The speed of the light reaction is proportional to the quantity of light of given wave length absorbed by the quinine alone unless the concentration of chromic acid is very small; this is consistent with the hypothesis that the light reaction runs in two stages.

Formulas are worked out from which the velocity produced by the incidence of known amounts of light of various wave lengths upon any mixture of quinine and chromic acid under the conditions prevailing throughout the research can be calculated.

The photochemical efficiency of a given amount of absolute light energy is found to decrease as the wave length of maximum absorption is approached. This result is predicted by theoretical considerations.

The effect of changing the thickness of the layer is tested experimentally. It is shown that the relative effect of two rays of different wave length must depend entirely on the thickness of the layer.

The experimental work described in this paper was carried out in the Physikalisch-Chemisches Institut of the University of Leipzig during the winter semester 1906–7.

ON THE OXIDATION OF HYDRAZINE. IV.

By A. W. Browne and F. F. Shetterly.

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Historical.

E. Fischer[1] has shown that by the oxidation of a cold aqueous emulsion of phenylhydrazine with an excess of Fehling's solution, benzene and aniline are formed. Baeyer[2] has made use of the action of copper sulphate upon the hydrazines in the preparation of hydrocarbons. Gallinek and V. v. Richter[3] have called attention to the possible use of copper sulphate in the gasometric determination of the nitrogen in certain hydrazine derivatives. Strache[4] has suggested the use of hot Fehling's solution in the determination of phenylhydrazine. By measuring the excess of unused phenylhydrazine he has also effected the determination of carbonyl oxygen in aldehydes and in ketones. In a subsequent communication[5] he calls attention to two possible sources of error in his method, and finally states[6] that no aniline is formed when boiling hot Fehling's solution is employed,

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[1] *Ann.*, **190**, 67–183 (1878).

[2] See Haller, *Ber.*, **18**, 89–94 (1885). See also Kijner, *J. Russ. Phys. Chem. Soc.*, **31**, 1033–62 (1899); *J. Chem. Soc.*, **78**, I, 333 (1900).

[3] *Ber.*, **18**, 3172–78 (1885).

[4] *Monatsh. Chem.*, **12**, 524–32 (1891). See also de Vries and Hollemann, *Rec. trav. chim.*, **10**, 228–30 (1891); Strache and Iritzer, *Monatsh. Chem.*, **14**, 33–38 (1893); Benedikt and Strache, *Ibid.*, **14**, 270–77 (1893); de Vries, *Ber.*, **27**, 1521–2 (1894); *Ibid.*, **28**, 2611–2 (1895); Kitt, *Chem.-Ztg.*, **22**, 358 (1898); *Chem. Centr.*, **1898**, I, 1310.

[5] *Monatsh. Chem.*, **13**, 299–315 (1892).

[6] Strache and Kitt, *Ibid.*, **13**, 316–19 (1892).

and that the nitrogen is liberated quantitatively under these conditions. A similar method has been applied by Jolles[1] for the detection and the determination of acetone in urine. Petersen[2] has described a nitrometric method for the determination of hydrazine, based upon the action of boiling hot Fehling's solution upon hydrazine salts.

Purgotti[3] has devised a method for the determination of copper, based upon the reaction expressed by the equation

$$4CuSO_4 + 10NaCl + N_2H_4.H_2SO_4 = 2Cu_2Cl_2 + 5Na_2SO_4 + 6HCl + N_2.$$

The solution containing the copper is boiled with the hydrazine sulphate solution in an apparatus modeled after that of Schultze and Tiemann.

Jannasch and Biedermann[4] have shown that copper may be precipitated quantitatively in the presence of sodium hydroxide by addition of a boiling 3 per cent. solution of hydrazine sulphate. This procedure is useful not merely for the determination of copper, but also for the separation of copper from zinc, aluminum, arsenic, and tin. Jannasch and Stephan[5] have studied the separation of platinum from a number of metallic elements, including copper in ammoniacal solution.

Riegler[6] has recommended the use of an alkaline solution of copper sulphate at room temperature, instead of the hot Fehling's solution, in effecting the gas volumetric determination of acetone in urine.

De Girard and de Saporta,[7] referring to the work of Purgotti,[8] have stated that a double sulphate of copper and hydrazine is formed when a 3.5 per cent. solution of copper sulphate is mixed with a 3 per cent. solution of hydrazine sulphate. They suggest the addition of sodium hydroxide to the solution, in case the reaction is to take place in the cold, and recommend the use of the Trubert calcimeter.

Ebler[9] has studied the reaction between ammoniacal cupric sulphate and hydrazine sulphate, reaching the conclusion that this reaction proceeds strictly in accordance with the equation

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[1] *Z. österr. Apoth. Vereins*, **30**, 198; *Z. anal. Chem.*, **31**, 576 (1892).

[2] *Z. anorg. Chem.*, **5**, 1–7 (1893).

[3] *Gazz. chim. ital.*, **26**, II, 559–73 (1896); *Chem. Centr.*, **1897**, I, 487.

[4] *Ber.*, **33**, 631–36 (1900).

[5] *Ibid.*, **37**, 1980–92 (1904). In connection with the further application of hydrazine salts in quantitative analysis, reference should also be made to the other investigations of Jannasch and his co-workers: *Ber.*, **31**, 2377–94 (1898); **37**, 2210–19, 2219–28, 2441–61 (1904); **38**, 1576–89, 2129–30, 2130–31 (1905). In connection with the application of hydrazine in qualitative analysis see Knoevenagel and Ebler, *Ber.*, **35**, 3055–67 (1902), and Ebler, Habilitationsschrift, Heidelberg, 1905.

[6] *Z. anal. Chem.*, **40**, 94–7 (1901).

[7] *Bull. soc. chim.* [3], **31**, 905–7 (1904). See also Rimini, *Atti accad. Lincei* [5], **14**, I, 386–92 (1905); *Chem. Centr.*, **1905**, I, 1546; Curtius and Schrader, *J. pr. Chem.*, *N. F.*, **50**, 311–346 (1894).

[8] *Loc. cit.*

[9] *Z. anorg. Chem.*, **47**, 371–6 (1905).

$$4CuSO_4.4NH_3 + N_2H_4.H_2SO_4 = 2Cu_2SO_4.4NH_3 + N_2 + 2NH_3 + 3(NH_4)_2SO_4,$$

and that quantitative liberation of the nitrogen of the hydrazine consequently takes place. From the results obtained when the copper and when the hydrazine, respectively, are taken in excess, the conclusion is drawn that the method may be employed in the determination either of hydrazine or of copper. In either case the Hempel-Oettel fluorometer is employed.

