In spite of the addition of ammonium iodide to the salt before fusion, the fused salt was slightly basic in all but one experiment. Since the density of strontium oxide is 4.6,[1] the basicity could not have affected the results.

Barium Iodide.—Barium nitrate was five times crystallized and converted into carbonate by precipitation with ammonium carbonate. From the carbonate the iodide was formed as in the case of calcium and strontium. Here also ammonium iodide failed to prevent basicity completely, but as in the cases of strontium and calcium, the error is too small to consider, since the density of barium oxide is about 5.3.[1]

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Percent. of BaO.	Density of BaI_2, $25°/4°$.
4.8746	0.8110	0.10	5.179
3.9124	0.6551	0.18	5.146
5.0750	0.8525	0.21	5.129
4.3577	0.7292	0.07	5.149
3.9504	0.6615	0.14	5.146
4.3432	0.7270	0.12	5.147
5.0332	0.8414	0.07	5.154

Average, 5.150[2]

It is to be noted that the values obtained by earlier experimenters are in most cases lower than ours, owing probably to the dangers mentioned at the beginning of this paper.

As a result of this investigation the densities of the following salts at $25°$ referred to water at $4°$ were found to be:

Sodium iodide............................ 3.665
Potassium iodide......................... 3.115
Rubidium iodide.......................... 3.438
Caesium iodide........................... 4.510
Calcium iodide........................... 3.956
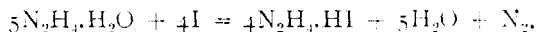Strontium iodide......................... 4.549
Barium iodide............................ 5.150

CAMBRIDGE, MASS.,
November 5, 1907.

ON THE OXIDATION OF HYDRAZINE. II.

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

Curtius and Schulz[3] have shown that alcoholic solutions of hydrazine hydrate and iodine react quantitatively in accordance with the equation

$$5N_2H_4.H_2O + 4I = 4N_2H_4.HI + 5H_2O + N_2.$$

[1] Landolt-Börnstein-Meyerhoffer.
[2] Filhol obtained the value 4.917. Ann. chim. phys. [3], **21**, 415 (1847).
[3] J. pr. Chem. [2], **42**, 521–49 (1890).

and that this reaction may be used as the basis of a method for determining the strength of solutions of hydrazine hydrate.

Rimini[1] found that the reaction between hydrazine sulphate and potassium iodate could be expressed by the equation

$$5N_2H_4.H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 4I.$$
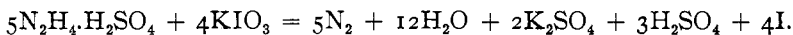
For the determination of hydrazine he recommended the following procedure: A weighed sample of the material to be examined is treated with a measured excess of potassium iodate. After the solution has been heated (in order to expel the liberated iodine) and then cooled, it is acidified with dilute sulphuric acid, and the excess of potassium iodate is determined in the usual way with a standard solution of sodium thiosulphate. Rimini stated that bromates react with hydrazine, when heated, but that chlorates do not react at all.

Riegler[2] devised a method for the determination of formaldehyde, which consists in the measurement of the volume of nitrogen liberated from a known amount of hydrazine sulphate (in presence of the formaldehyde) by the action of a solution of iodic acid. From the difference between the volume of nitrogen formed under these conditions, and the volume liberated from the same amount of hydrazine sulphate (in absence of formaldehyde), may be calculated the amount of formaldehyde present. In a subsequent article[3] Riegler suggested the use of a gasometric method of alkalimetry, based upon the reaction between hydrazine sulphate and sodium iodate. Still later[4] he recommended for the determination of iodides. a method consisting in the measurement of the nitrogen liberated by the addition of an excess of hydrazine sulphate to the iodate solution obtained by oxidizing the iodide in alkaline solution with potassium permanganate.

