

an alpha particle which captured an electron before it reached the cathode would have a value $e/m = 2.9 \times 10^8$. This value was actually determined for the particles which produced patch *c*.

There still remains the probability that a considerable number of alpha particles would combine with two electrons and form neutral helium atoms before reaching the cathode, and these would be undeflected in the space back of the cathode and would form the central bright patch. On the whole, then, it seems established within the limits of error of the experiment that alpha particles were given off from the anode and formed an important part of the *Kanalstrahlen*.

This explanation will also account for the sometimes unaccountable appearance of helium in vacuum tubes through which an electric charge has been passed. A striking example of this is given by Soddy in *Proc. Roy. Soc., London (A)*, 80, 94, and while the explanation which he there offers may be the correct one it seems not impossible that the one here suggested may be the true one, instead.

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THE OXIDATION OF HYDRAZINE. V. REACTION BETWEEN POTASSIUM IODATE AND HYDRAZINE SULFATE.¹

BY C. F. HALE AND H. W. REDFIELD.

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The most characteristic of the chemical properties of hydrazine is its vigorous reducing action. This behavior has led to the suggestion of several oxidimetric methods for use in the determination of hydrazine in its inorganic compounds. Among the oxidizing agents that have been employed are ammonium metavanadate,² potassium permanganate in acid³ or in alkaline⁴ solution, ammonium and potassium persulfates,⁵ Fehling's solution,⁶ ammoniacal cupric sulfate,⁷ mercuric chloride,⁸

¹ For the earlier articles of this series see Browne and Shetterly, *THIS JOURNAL*, 29, 1305-12 (1907); 30, 53-63 (1908); 31, 221-37 (1909); 31, 783-99 (1909).

² Hofmann and Kuspert, *Ber.*, 31, 64-7 (1897). See *THIS JOURNAL*, 29, 1305 (1907).

³ Petersen, *Z. anorg. Chem.*, 5, 1 (1893); Roberto and Roncali, *l'Industria chimica*, 6, 178 (1904); *Chem. Zentralbl.*, 1904, II, 616; Medri, *Gazz. chim. ital.*, 36, I, 373-8; *Chem. Zentralbl.*, 1906, II, 459. See also *THIS JOURNAL*, 31, 226 (1909).

⁴ Sabanejeff, *Z. anorg. Chem.*, 17, 480 (1898); 20, 21 (1899). See also *THIS JOURNAL*, 31, 230 (1909).

⁵ Pannain, *Gazz. chim. ital.*, 34, I, 500-4 (1904); Rimini, *Atti accad. Lincei*, [5] 15, II, 320-25; *Chem. Zentralbl.*, 1906, II, 1663. See also *THIS JOURNAL*, 31, 222 (1909).

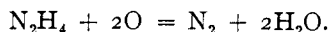
⁶ Petersen, *Loc. cit.* See also *THIS JOURNAL*, 31, 787 (1909).

⁷ Ebler, *Z. anorg. Chem.*, 47, 371-6 (1905).

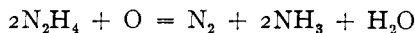
⁸ Rimini, *Atti accad. Lincei*, [5] 12, II, 376-81 (1903); 15, II, 320-5 (1906); *Chem. Zentralbl.*, 1904, I, 213; 1906, II, 1662. Ebler, *Z. anorg. Chem.*, 47, 377-85 (1905). See also *THIS JOURNAL*, 31, 790 (1909).

iodine,¹ and potassium iodate.²

The complete oxidation of hydrazine may be expressed by the equation



It has been shown in this laboratory³ that several oxidizing agents that have been employed in the determination of hydrazine either by an oxidimetric or by a nitrometric method fail, under certain conditions, at least, to oxidize hydrazine completely to nitrogen and water, yielding varying amounts of ammonia and hydronitric acid, in accordance with one or both of the equations:



