphate in the Presence of Sulphuric Acid.—Aqueous solutions of hydrazine sulphate and potassium persulphate, when heated together in the presence of free sulphuric acid, react with formation of considerable quantities of hydronitric acid and ammonia. This fact was discovered during the

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[1] *Gazz. chim. ital.*, 34 (I), 500 (1904).

[2] *Atti accad. Lincei* (5), 15, II, 320–5 (1906); *Chem. Zentralbl.*, **1906**, II, 1662.

[3] *Z. anorg. Chem.*, 5, 1 (1893).

[4] *L. Industria chimica*, 6, 178 (1904); *Chem. Zentralbl.*, **1904**, II, 616.

[5] *Z. anorg. Chem.*, 20, 21–9 (1899).

[6] *Loc. cit.*

[7] With reference to the behavior of hydrazine sulphate toward potassium chlorate, see THIS JOURNAL, 30, 53–63 (1908).

[8] THIS JOURNAL, 29, 1305–12 (1907); 30, 53–63 (1908).

[9] THIS JOURNAL, 27, 551–5 (1905).

[10] THIS JOURNAL, 29, 18 (1907).

[11] The procedure adopted in effecting the approximate colorimetric determination of small quantities of hydronitric acid in pure, aqueous solution, is briefly as follows: to equal amounts of an aqueous solution of ferric chloride, contained in two cylindrical vessels of the same size and shape, are added respectively a measured volume of the solution in which the percentage of hydronitric acid is to be determined, and a measured volume of a standard solution of hydronitric acid. The standard solution is added drop by drop, until the color intensity of the two solutions, after they have been brought to equal volume by dilution of one or the other with water, is exactly the same. The percentage of hydronitric acid in the solution of unknown strength may be calculated from the proportion

$$C_1 : C_2 = V_2 : V_1$$

in which C_1 and C_2 represent the respective percentages of hydronitric acid in the standard solution and in the solution of unknown strength, and in which V_1 and V_2 represent the volumes of the two solutions added.

performance of two preliminary experiments, and has been confirmed by a series of twelve experiments, the results of which are recorded in Table I.

The purity of the potassium persulphate employed throughout these experiments is attested by the results obtained in three determinations of the oxidizing power of the substance. These determinations were effected by a method essentially the same as that described by Treadwell and Hall.[1] The results obtained were as follows: Percentage of available oxygen in potassium persulphate, found, 5.89, 5.89, 5.89; theory, 5.92. With the aid of suitable blank experiments it was demonstrated that none of the materials employed contained any appreciable trace of ammonia, and that no hydronitric acid was produced by the interaction of sulphuric acid and hydrazine sulphate.

TABLE I.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	$K_2S_2O_8$. Grams.	Conc. H_2SO_4. cc.	AgCl obtained. Gram.	Yield HN_3. Per cent.	NH_3 obtained. Gram.	Yield NH_3. Per cent.
1	100	4.183	1	0.0178	3.23	0.0974	(148.9)
2	100	4.183	2.5	0.0447	8.11	0.0689	(105.2)
3	100	4.183	4	0.0639	11.6	0.0549	83.9
4	100	4.183	5	0.1159	21.0	0.0388	59.3
5	100	4.183	5	0.1526	27.7	0.0348	53.1
6	100	4.124	5	0.0904	16.4	0.0591	90.3
7	100	4.124	5	0.1152	20.9	0.0513	78.3
8	100	4.183	10	0.1565	28.4	0.0365	55.7
9	100	4.183	25	0.1990	36.1	0.0338	51.7
10	100	4.183	25	0.2037	37.0	0.0301	46.0
11	100	4.183	50	0.2154	39.1	0.0303	46.4
12	100	4.183	50	0.2223	40.3	0.0296	45.2

In all of the above experiments, with the exception of Experiments 6 and 7, the procedure was essentially as follows: The hydrazine sulphate solution and the solid potassium persulphate were placed together in a 1000 cc. distilling flask connected with a condenser and with the usual absorption apparatus. The concentrated sulphuric acid was then added drop by drop, and the solution was heated until the complete removal of the hydronitric acid had been effected. In order to accomplish this end it was usually found necessary to add 25 cc. of water, after the greater part of the water in the flask had been distilled over, and then to continue the distillation until white fumes just began to appear in the flask. It was found that in Experiments 9, 10, 11 and 12, the hydronitric acid was evolved more promptly than in the experiments in which smaller amounts of the sulphuric acid were employed. In Experiments 11 and 12, the greater part of the acid was evolved before heat was applied. These facts seem to be attributable not merely to the increased evolu-

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[1] *Analytical Chemistry*, Vol. II., 495 (1907).