Stollé[5] described an iodometric method for the determination of hydrazine. The titration is carried out in the presence of primary potassium or sodium carbonate. Rupp[6] maintained that the presence of sodium potassium tartrate or sodium acetate leads to more satisfactory results, but that the necessary delay of 15 minutes in awaiting the end of the reaction detracts from the practical value of the iodometric method.

Schlötter[7] found that the reduction of the alkali bromates with hydrazine sulphate proceeds quantitatively, and made use of this fact in his gas

[1] Gazz. chim. ital., 29, I, 265-69 (1899); Atti. accad. Lincei Roma [5], 15, II, 320; Chem. Zentr., 1906, II, 1662.

[2] Z. anal. Chem., 40, 92-4 (1901).

[3] Ibid., 41, 413-19 (1902).

[4] Ibid., 46, 315-18 (1907).

[5] J pr. Chem. [2], 66, 332-38 (1902).

[6] Ibid. [2], 67, 140-42 (1903).

[7] Z. anorg. Chem., 37, 164-71 (1903).

volumetric method for the determination of bromates.[1]   He also ascertained that iodic acid may be reduced quantitatively to hydriodic acid, by the action of hydrazine sulphate, but that potassium chlorate undergoes quantitative reduction only after prolonged boiling.[2]

Roberto and Roncali[3] expressed the reaction between chlorine water and hydrazine sulphate by means of the equation

$$N_2H_4.H_2SO_4 + 2Cl_2 = N_2 + 4HCl + H_2SO_4.$$
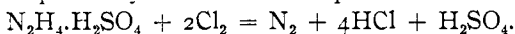
They recommended the use of hydrazine sulphate in the analysis of chloride of lime and of Javelle solution.   In a later article[4] they have described the action of oxidizing agents upon hydrazine sulphate with the aid of the following general equation:

$$N_2H_4.H_2SO_4 + 2O = H_2SO_4 + 2H_2O + N_2.$$
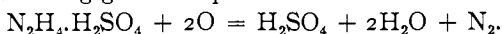
After expressing the reaction between potassium permanganate and hydrazine sulphate in acid solution by means of an erroneous equation,[5] they predicted the probable usefulness of hydrazine sulphate in the analysis of oxidizing agents in general, including peroxides and chlorates.

Jannasch and Jahn[6] found that in alkaline solutions potassium iodate and potassium bromate are easily reduced by hydrazine sulphate, but that potassium chlorate is decomposed only to a limited extent.   When potassium chlorate is treated with hydrazine sulphate in the presence of hydrogen peroxide and nitric acid, considerable quantities of hydronitric acid are formed.   This result was tacitly attributed by Jannasch and Jahn to the action of nitric acid[7] upon the hydrazine sulphate, in accordance with the observations of Sabanejeff and Dengin.[8]

The present article contains the description of a series of experiments illustrating the respective action of potassium chlorate, potassium bromate, potassium iodate, chlorine, bromine, and iodine upon hydrazine sulphate in acid solution.   These experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid as one product of the above reactions, and of determining the yield of the acid under certain specified conditions.

[1] Z. anorg. Chem., **37,** 172–76 (1903).

[2] *Ibid.*, **38,** 184–90 (1904).

[3] L'Industria chimica, 6, 93–5 (1904); Chem. Zentr., **1904,** I, 1294.

[4] L'Industria chimica, 6, 178–79 (1904); Chem. Zentr., **1904,** II, 616.

[5] Compare Petersen, Z. anorg. Chem., **5,** 1–7 (1893); also Medri, Gazz. chim. ital., **36,** I, 373 (1906); Chem. Zentr., **1906,** II, 459.

[6] Ber., **38,** 1576–89 (1905).

[7] In the light of certain experiments performed in this laboratory (Browne, This Journal, **27,** 551–55 (1905); see also the results shown in Table I of the present article) it is apparent that the formation of hydronitric acid under the conditions prevailing in the experiments of Jannasch and Jahn might also be attributed to the action of either one or both of the other oxidizing agents present: hydrogen peroxide and potassium chlorate.

[8] Z. anorg. Chem , **20,** 21–29 (1899).