Rimini[1] has suggested the use of mercuric chloride in the determination of hydrazine and its derivatives, and has recommended the converse application of the method for the determination of mercury. Ebler[2] has investigated the reaction between hydrazine sulphate and mercuric chloride under various conditions, with similar objects in view.

The use of hydrazine compounds for the quantitative reduction of chromates has been suggested by several authorities.[3] The reaction between hydrazine chloride and potassium dichromate in hydrochloric acid solution has been studied by Bach[4] in connection with his investigation of the heat of formation[5] of hydrazine. The reaction is considered to proceed as indicated by the equation

$$3N_2H_4.HCl + 2K_2Cr_2O_7 + 13HCl = 3N_2 + 4KCl + 4CrCl_3 + 14H_2O,$$

and ammonia is said to be formed in vanishingly small quantities only. Purgotti[6] has recommended a gas volumetric method for the determination of chromates, depending upon the reaction with hydrazine sulphate in sulphuric acid solution. Tanatar[7] found that by oxidizing a molecular mixture of hydrazine sulphate and hydroxylammonium chloride in acid solution with chromic acid, considerable quantities of hydronitric acid were obtained. Roberto and Roncali[8] express the reaction between potassium dichromate and hydrazine sulphate by means of equations substantially identical with that of Purgotti.[6] Medri[9] states that hydrazine is completely oxidized by potassium dichromate.

Seubert and Carstens[10] have studied the velocity of the reaction between

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[1] *Atti accad. Lincei* [5], 12, II, 376–81 (1903); *Chem. Centr.*, 1904, I, 213. See also *Boll. chim. farm.*, 47, 145–7 (1908); *Chem. Zentr.*, 1908, I, 1797.

[2] *Z. anorg. Chem.*, 47, 377–85 (1905). See also Rimini, *Atti accad. Lincei* [5], 15, II, 320–5 (1906); *Chem. Centr.*, 1906, II, 1662.

[3] Jannasch, "Praktischer Leitfaden der Gewichtsanalyse," 2nd Ed., Veit & Co., Leipzig, 1904, pages 30 and 439; Julius Schmidt, "Die Anwendung der Hydrazine in der Analytischen Chemie," Ferdinand Enke, Stuttgart, 1907, page 19. Herz, *Ber.*, 35, 949 (1902). See also Curtius and Schrader, *J. pr. Chem.*, *N. F.*, 50, 311–346 (1894).

[4] *Z. physik. Chem.*, 9, 241–63 (1892).

[5] See also Berthelot and Matignon, *Ann. chim. phys.* [6], 27, 289–302 (1892).

[6] *Loc. cit.*

[7] *Ber.*, 35, 1810–11 (1902).

[8] *L'Industria chimica*, 6, 178–9 (1904); *Chem. Centr.*, 1904, II, 616.

[9] *Gazz. chim. ital.*, 36, I, 373 (1906); *Chem. Centr.*, 1906, II, 459.

[10] *Z. anorg. Chem.*, 56, 357–364 (1907).

hydrazine and chromic acid. Relying upon the observation that the amounts of gas evolved from a given amount of hydrazine chloride in hydrochloric acid solution by the respective action of Fehling's solution and of potassium chromate are the same, they assume that ammonia is not formed as one of the reaction products. From their experimental results these investigators conclude that the reaction is bimolecular, and is to be expressed by the equation

$$H_2Cr_2O_7 + N_2H_4 = 2CrO_2 + 3H_2O + N_2,$$

or,

$$Cr_2O_7'' + N_2H_5^{\bullet} = 2CrO_2 + 2H_2O + OH'.$$

Chattaway[1] has investigated the behavior of several primary aromatic hydrazines toward a number of oxidizing agents, including free oxygen, metallic oxides, permanganates, and chromates.

Jannasch[2] has studied the behavior of hydrazine toward selenium and tellurium compounds. Gutbier[3] has employed a solution of hydrazine hydrate in the determination of tellurium, and in the separation of this element from antimony. Rimini and Malagnini[4] have described a selenate of hydrazine, a double selenate of hydrazine and copper, and a double selenate of hydrazine and zinc.

Experimental.

The behavior of hydrazine sulphate in aqueous solution toward a number of oxidizing agents has already been investigated in this laboratory, with especial reference to the formation of hydronitric acid and ammonia.[5] The substances thus far studied, however, constitute by no means the entire list of oxidizing agents capable of decomposing hydrazine under proper conditions. To make this part of the work more nearly complete it has seemed advisable to put upon record a brief statement of the results obtained in a series of experiments upon the behavior of hydrazine sulphate in aqueous solution toward the following additional substances: cupric sulphate, cupric oxide, Fehling's solution, potassium chromate, mercuric oxide, mercuric chloride, arsenic pentoxide, antimony pentoxide, ozone, chromic sulphate, selenious acid, selenic acid, telluric acid, molybdenum trioxide, ferric oxide, nickel sesquioxide, and cobalt sesquioxide. A number of other substances, including stannic oxide, stannic chloride, sodium bismuthate, tellurous acid, tungsten trioxide, and sodium pyrouranate, gave either indecisive or negative results under the conditions of the experiments performed, and have consequently received no attention in the present article.

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[1] *J. Chem. Soc.*, **91**, 1323–30 (1907); **93**, 270–80 (1908). See also Zincke, *Ber.*, **18**, 786 (1885); Wurster, *Ber.*, **20**, 2631–3 (1887).

[2] *Ber.*, **31**, 2386–94 (1898); "Praktischer Leitfaden der Gewichtsanalyse," 2nd Ed., 1904, p. 438; Schmidt, "Die Anwendung der Hydrazine in der Analytischen Chemie," 1907, page 19.

[3] *Ber.*, **34**, 2724–6 (1901); *Z. anorg. Chem.*, **31**, 331–9 (1902), foot-note, page 335; **32**, 260–71 (1902).

[4] *Atti accad. Lincei* [5], **15**, II, 561–3 (1906); *Chem. Zentr.*, **1907**, I, 86. *Gazz. chim. ital.*, **37**, I, 261–6 (1907); *Chem. Zentr.*, **1907**, II, 373.

[5] THIS JOURNAL, **27**, 551–5 (1905); **29**, 1305–12 (1907); **30**, 53–63 (1908); **31**, 221–37 (1909).

