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## ANHYDROUS HYDRONITRIC ACID. I. ELECTROLYSIS OF A SOLUTION OF POTASSIUM TRINITRIDE IN HYDRONITRIC ACID.<sup>1</sup>

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It has been shown by several investigators that anhydrous liquid ammonia is incapable of conducting the electric current except to a very limited extent;<sup>2</sup> that it exhibits remarkable power as a solvent,<sup>3</sup> and that its solutions are in general good conductors of the electric current.<sup>4</sup> It has also been shown that anhydrous hydrazine is a poor conductor of the electric current,<sup>5</sup> that it acts as a solvent toward a number of inorganic salts,<sup>6</sup> and that as an ionizing solvent it is comparable with water.<sup>7</sup>

The electrical conductivity of hydronitric acid in aqueous solution has been determined by Ostwald,<sup>8</sup> by Hantzsch,<sup>9</sup> and by West.<sup>10</sup> Hit-

<sup>1</sup> Reported at the thirty-eighth General Meeting of the American Chemical Society, held at New Haven, Conn., June 30–July 2, 1908.

<sup>2</sup> Cady, *J. Phys. Chem.*, **1**, 707–13 (1896); Goodwin and Thompson, *Phys. Rev.*, **8**, 38 (1899); Frenzel, *Z. Elektrochem.*, **6**, 477–80, 485–9, 493–500 (1900); Franklin and Kraus, *Am. Chem. J.*, **23**, 277–313 (1900); *THIS JOURNAL*, **27**, 191–222 (1905).

<sup>3</sup> Gore, *Proc. Roy. Soc.*, **20**, 441 (1872); **21**, 140 (1873); Franklin and Kraus, *Am. Chem. J.*, **20**, 820–36 (1898).

<sup>4</sup> Cady, *loc. cit.*; Goodwin and Thompson, *loc. cit.*; Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900); **24**, 83 (1900); *THIS JOURNAL*, **27**, 191 (1905); Franklin and Cady, *THIS JOURNAL*, **26**, 499 (1904).

<sup>5</sup> Cohen and de Bruyn, *Proc. K. Akad. Wetensch. Amsterdam*, **5**, 551–6 (1903); *J. Chem. Soc.*, **84**, II, 405 (1903).

<sup>6</sup> Lobry de Bruyn, *Rec. trav. chim.*, **15**, 174–84 (1896).

<sup>7</sup> Cohen and de Bruyn, *loc. cit.*

<sup>8</sup> See Curtius and Radenhausen, *J. pr. Chem.*, [2], **43**, 207 (1891).

<sup>9</sup> *Ber.*, **32**, 3066 (1899).

<sup>10</sup> *J. Chem. Soc.*, **77**, 705 (1900).

torf<sup>1</sup> has investigated the behavior of ammonium trinitride in aqueous solution toward the electric current. Peratoner and Oddo<sup>2</sup> have electrolyzed solutions of hydronitric acid and of sodium trinitride with a view of investigating the possible formation of polymeric nitrogen,<sup>3</sup> which they assumed might be obtained in the form of argon. Szarvasy,<sup>4</sup> in connection with a study of the behavior of the various hydrides of nitrogen toward the electric current, has electrolyzed solutions of hydronitric acid and of sodium trinitride. "Slight traces of ammonia, but no oxidation products of nitrogen were found in the electrolyzed liquid. In some of the experiments the ratio of hydrogen to nitrogen was found to be less<sup>5</sup> than that required by the expression  $H_2:3N_2$ . The deficiency of nitrogen seemed to indicate that some condensation of this element to a polymeride of the type  $N_3$  or  $N_6$  had taken place on the anode during the electrolysis. In order to test this possibility, density determinations of the gas evolved under two sets of conditions were made, but in each case the values obtained proved it to be pure nitrogen." Peratoner and Oddo<sup>6</sup> have expressed the opinion that the deficiency of nitrogen observed in the experiments of Szarvasy might be attributed to the influence of secondary reactions.

In 1891 Curtius and Radenhausen<sup>7</sup> prepared anhydrous hydronitric acid by dehydration, with calcium chloride, of the 91 per cent. acid obtained by repeated fractionation of an aqueous solution of the substance. The anhydrous acid is described as a colorless, mobile liquid which boils without decomposition at  $37^\circ$ , is miscible with water and alcohol, possesses an unbearable odor, explodes violently when brought into contact with a hot object, and sometimes explodes spontaneously even at room temperature. Dennis and Isham<sup>8</sup> prepared anhydrous hydronitric acid by treatment of dry potassium trinitride with sulphuric acid (two

<sup>1</sup> *Z. physik. Chem.*, **10**, 593 (1892).