Preparation of Solutions.— The solution of hydrazine sulphate contained 10.000 grams of the salt per liter. The solutions of potassium chlorate, bromate, and iodate contained 9.4226, 12.8418 and 16.4575 grams of the respective salts per liter. All four solutions were therefore almost exactly equimolecular.

General Procedure Followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a one liter round bottom flask provided with a four-hole rubber stopper through which passed (1) the stem of a separatory funnel, (2) a thermometer, (3) a glass tube serving as the air inlet, and reaching to the bottom of the flask, and (4) a glass elbow tube communicating with the condenser. After the desired amount of concentrated sulphuric acid had been added, the solution was heated to about 80°, and a measured amount of the oxidizing agent was added drop by drop through the separatory funnel. Throughout the entire experiment a current of air was in general drawn through the apparatus, in order to carry the hydronitric acid from the flask through the condenser into the absorption apparatus (which contained 5 cc. of a 10 per cent. solution of silver nitrate, 2 cc. of a 10 per cent. solution of sodium acetate and 35 cc. of distilled water), for a description of which reference may be made to the first article of the present series.[1] After the entire quantity of the oxidizing agent had been added, the solution was boiled until all of the hydronitric acid had been distilled from the flask. In the quantitative experiments the amount of hydronitric acid formed was determined as usual by the method of Dennis and Isham.[2] In certain experiments the yields of ammonia were determined by making the residual solution (after the hydronitric acid had been completely expelled) alkaline with sodium hydroxide and distilling with usual precautions into standard hydrochloric acid. The yields of both hydronitric acid and ammonia have been calculated on the basis of the equation[3]

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O.$$
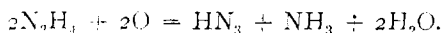
Results Obtained in the Experiments.—The results are tabulated under five different heads: (1) action of potassium chlorate upon hydrazine sulphate; (2) action of potassium bromate upon hydrazine sulphate; (3) action of potassium iodate upon hydrazine sulphate; (4) action of chlorine, bromine and iodine, respectively, upon hydrazine sulphate;

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[1] Browne and Shetterly, This Journal, **29,** 1305–12 (1907).

[2] *Ibid.*, **29,** 18 (1907).

[3] This equation recalls the work of E. Fischer (Ber., **10,** 1336 (1877)), who obtained diazobenzenimide and aniline (analogous to hydronitric acid and ammonia) by the action of iodine upon phenylhydrazine. This analogy in the behavior of the organic and the inorganic derivatives of hydrazine, as well as the interesting question of the possible formation of certain new inorganic compounds of hydrogen and nitrogen as intermediate products of the oxidation of hydrazine, is now under investigation in this laboratory, and will be discussed in detail in a future communication.

(5) action of potassium chlorate, bromate and iodate, respectively, upon hydrazine sulphate in presence of silver sulphate.

(1) *Action of Potassium Chlorate upon Hydrazine Sulphate.*—When heated together in presence of free sulphuric acid, aqueous solutions of these substances react with the formation of considerable quantities of hydronitric acid and ammonia. The acid was identified by the series of qualitative tests described in an earlier article.[1] The details of a number of experiments are given in Table I.

TABLE I.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	$KClO_3$ solution. cc.	Concentrated H_2SO_4 cc.	AgCl obtained. Gram.	Yield HN_3. Per cent.	Portion of distillate containing bulk of HN_3.
1	100	28.6	10.0	0.0738	13.39	..
2	100	28.6	10.0	0.0840	15.24	..
3	100	33.3	10.0	0.0814	14.77	..
4	100	33.3	10.0	0.0874	15.86	..
5	100	50.0	0.5	0.0204	3.70	6
6	100	50.0	5.0	0.1207	21.90	5
7	100	50.0	10.0	0.0822	14.91	4 and 5
8	100	50.0	25.0	0.0942	17.09	1 and 2
9	100	50.0	50.0	....	....	1
10	100	55.6	0.5	0.0299	5.42	6
11	100	55.6	5.0	0.0426	7.73	5
12	100	55.6	10.0	0.0947	17.18	4 and 5
13	100	55.6	25.0	0.0513	9.30	1 and 2
14	100	55.6	50.0	....	....	1
15	100	66.7	10.0	0.1091	19.79	..
16	100	66.7	10.0	0.1237	22.44	..

