

The amount of monohydrogen phosphate in the liquid phase was determined by means of a similar break obtained on adding increasing amounts of dilute nitric acid. In this case both the principle involved and its application to physico-chemical volumetry are given here for the first time.

6. The results of the conductivity titrations further verify the equation given in paragraph 2 above.

7. Furthermore, the deviation of the observed values of monohydrogen phosphate from the theoretical shows that the precipitated tricalcium phosphate undergoes partial hydrolysis, in such a way as to appear in the liquid phase as monohydrogen phosphate.

8. The extent of this hydrolysis is roughly proportional to the concentration of the dihydrogen phosphate present, and is slightly diminished by excess of calcium nitrate.

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## THE BEHAVIOR OF CERTAIN HYDRAZINE SALTS ON DECOMPOSITION BY HEAT.<sup>1</sup>

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In 1899 Sebanejeff<sup>2</sup> described a method for the preparation of hydronitric acid depending upon the action of nitric acid on hydrazine sulfate. It was observed that when hydrazine mononitrate was treated with concentrated sulfuric acid at ordinary temperature, nitric oxide was evolved, a reaction which did not occur at  $-15^{\circ}$ . On heating with dilute sulfuric acid, hydronitric acid was produced and was given off.

The hydrazine dinitrate, which proved to be much less stable than the corresponding monocompound, was decomposed under three sets of conditions and its decomposition products were studied—(1) at  $80^{\circ}$  to  $85^{\circ}$ ; (2) on a water bath, with a limiting temperature of  $100^{\circ}$ ; (3) at ordinary temperatures over sulfuric acid.

On warming this compound to  $80$  to  $85^{\circ}$ , this author found that the nitrate decomposed and yielded the volatile products, hydronitric acid, nitric acid, nitrogen and water, and the nonvolatile products, the neutral mononitrate and ammonium nitrate. Upon heating on the water bath, at  $100^{\circ}$ , the decomposition of the dinitrate occurred very much as it did at the temperature of  $80$ – $85^{\circ}$ , except that the decomposition was more complete, yielding a residue containing only ammonium nitrate.

When the hydrazine dinitrate was allowed to stand at ordinary temperature in a desiccator over sulfuric acid, there occurred a continuous evolu-

<sup>1</sup> A chapter from the thesis submitted by the author to the Faculty of Cornell University, May 1908, for the degree of Doctor of Philosophy.

<sup>2</sup> *Z. anorg. Chem.*, 20, 21 (1899).

tion of hydronitric acid accompanied by a disintegration of the crystals. The residual powder on analysis proved to be ammonium nitrate and hydrazine mononitrate.

Within the last few years<sup>1</sup> it has been shown in this laboratory that hydronitric acid may be obtained by the action of a number of different oxidizing agents in acid solution on hydrazine sulfate. With a view to determining whether hydrazine salts of acids, the action of whose other salts upon hydrazine sulfate have been previously studied, would yield hydronitric acid as one of their decomposition products, the investigation to be described in the present chapter was undertaken. The results obtained are classified under the following headings:

Decomposition of: (1) hydrazine monochlorate; (2) hydrazine dichlorate; (3) hydrazine monoperochlorate; (4) hydrazine diperochlorate; (5) hydrazine monosulfate; (6) hydrazine disulfate.

#### Decomposition in Solution.

The apparatus used for the decomposition of solutions consisted of a 200 cc. **distilling flask** and an ordinary condenser, the lower end of which was connected by means of a long-stemmed adapter with a receiver containing a few cubic centimeters of distilled water for the absorption of the hydronitric acid.

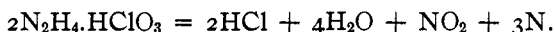
The procedure followed consisted in the careful distillation of a measured volume of the solution under consideration and in the cautious heating of the residue (in case any was obtained) until no further action was observed to take place. The distillate was divided into several fractions, each of which was treated with three drops of a 5% solution of ferric chloride. From the intensity of the color produced some idea was obtained of the relative amounts of the acid present.