tion of heat that takes place when the larger amounts of sulphuric acid are used, but also to the tendency toward the more prompt formation of hydronitric acid in concentrated than in dilute solutions of sulphuric acid, already observed by the authors in connection with their work upon the oxidation of hydrazine sulphate by means of potassium chlorate. In Experiments 6 and 7, the procedure was varied, as follows: The concentrated sulphuric acid was first mixed with the hydrazine sulphate solution in the distilling flask. Through a long-stemmed separatory funnel was then added, drop by drop, 235 cc. of an aqueous solution of potassium persulphate, containing 17.55 grams of the salt per liter. This procedure was shown, however, to be unfavorable to the production of the largest yields of hydronitric acid. In all of the experiments, a slow current of air was drawn through the apparatus to facilitate the quantitative removal of the acid, and after the completion of this operation, the amount of ammonia formed during the reaction was determined by the usual method. The percentage yield of the two substances has been calculated on the basis of the equation

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O.$$

In the last column of Table I it will be observed that the amount of ammonia formed in Experiments 1 and 2 was considerably in excess of the amount required on the basis of the above equation. For the sake of comparison, however, all results have been calculated on the same basis, the abnormal results being designated by placing them in parenthesis.

From the results obtained in the above experiments it is apparent that in general the yield of hydronitric acid varies directly, and the yield of ammonia inversely, with the concentration of the sulphuric acid in the solution, and that the yields of these substances approach equality with each other as the concentration of the sulphuric acid is increased.

Reaction between Hydrazine Sulphate and Potassium Persulphate in Alkaline Solution.—By means of a series of fourteen preliminary qualitative experiments, it was first shown that considerable quantities of ammonia, and small but determinable quantities of hydronitric acid are usually formed by the action of potassium persulphate upon hydrazine sulphate in the presence of potassium hydroxide. The following solutions were used in these preliminary experiments: hydrazine sulphate, 20 grams per liter; potassium persulphate, 27 grams per liter; potassium hydroxide, 40 grams per 100 cc. In the majority of the experiments, 50 cc. of the hydrazine solution were treated with 100 cc. of the oxidizing solution in the presence of from 1 to 25 cc. of the solution of potassium hydroxide. When the amount of potassium persulphate was increased to 155 cc., no indication of hydronitric acid was obtained. This was also the case when 10 cc. of hydrazine sulphate were treated with 20 cc. of potassium persulphate in the presence of 8 cc. of the potassium hydroxide solution. By proving in the case of a typical experiment that no potassium persulphate remained in the residual alkaline solution, the possible supposition that the hydronitric acid might have been formed by the action of residual potassium persulphate after the solution had been acidified, was rendered untenable.

The amount of hydronitric acid formed was determined in a series of four experiments. In each case, 25 cc. of the potassium hydroxide solution were added drop by drop to a mixture of 100 cc. of the potassium persulphate and 50 cc. of the hydrazine sulphate solution. The reaction was hastened by shaking, and after the evolution of nitrogen was complete, the ammonia formed was distilled into standard acid. To the solution remaining in the distilling flask was then added an excess of sulphuric acid, and the hydronitric acid was distilled into the usual absorbing solution. The amount of hydronitric acid ranged from 0.60 to 1.05 per cent. Some difficulty was experienced in determining the ammonia formed, because of the volatility of hydrazine in alkaline solution. The average yield of ammonia was in the neighborhood of 20 per cent.

On the Use of Hydrazine Sulphate in the Determination of Persulphates.—Pannain[1] has recently described a method for the determination of persulphates, which is based upon the action of hydrazine sulphate on the persulphates in the presence of potassium hydroxide. The substance to be analyzed, together with the hydrazine sulphate, is placed in the outer compartment of a gas evolution bottle, in the inner compartment of which is placed a solution of potassium hydroxide. The nitrogen evolved after mixing the two solutions, is measured in a Lunge nitrometer. It was taken for granted by Pannain that the hydrazine was completely oxidized, with quantitative evolution of free nitrogen, an assumption seemingly justified by the excellent results obtained by him in a series of twenty-one experiments with ammonium persulphate, and in a second series of eleven experiments with potassium persulphate. The average error amounted to but + 0.09 per cent. in the first, and to + 0.17 per cent. in the second series.

Rimini[2] has recommended the following procedure, which is to be regarded as a modification of the Pannain method: To a neutral solution of the persulphate is added first a solution of hydrazine sulphate, neutralized with potassium hydroxide, and then a measured quantity of a standard potassium hydroxide solution. After the solution has been shaken, and has been permitted to stand for five minutes, the excess of alkali is determined by titration. The reaction was considered by Rimini to proceed in accordance with the equation

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[1] *Gazz. chim. ital.*, 34, I, 500–4 (1904).

[2] *Atti accad. Lincei* [5], 15, II, 320–25; *Chem. Zentralbl.*, 1906, II, 1663.

$$2K_2S_2O_8 + N_2H_4.KHSO_4 + 5KOH = N_2 + 5K_2SO_4 + 5H_2O.$$

With a solution of potassium persulphate containing 1.76 per cent. of the salt Rimini obtained results varying between 1.657 and 1.562 per cent., corresponding to an error from —5.85 to —11.25 per cent. With an ammonium persulphate solution containing 1.13 per cent. of the salt he twice obtained the result 0.92 per cent., corresponding to an error of about —18.6 per cent. These low results were explained by Rimini himself on the ground that the persulphates analyzed were not absolutely pure.