<sup>2</sup> *Gazz. chim. ital.*, **25**, II, 13 (1895); *Chem. Centralbl.*, **1895**, II, 864.

<sup>3</sup> Dennstedt (*Chem.-Ztg.*, **19**, 2164 (1895); *Chem. Centralbl.*, **1896**, I, 191) has also suggested the possible identity of the hypothetical polymer,  $N_3$ , with argon. Dennstedt and Göhlich (*Chem.-Ztg.*, **21**, 876-7 (1897); *Chem. Centralbl.*, **1897**, II, 1093) have attempted to prepare this polymer by the oxidation of hydronitric acid in aqueous solution with potassium permanganate. Compare Dennis and Browne, *THIS JOURNAL*, **26**, 577-612 (1904), page 607, or *Z. anorg. Chem.*, **40**, 68-109 (1904), page 104. Hantzsch (*Ber.*, **33**, 522 (1900)) has endeavored to obtain the polymer ( $N_3$ )<sub>2</sub> by means of the reaction between silver trinitride and iodine trinitride, as expressed by the equation  $AgN_3 + IN_3 = AgI + (N_3)_2$ .

<sup>4</sup> *J. Chem. Soc.*, **77**, 603 (1900).

<sup>5</sup> That the author intended to make an exactly opposite statement is shown by his next sentence.

<sup>6</sup> *Gazz. chim. ital.*, **30**, II, 95-6 (1900); *Chem. Centralbl.*, **1900**, II, 660.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> *THIS JOURNAL*, **29**, 216-223 (1907).

parts of acid to one part of water, by volume). The liquid obtained by this method was shown by analysis to contain 99.94 per cent. of hydronitric acid. The melting point of the substance was found to be at  $-80^{\circ}$ . The results obtained in a determination of the vapor density indicate that at  $62^{\circ}$  hydronitric acid has the molecular formula  $\text{HN}_3$ .

From the behavior of anhydrous ammonia and anhydrous hydrazine toward the electric current, and from the ability of each of these substances to act as an ionizing solvent, it seems reasonable to suppose (1) that anhydrous hydronitric acid should show a very low electrical conductivity, (2) that it should possess the power of dissolving numerous substances, and (3) that solutions of inorganic salts in hydronitric acid should be relatively good conductors of the electric current.

In the present article is recorded the first of a series of researches undertaken for the purpose of demonstrating the foregoing statements, of studying the possible formation of the polymer,  $(\text{N}_3)_2$ , and of investigating the chemical behavior of anhydrous hydronitric acid toward a number of other substances. The work has been undertaken at the suggestion of Professor Dennis, and is to be regarded as a continuation of the researches of Dennis and Isham.<sup>1</sup>

*Preparation of Materials Used in the Experiments.*—The hydronitric acid employed in all experiments except the last four was prepared by the Wislicenus<sup>2</sup> method as modified by Dennis and Browne.<sup>3</sup> In order to eliminate the possible objection that certain phenomena observed during the experiments might be attributable to the presence of impurities in the acid prepared by this method, the acid used in the last four experiments was prepared by the entirely different hydrogen peroxide method.<sup>4</sup>

The potassium trinitride was invariably allowed to crystallize from an aqueous solution which had been slightly acidified with hydronitric acid,<sup>5</sup> and the crystals were thoroughly dried *in vacuo* at room temperature.

The anhydrous hydronitric acid was prepared by the method of Dennis and Isham. A weighed amount of the dry potassium trinitride was introduced into a 250 cc. distilling flask. Sulphuric acid (2 : 1) was slowly dropped upon the salt from a separatory funnel, and a slow current of pure, dry air was passed through the flask, which was in general partly immersed in water heated to about  $40^{\circ}$ . The hydrogen trinitride vapor was carried by the current of air from the flask through a glass-stoppered U-tube filled with calcium chloride, into the electrolytic cell, where it

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

<sup>2</sup> *Ber.*, 25, 2084 (1892).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *THIS JOURNAL*, 27, 551 (1905).

<sup>5</sup> *Ibid.*, 20, 225 (1898).

was condensed with the aid of liquid air. In one experiment the attempt was made to condense the vapor with the aid of ice. It was found, however, that the greater part of the vapor remained uncondensed, and was carried from the cell by the current of air. This indicates that hydronitric acid has a very appreciable vapor pressure at  $0^{\circ}$ , and that with the particular form of apparatus employed in these experiments, it is necessary to use a much more efficient refrigerant than ice, in order to insure complete condensation of the vapor.