The procedure adopted throughout the experiments was similar to that described in the preceding articles, unless otherwise specified. Whenever it seemed at all advisable the materials used were shown by means of suitable tests to be free from ammonia and from nitric acid. The presence of the latter substance might obviously give rise to erroneous conclusions concerning the ability of the oxidizing agent under consideration to form hydronitric acid from hydrazine, as nitric acid itself oxidizes hydrazine with this result. As an illustration of this difficulty it may be said that experiments with sodium metastannate in acid solution resulted in the formation of from 5.7 to 11.5 per cent. of hydronitric acid, while experiments with stannic oxide and stannic chloride gave negative results. It was then found that the sodium metastannate contained appreciable amounts of nitric acid.

The results obtained in the experiments are described under three principal heads: (1) action of cupric compounds upon hydrazine sulphate in alkaline solution; (2) action of potassium chromate upon hydrazine sulphate in acid solution; (3) action of various other oxidizing agents upon hydrazine sulphate in acid or in alkaline solution.

Action of Cupric Compounds upon Hydrazine Sulphate in Alkaline Solution. Cupric Sulphate.—A series of experiments was performed in which 50 cc. portions of a solution of hydrazine sulphate (10 gr. $N_2H_4.H_2SO_4$ per liter), to which had been added respectively 0, 5, 7.5, 10, 25, 40, and 50 cc. of a 20 per cent. solution of sodium hydroxide, were treated with an excess of a solution of copper sulphate (22.5 gr. $CuSO_4$ per liter). This solution was introduced drop by drop into the hydrazine solution, the temperature of which ranged from 20° to 100° in the different experiments. The reaction was in general found to proceed more rapidly as the temperature was raised, and as the concentration of sodium hydroxide was increased. In Experiment 1, in which no sodium hydroxide was used, no reaction was observed to take place. In each of the subsequent experiments the solution was distilled after the addition of the oxidizing agent. In Experiments 2, 3, and 4, the solutions were made strongly alkaline by the use of additional sodium hydroxide prior to distillation. Traces of ammonia were found in the distillates obtained in these experiments, but no ammonia was formed in Experiments 5, 6, and 7. The residual solutions, after acidification with sulphuric acid, were distilled. None of the distillates contained hydronitric acid.

Two additional experiments were performed in which the procedure recommended by Purgotti[1] for the determination of copper in copper salts by the use of hydrazine sulphate in the presence of sodium chloride, was duplicated as nearly as possible. Neither hydronitric acid nor ammonia could be identified as products of the reaction.

Cupric Oxide.—Four experiments were performed in which 50 cc. portions of a one per cent. solution of hydrazine sulphate were warmed gently with an excess of cupric oxide in the presence of 0, 2.5, 5, and 25 cc., respectively, of a 20 per cent. solution of sodium hydroxide. In the first experiment no reaction took place, but in the others a slight effervescence began at room temperature, and became more vigorous after the solutions had been heated. In Experiment 2 a copper mirror was deposited on the bottom of the flask. Appreciable amounts of ammonia were formed in the second and third experiments, but no trace of it could be detected in the fourth. No hydronitric acid was formed in any case. A second series of experiments in which freshly precipitated cupric oxide was used, under conditions similar to those just described, gave results substantially identical with those of the first series. Similar results were obtained, moreover, when an aqueous suspension of the copper oxide was introduced gradually into the hydrazine solution instead of being added all at once at the beginning of the experiment.

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[1] *Loc. cit.*

Fehling's Solution.[1]—In Table I are summarized the details of a series of experiments upon the behavior of Fehling's solution toward hydrazine sulphate.

TABLE I.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Fehling's. solution. cc.	Temperature.	Result.
1	50	125	100°	No HN_3; trace NH_3.
2	50	125	100°	No HN_3; trace NH_3.
3	50	125	15°–25°	No HN_3; large amount NH_3.
4	50	125	50°–60°	No HN_3; large amount NH_3.
5	50	125	60°–70°	No HN_3; large amount NH_3.
6	50	125	85°–95°	No HN_3; large amount NH_3.
7	50	125	85°–95°	No HN_3; large amount NH_3.
8	50	125	85°–95°	No HN_3; large amount NH_3.

In Experiments 1 and 2 the hydrazine solution was added drop by drop to the boiling Fehling's solution, and the mixture was allowed to distil slowly. In Experiments 3 to 8, inclusive, the procedure differed only in that the Fehling's solution was added slowly to the hydrazine solution at the various temperatures indicated. In every case oxidation of the hydrazine took place, but the velocity of the reaction was apparently accelerated as the temperature was raised. No evidence whatever of the formation of hydronitric acid was obtained in any experiment. In Experiments 7 and 8 the Fehling's solution was heated nearly to the boiling point before it was added to the hydrazine. In Experiment 8 the solution of hydrazine sulphate was made strongly alkaline by the addition of 25 cc. of a 20 per cent. potassium hydroxide solution prior to the introduction of the Fehling's solution. The amounts of ammonia formed during the reaction show some tendency to vary inversely with the temperature and with the concentration of the alkali, and are also dependent upon the method employed in bringing the reacting substances together. The results obtained in Experiments 1 and 2 and in other experiments not recorded in the table indicate that only negligible quantities of ammonia and no hydronitric acid whatever are formed when the Fehling's solution is kept at the boiling temperature, and is present in excess at all times during the course of the reaction. From this view-point, then, there can be no possible objection to the use of Fehling's solution, under these conditions, in the determination of hydrazine.

Action of Potassium Chromate upon Hydrazine Sulphate in Acid Solution.—The results obtained in certain typical experiments are shown in Table II.

TABLE II.

No. of experiment.	$N_2H_4.H_2SO_4$ (10 grams per liter). cc.	Conc. H_2SO_4. cc.	K_2CrO_4 (33 grams per liter). cc.	Result.
1	50	0	45	No HN_3; small amount NH_3.
2	50	10	45	No HN_3; large amount NH_3.
3	50	25	45	Trace HN_3; large amount NH_3.
4	100	2	60	Trace HN_3; large amount NH_3.
5	50	5	excess	No HN_3; large amount NH_3.
6	100	5	75	Small amount HN_3; large amount NH_3.
7	100	25	75	No HN_3; large amount NH_3.
8	100	10	75	37 per cent. NH_3.
9	100	25	75	66 per cent. NH_3.

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[1] This solution contained 34.639 grams of copper sulphate, 173 grams of sodium potassium tartrate, and 100 cc. of sodium hydroxide solution (sp. gr. 1.12) per liter.