In the authors' experiments on the reaction between hydrazine sulphate and potassium persulphate in alkaline solution, the conditions were chosen with a view to duplicating, so far as practicable, the conditions prevailing in the work of Pannain and of Rimini, respectively. In these experiments, as has been stated above, it was found that small but determinable amounts of hydronitric acid, and considerable quantities of ammonia were usually formed. The formation of either of these substances during the determination of a persulphate by means of hydrazine sulphate will obviously give rise to error both when the nitrometric method and when the acidimetric method are employed. Any discussion of this error would be foreign to the purpose of the present article, and will consequently be reserved for a later communication, in which the entire subject of the determination of hydrazine and of the use of weighed amounts of hydrazine in the determination of oxidizing agents will be considered from the view-point of analytical chemistry. One precaution that should be borne in mind during the selection of a particular method for either of these determinations is to ascertain whether it is possible, under easily reproducible conditions, to effect the quantitative oxidation of the hydrazine to nitrogen and water. If under the conditions most favorable to this purpose, appreciable quantities of hydronitric acid and ammonia be formed, then the method is as a rule to be regarded with suspicion.

Reaction between Hydrazine Sulphate and Potassium Permanganate in the Presence of Sulphuric Acid.—In 1893, Petersen[1] expressed the reaction between hydrazine sulphate and potassium permanganate in the presence of sulphuric acid by means of the equation

$$17N_2H_4.H_2SO_4 + 13O = 13H_2O + 7(NH_4)_2SO_4 + 10N_2 + 10H_2SO_4.$$

This equation was verified experimentally by determinations of the amount of oxygen consumed, and of the amounts of ammonia and nitrogen formed. The reaction was suggested as the basis of a method for the determination of hydrazine in its salts.

In 1902, Herz[2] recommended the use of hydrazine sulphate in the

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[1] *Loc. cit.*

[2] *Ber.*, 35, 949 (1902).

determination of potassium permanganate. His procedure consisted in weighing the oxides of manganese precipitated by addition of a soluble carbonate to the solution obtained by treatment of a weighed amount of the permanganate in aqueous solution, with hydrazine sulphate.

In 1904, Roberto and Roncali[1] stated that when potassium permanganate is gently heated with hydrazine sulphate, the reaction takes place in accordance with the equations

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O + 3H_2O$$

$$5N_2H_4.H_2SO_4 + 5O_2 = 10H_2O + 5H_2SO_4 + 5N_2$$

and that the reaction between hydrazine sulphate and oxidizing agents in general may be expressed by means of the equation

$$N_2H_4.H_2SO_4 + O_2 = H_2SO_4 + 2H_2O + N_2.$$

In 1906, Medri[2] criticized the work of Roberto and Roncali, and further established the equation given by Petersen. He showed, moreover, that the percentage of free sulphuric acid may be varied over a considerable range without influencing the results, but that in the absence of the acid, the oxidation of the hydrazine is more nearly complete.

From the behavior of numerous other oxidizing agents toward hydrazine sulphate under similar conditions, it seems reasonable to suppose that potassium permanganate in acid solution should oxidize hydrazine with the formation of at least small quantities of hydronitric acid. It has already been shown in this laboratory, however, that potassium permanganate is capable of oxidizing hydronitric acid[3] itself to nitrogen and water. Consequently, it was necessary to choose the conditions with a view to permitting the escape of any hydronitric acid that might be formed during the experiment without subjecting the acid to the action of an excess of permanganate.

TABLE II.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	$KMnO_4$ (Grams per liter indicated in parenthesis). cc.		Results.
1	100	25	50	(6)	HN_3 formed
2	100	50	50	(6)	HN_3 formed
3	100	50	100	(3)	HN_3 formed
4	100	100	50	(6)	Very little HN_3 formed
5	100	25	225	(1.5)	HN_3 formed
6	100	50	225	(1.5)	HN_3 formed
7	100	0	450	(1.5)	Very little HN_3 formed
8	50	25	150	(1.2)	HN_3 formed
9	50	50	150	(1.2)	HN. formed
10	100	5	ca. 150	(2.491)	No HN_3
11	100	7	ca. 150	(2.491)	No HN_3
12	100	5	ca. 150	(2.491)	HN_3 formed
13	100	7	ca. 150	(2.491)	HN_3 formed

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[1] *Loc. cit.*

[2] *Gazz. chim. ital.*, 36, I, 373–8; *Chem. Zentralbl.*, 1906, II, 459.

[3] Dennis and Browne. THIS JOURNAL, 26, 577 (1904).

In Table II is recorded a series of qualitative experiments in which the permanganate was added drop by drop after the acidified hydrazine solution had been heated nearly to the boiling point, except in the case of Experiments 10 and 11, in which the solution was held at a temperature of from 60° to 70°, in accordance with the procedure of Petersen. In every experiment except numbers 10 and 11, a distinctly recognizable amount of hydronitric acid, and a large amount of ammonia were obtained.