**Decomposition of a Solution of Hydrazine Monochlorate.**—Salvadori,<sup>2</sup> anticipating us in our work on the chlorates and perchlorates, while the work was still in progress in this laboratory published in complete form a description of the methods of preparation and properties of the monochlorate and the monoperochlorate of hydrazine. His interest in, and study of these compounds, however, was in connection with their explosibility. He found that the chlorate crystallizes in unstable, hygroscopic, laminated crystals and, when placed in hydrochloric acid, evolves chlorine. In concentrated sulfuric acid it explodes; if the sulfuric acid has been warmed to 80° explosion occurs with a loud report and a terrific local effect. A study of the decomposition products formed when the decomposition occurs explosively led the author to the conclusion that

<sup>1</sup> Browne, *THIS JOURNAL*, 27, 551 (1905); *Ber.*, 38, 1825 (1905); Browne and Shetterly, *THIS JOURNAL*, 29, 1305 (1907); 30, 53 (1908); 31, 221, 783 (1909); *Ber.*, 40, 3953 (1907).

<sup>2</sup> *Gazz. chim. ital.*, 37, 32 (1907).

the intramolecular oxidation took place as indicated by the equation



In these experiments the explosions were induced by percussion.

**Preparation of Hydrazine Monochlorate.**—To prepare 5 g. of hydrazine monochlorate, 6.8 g. of barium chlorate were added to 5.6 g. of hydrazine sulfate; to this were then added 6.4 g. of barium hydroxide,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , the precipitated barium sulfate was removed by filtration and the solution was allowed to concentrate by spontaneous evaporation in the open air, at room temperature. All attempts made to crystallize the salt in mass, even at low temperatures over sulfuric acid, resulted in the spontaneous decomposition of the compound with the evolution of chlorine. When evaporated in small bulk on the stage of a microscope, laminated crystals made their appearance, only to decompose at one with the evolution of gas. A slight residue was left which, on examination, proved to be hydrazine chloride.

**Experiments 1-4.**—A solution of hydrazine monochlorate, prepared as described above, 1 cc. of which contained 0.035 g. of the salt, was treated in accordance with the procedure outlined. The 5 cc. portions, together with 30 cc. of water, were introduced into the distilling flask and the resulting solution was distilled.

On examining the distillate, no indication of the presence of hydronitric acid in any fraction was obtained.

**Experiments 5 and 6.**—Conditions identical with those of the preceding experiments were chosen except that in each of these cases 0.5 cc. of concentrated sulfuric acid was added. The distillate was caught in each experiment in 5 cc. fractions, in each of which the presence of hydronitric acid was clearly demonstrated. The amounts of acid increased as the distillation progressed until the last fraction was reached, in which no indication of the presence of the acid could be obtained.

**Decomposition of a Solution of Hydrazine Dichlorate.**—A solution of hydrazine dichlorate was prepared by treating 3.2 g. of hydrazine sulfate with 7.9 g. of barium chlorate. The solution was filtered and was concentrated by evaporation at room temperature until 1 cc., as shown by analysis, contained 0.05 g. of hydrazine dichlorate. Treatment of small portions of the solution with sulfuric acid and with barium chloride, respectively, gave no indications of the presence of appreciable quantities of barium or of sulfuric acid.

In concentrated solution this compound likewise proved so unstable that it rapidly decomposed. Crystals could be obtained when small amounts of the solution were evaporated to dryness under the microscope, but their disintegration was so rapid that they could not be subjected to an examination. Here, also, a slight, solid residue, consisting of a chloride of hydrazine, remained from the destruction of the compound. The main products of the decomposition of hydrazine dichlorate, as is also true of the monochlorate, are gaseous.