The selection of an oxidizing agent entirely suitable for use in the determination of hydrazine has long been a matter of considerable interest in this laboratory, because of the frequent necessity for numerous determinations of this substance in connection with researches now completed or still in progress. Naturally, the choice was limited to those substances which had been observed to yield, under ordinary conditions, neither ammonia nor hydronitric acid when allowed to act upon hydrazine. Among these substances are potassium iodate and iodine. Complete reliance could scarcely be placed upon either of these substances, however, until the merely negative evidence of its inability to yield ammonia or hydronitric acid had been supplemented by positive proof of its ability to oxidize hydrazine quantitatively to nitrogen and water.

The importance of bearing in mind the behavior of iodine toward hydrazine before deciding upon potassium iodate as a thoroughly reliable substance for use in the determination of hydrazine is apparent from the results obtained in an earlier research conducted in this laboratory.⁴ When potassium iodate was allowed to act upon hydrazine sulfate in acid solution and in the presence of silver sulfate, which served to prevent the liberation of iodine, very appreciable amounts of ammonia and hydronitric acid were formed. It seems probable, therefore, that potassium iodate owes its apparent ability to oxidize hydrazine completely to nitrogen and water to the iodine set free during the course of the reaction.

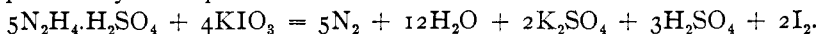
¹ Curtius and Schulz, *J. prakt. Chem.*, [2] 42, 521-49 (1890); Stollé, *Ibid.*, 66, 332-8 (1902); Rupp, *Ibid.*, 67, 140-2 (1903). See also *THIS JOURNAL*, 30, 60 (1908).

² Rimini, *Gazz. chim. ital.*, 29, I, 265-9 (1899); *Atti accad. Lincei*, [5] 15, II, 320; *Chem. Zentralbl.*, 1906, II, 1662. See also *THIS JOURNAL*, 30, 59 and 62 (1908). Baxter and Tilley, *THIS JOURNAL*, 31, 201-21 (1909), have employed hydrazine hydrate in the reduction of the iodic acid used in determining the atomic weights of silver and iodine. See also Riegler, *Z. anal. Chem.*, 40, 92-4 (1901); 41, 413-19 (1902); 46, 315-18 (1907); and Schlötter, *Z. anorg. Chem.*, 37, 172-6 (1903).

³ Browne and Shetterly, *Loc. cit.*

⁴ *THIS JOURNAL*, 30, 62 (1908).

Rimini¹ has shown that the reaction between potassium iodate in excess and hydrazine sulfate in the presence of sulfuric acid may be expressed by the equation



He submits no analytical data, however, nor does he describe the exact procedure to be followed in carrying out the analysis. Possibly for these reasons the Rimini method has not enjoyed the wide application that would seem to be justified by its convenience and accuracy.

The purpose of the experimental work to be described in the following paragraphs has been to subject the Rimini potassium iodate method for the determination of hydrazine to a rigorous experimental test. Three series of experiments have been performed. In the first, a number of simultaneous oxidimetric and nitrometric determinations have been carried out, the reaction having been allowed in each case to take place in a current of pure carbon dioxide. In the second series the procedure was similar to that of the first except that the reaction took place in a current of steam. In the third, the oxidimetric method alone was studied under ordinary laboratory conditions.

Materials Used in the Experiments.—The purity of the hydrazine sulfate (obtained from Kahlbaum, Berlin) used in the first two series was tested by the determination of sulfur in six different samples of the material. The average of the six closely agreeing results was 24.57 per cent. Theory for S in $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, 24.64 per cent. In the first and second series two potassium iodate solutions were employed having the respective concentrations 7.07 grams and 14.13 grams per liter. The former was used for small samples weighing 0.22 gram or less, and the latter for the larger samples. In effecting the standardization of these solutions the usual procedure was followed. This consists in the reduction of a measured volume of the iodate solution by means of a slight excess of a 10 per cent. solution of potassium iodide, in the presence of dilute sulfuric acid, and subsequent titration of the resulting solution against standard thiosulfate. The latter solution was in turn standardized against twice resublimed iodine. The thiosulfate was added in slight excess, and the blue color of the starch indicator was restored by an iodine solution of which the strength in terms of the thiosulfate solution was known.