In two additional experiments, the procedure was reversed by dropping the hydrazine solution into boiling, acidified permanganate. No indication whatever of the formation of hydronitric acid was obtained.

Table III contains the results of several quantitative experiments, in which the amounts of hydronitric acid and ammonia have been determined. In Experiments 1 and 2, the permanganate solution, diluted with an equal volume of water, was gradually added to the boiling, acidified hydrazine solution. The permanganate was diluted in Experiments 3 and 4 with three times, in 5 and 6 with five times, and in 7 to 10 inclusive with one and one-half times its volume of water. In every case the hydronitric acid vapor was drawn over by suction into the usual absorbing solution. In the last two experiments, the hydrazine solution was held at a temperature of from 60° to 70° during the addition of the permanganate.

TABLE III.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated. H_2SO_4. cc.	$KMnO_4$ (6.308 grams per liter). cc.	AgCl obtained. Grams.	Yield HN_3. Per cent.	NH_3 obtained. Gram.	Molecules of NH_3 per two molecules of N_2H_4.
1	100	25	62.5	0.0080	1.45	0.10317	1.576
2	100	50	62.5	0.0070	1. 7	0.10325	1.578
3	100	25	66.4	0.0157	2.85	0.10156	1.552
4	100	50	64.0	0.0113	2.05	0.10516	1.607
5	100	25	65.0	0.0128	2.32	0.10283	1.571
6	100	50	65.0	0.0176	3.19	0.10240	1.564
7	100	5	64.0	0.0064	1.16	0.10410	1.590
8	100	7	64.0	0.0048	0.87	0.10494	1.603
9	100	5	62.0	..	0.1	0.10812	1.652
10	100	7	62.0	..	0.1	0.10724	1.639

It will be observed that, in general, the yields of hydronitric acid vary inversely with the yields of ammonia. On the basis of the equation suggested by Petersen, the yield of ammonia should amount to 0.10780 gram per gram of hydrazine sulphate, or to 1.647 molecules of ammonia from two molecules of hydrazine. As the yield of hydronitric acid decreases, the yield of ammonia closely approaches this value, as may be noted in the case of Experiments 9 and 10.

In order to ascertain the relative amounts of hydronitric acid, ammonia, and free nitrogen formed under conditions substantially similar to those prevailing in the work already described, a series of experiments were performed in which the reaction was caused to proceed in an apparatus so constructed as to permit the simultaneous determination of these products. A measured, slight excess of the permanganate solution, diluted with five times its volume of water, was slowly added through a dropping funnel to the boiling, acidified solution of hydrazine sulphate, contained in a distilling flask which communicated with a condenser and with the usual absorption apparatus for hydronitric acid. With the aid of a generator modeled after that of Bradley and Hale,[1] the air in the apparatus was displaced with carbon dioxide, and a current of this gas was used throughout each experiment to carry the hydronitric acid into the absorption apparatus, and the nitrogen to the nitrometer tube located at the end of the chain. From the nitrometer, which was filled with a solution of potassium hydroxide at the beginning, the gas was transferred at the end of each experiment to a Hempel gas burette, and was then passed successively into Hempel pipettes filled with potassium hydroxide and with alkaline pyrogallol. The residual gas was assumed to be nitrogen. One nearly constant source of error, which could not be entirely eliminated without the use of rather elaborate precautions, arose from the solubility of atmospheric oxygen and nitrogen in the solutions employed. A correction based upon the work of Pettersson and Sonden[2] was consequently introduced in each case.

In Table IV are given the results obtained in these experiments.

TABLE IV.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	$KMnO_4$ (6.308 grams per liter). cc.	Nitrogen in form of HN_3. Gram.	Nitrogen in form of NH_3. Gram.	Nitrogen gas. cc. (corr.)	Nitrogen gas. Gram.	Total nitrogen accounted for. Gram.
1	100	25	62.5	0.00126	0.0892	97.80	0.1223	0.2128
2	100	25	62.0	0.00154	0.0878	97.81	0.1223	0.2116
3	100	10	61.0	0.00079	0.0858	100.96	0.1263	0.2129
4	100	10	61.0	0.00088	..	99.71	0.1247	..
5	100	25	61.0	0.00088	..	100.69	0.1259	..
6	100	50	61.0	0.00127	0.0884	99.47	0.1244	0.2141
7	100	25	61.0	0.00090	0.0866	100.17	0.1253	0.2128
Average (excluding 4 and 5)				0.00115	0.08756		0.12412	0.21284

From the data shown in the last column, it is to be noted that the total amount of nitrogen determined as ammonia, hydronitric acid and free nitrogen, has the average value of 0.21284 gram, or 98.8 per cent. of the theoretical amount, 0.21532 gram. The average result of these experiments may be expressed in round numbers as follows:

$$281\ N_2H_4 \longrightarrow 228\ NH_3 + 162\ N_2 + HN_3.$$

It will be seen that seven of the 562 nitrogen atoms, or about 1.2 per

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[1] THIS JOURNAL, **30**, 1090–6 (1908).