In all of these experiments the chromate solution was added drop by drop to the hydrazine solution. In Experiments 1, 2, 3, 8, and 9, the hydrazine solution was heated to the boiling point; in 4 and 5 it was held at room temperature; in 6 and 7 the temperature was gradually raised, during the addition of the oxidizing agent, from about 20° to 100°. In no case was more than a small amount of hydronitric acid formed, but ammonia was invariably found to be one of the reaction products. The two quantitative experiments, 8 and 9, serve to show the magnitude of the yields of ammonia, and to illustrate the influence of a large excess of sulphuric acid upon the yield. With regard to the effect of temperature it may be said that in general the reaction proceeds more rapidly, and with formation of larger amounts of ammonia, as the temperature is raised. Two additional experiments were performed in which the reacting substances were mixed and were allowed to stand at room temperature for 30 hours. Traces of hydronitric acid and appreciable amounts of ammonia were formed.

By means of a second series of experiments, the details of which are not given in the table, it has been demonstrated that hydrazine dichloride in the presence of hydrochloric acid reacts with chromic acid, yielding considerable amounts of ammonia, and in some instances traces of hydronitric acid. Even at room temperature, under conditions identical with those prevailing in the experiments of Seubert and Carstens,[1] small amounts of ammonia were invariably formed.

In the attempt to throw some light upon the reaction that takes place when hydrazine and hydroxylamine are simultaneously oxidized in acid solution by means of chromic acid,[2] a number of experiments have been performed, with the following results: (1) Traces, only, of hydronitric acid were formed when hydrazine alone was treated in acid solution with chromic acid; (2) no hydronitric acid was formed when hydrazine and hydroxylamine were heated together in the absence of oxidizing agents, in acid solution; (3) appreciable amounts of hydronitric acid were obtained when hydrazine sulphate in the presence of sulphuric acid was treated at 100° either (*a*) with the solution obtained by bringing hydroxylamine, in acid solution, into contact with the proper amount of chromic acid to destroy the hydroxylamine without leaving an excess of the oxidizing agent, or (*b*) with the gaseous oxidation products of the reaction between hydroxylamine and chromic acid in acid solution. Although the amounts of hydronitric acid obtained in the third series of experiments are much smaller than those obtainable by the simultaneous oxidation of hydrazine and hydroxylamine, it seems reasonable to suppose that the formation of the acid may be ascribed, at least in part, to the initial oxidation of the hydroxylamine and subsequent reaction between the hydrazine and the products of the first reaction.

Action of Various Other Oxidizing Agents upon Hydrazine Sulphate. (*a*) *Mercuric Oxide.*—In the first three experiments 75 cc. of a one per cent. solution of hydrazine sulphate, to which had been added respectively 0 cc., 10 cc., and 25 cc. of concentrated sulphuric acid, were heated in a distilling flask with an excess of red mercuric oxide. In the fourth experiment 10 cc. of a concentrated solution of sodium hydroxide were added instead of the sulphuric acid. In the fifth, sixth, and seventh, 50 cc. of the hydrazine solution, to which 0 cc., 10 cc., and 25 cc. of concentrated sulphuric acid had been added, were heated with an excess of yellow mercuric oxide. In the eighth experiment 20 cc. of the sodium hydroxide solution were added instead of the acid. The hydrazine was oxidized in each case, but no perceptible amount of either hydronitric acid or ammonia was formed during the reaction. When yellow mercuric oxide was added a little at a time, however, to a slightly alkaline solution of hydrazine sul-

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[1] *Loc. cit.*

[2] Tanatar, *Ber.*, **35**, 1810–11 (1902).

phate held at a temperature of 0°, appreciable amounts of both hydronitric acid and ammonia were formed.

(*b*) *Mercuric Chloride.*—Three experiments were performed, in which an excess of a saturated solution of the mercuric salt was added drop by drop to 75 cc. of the hydrazine solution containing respectively 0 cc., 10 cc., and 25 cc. of sulphuric acid, and heated to the boiling point. The hydrazine was oxidized, but no hydronitric acid or ammonia could be detected in the products of the reaction.

(*c*) *Arsenic Pentoxide.*—Fifty cc. portions of the hydrazine sulphate solution were treated respectively with 10 cc. and 25 cc. of sulphuric acid, and were then heated to boiling in the presence of an excess of solid arsenic pentoxide. Distinct indications of the formation of hydronitric acid and ammonia were obtained in each case. The reaction apparently proceeded very slowly.

(*d*) *Antimony Pentoxide.*—No hydronitric acid was formed when 50 cc. portions of the hydrazine solution in the presence of 10 cc. of sulphuric acid were heated with an excess of sodium pyroantimonate, potassium antimonate, or antimony pentoxide, respectively. In the presence of 10 cc. of a concentrated solution of sodium hydroxide, however, both hydronitric acid and ammonia were formed in each case.

(*e*) *Ozone.*—Several experiments were performed in which ozonized oxygen was passed through acid, neutral, and alkaline solutions of hydrazine sulphate at various temperatures. In every case the hydrazine was gradually oxidized, at a rate that did not appear to undergo any very marked change when the temperature was raised. In one experiment the ozone was passed for over three hours through 100 cc. of a strongly alkaline solution of hydrazine sulphate held at a temperature of from 60° to 90°. Neither hydronitric acid nor ammonia was formed under these conditions, although all of the hydrazine was decomposed. In another experiment, in which an alkaline solution of hydrazine sulphate, heated to the boiling point, was subjected to the action of a current of ozonized oxygen for about 75 minutes, a very appreciable amount of hydronitric acid was obtained. The residual solution was found to contain a considerable quantity of unoxidized hydrazine. In none of the experiments was ammonia positively identified as one of the oxidation products.

(*f*) *Chromic Sulphate.*—A 50 cc. sample of the hydrazine solution, to which had been added 10 cc. of sulphuric acid, was heated to the boiling point. A solution of chromic sulphate was introduced drop by drop. Shortly before the point in the distillation had been reached at which white fumes began to appear in the flask, hydronitric acid was formed.

(g) *Selenious and Selenic Acids.*—No hydronitric acid was formed in either acid or alkaline solution by the action of selenious acid or of selenium dioxide upon hydrazine sulphate. By the gradual addition of a dilute solution of selenic acid, however, to 50 cc. of the hydrazine solution with 10 cc. or with 15 cc. of sulphuric acid, appreciable amounts of hydronitric acid were obtained.

(*h*) *Telluric Acid.*—Large quantities of both hydronitric acid and ammonia were formed by the action of an excess of solid telluric acid upon 100 cc. portions of the hydrazine solution, to which had been added from 10 to 25 cc. of sulphuric acid.