*Apparatus Employed in the Experiments.*—In designing a suitable electrolytic cell it was found necessary to keep in mind the following desiderata: The cell should be of such form or character that (1) the hydronitric acid may be readily condensed and readily distilled off, as occasion requires; (2) the hydronitric acid may be kept at any desired temperature within reasonable limits; (3) the gases liberated during the electrolysis of solutions of potassium trinitride in hydronitric acid may be collected and drawn from the cell; (4) leakage of the poisonous fumes of the acid is prevented; (5) the smallest possible amount of the acid suffices for the work. The desirability of the fifth precaution becomes evident when the explosive character of the acid is borne in mind.

After considerable preliminary experimentation the form of apparatus shown in Fig. 1 was adopted. This consists essentially of the U-tube *A* (10 cm. high, 1 cm. inner diameter), the left arm of which is provided with a small bulb. Each arm of the U-tube is furnished with a side-tube, *S* and *S'*, of 4 mm. inner diameter, which slopes in slightly toward the center. The bottom of the U-tube is made as nearly as possible horizontal except for a slight depression exactly below each arm, which serves the purpose of reducing to the smallest possible amount the necessary quantity of hydronitric acid used. Each arm is carefully fitted with a small cork through which passes a three-way stop-cock, *C* and *C'*, the side-arm of which communicates, through a short capillary elbow-tube, *E* and *E'*, with a Hempel gas burette, *F* and *F'*, which is filled with mercury. Sealed to the stop-cocks are the graduated and calibrated tubes, *B* and *B'*, which have a working capacity of about one cc. each, and which are of sufficiently small diameter to permit the reading of the meniscus level to within 0.01 cc., with a fair degree of accuracy. Through each of these tubes, which extend nearly to the bottom of the depressions in *A*, is fused a platinum wire of 0.3 mm. diameter, to the lower end of which is welded a platinum electrode, *L* and *L'*, 1.0 cm. long and 0.25 cm. wide. From the point at which it is fused into the tube, each of these wires passes upward through the cork to the outside, where connection is made with the rest of the circuit.

A diagrammatic representation of the circuit in which the cell was placed is shown in Fig. 2. The Weston milliammeter used in the ex-

periments is represented by A, and the voltmeter by V. The voltmeter was never thrown into the circuit for more than a moment at a time,

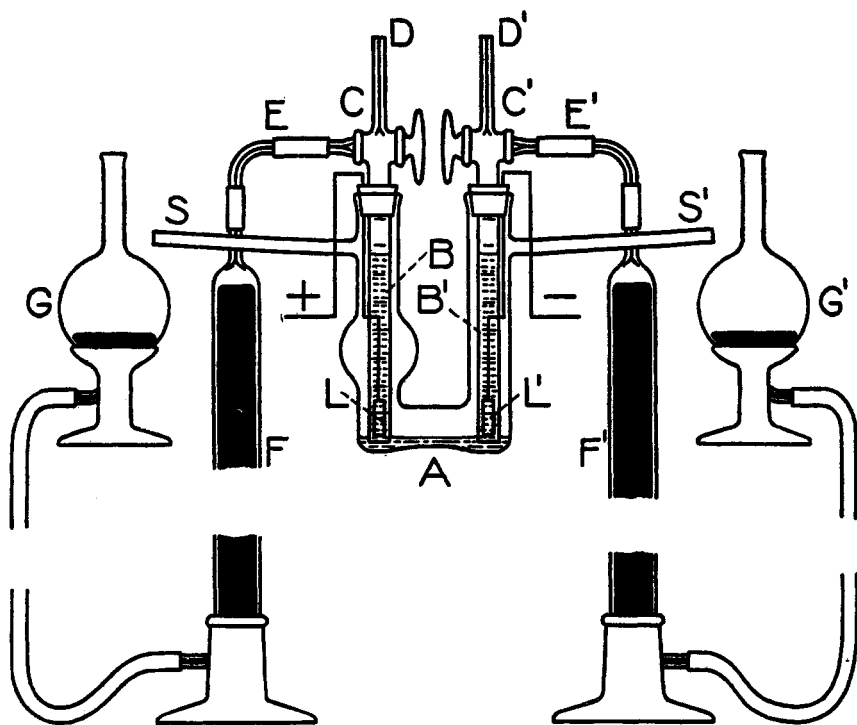


Fig. 1.

and of course this was never done without cutting out the voltmeter. It was at first hoped that the voltmeter readings would furnish a definite indication either of the formation or of the non-formation of a polymeric form of nitrogen. When it was found, however, that apprecia-