Apparatus Used in the Experiments.—In the first two series of experiments a nitrometer not very different from that used by Petersen² in his study of the action of boiling hot Fehling's solution upon hydrazine salts, or from the modified Schultze and Tiemann apparatus employed by Purgotti³ in his investigation of the behavior of certain oxidizing agents

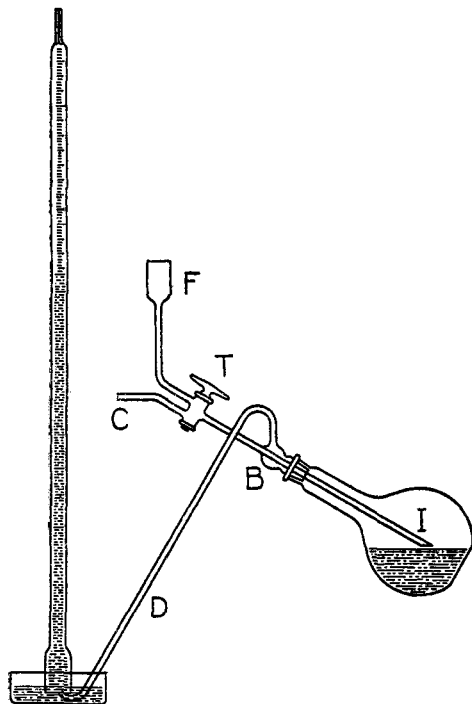
¹ *Loc. cit.*

² *Z. anorg. Chem.*, 5, 1 (1893).

³ *Gazz. chim. ital.*, 26, II, 559 (1896); *Chem. Zentralbl.*, 1897, I, 487.

toward hydrazine, was employed. The essential parts of this apparatus are shown in the accompanying sketch. From the fact that iodine is abundantly liberated during the course of the reaction to be studied arose the necessity that the apparatus should be constructed entirely of glass.

An ordinary 500 cc. glass stoppered wash bottle was modified by fusing on the two-way stopcock T, and the delivery tube D. The measuring tube consisted of a Hempel gas buret, to the lower end of which had been sealed a short tube of larger diameter, which served to prevent loss of gas when a rapid current was being passed through D. The funnel tube F served to admit the sample of hydrazine sulfate, and the tube C was used, in the first series, for establishing connection with an apparatus for generating pure carbon dioxide, modeled after that of Bradley and Hale.¹ The connection at this point was rendered impervious to air by means of a mercury seal. During the progress of the experiments the evolution flask was inclined at such an angle that no gas trap was



formed either in the flask itself or in the bulb B. Both the stopper and the stopcock were found to be gas-tight under all pressures to which the flask was subjected. Inasmuch as the pressure in the flask during the experiments varied but slightly, if at all, from that of the atmosphere it was considered sufficient to test the apparatus at pressures from 23 cm. of mercury below atmospheric, to 27 cm. above atmospheric pressure. The nitrometer tube was filled with a concentrated solution of potassium hydroxide (3 : 2) at the beginning of each experiment in the first series, and with water in the second series. For heating the evolution flask, a bath of strong calcium chloride solution was found to be very convenient.