(*i*) *Molybdenum Trioxide.*—In alkaline solution the reaction was found to take place very slowly. Ammonia was found in the products of the reaction, but no hydronitric acid. When 75 cc. portions of the hydrazine solution, acidified respectively with 10 cc. and 25 cc. of sulphuric acid, were subjected to the action of an excess of molybdenum trioxide, appreciable quantities of both hydronitric acid and ammonia were formed. By means of a blank experiment it was shown that the molybdenum trioxide employed in the experiments contained no recognizable trace of ammonia. Two 100 cc. samples of the hydrazine solution were treated with 10 cc. and 25 cc. of sulphuric acid, and were heated to boiling. An excess of the oxidizing agent in the form of an aqueous suspension was added drop by drop. In each case appreciable amounts of hydronitric acid were formed. In the first experiment 26.1 per cent. of ammonia was obtained, and in the second experiment 18.2 per cent.

(*j*) *Ferric Oxide.*—Three qualitative experiments were first performed in which 75 cc. samples of the hydrazine solution, treated with 5 cc., 10 cc., and 25 cc. of sulphuric acid, were subjected to the action of an excess of hydrated ferric oxide. No trace of hydronitric acid was found in the distillates, but large quantities of ammonia were formed during the reaction. From two 100 cc. samples, similarly oxidized in the presence of 10 cc. and 25 cc. of sulphuric acid, were obtained quantities of ammonia corresponding to a yield of 1.73 and 1.65 molecules of ammonia, respectively, from 2.00 molecules of hydrazine. The ferric oxide and the sulphuric acid used throughout the experiments were found to contain no detectable amount of ammonia.

(*k*) *Nickel Sesquioxide.*—Three 50 cc. portions of the hydrazine solution, to which had been added 0 cc., 10 cc., and 25 cc. of sulphuric acid, were treated with an excess of nickel sesquioxide, which was suspended in water and added drop by drop. In the third experiment a very faint indication of the formation of hydronitric acid was obtained. In the other two no perceptible trace of the acid was formed. Ammonia was formed in all of the experiments. By means of a blank test it was shown that the oxidizing agent used throughout the work contained no ammonia.

(*l*) *Cobalt Sesquioxide.*—Three 50 cc. samples of the hydrazine solution, containing 0 cc., 10 cc., and 25 cc. of sulphuric acid were treated with an excess of the oxidizing agent, which was shown by means of a blank experiment to be free from ammonia. In the second and third experiments traces of hydronitric acid were formed. Ammonia was obtained in all of the experiments.

Summary and Discussion of Experimental Results.

In performing the experiments described in the four articles thus far published in the present series the authors have had the following ultimate objects in view:

(1) Investigation of the mechanism of the reaction that takes place between hydrazine and the numerous oxidizing agents under various conditions, and formulation of a suitable theory to account for the observed facts.

(2) Tentative classification of the oxidizing agents on the basis of their behavior toward hydrazine.

(3) Selection of the oxidizing agent best adapted for the preparation of hydronitric acid from hydrazine.

(4) Selection of the oxidizing agent best adapted for the detection of hydrazine.

(5) Study of the reactions that have been used by previous investigators in the determination of hydrazine, or in the determination of certain oxidizing agents.

(6) Expression of the analogy existing between the reactions involved in the oxidation of hydrazine, and those involved in the oxidation of certain organic substitution products of hydrazine.

These topics will now be discussed in the order given.

Mechanism of the Reactions Involved in the Oxidation of Hydrazine.—Methods for the formation of hydronitric acid from hydrazine may be separated into two divisions, according as the other substance used in the reaction does or does not contain nitrogen. The behavior of hydrazine toward such substances as nitrous acid[1] or its salts[2] and esters,[3] nitrogen trichloride,[4] and nitric acid[5] has already been studied by previous investigators.

The action of hydrazine upon nitrous acid is assumed by Angeli to be in conformity with the equations

$$N_2H_4 + HNO_2 = NH_2.N:N.OH + H_2O$$
$$NH_2.N:N.OH = HN_3 + H_2O.$$

Francke has shown that nitrous oxide and ammonia[6] are formed by the interaction of hydrazine sulphate and sodium nitrite.

Thiele suggests that the formation of nitrous oxide in the experiments of Dennstedt and Göhlich may be due either to the intermediate formation of "dinitrosohydrazine" or to the interaction of hydronitric acid with nitrous acid, the final products in either case being nitrous oxide, nitrogen, and water.

There is still much to be learned concerning the mechanism of the reactions between hydrazine and nitrogen trichloride or nitric acid, and the reactions involved in the simultaneous oxidation[7] of hydrazine and

[1] Curtius, *Ber.*, **26**, 1263 (1893).

[2] Angeli, *Atti accad. Lincei* [5], **2**, I, 569 (1893); *Chem. Centr.*, **1893**, II, 559. Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876 (1897); *Chem. Centr.*, **1897**, II, 1093. De Girard and de Saporta, *Bull. soc. chim.* [3], **31**, 905–7 (1904). See also Rimini, *Atti accad. Lincei* [5], 14, I, 386–92 (1905); *Chem. Centr.*, **1905**, I, 1546. E. Francke, *Ber.*, **38**, 4102 (1905).

[3] Thiele, *Ber.*, 41, 2681–3, 2806–11 (1908). Stollé, *Ber.*, 41, 2811–13 (1908).

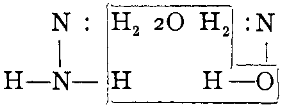
[4] Tanatar, *Ber.*, **32**, 1399 (1899).

[5] Sabanejeff and Dengin, *Z. anorg. Chem.*, 20, 21 (1899).

[6] The formation of ammonia by the action of nitrous acid upon hydrazine has been corroborated by a series of hitherto unpublished experiments performed in this laboratory some months ago by Mr. M. J. Brown. From 115 to 150 cc. of a one per cent. solution of potassium nitrite were introduced drop by drop into 100 cc. portions of a one per cent. solution of hydrazine sulphate containing from 0.5 to 5.0 cc. of concentrated sulphuric acid. The amounts of hydronitric acid formed under these conditions correspond to from 0.18 to 0.28 molecule per molecule of hydrazine used. The amounts of ammonia correspond to from 0.19 to 0.66 molecule per molecule of hydrazine. In the opinion of the authors the reaction between nitrous acid and hydrazine in aqueous solution has not yet been studied under various conditions in sufficient detail to warrant the formulation of a satisfactory hypothesis to account for the observed phenomena. From the facts thus far known it seems reasonable to suppose that while a part of the nitrous acid may act in aqueous solution as ethyl nitrite acts in ethereal solution, condensing with the hydrazine to form hydronitric acid, another part may decompose the hydrazine after the manner of certain oxidizing agents containing no nitrogen, with formation of hydronitric acid and ammonia. It is also conceivable that during this process the nitrous acid might under proper conditions be reduced to hyponitrous acid or nitrous oxide.