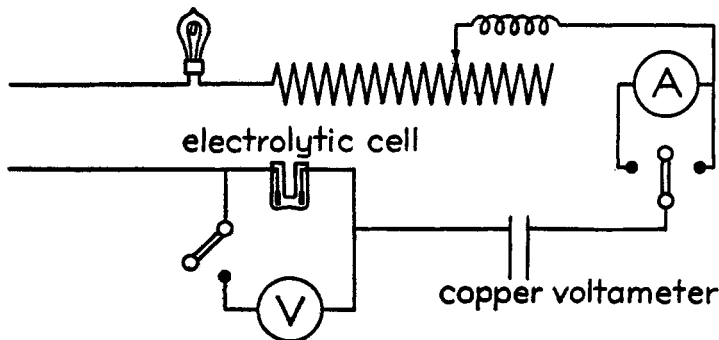


Fig. 2.

ble amounts of ammonia were formed during the electrolysis, it was recognized that the voltameter could give information of but little value for this purpose, and that reliance must be placed upon direct tests or observations rather than upon the voltameter readings.

The apparatus shown in Fig. 3 was constructed with a view of ascertaining whether any indication of the presence of an oxidizing agent could be found in the gaseous products of electrolysis at the anode. The gas burettes shown in Fig. 1 are replaced by small gas pipettes, *F* and *F'*, of 50 cc. capacity, which are joined to the respective stop-cock tubes

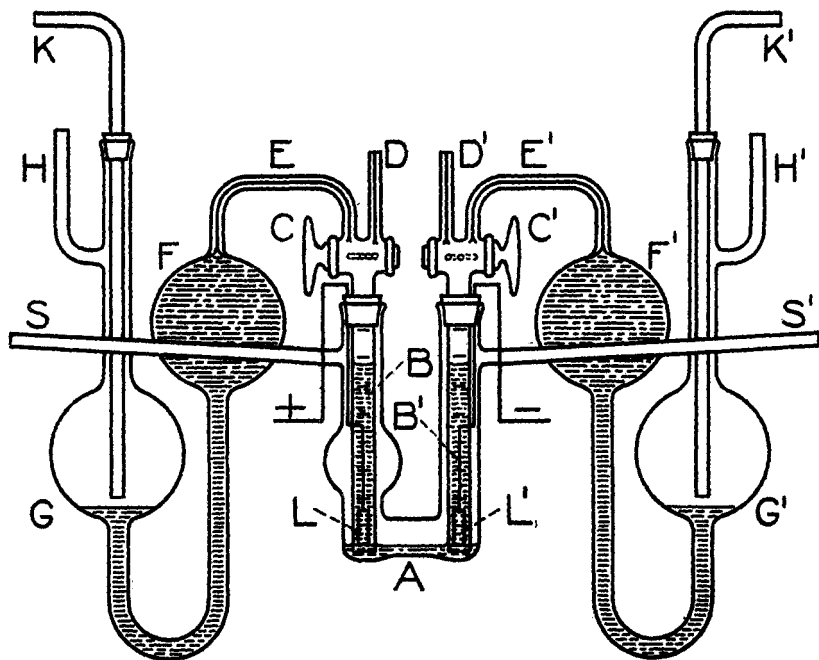


Fig. 3.

*E* and *E'* without the aid of rubber connections. Stop-cocks of a different sort are used, to which are sealed, as before, the graduated and calibrated tubes *B* and *B'*. The pipettes are filled with a one per cent. solution of pure potassium iodide. The solution in the anode pipette *F* is saturated at the outset with nitrogen gas, and that in the cathode pipette *F'* with hydrogen gas. To prevent loss of the collected gases in the pipettes by gradual diffusion through the liquids, slow currents of nitrogen and hydrogen are passed through the tubes *K* and *K'*, respectively, during the course of the experiment. Small test-tubes are inverted over the side-tubes *H* and *H'* in order to prevent diffusion of air into *G* and *G'*.

In Figs. 1 and 3 it has been found necessary, for the sake of clearness, to represent the U-tube and the calibrated tubes within it as having a diameter nearly twice as large, with reference to their length, and with reference to the dimensions of the other parts of the apparatus, as they had in actual practice. Moreover, in the actual apparatus both stop-cocks were in each case turned to the front, so that it was possible to open or to close them from a distance with the aid of a long wooden stick.

In every case the apparatus for the generation of the anhydrous acid was connected to the side-tube  $S'$  of the electrolytic cell. To prevent the escape of fumes into the air, the side-tube  $S$  was closed by a glass stop-cock which was connected on the other side with a chain of absorption bottles containing either an aqueous solution of potassium hydroxide, or, in some experiments, an aqueous or an alcoholic solution of potassium iodide. During the collection of the acid, and during its evaporation at the conclusion of an experiment, the stop-cock was left open; during the electrolysis it was kept closed.