Action of Potassium Iodate upon Hydrazine Sulfate in an Atmosphere of Pure Carbon Dioxide.—In each of the six experiments of the first series a volume of the potassium iodate solution from 2–5 cc. in excess of the

¹ THIS JOURNAL, 30, 1090–6 (1908).

amount theoretically required for the complete oxidation of the hydrazine sample was introduced into the evolution flask and was diluted to about 200 cc. After connection with the carbon dioxide generator had been established, the stopcock T was adjusted to permit the current of gas to pass through the flask, and out through the delivery tube into the room. The solution in the flask was boiled for ten minutes and was then allowed to cool in a current of carbon dioxide. When the circulation of the gas had continued for an hour, a half-hour sample was collected in the nitrometer, and the residual bubble of gas, not absorbed by the potassium hydroxide solution, was drawn off into a narrow tube mounted upon the top of a Hempel gas burette and provided with a stopcock at its upper end. Measured under atmospheric pressure, the volume of this bubble rarely amounted to more than a few tenths of a cubic centimeter. The sample of hydrazine sulfate, dissolved in 25 cc. of previously boiled hot water, was introduced into the flask from the funnel tube F by suitably adjusting the stopcock T. The container and the funnel tube were rinsed with four successive 25 cc. portions of hot water. At this point the current of carbon dioxide was diverted from the flask by closing T, and the contents of the flask were boiled until the liberated iodine had been driven off. As a rule it was found necessary to continue the boiling for from twenty to thirty minutes in order to insure the complete expulsion of the iodine. That the prolonged boiling effected also the removal of all evolved nitrogen from the flask was evident from the fact that on renewing the carbon dioxide circulation practically all of the gas issuing from the delivery tube was absorbed before the bubbles reached the meniscus of the potassium hydroxide solution in the nitrometer. To insure the complete transfer of the nitrogen, however, a current of carbon dioxide was sent through the apparatus for fifteen minutes after the boiling was discontinued. In order to permit correction of the volume of nitrogen for the small volume of unabsorbable gas present in the carbon dioxide, care was of course taken to keep the speed of the gas constant throughout each experiment, and to record the exact length of time that the gas was used. At the expiration of the fifteen minutes the delivery tube was removed from the absorbing solution, and the current of carbon dioxide cut off. The flask was then allowed to cool to room temperature. After the solution had been shown, by means of the starch test, to be free from uncombined iodine, the excess of potassium iodate was determined by the method already indicated in connection with the standardization of the solution.

The nitrogen was drawn from the nitrometer into a Hempel simple mercury pipet¹ containing 10 cc. of potassium hydroxide solution, and thence into a water-jacketed Hempel gas buret, in which mercury was used as the confining liquid, where the volume was accurately measured.

¹ Hempel-Dennis, "Methods of Gas Analysis," 1902, p. 67.

It was next introduced into a pipet containing 10 cc. of alkaline pyrogallol, and was then transferred to the buret for final measurement. Both reagents had previously been saturated with nitrogen, as well as the small volume of pure water (about 1 cc.) introduced into the buret to insure saturation of the gas with aqueous vapor. The final volume was thus virtually measured over water, and a correction for the tension of aqueous vapor was consequently introduced in calculating the volume of the gas at 760 mm. and 0°.

Small amounts of oxygen, varying in different experiments from 0.2–0.5 cc., were always found. The proper manner of introducing a correction for the nitrogen, which undoubtedly accompanied this volume of oxygen, was at first by no means obvious. To be sure, a very small amount of air was admitted as an impurity in the carbon dioxide. The correction for this volume would be, clearly, four-fifths of the residue unabsorbed by potassium hydroxide in the half-hour test run, apportioned for the time during which the carbon dioxide current was passing through the apparatus after the collection of the nitrogen had begun. This correction, however, did not account for all of the oxygen found. Another source from which small volumes of oxygen and nitrogen could be introduced into the apparatus was to be found in the solutions employed. Obviously the error due to this source could be estimated by dispensing with the carbon dioxide, as has been done in the second series of experiments. The only other source of air considered was the absorbing solution in the nitrometer. This solution was always boiled immediately before each experiment and was kept hot by the steam escaping from the delivery tube. The possible error due to the diffusion out of oxygen remaining in the absorbing solution was assumed to be negligible. These considerations and the results of experiments in which no carbon dioxide was used, led to a correction for air dissolved in the solutions introduced into the flask. For this correction recourse was had to the work of Petterson and Sonden¹ and a correction amounting to twice the volume of oxygen found was applied in all cases.