**Experiment 7.**—A 5 cc. portion of the above solution, with 30 cc. of  $H_2O$ , was distilled and collected in 5 cc. fractions. Appreciable quantities of hydronitric acid were formed, the most distinct indications of its presence being obtained in the sixth fraction.

**Experiment 8.**—The conditions prevailing in Expt. 7 were closely duplicated except that 0.5 cc. of concentrated sulfuric acid was added to the solution. Hydronitric acid was found to be present in the successive fractions of the distillate in increasing amount up to the fifth fraction. The last fraction, containing other products of the reaction, gave no indications of the presence of the acid.

**Decomposition of a Solution of Hydrazine Monoperchlorate.**—This substance was prepared by Salvadori<sup>1</sup> and by the author independently. Salvadori ascribed to it the formula  $N_2H_2ClO_4 \cdot \frac{1}{2}H_2O$ , a formula upheld by his analytical results. The salt readily can be crystallized from water on the water bath, which fact bespeaks for its remarkable stability. It is nonhygroscopic, soluble in water and alcohol and insoluble in ether, carbon disulfide, benzene and chloroform. It melts at  $131-132^\circ$ . Like the chlorate, hydrazine monoperchlorate on heating and on being subjected to percussion is violently explosive.

A solution of this compound was obtained by treating 3.3 g. of hydrazine sulfate with 4.3 g. of hydrated barium hydroxide and 4.3 g. of barium chlorate, in solution. After the barium sulfate had been removed by filtration, the solution of hydrazine monoperchlorate was evaporated until the compound crystallized out. As a check upon the purity of the compound so obtained, the percentage of nitrogen was determined by the method of Rimini.<sup>2</sup>

Per cent. nitrogen: calculated for  $N_2H_4ClO_4 \cdot H_2O$ : 11.17%; found (av. of two): 10.51%.

Determinations of so-called water of crystallization by desiccation methods shown in Table I, made before the appearance of Salvadori's work, had led us to the belief that the monoperchlorate crystallized with one molecule of water of crystallization.

TABLE I.

No.	$N_2H_4 \cdot HClO_4 \cdot H_2O$ Weight taken.	Loss.	Theory.	
			$\frac{1}{2} H_2O$ .	1 $H_2O$ .
1.....	0.2737	0.0175	0.0128	0.0196
2.....	0.5194	0.0335	0.0193	0.0372

In Experiment 1 the sample was dehydrated to constant weight over sulfuric acid; in Experiment 2 the sample was heated at  $100^\circ$  on a water bath until its weight became constant. These results show that the water is quite readily removed from the monoperchlorate, both by desiccating agents and by heat. No attempt is here being made to refute the statements of Salvadori.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Gazz. chim. ital.*, 29, 1, 265 (1899); *Atti. accad. Lincei*, [5] 15, II, 320; *Zentr.*, 11, 1662 (1906).

**Experiments 9 and 10.**—A volume of 25 cc. of a solution of hydrazine monoperchlorate containing 0.004 g. per cc. was distilled until the solution came to dryness. Collected in 5 cc. fractions. No test for hydronitric acid was obtained in any fraction. On coming to dryness, the residue exploded. From the products of the decomposition remaining in the flask, after being dissolved in water, were obtained, by means of the usual tests, indications of the presence of hydrochloric acid and hydrazine. The last fraction of the distillate gave an acid reaction and emitted the odor of chlorine.

**Experiments 11 and 12.**—In these experiments the conditions which obtained in Experiments 9 and 10 were observed as closely as possible, with the single exception that 0.5 cc. of concentrated sulfuric acid was added to the solution before the distillation. No test for hydronitric acid was obtained in any fraction. The last portions of the distillate gave an acid reaction with litmus. Some sulfur dioxide was produced. The residue in the flask consisted of hydrazine sulfate and gave no tests for chlorine ions.