[7] Tanatar, *loc. cit.*

hydroxylamine. It is impossible at the present time to state with certainty whether or not the nitrogen of these other substances participates in every case in the synthesis of the nitrine group. It is presumable, however, that at least a part of the nitrogen is utilized in this way. If this is true, the reactions involved in the simultaneous oxidation of hydrazine and hydroxylamine, whether explained by a direct condensation as indicated in the following expression



$$\begin{array}{ll} \mathrm{N:} & \mathrm{H_2\ 2O\ H_2\ :N} \\ | & \qquad\qquad\ \ | \\ \mathrm{H{-}N{-}} & \mathrm{H\qquad\ H{-}O} \end{array}$$

or by the initial formation of nitrous acid, nitric acid, or some other nitrogen compound by oxidation of the hydroxylamine,[1] and subsequent condensation of the hydrazine with these substances, are comparable with the reactions between hydrazine and substances containing nitrogen, rather than with the reactions between hydrazine and nitrogen-free oxidizing agents.

The oxidation of hydrazine by means of substances containing no nitrogen[2] proceeds in all probability in a different way from that just illustrated. In connection with the work described in the four articles of the present series, the behavior of hydrazine toward more than thirty of these oxidizing agents has been studied with especial reference to the formation of hydronitric acid and ammonia. From this view-point the reaction seems to proceed, with different oxidizing agents in acid solution, in at least three different ways: (*a*) with formation of fairly large amounts of hydronitric acid and ammonia; (*b*) with formation of little or no hydronitric acid, but large amounts of ammonia; (*c*) with formation of little or no hydronitric acid and ammonia. Typical of the oxidizing agents ordinarily reacting with hydrazine in acid solution in the three ways, respectively, are (*a*) hydrogen peroxide, potassium chlorate, and potassium persulphate; (*b*) potassium permanganate, manganese dioxide, and ferric oxide; (*c*) potassium iodate, mercuric oxide, and mercuric chloride.

On the assumption that the first step in the oxidation of a hydrazine molecule is the removal from it of two hydrogen atoms, there are two different ways in which the process of oxidation may be considered to commence. First, by removal of two hydrogen atoms joined to the same nitrogen atom. The residue H_2: N.N: might then undergo further loss of hydrogen, with liberation of molecular nitrogen, or else under proper conditions combine, at least transitorily, with another residue of the same

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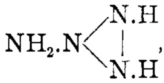
[1] Bertoni, *Gazz. chim. ital.*, **9**, 571; *J. Chem. Soc. London*, **38**, 298 (1880).

[2] Ammonium metavanadate in the presence of an excess of sulphuric acid may for the present purpose be included in this class of substances. See THIS JOURNAL, **29**, 1305 (1907).

sort, forming "tetrazone."[1] Second, by removal of two hydrogen atoms joined to different nitrogen atoms. The residue $H.\dot{N}.\dot{N}.H$ might then by further oxidation yield free nitrogen, it might take the form of "diimide," $H.N:N.H$,[2] or it might unite with another residue of the same sort, yielding "tetrimide." By simultaneous oxidation of "diimide" and hydrazine, with subsequent combination of the residues, it is conceivable that the hypothetical "buzylene"[3] or "diazohydrazine" might be formed as an intermediate product. The union of $H_2:N.N:$ with $H.\dot{N}.\dot{N}.H$ would result in the formation of "aminotriimide." The condensation of two "diimide" molecules would yield "diiminohydrazine,"[4] $H.N:N.N:N.H$.

On the assumption that the first step in the process of oxidation is the removal of one hydrogen atom from each of two hydrazine molecules, it is possible that "buzane"[5] or "hydrotetrazone," $NH_2.NH.NH.NH_2$, might be formed at first, yielding on further oxidation one or more of the intermediate products to which reference has been made in the preceding paragraph.

The behavior of hydrazine toward the three groups of oxidizing agents may be explained as follows:

(*a*) Oxidizing agents such as hydrogen peroxide, potassium chlorate, and potassium persulphate decompose hydrazine sulphate in acid solution, yielding varying amounts of some such intermediate condensation product as "buzylene," $HN:N.NH.NH_2$, or "aminotriimide,"  $NH_2.N\genfrac{}{}{0pt}{}{\diagup N.H}{\diagdown N.H}$,

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[1] Numerous derivatives of this hypothetical compound, including aliphatic, aromatic, and mixed substitution products, have been prepared, usually by cautious oxidation of unsymmetrical secondary hydrazines with mercuric oxide or ferric chloride. See E. Fischer, *Ann.*, **190,** 67–183 (1878), page 166; **199,** 281–332 (1879), page 319; Renouf, *Ber.*, **13,** 2169–2174 (1880); Michaelis, *Ann.*, **252,** 266–317 (1889); Franchimont and Van Erp, *Rec. trav. chim.*, **14,** 317–26 (1895); Angeli, *Atti accad. Lincei* [5], **9,** II, 180–3 (1900); *Chem. Centr.*, 1900, II, 857. J. R. Bailey, THIS JOURNAL, **26,** 1006 (1904); **30,** 1412–18 (1908).

[2] The diazo and azo compounds may obviously be regarded as derivatives of this hypothetical compound.

[3] Derivatives have been prepared by Curtius (*Ber.*, **26,** 1263 (1893)), by Wohl (*Ber.*, **26,** 1587 (1893); see also Wohl and Schiff, *Ber.*, **33,** 2741–58 (1900)), and by Stollé (*J. pr. Chem.* [2], **66,** 332–8 (1902)).

[4] Betti, *Gazz. chim. ital.*, **34,** I, 201–12 (1904); *Chem. Centr.*, **1904,** I, 1485.