From these experiments it is apparent that the yield of hydronitric acid does not vary in any regular way with the concentration of the oxidizing agent or of the sulphuric acid. In fact, the magnitude of the yield seems to depend fully as much upon the method adopted in bringing the two substances together, in heating the mixture, and in distilling off the hydronitric acid, as upon any other factor. The liberation of chlorine during the experiment militates against the production of a large yield of the acid. That the presence of a considerable amount of sulphuric acid is necessary seems to be shown by the low yields obtained in Experiments 5 and 10. A separate series of experiments (each performed in duplicate), the results of which are given in column 7 of Table I, has shown, moreover, that the formation of hydronitric acid takes place most readily within a certain range of concentration of sulphuric acid. In each of these experiments the distillate was divided into six 25 cc. fractions. To each fraction was added 1 cc. of a 9 per cent. ferric chloride solution. From the depth of color shown by the various fractions the relative amounts of hydronitric acid present were then roughly estimated.

[1] Browne, This Journal, **27**, 551-55 (1905).

In every case the bulk of the acid was found in one or at most two of the fractions; moreover, as the concentration of sulphuric acid was increased, the formation of the hydronitric acid took place earlier in the experiment. Thus in Experiments 5 and 10, in which but 0.5 cc. of sulphuric acid was present, the hydronitric acid came over in the sixth fraction, while in Experiments 9 and 14, in which 50 cc. of sulphuric acid were present, the hydronitric acid appeared in the first fraction. These facts cannot be explained on the ground that hydronitric acid might be expected to distil over more rapidly from solutions strongly acidified than from solutions but slightly acidified with sulphuric acid. Curtius and Rissom[1] have shown that when an aqueous solution of hydronitric acid is distilled, almost the entire amount of the acid passes over with the first fourth of the liquid. It is consequently legitimate to infer from the presence of the greater part of the hydronitric acid in the sixth fraction obtained in Experiments 5 and 10, for example, that the formation of the acid does not readily take place until toward the close of the experiment. when the concentration of the sulphuric acid has become sufficiently high.

For the purpose of determining the yield of ammonia formed under conditions substantially similar to those under which the largest yield of hydronitric acid had been obtained, four additional experiments were performed. Care was of course taken to use sufficient potassium chlorate to insure the complete oxidation of the hydrazine, since any hydrazine remaining unoxidized would have been at least in part distilled over with the ammonia when the residual solution was heated after having been made alkaline. In each of the experiments, 100 cc. of the hydrazine sulphate solution and 10 cc. of concentrated sulphuric acid were employed. In the first two, 66.7 cc. of the potassium chlorate solution were used in each case; in the last two, 77.8 cc. The yield of ammonia in the four experiments amounted respectively to 48.76, 40.99, 31.64 and 30.06 per cent.

(2) *Action of Potassium Bromate upon Hydrazine Sulphate.*—Aqueous solutions of these substances react when heated together in presence of free sulphuric acid, forming appreciable quantities of hydronitric acid and ammonia. The results obtained in a series of experiments (parallel in the main with the experiments in which potassium chlorate was used) are shown in Table II.

The best yields of hydronitric acid were obtained when 5 cc. of sulphuric acid were taken. The decrease in yield observed as the concentration of sulphuric acid was increased beyond this limit is at least partially attributable to the greater difficulty of preventing, in strongly acid solution, the liberation of free bromine during the course of the reaction.

[1] J. pr. Chem. [2], **58**, 261–309 (1898).