[2] *Ber.*, **22**, 1443 (1889).

cent., have not been accounted for. This error may possibly be explained on the ground that small quantities of other substances are formed during the reaction. It seems more probable, however, that the deficit is to be attributed simply to unavoidable experimental error. For the purpose of the present investigation, the work has demonstrated satisfactorily that the greater part of the hydrazine is converted into nitrogen and ammonia, as stated by Petersen, but that determinable quantities of hydronitric acid are formed under certain conditions.

Reaction between Hydrazine Sulphate and Potassium Permanganate in Alkaline Solution.—Sabanejeff[1] has utilized potassium permanganate in alkaline solution for the determination of hydrazine in a number of its inorganic compounds. From the circumstance that of nineteen analyses reported in his work, all but one of the results are slightly lower than the theoretical value, showing an average percentage error of about —1.1 per cent., it has seemed possible that at least small quantities of hydronitric acid might be formed during the interaction of the substances. In Table V are shown the results of a series of experiments performed with a view to investigating this possibility.

TABLE V.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	KOH (200 grams per liter). cc.	$KMnO_4$ (20 grams per liter). cc.	Results.
1	50	10	5	Small amount HN_3 formed
2	50	10	5	Small amount HN_3 formed
3	50	10	5	1.2 per cent. HN_3 formed
4	50	10	5	1.5 per cent. HN_3 formed
5	50	10	25	Small amount HN_3 formed
6	50	10	25	Small amount HN_3 formed
7	50	10	25	Small amount HN_3 formed
8	50	10	25	Small amount HN_3 formed
9	50	10	50	No HN_3 formed
10	50	10	50	No HN_3 formed
11	50	10	50	No HN_3 formed
12	50	10	50	Small amount HN_3 formed

After the addition of the permanganate to the alkaline hydrazine solution in these experiments, the mixture was heated for about half an hour on the steam bath, before the solution was acidified in order to liberate the hydronitric acid formed. In Experiments 5 and 6, the oxides of manganese were removed by filtration before the solution was acidified. In 9 and 10 the excess of permanganate present undoubtedly oxidized the hydronitric acid when the solution was acidified.[2] In 11 and 12, 25 cc. and 75 cc. respectively of a 2 per cent. solution of oxalic acid were added to the solution before acidification.

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[1] *Z. anorg. Chem.*, 17, 480 (1898); 20, 21 (1899).

[2] Dennis and Browne, *Loc. cit.*

A second series of experiments, in which potassium hydroxide and potassium permanganate solutions of various concentrations were employed, and in which the temperature was varied from 0° to 100°, has led to the conclusion that, in general, traces of hydronitric acid are formed by the interaction of hydrazine sulphate and potassium permanganate in alkaline solution, provided that the permanganate is not present in excess.

Reaction between Hydrazine Sulphate and Hydrogen Peroxide in the Presence of Sulphuric Acid.—It has already been demonstrated in this laboratory[1] that considerable quantities of hydronitric acid may be formed by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid. In a series of ten experiments the yield of the acid as calculated on the basis of the simple equation

$$3N_2H_4 + 5H_2O_2 = 2HN_3 + 10H_2O$$

was found to vary between 11.4 and 28.4 per cent. This method has since been used repeatedly in this laboratory for the preparation, on a comparatively large scale, of pure solutions of hydronitric acid. In the first series of experiments no attention was given to the possible formation of ammonia as one of the reaction products. Subsequent experiments have shown, however, that large percentages of ammonia are formed by the reaction.

Two qualitative experiments were first performed, in which 100 cc. of a one per cent. solution of hydrazine sulphate were treated respectively with 5 and 25 cc. of concentrated sulphuric acid. In each case, 10 cc. of 3 per cent. hydrogen peroxide mixed with 15 cc. of water were added to the slowly boiling solution of hydrazine sulphate. The distillate was divided into 30 cc. fractions, each of which was tested for hydronitric acid. In the first experiment, the greater part of the acid was found in the third fraction; in the second experiment, large quantities of the acid were found in the first three fractions. The residual solutions, when made alkaline with sodium hydroxide, were in each case found to contain large amounts of ammonia.

The results obtained in a series of quantitative experiments are presented in Table VI. The yields of hydronitric acid and ammonia have been calculated on the basis of the equation

$$2N_2H_4 + 2H_2O_2 = HN_3 + NH_3 + 4H_2O.$$

In comparing these results with the yields of the acid obtained in the earlier work done in this laboratory, it should be borne in mind that when the earlier yields are recalculated on the basis of the new equation, they range from 15.2 to 37.8 per cent., instead of from 11.4 to 28.4 per cent.

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[1] THIS JOURNAL, **27**, 551–5 (1905).