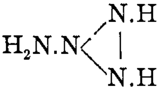
[5] Minunni, *Gazz. chim. ital.*, **22,** II, 217–30 (1892); *J. Chem. Soc. London*, **64,** I, 97 (1893); V. Pechmann, *Ber.*, **26,** 1045–7 (1893); V. Pechmann and Runge, *Ber.*, **27,** 2920 (1894); Ingle and Mann, *J. Chem. Soc. London*, **67,** 606–16 (1895); Minunni and Rap, *Gazz. chim. ital.*, **26,** I, 441–56 (1896); *J. Chem. Soc. London*, **72,** I, 40 (1897); Minunni, *Gazz. chim. ital.*, **27,** II, 215–35, 244–62, 277–92 (1897); **29,** II, 420–34 (1899); *J. Chem. Soc. London*, **74,** I, 190, 191, 192 (1898); **78,** I, 259 (1900); Curtius, *J. pr. Chem.* [2], **62,** 83–126 (1900), page 105.

which in turn decomposes with formation of hydronitric acid and ammonia. This reaction may be considered to take place in two stages:

$$2N_2H_4 + 2O = N_4H_4 + 2H_2O$$
$$N_4H_4 = HN_3 + NH_3$$

The following facts may be cited in support of this hypothesis. E. Fischer[1] has shown that diazobenzenimide and aniline are obtained by the oxidation of phenylhydrazine under certain conditions. Curtius[2] has obtained similar products by the decomposition of certain buzylenes, and has expressed the reaction by means of the equations

$$R_I NH.NH.N\!:\!N.R_{II} = R_I N_3 + R_{II} NH_2$$
$$R_I NH.NH.N\!:\!N.R_{II} = R_{II} N_3 + R_I NH_2.$$

Wohl and Schiff[3] consider that the formation of the azoimides and amines either directly by the action of diazo compounds upon hydrazines, or indirectly by decomposition of the diazohydrazines, is probably due to the intermediate formation of a derivative of the hypothetical compound  which breaks up, especially in acid solution, with formation of the derivatives of hydronitric acid and ammonia.

(*b*) Oxidizing agents of the second class, typified by potassium permanganate, manganese dioxide, and ferric oxide, decompose hydrazine sulphate in acid solution yielding varying amounts of some such intermediate condensation product as "tetrazone," $H_2N.N\!:\!N.NH_2$, which breaks up under the conditions of the experiment with formation of nitrogen and ammonia. The reaction may perhaps be considered to take place in accordance with the equations

$$2N_2H_4 + 2O = N_4H_4 + 2H_2O$$
$$N_4H_4 + H_2O = N_2 + 2NH_3 + O,$$

or may be briefly expressed by means of the single equation

$$2N_2H_4 + O = N_2 + 2NH_3 + H_2O.$$

In support of this hypothesis may be mentioned the following facts. It has been found by E. Fischer[4] that during the oxidation of methylphenylhydrazine with mercuric oxide two distinct processes always take place. A part of the hydrazine is decomposed, with formation of nitrogen and methylaniline, in accordance with the equation

$$2(CH_3)(C_6H_5)N.NH_2 + O = N_2 + 2(CH_3)(C_6H_5)NH + H_2O,$$

while another part yields dimethyldiphenyltetrazone, as follows:

$$2(CH_3)(C_6H_5)N.NH_2 + 2O = (CH_3)(C_6H_5)N.N\!:\!N.N(C_6H_5)(CH_3) + 2H_2O.$$

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[1] *Ber.*, **10**, 1336 (1877).

[2] *Ibid.*, **29**, 759–83 (1896), page 781.

[3] *Loc. cit.*

[4] *Ann.*, **199**, 281–332 (1879), page 323.

It has been shown, moreover, by the same author, that by heating a dilute solution of tetrethyltetrazone with hydrochloric acid to a temperature of from 70° to 80°, decomposition is effected as indicated by the equation

$$(C_2H_5)_2N.N:N.N(C_2H_5)_2 + H_2O = N_2 + (C_2H_5)_2NH + C_2H_5NH_2 + C_2H_4O.$$

Renouf[1] has studied the decomposition of tetramethyltetrazone in acid solution, and has expressed the reaction by means of an equation corresponding exactly with that given by Fischer for tetrethyltetrazone.

(*c*) Oxidizing agents of the third class, as for example potassium iodate, mercuric oxide, and mercuric chloride, decompose hydrazine sulphate in acid solution at a temperature of 100° apparently without formation of intermediate condensation products. In case such products are formed at first, as might be thought possible in consideration of the behavior of mercuric oxide, for example, toward unsymmetrical secondary hydrazines, it seems certain that they are soon completely oxidized, without formation of hydronitric acid or ammonia.

With certain of the oxidizing agents it seems reasonable to suppose that the reaction may proceed in two ways, or even in all three ways, at once. In general it may be said that the progress of the reaction in any case is very largely influenced by the temperature, by the concentration of the hydrazine, of the sulphuric acid or the alkali, and of the oxidizing agent, by the potential of the oxidizing agent, and by the method adopted in bringing the substances together. Against the possible contention[2] that the differences in the yields of hydronitric acid obtained under different conditions with a given oxidizing agent, or under similar conditions with various oxidizing agents, are to be accounted for wholly or chiefly by the varying oxidizability of hydronitric acid under different conditions, may be cited the following arguments: The amounts of ammonia actually formed by oxidizing agents of the second class are very often considerably larger than the theoretical amount required from those of the first class. Moreover, with a given oxidizing agent of the first class the yields of hydronitric acid usually vary inversely with the yields of ammonia. If the lowering of the yield of hydronitric acid effected by changing the oxidizing agent, or by varying the conditions with a given oxidizing agent, be attributed to the oxidation of the acid, then it would be difficult to account for the concomitant rise in the percentage of ammonia formed, without the assumption that ammonia might be obtained as a product of the oxidation of hydronitric acid. It has already been shown in this laboratory that no ammonia is formed by the oxidation of the acid with potassium permanganate.[3]

Chattaway[1] has explained the behavior of primary aromatic hydrazines

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[1] *Loc. cit.*

[2] In this connection see Thiele, *Ber.*, 41, 2681 (1908).

[3] Dennis and Browne, THIS JOURNAL, 26, 577–612 (1904), page 608.

toward oxidizing agents on the assumption that one of the hydrogens of the hydrazino group is first attacked, with the result that a hydroxyhydrazine, R.NH.NH.OH, is produced. This substance is then supposed to decompose, yielding the corresponding hydrocarbon RH, nitrogen, and water. When a very energetic oxidizing agent is employed, a dihydroxyhydrazine, R.NH.N$(OH)_2$, may be first formed, and this compound may be subsequently broken up so as to form a phenol, nitrogen, and water. This hypothesis is in no way contradictory to that stated in the preceding paragraphs, but it offers no explanation of the nitrogen coupling involved in the formation of hydronitric acid.