TABLE II.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	$KBrO_3$ solution. cc.	Concentrated H_2SO_4. cc.	AgCl obtained. Gram.	Yield HN_3 Per cent.
1	100	28.6	5.0	0.0298	5.41
2	100	28.6	10.0	......	....
3	100	33.3	5.0	0.0368	6.68
4	100	33.3	10.0	0.0217	3.94
5	100	50.0	0.0	0.0058	1.05
6	100	50.0	0.5	0.0104	1.88
7	100	50.0	5.0	0.0341	6.18
8	100	50.0	10.0	0.0252	4.57
9	100	55.6	0.5	0.0179	3.25
10	100	55.6	5.0	0.0346	6.28
11	100	55.6	10.0	0.0095	1.72
12	100	55.6	25.0	0.0017	0.31

The yield of ammonia was determined in four additional experiments, in each of which 100 cc. of hydrazine sulphate solution were taken. The other details were respectively as follows: potassium bromate solution, 66.7, 66.7, 77.8, 77.8 cc.; concentrated sulphuric acid, 5, 10, 5, 10 cc.; yield of ammonia, 9.77, 3.91, 1.21, 1.21 per cent.

(3) *Action of Potassium Iodate upon Hydrazine Sulphate.*—Preliminary experiments seemed to indicate that no hydronitric acid was formed by the interaction of these substances. In the four experiments subsequently performed, distilled water was consequently substituted for the usual absorbing solution (containing silver nitrate and sodium acetate), in order to facilitate the detection of minute amounts of hydronitric acid. In each of the experiments 100 cc. of hydrazine sulphate solution were employed. The amounts of the other substances were respectively as follows: potassium iodate solution, 28.5, 33.3, 50, 50 cc.; concentrated sulphuric acid, 5, 5, 5, 10 cc. Some difficulty was experienced in keeping the iodine that was liberated during the reaction from passing over into the distillate, especially in the fourth experiment, in which 10 cc. of sulphuric acid were employed. In certain cases it was found necessary to shake a portion of the distillate (to be tested for hydronitric acid) with metallic mercury before adding the ferric chloride solution, in order to remove the small quantities of free iodine that were unavoidably distilled over. In no case was the slightest indication of the presence of hydronitric acid observed.

In the fifth experiment 200 cc. of the hydrazine sulphate solution, to which had been added 20 cc. of sulphuric acid, were treated with 133.3 cc. of the potassium iodate solution. The solution was heated until the evolution of gas had ceased, and was then made alkaline with sodium hydroxide. No indication of the presence of ammonia was observed when a moistened piece of red litmus paper was suspended above the liquid in the flask. The subsequent addition of 2 mg. of solid ammonium

chloride (corresponding to 0.5 per cent. yield of ammonia) to the same solution caused the litmus paper to turn distinctly blue.

(4) *Action of Chlorine, Bromine, and Iodine, Respectively, upon Hydrazine Sulphate.*—In the foregoing experiments it was observed (as might have been expected) that the tendency for the free halogen to appear during the course of the reaction varied directly with the atomic weight of the halogen. In the experiments with potassium chlorate, for example, it was comparatively easy to keep the free chlorine from passing over into the absorption apparatus, while in the experiments with potassium iodate it was found necessary to employ some caution in the addition of the oxidizing agent, and in the regulation of the temperature at which the reaction was permitted to take place, in order to prevent the carrying over of considerable quantities of free iodine. In almost every case it was found possible, however, by the exercise of proper precautions, to effect the reduction of the free halogen by the hydrazine sulphate still remaining in the solution. From these facts it is obvious that the hydrazine sulphate is in each case virtually subject to the action of two different oxidizing agents during the course of the experiment, either one or both of which might be responsible for the production of the hydronitric acid.