**Decomposition of a Solution of Hydrazine Diperchlorate.**—To prepare 10 g. of hydrazine diperchlorate, 13.5 g. of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  were neutralized with perchloric acid which had been freed from hydrochloric acid by precipitation with a solution of silver perchlorate, prepared by dissolving silver carbonate in perchloric acid. To the solution of barium perchlorate thus formed was added the theoretical amount, 5.56 g., of hydrazine sulfate. After removing by filtration the precipitated barium sulfate, the clear solution was evaporated to dryness over steam coils and with the aid of a blast of dry air.

**Experiments 13-16.**—Distillation of the unacidified (Expts. 13 and 14) and the acidified (Expts. 15 and 16) solutions, respectively, gave no detectable amount of hydronitric acid. The residue from the former showed the presence of hydrazine and of chloride; that from the latter, hydrazine sulfate.

### Decomposition of Solids.

The apparatus used for the decomposition of the solid substances consisted essentially of three parts, which, in the order in which they were connected, were (1) a carbon dioxide generator, especially constructed with a view to furnishing very pure, air-free gas, (2) an ignition tube, containing a thermometer, in which the substance under examination was heated, and (3) an absorption apparatus, designed for the subsequent detection of hydronitric acid.

The absorption apparatus, connected with the farther end of the ignition tube, consisted of two large test tubes, each of which contained a few cubic centimeters of distilled water. These were so connected by means of glass tubes and stopcocks that the current of gas could be passed either through the two tubes in series, or through the farther tube only. By this device it was possible to prevent the contamination of the solution to be tested for hydronitric acid by other products formed at certain stages of the decomposition. After the current of gas had passed through the two tubes it entered the third, to the inside wall of which were fastened several strips of filter paper impregnated with manganous sulfate.

By moistening one of these slips with a few drops of potassium hydroxide solution, introduced through a small separatory funnel, it was possible to detect the presence of oxygen in the tube at any time. To facilitate the successive application of this test without dismantling the apparatus, the stem of the separatory funnel was bent at right angles. By slightly turning the funnel, the end of the stem could be brought into contact with successive strips of the paper.

The gas finally passed through a short tube into a eudiometer filled with a solution of potassium hydroxide.

**Procedure Followed.**—When the air in the entire apparatus had been displaced by carbon dioxide, as indicated by the failure to obtain a brown coloration on the manganous sulfate paper, heat was applied slowly to a weighed sample of the hydrazine salt contained in a porcelain boat, which previously had been introduced into the ignition tube. A slow stream of carbon dioxide was passed through the apparatus throughout the decomposition of the salt and until all decomposition products had been swept into the absorption apparatus. When it became evident in any case that products of decomposition capable of interfering with the detection of hydronitric acid were being formed in any considerable quantity, the current of gas which previously had passed through both absorption tubes was directed so as to pass through the second only. By this means the hydronitric acid, which seemed ordinarily to be formed in the early stages of the decomposition, was not contaminated by the products of the final stages.

The acid was identified by the usual method. The unabsorbable, gaseous products of decomposition were collected in the eudiometer and, whenever it seemed desirable, were subjected to further examination.

**Decomposition of Hydrazine Monoperchlorate. Experiment 17 (and duplicate, 18).**—A sample of hydrazine monoperchlorate of 0.10 g. was treated as outlined under "procedure." The salt first melted, then began to boil slowly, giving off gas and water vapor. At this stage of the decomposition, as shown by the reddening of the ferric chloride in the first of the absorption tubes, hydronitric acid was produced.

When the visible evolution of gas from the substance undergoing decomposition had ceased, as marked by the cessation of the formation of bubbles, the course of the stream of gas through the apparatus was diverted into the second absorption tube. On further heating then, the substance in the boat exploded, emitting light, and filling the apparatus with fumes ( $H_2O$  and  $HCl$ ?) which soon condensed. It was subsequent to this violent stage of the decomposition that a nonabsorbable gas appeared in the eudiometer. A slight, white residue was left.