In view of the fact that from two to nine grams of anhydrous hydronitric acid were employed in each experiment, it seemed advisable to adopt unusual precautions to insure the safety of the operators. Two wooden screens, six feet high and three feet wide, made of two-inch pine planks, were placed in front of the apparatus. The stop-cocks were adjusted with the aid of a long stick which passed through a small hole in the screen, and which was provided with a suitable slot at one end. The electrical instruments were located at a distance of about fifteen feet from the cell. By the use of a cathetometer telescope it was found possible to make many of the readings of the gas volumes at some distance from the apparatus. Whenever it became necessary to handle the apparatus, or to stand in its immediate neighborhood, the eyes of the operator were invariably shielded with goggles made of heavy plate glass, and the hands were protected by heavy gloves. When any unusual risk was taken, the additional precaution of holding a plate glass screen before the face, or of wearing a sheet-iron mask, was adopted.

*Electrical Conductivity of Hydronitric Acid.*—It was found by repeated experiments upon different samples of anhydrous hydronitric acid prepared by the methods described in one of the preceding paragraphs, that the acid offers a remarkably high resistance to the passage of the electric current. With a potential difference of about 100 volts between the electrodes, a current of from 0.03 to 0.15 milliampere was obtained at a temperature of 0°. The resistance capacity of the cell shown in Figs. 1 and 3, determined by the Kohlrausch bridge and telephone method,<sup>1</sup> with the aid of a 0.02  $N$  solution of potassium chloride, was 23.55 at 23°. It was found by experiment that the introduction of small amounts

<sup>1</sup> *Wied. Ann.*, 64, 417 (1898); see also *Das Leitvermögen der Electrolyte*, page 1, 1898.

of water, or of dry potassium trinitride, increased the conductivity very greatly. When platinum electrodes were used, without previous treatment with hydrochloric acid to remove the iron, the hydronitric acid soon assumed a brownish-red tint, due to the presence of ferric trinitride. The conductivity of the solution obtained in this way was of course considerably higher than that of the pure acid. No accurate measurements of the conductivity of the acid, or of its solutions, have been made during the present investigation. This work is now in progress, however, and will be made the subject of a separate communication in the near future. From the preliminary work already performed it seems reasonable to expect that when rigid precautions shall have been taken to exclude the minutest traces of moisture, the hydronitric acid will be found to have a specific conductivity of about the same order of magnitude as that of very pure ammonia.

*Purposes of the Electrolytic Experiments.*—The experiments to be described in the following paragraphs have been conducted primarily for the purposes of (1) determining the ratio in which nitrogen and hydrogen are liberated by the action of the current upon solutions of potassium trinitride in hydronitric acid, and of (2) ascertaining whether any preliminary indication may be obtained, under various conditions, of the formation of the hypothetical polymeric modification of nitrogen,  $(N_3)_2$ .

If the liberation of nitrogen and hydrogen gas were to take place quantitatively, the ratio of the gases would obviously correspond to the expression  $3N_2 : H_2$ . The formation of a polymeric modification of nitrogen should tend to lower this ratio, whether the polymer proved to be an insoluble gas, or a soluble gas or liquid which would remain dissolved in the electrolyte. The formation of either ammonia or hydrazine by reduction<sup>1</sup> of a part of the electrolyte, would tend to increase the ratio. The presence of water would tend to lower the ratio, provided that the oxygen and hydrogen gas were liberated quantitatively. In case part of the oxygen were to appear as ozone, the ratio would of course be still further lowered.

Hydronitric acid and its compounds show in many respects a close analogy with the halogen hydracids, especially hydrochloric acid, and their derivatives. Curtius and Rissom<sup>2</sup> have pointed out, for example, that from a comparison of the solubility of the alkali trinitrides with that of the alkali halides, the conclusion may be drawn that the nitrine group  $(N_3)'$  is to be placed between chlorine and bromine in the halogen series. This arrangement is obviously in harmony with the relationship existing between the atomic weights of the halogens and the formula weight of the nitrine group. From the foregoing analogy, and from the

<sup>1</sup> W. T. Cooke, *Proc. Chem. Soc.*, **19**, 213 (1903).

<sup>2</sup> *J. pr. Chem.* [2], **58**, 261–309 (1898), page 306.



repeated failure of attempts made to identify the nitrine group with argon<sup>1</sup> it seems reasonable to infer that the hypothetical polymer nitrine  $(N_3)_2$  should be an active oxidizing agent rather than an inert substance, that it should be able to liberate iodine from acidified solutions of potassium iodide,<sup>2</sup> and that certain of its physical properties should be in conformity with its intermediate position between chlorine and bromine.