TABLE VI.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	H_2O_2 (3%) cc.	Concentrated H_2SO_4. cc.	AgCl obtained. Grams.	Yield HN_3. Per cent.	NH_3 obtained. Gram.	Yield NH_3. Per cent.
1	100	15	5.0	0.0405	7.35	0.0411	62.8
2	100	15	25.0	0.1579	28.6	0.0379	57.9
3	100	25	15.0	0.1564	28.3	0.0446	68.1
4	100	25	50.0	0.2018	36.6	0.0392	59.8
5	100	20	2.5	0.0323	5.86	0.0717	(109.6)
6	100	20	25.0	0.1673	30.9	0.0515	78.7
7	100	20	50.0	0.2123	38.5	0.0353	53.9
8	100	20	50.0	0.1893	34.3	0.0420	64.1

In all of the experiments except No. 7, the measured quantity of hydrogen peroxide was diluted with twice its volume of distilled water, and the resulting solution was added drop by drop through a separatory funnel, the stem of which extended beneath the surface of the liquid in the distilling flask. Small additional quantities of water were usually added during the progress of the distillation to insure the quantitative removal of the hydronitric acid. After this operation had been completed, 5 cc. of 3 per cent. peroxide solution were added and the distillation was resumed. In no case, however, was the formation of hydronitric acid noted as the result of this procedure, a fact which indicated that sufficient hydrogen peroxide had been previously used in the experiment to effect the complete oxidation of the hydrazine present. In Experiments 7 and 8, 50 cc. of water were distilled from the solution of hydrazine sulphate before the addition of the peroxide solution. In Experiment 7, the peroxide solution was added all at once, and without previous dilution. By this procedure, which exactly duplicated the conditions found in the earlier series of experiments to be most favorable for the production of hydronitric acid, the largest yield of the acid was obtained. It may be said, in general, that the yield of ammonia showed a tendency to vary inversely with the yield of hydronitric acid.

Reaction between Hydrazine Sulphate and Hydrogen Peroxide in Alkaline Solution.—Six qualitative experiments were performed, in which 100 cc. of a one per cent. hydrazine sulphate solution were treated, in the presence of from 2.5 to 25 cc. of concentrated sodium hydroxide solution, with from 30 to 45 cc. of one per cent. hydrogen peroxide. The alkaline hydrazine solution was, in general, heated to boiling, and the peroxide was added drop by drop. The distillate obtained from the alkaline solution was tested for ammonia, and the distillate from the residual solution, after acidification with sulphuric acid was tested for hydronitric acid. In one experiment, in which the peroxide was added to the hydrazine at room temperature, and the mixture permitted to stand over night before distillation, no indication of the formation of hydronitric acid was obtained, although ammonia was found in considerable amount.

In the other five experiments, hydronitric acid was formed in small, and ammonia in moderately large quantities. Similar results were obtained when precautions were taken to insure the complete decomposition of the hydrogen peroxide before the solution was acidified.

Reaction between Hydrazine Sulphate and Potassium Perchlorate.—The behavior of these substances in acid solution is illustrated by the experiments recorded in Tables VII and VIII.

TABLE VII.

No. of experiment.	$N_2H_4 H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	$KClO_4$. Grams.	Results.
1	100	5.0	0.7	Trace HN NH formed
2	100	10.0	0.7	Trace HN ; NH_3 formed
3	100	25.0	7.0	HN_3 and NH_3 formed
4	100	50.0	7.0	HN_3 and NH_3 formed
5	50	12.5	4.0	HN_3 formed
6	50	50.0	6.0	HN_3 formed
7	50	5.0	7.0	HN_3 and NH_3 formed
8	50	10.0	9.0	HN_3 and NH_3 formed

The procedure adopted in these qualitative experiments was briefly as follows: the solid potassium perchlorate was added to the acidified hydrazine sulphate solution, and the successive 30 cc. fractions of the distillate obtained on heating the mixture to boiling were tested for hydronitric acid. In Experiments 3 and 4, the perchlorate was added from time to time in 1 gram portions. Whenever it was found necessary, small quantities of water were added to the reacting mixture during the course of the distillation. The point at which the appearance of the hydronitric acid in the distillate took place was found to depend chiefly upon the concentration of the sulphuric acid.[1] No tests for ammonia were made in Experiments 5 and 6.

TABLE VIII.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	$KClO_4$. Grams.	AgCl obtained. Gram.	Yield HN_3. Per cent.	NH_3 obtained. Gram.	Yield NH_3. Per cent.
1	100	5	14	0.1237	22.4	0.0257	39.2
2	100	10	14	0.1140	20.7	0.0288	44.0
3	100	15	14	0.0494	8.96	0.0267	40.8
4	100	20	14	0.0510	9.25	0.0276	42.2

In the foregoing experiments, the distillation was effected rather slowly, and small quantities of water were added from time to time to the mixture. In Experiments 3 and 4, some difficulty was experienced owing to the liberation of chlorine. As was expected, the yields of hydronitric acid were found to decrease when the percentage of sulphuric acid was raised so high that the liberation of chlorine in considerable

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[1] Compare THIS JOURNAL, 30, 57 (1908).

quantity could not well be avoided. After the ammonia had been distilled over, both the residual solution and the distillate were in each case tested for hydrazine, with negative results. It was thus demonstrated that no hydrazine had escaped the action of the oxidizing agent.