The solution from the second absorption tube, on examination, showed the presence of chlorine ions with silver nitrate in the presence of nitric acid; of hydrogen ions, with blue litmus; of chlorine, with potassium iodide and carbon disulfide and, perhaps, of nitrates. Water was a further product of the decomposition. The gas accumulated in the eudiometer at the end of the run proved to be 14.0 cc. of nitrogen, and 7.6 cc. of oxygen. The presence of oxygen was indicated also by the manganous sulfate paper.

**Decomposition of Hydrazine Diperchlorate. Experiment 19 (and duplicate, 20).—**Following the procedure already described for preceding experiments, a portion of hydrazine diperchlorate of 0.057 g. was decomposed and its decomposition products studied. These proved to be hydronitric acid in considerable quantities; oxygen, chlorine, and chlorine and hydrogen ions, as determined by the usual tests. The unabsorbed gases proved to be 9.0 cc. of nitrogen, and 8.0 cc. of oxygen.

This substance in decomposing behaved very much as did the monopерchlorate in that the decomposition at first was gradual and was accompanied by a slow bubbling. After this had ceased an explosion occurred which filled the tube with a yellow-green gas of chlorine or of chlorine peroxide, or both. The odor indicated chlorine peroxide. It was subsequent to the explosion, also in this case, as in the preceding instance, that the nitrogen and oxygen made their appearance in the gas collector, a fact which would indicate that they were liberated at the time of the explosion. A white residue, presumably of ammonium chloride, remained.

**Action of Potassium Perchlorate upon Hydrazine Sulfate. A Correction.**—In connection with their study of the oxidation of hydrazine,<sup>1</sup> Browne and Shetterly found that potassium perchlorate (Baker and Adamson, "C. P."), when used in comparatively large quantities, oxidized hydrazine in sulfuric acid solution, with formation of both hydronitric acid and ammonia. The former product, under most favorable conditions, was obtained in exactly the same amount, 22.4%, with potassium perchlorate, as with potassium chlorate<sup>2</sup> as oxidizing agent. The possible significance of this fact was overlooked until the attention of one of the authors was directed to the matter by Dr. H. H. Willard, who has done extensive work with the perchlorates.<sup>3</sup> Dr. Willard very kindly furnished a liberal sample of the very pure potassium perchlorate prepared during the course of his investigations.

In a series of additional experiments performed by Dr. Shetterly under conditions similar to those prevailing in the earlier work, except that the very pure potassium perchlorate, which was found to be entirely free from chlorates, was used, no indication whatever of the oxidation of the hydrazine was obtained. The tests for both hydronitric acid and ammonia gave negative results. Examination of two samples of the Baker and Adamson perchlorate used in the earlier work showed that this product contained a considerable quantity of potassium chlorate ( $KClO_3$  found, (1) 4.22, (2) 4.23%). It may, therefore, be concluded that chlorate-free potassium perchlorate is without action upon hydrazine sulfate under the conditions of the experiments, and that the oxidizing action noted in the earlier experiments was due to the presence of potassium chlorate in the perchlorate used.

This conclusion is of particular interest when considered in connection with the results obtained in the decomposition of the perchlorates of

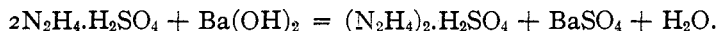
<sup>1</sup> THIS JOURNAL, 31, 221-37 (1909), page 233.

<sup>2</sup> *Ibid.*, 30, 53-63 (1908), page 57.