Tentative Classification of the Oxidizing Agents on the Basis of Their Behavior toward Hydrazine.—It was at first hoped that it might be possible to establish a simple relationship between the potential of the various oxidizing agents and their ability to produce hydronitric acid from hydrazine. So many different factors have been found to influence the reactions, however, that the project was soon abandoned. In the foregoing paragraphs it has been shown that the oxidizing agents may in general be divided into three classes, the characteristics of which have already been discussed. On the basis of the maximum yields of hydronitric acid obtained in each case, the principal oxidizing agents may be arranged in the following order: Potassium persulphate, 40.3; hydrogen peroxide, 38.5; potassium chlorate, 22.4; potassium perchlorate, 22.4; vanadium pentoxide, 13.6; potassium bromate in the presence of silver sulphate, 11.7; potassium iodate in the presence of silver sulphate, 11.2; potassium bromate, 6.68; lead dioxide, 4.10; potassium permanganate, 3.19; manganese dioxide, 2.32.

One interesting fact that becomes apparent from a study of the numerous oxidizing agents is the similarity that seems to exist between oxidizing agents derived from elements related more or less closely in the periodic arrangement. It has been shown, for example, that the tendency of chlorates, bromates, and iodates, as well as the tendency of free chlorine, bromine, and iodine, to produce hydronitric acid, varies inversely with the atomic weight of the halogen; that while sulphuric acid yields no hydronitric acid, selenic acid yields an appreciable amount, and telluric acid a larger amount of this substance; that the behavior of potassium permanganate is rather similar to that of potassium chromate, while the behavior of ferric oxide is not widely different from that of the nickel and cobalt sesquioxides. Appreciable amounts of hydronitric acid were obtained by the action of the pentoxides of vanadium, arsenic, and antimony. While certain of these apparent analogies may be merely superficial or accidental, it seems probable that the behavior of oxidizing agents toward hydrazine sulphate is at least to some extent dependent upon their position in the periodic arrangement.

Preparation of Hydronitric Acid from Hydrazine.—Hydrogen peroxide has been found to be the most satisfactory of the oxidizing agents studied in the present series, for the preparation of hydronitric acid from hydrazine. Both hydrogen peroxide and hydrazine sulphate are of course readily obtainable in a reasonably pure state, and by means of a single distillation under proper conditions will yield hydronitric acid of a very fair degree of purity. This method has been repeatedly used for the preparation of the acid in this laboratory under circumstances rendering the convenience of the process and the purity of the product of rather greater importance than the yield of acid obtained.[1] No particular effort has been made, in fact, to increase the yield obtainable by this method, although it is possible that by working in non-aqueous solution, or by using an organic derivative of the oxidizing agent, the yield might be greatly improved. Even if this is found to be true, however, it is very unlikely that from given amounts of hydrazine quantities of hydronitric acid approaching in magnitude those obtained by Thiele and by Stollé[2] by the action of alkyl nitrites upon hydrazine will ever be obtained. This is chiefly attributable to the inherent difficulty that ammonia is formed by the action of hydrogen peroxide or similar oxidizing agents upon hydrazine, so that yields corresponding to but one molecule of hydronitric acid from two molecules of hydrazine are probably the highest that can be expected. In the method of Thiele, on the other hand, the yield is twice as great as this theoretical maximum, since the nitrogen atoms of both hydrazine and nitrous acid participate in the synthesis of the nitrine ring.

Detection of Hydrazine.—Since the presence of minute amounts of hydronitric acid may be detected by means of the ferric chloride test,[3] and since hydrazine may be efficiently converted into hydronitric acid, it is apparent that a possible method for the detection of hydrazine consists in converting this substance into the acid by some convenient method, and then identifying the acid in the usual way. The sensitiveness of the method varies of course with the efficiency of the production of hydronitric acid. The method of Thiele, involving the use of ethyl nitrite, is consequently the one to be recommended when very small amounts of hydrazine are to be detected. In certain cases, however, such substances as nitric acid, hydrogen peroxide or potassium chlorate may be used to advantage in the identification of larger amounts of hydrazine. The presence of hydronitric acid or its hydrolyzable derivatives in the substance to be examined for hydrazine would of course interfere with the

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[1] See for example Browne and Lundell, THIS JOURNAL, 31, 435–48 (1909), page 437.

[2] *Loc. cit.*

[3] Dennis and Browne, *Loc. cit.*, page 603.

test. The presence of sulphocyanic, formic, acetic or meconic acid, or of any other substance giving with ferric chloride a reddish coloration, would necessitate the performance of confirmatory tests,[1] unless care had been taken at the outset to remove these substances from the sample.

Determination of Hydrazine by Oxidation Methods, and Determination of Oxidizing Agents by Reduction with Hydrazine.—On the assumption that hydrazine is completely oxidized to nitrogen and water several different methods for its determination have been based upon the action of oxidizing agents. In some cases ammonia is formed as one of the products of the reaction, and in others both ammonia and hydronitric acid. This is also true in the case of certain reactions in which weighed amounts of hydrazine have been utilized in the determination of oxidizing agents. It is entirely possible, of course, that conditions might be found under which in any of these cases the oxidation might be made complete. Positive proof of the quantitative conversion of the hydrazine to nitrogen and water should be obtained, however, before reliance is placed upon any method which under ordinary conditions is subject to the error just mentioned.

Analogy between Hydrazine and its Substitution Products.—In addition to the analogies to which reference has already been made in this summary, may be mentioned the following: (1) Formation of aniline and ammonia, respectively, by the action of Fehling's solution upon phenylhydrazine[2] and hydrazine; (2) formation of diazobenzenimide and hydronitric acid, respectively, by the oxidation of phenylhydrazine[3] and hydrazine with hydrogen peroxide; (3) formation of aromatic azoimides and hydronitric acid, respectively, by the oxidation of primary aromatic hydrazines[4] and hydrazine with various oxidizing agents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ELECTROLYTIC PREPARATION OF THE AMALGAMS OF THE ALKALI AND ALKALI-EARTH METALS.

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The four methods by which alkali and alkali-earth amalgams have been prepared are: 1. Directly from metals. 2. By the action of an amalgam on a salt solution. 3. By the electrolysis of a complex alkali-mercury salt in aqueous solution, with platinum electrodes. 4. By the electrolysis of a salt solution with a mercury cathode.

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

[2] E. Fischer, *Ann.*, 190, 67–183 (1878).

[3] Wurster, *Ber.*, 20, 2631–3 (1887).

[4] Chattaway, *Loc. cit.*