In order to investigate qualitatively the behavior of the free halogens toward hydrazine sulphate, with reference to the formation of hydronitric acid, a series of experiments was performed in which hydrazine sulphate was treated in both acid and alkaline solution with chlorine, bromine and iodine solutions, respectively. The chlorine solution was prepared (immediately before the experiments were performed) by saturating distilled water at room temperature with chlorine gas. The bromine solution contained about 6.9 grams of bromine per liter. The iodine solution contained about 11.0 grams of iodine, and 22 grams of potassium iodide per liter. The details of the experiments are given in Table III.

TABLE III.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	Oxidizing solution. cc.	Conc. H_2SO_4. cc.	NaOH. Grams.	Result of tests for HN_3.
1	50	100 (chlorine)	5	.	Small amount of HN_3
2	50	100 "	5	.	" " " "
3	50	100 "	.	5	" " " "
4	50	100 "	.	5	" " " "
5	50	100 (bromine)	5	.	No HN_3
6	50	100 "	5	.	" "
7	50	100 "	.	5	Trace of HN_3
8	50	100 "	.	6	" "
9	50	100 (iodine)	5	.	No HN_3
10	50	100 "	5	.	" "
11	50	100 "	.	5	" "
12	50	100 "	.	5	" "

For the experiments in which sulphuric acid was used the general procedure was briefly as follows: the oxidizing solution was first added slowly to the acidified hydrazine sulphate solution, with frequent shaking in order to hasten the reaction. When the reduction of the halogen was complete (in the experiments with iodine it was found necessary to heat the solution at intervals), the solution was distilled, and the first fractions were carefully tested for hydronitric acid. For the experiments in which sodium hydroxide was used, the general procedure was as follows: The oxidizing solution was first brought into contact with the sodium hydroxide (in the form of a 20 per cent. solution). The hydrazine sulphate was then added, and the solution was shaken until the evolution of gas had nearly ceased. After having been heated for a short time, the solution was slightly acidified with sulphuric acid and was distilled. Careful tests for hydronitric acid were made, as before, upon the first fractions of the distillate. In no case were indications given of the formation of any very considerable quantity of hydronitric acid. When chlorine was used it was found that a small amount of hydronitric acid was formed in both acid and alkaline solution. With bromine, traces of the acid were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. From these results the conclusion may be drawn that the tendency of the free halogens to form hydronitric acid as one of the oxidation products of hydrazine sulphate is but slight in any case, and that this tendency varies inversely with the atomic weight of the halogen.

It seems reasonable also to infer that the liberation of the halogens in the chlorate, bromate and iodate experiments must be unfavorable to the production of large yields of hydronitric acid, even though precautions are taken to keep the free halogen in any case from passing over into the absorption apparatus. Since the liberation of a given amount of iodine would presumably militate more strongly against the production of hydronitric acid than would the liberation of a corresponding amount of bromine or of chlorine, and since the liberation of iodine takes place more extensively than that of the other halogens, it is by no means surprising that hydronitric acid was not formed in the experiments with potassium iodate. It has moreover been shown by experiment that even potassium chlorate, under conditions otherwise very favorable to the formation of hydronitric acid, does not produce appreciable yields of the acid in presence of potassium iodide. Two experiments were performed in which the procedure adopted in Experiments 6 and 16, Table I, was carefully duplicated. In these cases, however, 0.64 gram and 0.85 gram of potassium iodide were dissolved in the acidified hydrazine sulphate solution before the (gradual) addition of the potassium chlorate solution. In both cases the tests for hydronitric acid gave negative results.

(5) *Action of Potassium Chlorate, Bromate and Iodate, Respectively, upon Hydrazine Sulphate in Presence of Silver Sulphate.*—A natural supposition to be made on the basis of the facts discussed in the preceding paragraphs is that if the liberation of halogen in the chlorate, bromate, and iodate experiments could be entirely prevented, the yield of hydronitric acid might be appreciably increased. In the experiments recorded in Table IV this condition has been realized by the addition in each case, of 1 gram of silver sulphate, in solid form, to the acidified solution of hydrazine sulphate, prior to the introduction of the oxidizing solution. The procedure was in all other particulars the same as in the earlier experiments with these oxidizing agents.