By plotting the boiling points and the melting points of chlorine and bromine against the atomic weights of these elements, curves may be obtained from which the probable boiling and melting temperatures for nitrine may be read by interpolation. The boiling point should be located in the neighborhood of  $-19.3^\circ$ , and the melting point at about  $-88^\circ$ . A further reason for the hope that a polymeric form of nitrogen should possess some oxidizing power is furnished by the close proximity of nitrogen to oxygen in the periodic arrangement of the elements, from which it might be argued that a polymeric form of nitrogen would be in a sense analogous to ozone.

*General Procedure Followed in the Electrolytic Experiments.*—At the beginning of each experiment a weighed quantity of dry potassium trinitride, more than sufficient for the preparation of a saturated solution, was introduced through one of the side-tubes *S* and *S'* into the liquefied hydronitric acid. Solution was effected with the aid of a current of dry air. In the experiments during which the electrolytic gases were collected for measurement and analysis, the air present in the tubes *B* and *B'* was then forced out through the capillary tubes *D* and *D'*. This was accomplished by increasing the pressure in the cell, by means of a current of dry air admitted through one or both of the side-tubes *S* and *S'*. By opening each of the stop-cocks *C* and *C'*, the hydronitric acid was caused to rise slowly in the tubes. When the meniscus had been permitted to approach the top of each tube as closely as possible without risk of losing part of the liquid, the stop-cocks were closed, and the electric current was allowed to pass through the cell until the tubes were partly filled with gas. This gas was then caused to escape through *D* and *D'*, and the process of filling and emptying the tubes was once more carried out, in order to complete the removal of the air. The level of the acid in the tubes was then accurately noted, and after the electrical instruments

<sup>1</sup> Peratoner and Oddo, Dennstedt and Göhlich, *Loc. cit.*

<sup>2</sup> The credibility of this hypothesis is enhanced by the hitherto unpublished results of certain experiments performed in this laboratory by Mr. Mortimer J. Brown, in April, 1907. By treating an anhydrous ethereal solution of iodine trinitride, prepared according to the method of Hantzsch (*Ber.*, 33, 522 (1900)), with an insufficient amount of metallic sodium to unite with both nitrine and iodine, Mr. Brown found that iodine was liberated, and sodium trinitride was formed. When an excess of sodium was used, the solution at first assumed a reddish tint, owing to the liberation of iodine, but subsequently lost its color as the iodine combined with the sodium.

had been arranged in the circuit as shown in Fig. 2, the electrolysis was commenced. For the purpose of gaining information concerning the progress of the electrolysis at every stage of the experiment, the current was interrupted, and the gas volumes were read, as soon as one of the tubes had been nearly filled with the gas. The stop-cocks were then turned so that communication was established between the tubes and the gas burettes or pipettes, which had been previously filled with mercury or with an aqueous solution of potassium iodide, and the gas was carefully forced over into the burettes or pipettes. The level of the acid in the tubes was again noted, the circuit was closed, and the gas was collected and transferred as before. These operations were repeated until the samples of gas collected were of convenient volume for analysis. The progressive readings of the volumes of gas in the graduated tubes were of but little value in indicating the absolute amount of gas evolved, as the gases were invariably saturated with hydronitric acid vapor, and were always under slightly reduced pressure. As a means of indicating in a relative way the ratio of nitrogen to hydrogen evolved throughout the entire experiment, however, they were of considerable value. After the conclusion of each experiment, the hydronitric acid was driven from the apparatus by immersing the U-tube in water at a temperature of about  $40^{\circ}$ , and passing a current of air through the tube. In general the acid was absorbed in a solution of potassium hydroxide, with formation of potassium trinitride, which was recovered, dried, and set aside for use in subsequent experiments. In analyzing the samples of gas, use was made of a series of Hempel simple mercury absorption pipettes,<sup>1</sup> each of which contained about 10 cc. of the desired reagent. In the analysis of the anode and cathode gases, reagents saturated respectively with nitrogen and with hydrogen were used. The gas was in each case passed first into a pipette containing potassium hydroxide, to remove the hydronitric acid vapor. The volume was then accurately measured in a burette provided with a water jacket, and containing mercury as the confining liquid. The gas was transferred to a pipette containing alkaline pyrogallol solution, and was then returned to the burette for the final measurement. Small amounts of oxygen were uniformly found in both anode and cathode gases. This was no doubt due to the unavoidable leakage of small amounts of air into the apparatus, which resulted during the frequent opening and closing of the stop-cocks. Corrections were introduced for these small volumes of air. With the apparatus shown in Fig. 3, the following procedure was necessary in removing the gases for analysis. After the hydronitric acid had been distilled off, the U-tube was removed, and the tubes *L* and *L'* were connected in turn with a jacketed Hempel burette filled with mercury. Before the samples of gas were

<sup>1</sup> Hempel-Dennis, *Methods of Gas Analysis*, 1902, page 67.

drawn over into the burette, mercury was caused to rise through *L* and *L'* into *D* and *D'*, the tubes *K* and *K'* were removed, and water was poured into *G* and *G'* until the tubes *H* and *H'* were partly filled. The stop-cocks *C* and *C'* were finally turned so as to establish communication between *F* and *B* and between *F'* and *B'*, and the gases were drawn over into the burette.