The results obtained in the experiments in which a current of carbon dioxide was employed are given in Table I.

The percentages of hydrazine have been calculated oxidimetrically—that is, on the basis of the iodate used. These results clearly indicate that the hydrazine is oxidized quantitatively under the described conditions to water and nitrogen. It was considered wise, however, as an additional precaution, to test the residual solutions for ammonia after the titrations had been completed. To carry out this test, the solutions were made strongly alkaline with solid potassium hydroxide and one-quarter of the liquid was in each case distilled off into standard acid. After the

¹ *Ber.*, 22, 1443 (1889).

acid had been titrated, the solution was again made alkaline and Nessler's reagent was added. The titration of the acid was in every case well within the limits of experimental error, and the test with Nessler's reagent was no more pronounced than could be obtained with an equal volume of distilled water to which the same amounts of the various solutions used had been added.

TABLE I.

Number of experiment.	N ₂ H ₄ .H ₂ SO ₄ used. Gram.	Hydrogen found.		Per cent. N ₂ H ₄ .	Nitrogen found.		
		Gram.	Per cent.		Corrected volume. cc.	Weight. Gram.	Per cent.
1.....	0.1183	0.00367	3.10	24.64	20.4	0.0255	21.49
2.....	0.2088	0.00645	3.09	24.56	35.9	0.0448	21.48
3.....	0.2100	0.00648	3.09	24.54	36.6	0.0458	21.79
4.....	0.2099	0.00647	3.08	24.50	36.2	0.0452	21.54
5.....	0.2014	0.00622	3.09	24.55	35.1	0.0439	21.80
6.....	0.2044	0.00632	3.10	24.59	35.1	0.0439	21.46
Average.....			3.09	24.56			21.59
Theory.....				24.63			21.53

Action of Potassium Iodate upon Hydrazine Sulfate at 100° in an Atmosphere of Steam.—The only change in the apparatus already described was the replacing of the inner tube I with a capillary tube which was bent downward so that it reached the bottom of the flask when the apparatus was set up as shown in the figure. The lower end of this tube was drawn out to a small diameter in order that the solution of the sample could be admitted in a thin stream below the surface of the oxidizing solution. It was the practice to fill this tube with hot boiled water just before attaching the flask. The iodate solution was then boiled for twenty minutes to expel the air in the flask and delivery tube. The sample was slowly introduced as in the first series of experiments, and the boiling was continued until the iodine had been entirely driven off. It was clearly evident that the evolution of nitrogen had ceased and that the gas had all been swept over into the nitrometer long before the iodine color disappeared. The solution, cooled to room temperature, was tested for the free iodine and was titrated in the manner already outlined. The average amount of oxygen present in the nitrometer gas was the same as in the first series, although no oxygen at all was found in the third experiment.

In Table II will be found the results of the series of experiments in which no carbon dioxide was used.

A comparison of the results obtained in the two series of experiments shows that those of the second series are not quite so closely in accord with theory as are those of the first series. That this difference is attributable to experimental error that is not readily avoidable in the second series, rather than to any change in the reaction when the sample is added

to boiling iodate solution, seems evident. A change in the reaction in the direction of incomplete oxidation would be accompanied by a shrinkage in the amount of nitrogen and it is plain that any oxidation of nitrogen, that is ultra-oxidation of hydrazine, would have the effect of raising the percentage of hydrazine found. Tests for ammonia were made as in the earlier experiments with the same negative results.

TABLE II.