<sup>3</sup> Richards and Willard, *Ibid.*, 32, 4 (1910); Willard, *Ibid.*, 34, 1480 (1912).

hydrazine. The formation of hydronitric acid in this decomposition in the dry way suggests the query: Is this formation not due to the action of the chloric acid radical on the hydrazine instead of the perchloric radical? It may be regarded as possible that the decomposition of the perchlorate takes place in such a way that its initial stage is marked by the liberation of oxygen, yielding chlorate, a decomposition characteristic of the more stable perchlorates, and that the chlorate in turn reacts intramolecularly to form hydronitric acid. The presence of free oxygen in the gaseous products of the decomposition may be interpreted to indicate such a liberation. The freedom from chlorate of the hydrazine perchlorates dealt with is suggested by the absence of hydronitric acid from the products obtained from these when decomposed in the wet way, a suggestion borne out by their analysis.

**Decomposition of Hydrazine Monosulfate.**—Hydrazine monosulfate was prepared by treating 2.28 g. of hydrazine disulfate in solution with a solution of barium hydroxide containing 2.76 g. of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  transposition taking place analytically according to the equation



After filtering, the clear solution was evaporated over steam coils. A clear syrup, or gum, resulted which, on being touched with spatula or rod, rapidly became an opaque mass of white crystals, the crystals growing out in fronds from the point of the surface to which the rod had been touched. The analysis of the dry substance gave the following:

N calc. for  $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ : 34.52; found (av. of 4): 33.45%. S calc.: 19.76; found (av. of 2): 19.76%.

**Experiment 21.**—A portion, 0.2 g. in weight, when heated gradually, melted at 70–80° and at 120° began to decompose, as evidenced by the appearance of a white sublimate on the cooler portions of the combustion tube. It was not until a temperature of 160° was reached, however, that the decomposition became so rapid as to produce frothing. The sublimate then became yellow, revealing its identity as sulfur. When the temperature had been raised to 180° the visible activity had ceased. There was a free evolution of water and hydrogen sulfide. No test for hydronitric acid, on account of the presence of hydrogen sulfide, could be obtained. A white residue remained which, qualitatively, proved to be hydrazine sulfate.

**Experiment 22.**—Experiment 21 was duplicated with modifications designed to test successive portions of the gaseous products of the decomposition, still yielding negative results with respect to hydronitric acid.

It was noticed that as the condensed moisture on the inside of the tube was driven out by re-evaporation, a white crystalline substance remained. On examination, this substance was shown to be ammonium carbonate.

**Decomposition of Hydrazine Disulfate. Experiments 23 and 24.**—Hydrazine disulfate in 1 g. portions, finely pulverized, was subjected to decomposition under the conditions shown above. Once the temperature of incipient decomposition had been reached, the intramolecular oxidation became self-propagating. There ensued a lively evolution of gas accompanied by a bubbling of the melted mass. Sulfur was evolved and formed an abundant white sublimate, deepening to a yellow color where the sub-



limate was thickest, over the interior of the apparatus. Water was formed. And among the gaseous products of the decomposition were found volumes of hydrogen sulfide and sulfur dioxide.

No hydronitric acid was found in any experiment with the disulfate.

Sulfurous acid gives a reaction with both silver nitrate and ferric chloride which superficially resembles and effectively masks that of the hydronitric acid with these reagents—namely, a white precipitate with silver nitrate, which gives a red coloration when treated with ferric chloride, and a red coloration direct with ferric chloride, due to the formation of ferric sulfite. Practically the only differences which easily are shown between the reactions of sulfur dioxide and hydronitric acid with these two favorite reagents for the detection of hydronitric acid are that silver trinitride is readily and violently explosive, while silver sulfite is not and that the color obtained from ferric chloride and hydronitric acid, due to ferric trinitride, slowly fades, while that due to ferric sulfite fades more rapidly. The change of color in solution of ferric sulfite is brought about by the reduction of the ferric iron to the ferrous by the sulfite and the oxidation of the sulfite to the sulfate by the ferric iron. Ferrous sulfate results.

It is necessary, therefore, if one is to test for hydronitric acid in the presence of sulfur dioxide, first to eliminate the sulfur dioxide. The method as applied in the following paragraphs is recommended.