*Details of the Electrolytic Experiments. Experiment 1.*—Four and one-half grams of potassium trinitride, corresponding to 2.4 grams of the anhydrous acid, were introduced into the generator. To the liquefied hydronitric acid was added 0.05 gram of dry potassium trinitride, a part of which soon went into solution, as was subsequently indicated by the formation of a crystalline residue around the upper surface of the liquid after some evaporation had taken place. The solution was subjected to the action of the electric current at temperatures varying from about 0° to -80°, with the result that an evolution of gas was observed to take place at both electrodes. The experiment was of a purely qualitative nature.

*Experiment 2.*—Five grams of potassium trinitride were used in the generator, and 0.03 gram in the electrolytic cell. The electrolysis was continued through a period of over three hours, during which time the graduated tubes were partially filled 34 times. The cell was maintained at a temperature of 0° throughout this experiment, and a current of about 3 milliamperes was passed through the solution. The successive readings of the gas volumes indicated the ratio of nitrogen to hydrogen to be in the neighborhood of three to one. The total volume of gas liberated at the anode was 15.9 cc.; the total volume at the cathode was 5.4 cc.

*Experiment 3.*—Five grams of potassium trinitride were used in the generator, and 0.03 gram in the cell. The electrolysis covered a period of about four and one-half hours, and the cell was kept at a temperature considerably below 0°, but always above -80°. A current of about 7 milliamperes was employed. At one time the cathode became covered with a white solid, in all probability potassium trinitride, which for a time greatly hindered the passage of the current. Analysis of the gases obtained at the electrodes showed that 22.7 cc. of nitrogen were liberated at the anode, and 9.0 cc. of hydrogen at the cathode. This corresponds to a ratio of 2.52 to 1. In this experiment, and also in Experiment 2, it was noticed that the surface of the mercury in the anode burette (Fig. 1) was corroded. In neither case was a similar corrosion noted in the cathode burette. Two possible explanations may be offered in attempting to account for this phenomenon: (1) small quantities of ozone may have been formed at the anode, as a result of the possible presence of traces of moisture in the hydronitric acid; (2) small amounts of a polymeric form of nitrogen may have been formed.

*Experiment 4.*—Five grams of potassium trinitride were used in the generator, and 0.03 gram in the cell. The duration of the electrolysis was over two hours, during which time the tubes were partially filled 22 different times. The temperature was held as nearly as possible at -80°, and a current of about 7 milliamperes was passed through the cell. The successive readings of the gas volumes indicated the average ratio of nitrogen to hydrogen to be 2.43 to 1. One very peculiar phenomenon observed throughout this experiment was the sudden liberation of numerous small bubbles of gas in the anode tube, whenever it was refilled with hydronitric acid. This seemed to take place as the result of the slight increase in temperature to which the acid was subjected whenever it was forced up into the tube, which was never cooled to a temperature quite as low as that of the lower part of the cell. This spontaneous evolution of gas was not observed in the cathode tube, except when the acid in this tube was raised so high that a part of the liquid previously located in the neighborhood of the anode was drawn up.

Three possible explanations may be offered: (1) small quantities of ozone may have been formed, and may have decomposed a part of the hydronitric acid, with liberation of gas, when the temperature was very slightly raised; (2) appreciable amounts of nitrogen gas may possibly have remained in solution in the electrolyte at  $-80^{\circ}$ , and may have been liberated at slightly higher temperatures; (3) small amounts of a polymeric form of nitrogen, soluble in hydronitric acid, comparatively stable at  $-80^{\circ}$ , but decomposable at slightly higher temperatures, may possibly have been formed.

*Experiment 5.*—Five grams of potassium trinitride were used in the generator, and 0.03 gram in the cell. The electrolysis was conducted at a temperature of about  $-80^{\circ}$ , without making any effort to read the volume of the gases liberated. When the passage of the current through the cell was discontinued, and the temperature of the electrolyte permitted to rise gradually, a spontaneous evolution of gas was noticed throughout the body of the liquid. After a current of about 7 milliamperes had been again passed through the cell at  $-80^{\circ}$  for some time, the circuit was broken, and 5 cc. of an aqueous solution of potassium iodide were introduced into the cell. A small quantity of iodine, shown by subsequent titration to be equivalent to two drops of a tenth-normal solution of sodium thiosulphate, was liberated.