Number of experiment.	N ₂ H ₄ . H ₂ SO ₄ used. Gram.	Hydrogen found.		Per cent. N ₂ H ₄ .	Nitrogen found		
		Gram	Per cent.		Corrected volume cc.	Weight. Gram.	Per cent.
1.....	0.2184	0.00674	3.09	24.54	38.1	0.0475	21.77
2.....	0.2124	0.00654	3.08	24.48	36.8	0.0460	21.68
3.....	0.2135	0.00659	3.09	24.54	36.9	0.0461	21.60
4.....	0.4138	0.01277	3.09	24.53	71.0	0.0888	21.47
5.....	0.4190	0.01292	3.08	24.52	72.5	0.0907	21.64
6.....	0.3365	0.01120	3.08	24.47	62.4	0.0781	21.53
Average.....			3.09	24.51			21.61
Theory.....				24.63			21.53

It is obvious that a further change in the method of introducing the sample might be made. By a cradle-like arrangement on the upper side of the inner tube I (Fig. 1), the weighed sample, contained in a small test tube, could be placed inside the flask at the beginning of the experiment. After the requisite preliminary boiling the test tube could be dislodged by a slight jarring of the apparatus. This method would obviate the introduction of 125 cc. of water with the sample, the air in the test tube being displaced by a few cubic centimeters of water before putting the tube into the cradle. On attempting to employ this method it was found that the reaction was too violent when the solid hydrazine sulfate was suddenly thrown into the boiling iodate solution. Some of the nitrogen was carried out under the nitrometer in the early stages of the reaction. This difficulty was not entirely overcome by immersing the mouth of the nitrometer under a few centimeters of mercury. It became evident that these experiments could contribute nothing to the present purpose, and after a few trials they were abandoned.

Study of the Rimini Method under Ordinary Conditions.—The results of the simultaneous oxidimetric and nitrometric determinations carried out in the two preceding series of experiments demonstrate that within the limits of experimental error, the reaction between potassium iodate and hydrazine sulfate takes place in accordance with the equation given by Rimini. The only remaining step, then, in the complete vindication of the Rimini method as a reliable means of determining hydrazine consists in a test of the method under ordinary laboratory conditions.

The hydrazine sulfate used in this third series of experiments was ob-

tained from Raschig, and was marked 100 per cent. pure. One kilogram of this material was dissolved in water, and the solution was evaporated until crystallization started. The hot solution was then filtered and the filtrate was thoroughly agitated by means of mechanical stirrers until it had cooled to room temperature. The crystals were filtered upon a Buchner funnel, were washed with 10 liters of cold distilled water, and were dried for ten hours in an air bath at 110°. This product was shown by titration with tenth-normal sodium hydroxide to be slightly deficient in sulfuric acid. It was consequently recrystallized from dilute sulfuric acid by the method just described, with the result that a product of entirely satisfactory composition was obtained. The solution of hydrazine sulfate used in the experiments contained 5.4000 grams of the salt per liter. The potassium iodate solution contained 7.1045 grams per liter, and was consequently of such strength that 1 cc. was equivalent to 1 cc. of the hydrazine sulfate solution. The sodium thiosulfate solution was standardized very carefully against solutions of resublimed iodine, and of potassium dichromate, and was made exactly tenth-normal.

The details of a series of ten experiments are summarized in Table III.

TABLE III.