#### **A Test for Hydronitric Acid in the Presence of Sulfites.**

To 10 cc. of a standard solution of hydronitric acid were added 100 cc. of a 5% solution of sodium hydroxide, 10 cc., 10% sodium sulfite solution and 15 cc. of a 3% solution of hydrogen peroxide. This solution was boiled until effervescence had ceased upon which it gave negative tests for both hydrogen peroxide and sulfites with the potassium iodide and potassium iodate tests, respectively. The solution was then transferred to a distilling apparatus and, after acidification, it was distilled until a few drops of the distillate gave no test for hydronitric acid. To the distillate were then added 10 drops of ferric chloride and the solution was diluted with distilled water to a definite volume. Another portion of 10 cc. of the standard solution of hydronitric acid was then treated with the same amount of ferric chloride and was diluted to an equal volume. The two solutions were then compared in comparison cylinders and their color intensity was found to be equal, showing that no hydronitric acid was oxidized by hydrogen peroxide in alkaline solution.

The solution from the absorption apparatus, which contained the decomposition products of the hydrazine disulfate, was then treated with 10 cc. of a 5% solution of sodium hydroxide, and 10 cc. of a 3% solution of hydrogen peroxide. The resulting solution was placed in a distilling apparatus and boiled until effervescence had ceased. The cessation of the effervescence in this case was taken as an indication of the complete

removal of the excess of hydrogen peroxide. The solution was then acidified with 1 : 1 sulfuric acid and was distilled. The distillate gave no tests for hydronitric acid with ferric chloride.

#### Summary.

The decomposition of hydrazine monochlorate, by heat, in neutral, aqueous solution yielded no hydronitric acid; in ( $\text{H}_2\text{SO}_4$ ) acid solution hydronitric acid resulted. The corresponding di-salt yielded hydronitric acid both in the presence and absence of sulfuric acid. The mono- and diperchlorate of hydrazine yielded no hydronitric acid in either acidified or unacidified solution. When the dry crystallized salt was decomposed by heat in a stream of carbon dioxide, hydronitric acid was produced from the latter, but not from the former. Both liberated gaseous chlorine, nitrogen and oxygen, and chloride and hydroxide ions. The mono- and disulfates of hydrazine, under similar conditions, gave off water, hydrogen sulfide, sulfur dioxide and sulfur, but no hydronitric acid. A method is described for the detection of hydronitric acid in the presence of sulfur dioxide.

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## ELECTROCHEMICAL OXIDATION OF HYDRAZINE SULFATE AND AMMONIUM HYDROXIDE.<sup>1</sup>

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Szarvasy<sup>2</sup> has shown that hydrazine, on electrolysis, yields nitrogen at the anode and hydrogen at the cathode in the ratio in which these two elements exist in the hydrazine molecule, namely,  $\text{N}_2 : 2\text{H}_2$ . These results were obtained from the electrolysis of solutions of hydrazine hydrate, sulfate and chloride at varying concentrations of solution, current densities and temperatures. The hydrazine cations, he explains, are oxidized at the anode by the discharge anions, oxygen, chlorine, with the formation, respectively, of water and hydrochloric acid, evolving nitrogen; and at the cathode "the free base reacts with two molecules of water, the hydrate being re-formed and hydrogen liberated." Under the conditions of his experiments, as his figures indicate, the hydrazine cation was oxidized at the anode quantitatively to nitrogen without any indication of a reduction at the cathode.

These experiments show conclusively that oxygen and chlorine liberated by electrolysis, under the conditions named, do not oxidize hydrazine in the alkaline solution of the hydrate or in the neutral or weakly acid solution

<sup>1</sup> In part a chapter from the thesis submitted by the author to the Faculty of Cornell University for the degree of Doctor of Philosophy, May, 1908.

<sup>2</sup> "Electrolysis of the Nitrogen Hydrides and of Hydroxylamine, *J. Chem. Soc.*, [1] 11, 603 (1900).