It will be observed that the yields of hydronitric acid and ammonia are of about the same magnitude as the yields obtained by the action of potassium chlorate upon hydrazine sulphate.[1]

Reaction between Hydrazine Sulphate and Sodium Periodate.—In view of the similarity that has been shown to exist between the action of potassium perchlorate and that of potassium chlorate upon hydrazine sulphate, the following experiments have been performed in order to ascertain whether a like relationship could be shown to exist between the behavior of a periodate and that of a typical iodate toward hydrazine sulphate.

Experiment 1.—50 cc. of a 1 per cent. solution of hydrazine sulphate were added drop by drop to an excess of sodium periodate dissolved in 50 cc. of water and 5 cc. of concentrated sulphuric acid. Iodine was instantly liberated. No indication of the formation of hydronitric acid was obtained.

Experiment 2.—The conditions prevailing in the preceding experiment were duplicated, but the liberation of iodine was prevented by the addition of solid silver sulphate. Traces of hydronitric acid and ammonia were formed.

Experiment 3.—The acidified periodate solution was added drop by drop to 50 cc. of the hydrazine solution, which had previously been treated with 10 cc. of concentrated sulphuric acid, and heated to boiling. Iodine was liberated, and no indication of the formation of hydronitric acid was obtained.

Experiment 4.—The preceding experiment was duplicated, except for the addition of about one gram of solid silver sulphate to the acidified hydrazine solution prior to the introduction of the periodate solution. No iodine was liberated. Considerable quantities of hydronitric acid and ammonia were formed.

From these experiments it appears that the behavior of sodium periodate toward hydrazine sulphate in acid solution is similar to that of potassium iodate under corresponding conditions, at least so far as the tendency to form hydronitric acid is concerned.[2]

Reaction between Hydrazine Sulphate and Lead Dioxide.—In Experiments 2 to 5 inclusive, Table IX, the solid lead dioxide was added to the hydrazine sulphate solution prior to the addition of the sulphuric acid. The solution was then in each case heated to boiling. In Experiments

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[1] THIS JOURNAL, 30, 57 (1908).

[2] *Ibid.*, 30, 59 (1908).

6 and 7, the dioxide was suspended in 50 cc. of water, the sulphuric acid was added, and finally the hydrazine solution was introduced drop by drop into the mixture which had been heated to a temperature of 90°. The amounts of hydronitric acid formed in this preliminary series of experiments were found to vary in general with the amounts of sulphuric acid added.

TABLE IX.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	PbO_2 Grams.	Results.
1	100	0	4	Small amount HN_3 formed
2	100	5	4	Considerable HN_3 formed
3	100	10	4	HN_3 and NH_3 formed
4	100	20	4	HN_3 and NH_3 formed
5	100	50	4	HN_3 and NH_3 formed
6	100	50	4	HN_3 and NH_3 formed
7	100	10	4	HN_3 and NH_3 formed

By means of suitable blank experiments, it was demonstrated that the lead dioxide employed in this work contained no ammonia. No tests for ammonia were made in connection with Experiments 1 and 2.

In Experiments 2 to 8, inclusive, Table X, the lead dioxide was first added to the hydrazine solution, and then the sulphuric acid was introduced. In Experiments 9 to 12 inclusive an excess of the dioxide suspended in from 80 to 100 cc. of water was added drop by drop to the acidified hydrazine sulphate solution during the process of distillation. The residual solution was filtered in each case before the ammonia was determined.

TABLE X.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	PbO_2 Grams.	AgCl obtained. Gram.	Yield HN_3 Per cent.	NH_3 obtained. Gram.	Yield NH_3 Per cent.
1	100	0	4.5	..	..	0.00151	2.3
2	100	10	4.5	0.0090	1.63	0.00667	10.2
3	100	20	6.0	0.0040	0.73	0.00538	8.22
4	100	30	6.0	0.0054	0.98	0.00538	8.22
5	100	40	6.0	0.0064	1.16	0.00495	7.56
6	100	50	6.0	0.0099	1.79	0.00495	7.56
7	100	50	6.0	0.0080	1.45	...	...
8	100	50	4.5	0.0086	1.56	...	...
9	100	5	Excess	0.0159	2.88	0.00861	13.2
10	100	10	Excess	0.0167	3.03	0.00710	10.8
11	100	25	Excess	0.0146	2.65	...	...
12	100	50	Excess	0.0226	4.10	0.00628	9.59

Reaction between Hydrazine Sulphate and Red Lead.—Five qualitative experiments were performed, in each of which an excess of red lead suspended in water was gradually introduced into 100 cc. of a boiling, one per cent. solution of hydrazine sulphate, to which a measured amount of concentrated sulphuric acid had previously been added. The amounts of sulphuric acid employed were respectively as follows: 10, 10, 25, 25 and 50 cc. Hydronitric acid was found in each case in the first three or four 30 cc. fractions of the distillate. Ammonia was found in each experiment except No. 5, in which no test was made for it.