Number of experiment.	Cc. of hydrazine sulfate solution used.	Cc. of potassium iodate solution added.	Calculated excess of potassium iodate solution in cc.	Cc. water added.	Grams of potassium iodide added.	Cc. 1:4 sulfuric acid added.	Cc. tenth normal sodium thiosulfate required.	Cc. excess of potassium iodate solution calculated from sodium thiosulfate required.	Cc. of potassium iodate solution used up by hydrazine sulfate taken.	Equivalent in grams of hydrazine	Percentage of hydrazine in hydrazine sulfate.
1.....	20.0	25.0	5.0	155.0	1.0	15.0	10.10	5.07	19.93	0.0265	24.54
2.....	20.0	30.0	10.0	150.0	2.0	25.0	19.85	9.97	20.03	0.0266	24.67
3.....	30.0	35.0	5.0	135.0	1.0	15.0	9.95	5.00	30.00	0.0399	24.63
4.....	30.0	40.0	10.0	130.0	2.0	25.0	19.95	10.01	29.99	0.0398	24.56
5.....	40.0	45.0	5.0	115.0	1.0	15.0	10.00	5.02	39.98	0.0532	24.62
6.....	40.0	50.0	10.0	110.0	2.0	25.0	19.90	9.99	40.01	0.0532	24.64
7.....	50.0	55.0	5.0	95.0	1.0	15.0	9.90	4.97	50.03	0.0665	24.64
8.....	50.0	60.0	10.0	90.0	2.0	25.0	19.85	9.97	50.03	0.0665	24.64
9.....	60.0	65.0	5.0	75.0	1.0	15.0	10.00	5.02	59.98	0.0798	24.62
10.....	60.0	70.0	10.0	70.0	2.0	25.0	20.00	10.04	59.96	0.0798	24.61
Average.....											24.617
Theory.....											24.629

The results of these experiments indicate very clearly that the Rimini method is sufficiently accurate for all ordinary purposes, and show that the oxidimetric method is more satisfactory than the nitrometric method for work in which considerable accuracy is required.

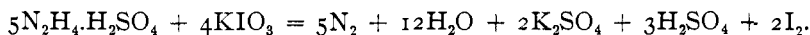
The exact procedure to be recommended in carrying out the Rimini method is briefly as follows:

Weigh out about 0.3 gram of the hydrazine salt or of the solid substance in which the percentage of hydrazine is to be determined and dissolve if possible in about 50 cc. of distilled water. Transfer to a 300 cc. tall narrow-mouthed Erlenmeyer flask and add such a carefully measured amount of potassium iodate solution (containing about 7.1045 grams to the liter) as will give from 5–10 cc. excess of the iodate. (This will be from 60–65 cc., if hydrazine sulfate is being analyzed.) Then add sufficient distilled water to bring the volume up to 200 cc., and boil over a free flame for thirty minutes. During the boiling, the volume will be reduced to about 100 cc. Cool the solution to about 20° and add from 1–2 grams of potassium iodide (free from iodate), to decompose completely the excess of potassium iodate and also to dissolve the iodine that is liberated. After having added about 20 cc. of 1 : 4 sulfuric acid, titrate the solution immediately with 0.1 *N* sodium thiosulfate until a straw-yellow color is reached. Now add 1 cc. of starch solution¹ (previously made by boiling 1 gram of starch with 200 cc. of distilled water for ten minutes, cooling, allowing to settle and decanting off the clear solution) and titrate to disappearance of the blue color.

Summary.

The principal results obtained in the present investigation may be summarized as follows:

1. The oxidation of hydrazine sulfate by potassium iodate has been shown by simultaneous oxidimetric and nitrometric determinations to proceed quantitatively in accordance with the Rimini equation



2. The reaction is the same whether the hydrazine is added to the potassium iodate in the cold (in an atmosphere of carbon dioxide) or at the boiling temperature (in an atmosphere of steam).

3. Under ordinary laboratory conditions the oxidimetric procedure, essentially as recommended by Rimini, affords an accurate method for the determination of hydrazine.

The chief disadvantage of the method lies in the length of time (thirty minutes) required for the expulsion of the liberated iodine. In a future communication attention will be given to several other methods for the determination of hydrazine.

The present investigation was undertaken at the suggestion of Professor A. W. Browne, and was carried out under his supervision.

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¹ Mr. Welsh, of this laboratory, reports that under certain conditions methylene blue is preferable to starch as an indicator in this titration. See F. S. Sinnatt, *Analyst*, 35, 309 (1910).