TABLE IV

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	Oxidizing solution. cc.	Concentrated H_2SO_4. cc.	AgCl obtained. Gram.	Yield HN_3. Per cent.	Yield NH_3. Per cent.
1	100	($KClO_3$) 78.0	10	0.0734	13.32	15.64
2	100	" 78.0	10	0.0707	12.83	16.96
3	100	($KBrO_3$) 66.7	10	0.0374	6.79	25.25
4	100	' 66.7	10	0.0642	11.65	27.42
5	100	(KIO_3) 66.7	10	0.0520	9.43	12.68
6	100	" 66.7	10	0.0615	11.16	16.16

These experiments show clearly that while in the case of the chlorate solution the presence of silver sulphate does not increase the yield of hydronitric acid, with the bromate solution a slight increase, and with the iodate solution a very marked increase is to be noted. In other words, the influence of the silver sulphate in augmenting the tendency of the chlorate, bromate, and iodate solutions to form hydronitric acid from hydrazine sulphate in acid solution, varies directly with the atomic weight of the halogen.

Summary.

When potassium chlorate or bromate is brought into contact with hydrazine sulphate in the presence of sulphuric acid, the hydrazine is not completely oxidized to nitrogen and water. A secondary reaction takes place which may be expressed by the equation

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

With potassium chlorate the highest yields obtained were 22.44 per cent. HN_3, 48.76 per cent. NH_3; with potassium bromate, 6.68 per cent. HN_3, 9.77 per cent. NH_3. With potassium iodate under similar conditions no formation of HN_3 or of NH_3 was observed. The amount of hydronitric acid formed, consequently, decreases with increase of the atomic weight of the halogen.

By the action of the free halogens upon hydrazine sulphate but little hydronitric acid was obtained in any case. When chlorine was used, a small amount of the acid was formed in both acid and alkaline solution.

With bromine, traces were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. The slight tendency of the free halogens to produce hydronitric acid from hydrazine sulphate, consequently decreases with increase of the atomic weight of the halogen.

The maximum yields of hydronitric acid and ammonia obtained in a series of experiments with potassium chlorate, bromate, and iodate, in the presence of sulphuric acid and silver sulphate, were as follows: with potassium chlorate, 13.32 per cent. HN_3, 16.96 per cent. NH_3; with potassium bromate, 11.65 per cent. HN_3, 27.42 per cent. NH_3; with potassium iodate, 11.16 per cent. HN_3, 16.16 per cent. NH_3. The influence of the silver sulphate in augmenting the yield of hydronitric acid consequently varies directly with the atomic weight of the halogen.

The behavior of a number of other oxidizing agents toward hydrazine sulphate is now under investigation in this laboratory.

CORNELL UNIVERSITY.
October, 1907.

ON THE REACTION BETWEEN LIME AND SULPHUR.

BY R. W. THATCHER.

The compounds which may be formed by the union of calcium and sulphur, either with or without oxygen, are quite numerous and varied in their properties. They have been extensively studied in connection with the theoretical principles involved in the replacement of oxygen by its analogous element sulphur. Recently, the subject has been given a very important economic bearing by the very extensive use of solutions prepared by boiling together in water, lime, sulphur, and sometimes other ingredients, and applied as insecticides for scab on animals and for soft-bodied scale insects on fruit trees. Some idea of the extent to which this wash is being used on the Pacific Coast States may be obtained from the fact that a single firm has recently installed in California a plant which is producing at each single boiling fourteen carloads of a concentrated lime-sulphur solution of twelve times the strength in which it is used in orchard practice, while at least two other firms are manufacturing similar concentrated solutions on a large scale, and a very much larger amount of the wash is produced by home-boiling in orchards and sheep camps.

The formulae which have been used for the preparation of the insecticide wash have differed widely. The various modifications of the original formula have been based on a great variety of conceptions as to the nature of the compounds formed in the wash and their insecticidal properties, none of which, however, were based on any accurate knowl-