Tanatar[1] has shown that both lead dioxide and red lead, as well as chromic acid, hydrogen peroxide, bromine water, and permanganic acid, will oxidize a molecular mixture of hydrazine sulphate and hydroxylammonium chloride, with formation of hydronitric acid.

Reaction between Hydrazine Sulphate and Manganese Dioxide.—In seven preliminary experiments, the two substances were brought together in various ways in the presence of sulphuric acid, with the result that large quantities of ammonia and appreciable amounts of hydronitric acid were usually formed. The yields were determined in a second series of experiments recorded in Table XI.

TABLE XI.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Concentrated H_2SO_4. cc.	MnO_2. Grams.	AgCl obtained. Gram.	Yield HN_3. Per cent.	NH_3 obtained. Gram.	Molecules of NH_3 per two molecules N_2H_4.
1	100	1.0	1.6	0.0076	1.38	0.0433	0.66
2	100	2.5	1.6	0.0081	1.47	0.0521	0.80
3	100	5.0	1.6	0.0128	2.32	0.0588	0.90
4	100	10.0	1.6	0.0068	1.23	0.0551	0.84
5	100	2.5	1.6	0.0072	1.30	0.0545	0.85
6	100	10.0	1.6	0.0060	1.09	0.0717	1.10
7	100	5.0	Excess	0.0096	1.74	0.0899	1.37
8	100	5.0	Excess	..	..	0.0356	0.54
9	100	25.0	Excess	0.0042	0.76	0.1004	1.53
10	100	25.0	Excess	..	..	0.0532	0.81
11	100	2.5	Excess	0.0084	1.52	0.0816	1.25
12	100	2.0	Excess	0.0060	1.09	0.0487	0.74

In Experiments 1 to 4 inclusive, the solid manganese dioxide was suspended in the hydrazine solution, the sulphuric acid was added, and the mixture was gradually heated. Water was added from time to time during the progress of the distillation. In Experiments 5 and 6, the dioxide was suspended in 75 cc. of water, and was treated with the measured amount of sulphuric acid. The mixture was heated to about 90°, and the hydrazine solution was introduced drop by drop. In the remaining experiments, an excess of dioxide, suspended in from 50 to 100 cc. of water, was slowly introduced into the acidified hydrazine sulphate solution. In Experiments 8, 10 and 12, freshly precipitated manganese dioxide was employed. By means of blank experiments, it was demonstrated that neither variety of the dioxide used contained ammonia. Hydronitric acid was formed in Experiments 8 and 10 in sufficient quantity to give the characteristic tests.

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[1] *Ber.*, **35**, 1810 (1902).

Purgotti[1] has recommended the general use of hydrazine sulphate for the gasometric determination of oxidizing agents, relying upon the assumption that the oxidation of hydrazine takes place with quantitative evolution of nitrogen. The action of manganese dioxide upon hydrazine sulphate in acid solution is expressed by this investigator with the aid of the equation:

$$2MnO_2 + N_2H_4.H_2SO_4 + 2H_2SO_4 = 2MnSO_4 + 4H_2O + N_2 + H_2SO_4,$$

and the action in neutral solution by the equation:

$$2MnO_2 + 2N_2H_4.H_2SO_4 + H_2O = 2MnSO_4 + 4H_2O + N_2 + N_2H_4.H_2O.$$

Summary.

The maximum yields of hydronitric acid and ammonia obtained under specified conditions by the action of certain oxidizing agents upon hydrazine sulphate in aqueous solution, and calculated (when given as percentages) from the equation

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O,$$

are as follows:

(1) With potassium persulphate in acid solution, 40.3 per cent. HN_3, 1.5 molecules NH_3 from 2 molecules of N_2H_4; in alkaline solution, small amounts of HN_3, and about 20 per cent. of NH_3.

(2) With potassium permanganate in acid solution, 3.19 per cent. HN_3, 1.65 molecules NH_3 from 2 molecules N_2H_4; in alkaline solution, small amounts of HN_3.

(3) With hydrogen peroxide in acid solution, 38.5 per cent. HN_3, 1.10 molecules NH_3 from 2 molecules of N_2H_4; in alkaline solution, small amounts of HN_3, fairly large amounts of NH_3.

(4) With potassium perchlorate in acid solution, 22.4 per cent. HN_3, 44.0 per cent. NH_3.

(5) With sodium periodate in acid solution, considerable quantities of hydronitric acid and ammonia, when silver sulphate was present.

(6) With lead dioxide in acid solution, 4.1 per cent. HN_3, 13.2 per cent. NH_3.

(7) With red lead, HN_3 and NH_3 in acid solution.

(8) With manganese dioxide in acid solution, 2.32 per cent. HN_3, 1.53 molecules NH_3 from 2 molecules N_2H_4.

CORNELL UNIVERSITY, November, 1908.

THE WEIGHT OF CARBON DIOXIDE WITH A TABLE OF CALCULATED RESULTS.

BY S. W. PARR.

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In making use of analytical methods involving the evolution and measurement of constituents in the gaseous form, two difficulties are met

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[1] *Gazz. chim. ital.*, **26**, II, 559–73 (1896).