*Experiment 6.*—The conditions prevailing in Experiment 3 were approximately duplicated, except that a current from two to three times as large was employed. Toward the close of the experiment the temperature of the cell was allowed to rise to about  $20^{\circ}$ . The tubes had just been filled, and the electrolysis was apparently proceeding as usual, when a deafening explosion, accompanied by a clearly perceptible flash of light, took place, with the result that all glass apparatus in the neighborhood of the cell was reduced to an almost impalpable powder. In spite of the extreme violence of the explosion, however, no serious personal injury was experienced by the investigators, both of whom happened to be standing, with faces protected only by goggles, within about three feet of the cell.

*Experiment 7.*—Ten grams of potassium trinitride were introduced into the generator, and 0.2 gram into the cell. The electrolysis covered a period of about two hours, during which time 34 readings were made. The temperature was held at  $0^{\circ}$ , and a current of from 11 to 17 milliamperes was employed. The successive readings of the gas volumes indicated a ratio of somewhat less than 2 : 1. No particular emphasis can be laid upon this experiment, although it was duplicated with substantially identical results, on account of the fact that the platinum electrodes used were found to contain appreciable amounts of iron. The liquid gradually assumed a reddish tint, without doubt due to the formation of ferric trinitride, and on evaporation left a very explosive solid residue of a dark red color.

*Experiment 8.*—Seventeen grams of potassium trinitride were used in the generator, and 0.2 gram in the cell. The electrolysis was continued through a period of six hours, during which time 70 readings were made. The cell was kept at a temperature of  $0^{\circ}$ , and a current of about 7 milliamperes was employed. Analysis of the gases obtained at the electrodes showed that 15.98 cc. of nitrogen (corrected) were liberated at the anode, and 5.22 cc. of hydrogen (corrected) at the cathode, corresponding to a ratio of 3.06 to 1. The residue left after removal of the hydronitric acid from the cell was found to contain appreciable amounts of ammonia, but no hydrazine.

*Experiment 9.*—Seventeen grams of potassium trinitride were used in the generator, and 0.2 gram in the cell. Over 80 readings were made during the seven hours devoted to the electrolysis. A current of about 6 milliamperes was passed through the cell, which was kept at a temperature in the neighborhood of  $-80^{\circ}$ . The corrected volumes of the gases evolved were shown by analysis to be as follows: nitrogen, 21.87 cc.; hydrogen, 7.41 cc. The ratio is consequently 2.95 to 1. The successive readings of

the gas volumes, however, indicated throughout the entire experiment a ratio of about 2.5 to 1. This discrepancy is probably to be explained by the fact that a spontaneous evolution of gas, similar to that noted in Experiment 4, was observed throughout the present experiment. This evolution took place chiefly during the intervals between the reading of the gas volume, and the transfer of the gas to the pipette, and consequently the gas evolved was not taken into account in the successive readings. Appreciable amounts of ammonia were formed during the electrolysis, but no indication of the formation of hydrazine was obtained. The amount of copper precipitated on the voltameter cathode was 0.0239 gram, corresponding to 0.0316 gram of nitrogen, and to 0.000758 gram of hydrogen. The actual weight of nitrogen and hydrogen obtained in the experiment was 0.0275 gram and 0.000666 gram, respectively.

*Experiment 10.*—For the purpose of investigating the results obtainable with a comparatively high current density at the anode, the electrolytic cell was remodeled as follows: The pipettes, stop-cocks, and graduated tubes (Fig. 3) were replaced by simple glass tubes, one in each arm of the U-tube, reaching just to the surface of the liquid hydronitric acid, and connected above with a chain of Muencke gas wash-bottles containing concentrated sulphuric acid. At a distance of about 3 cm. below each of the side-tubes S and S', was attached another tube, bent at an angle of 90°, and extending downward along the side of the U-tube for a distance of a few centimeters. Each of these tubes reached to the bottom of a small test-tube, about 3 cm. long and one cm. in diameter, which was provided with a tight-fitting two-hole cork. Through the second opening in each cork passed a glass tube connected with a suction pump. A platinum wire of 0.3 mm. diameter served as the anode, and a piece of platinum foil 1.0 cm. long and 0.5 cm. wide was used for the cathode. The average current density at the anode amounted to about 7.7 amperes per sq. dcm. Thirteen grams of potassium trinitride were used in the generator, and about 0.3 gram in the cell. The test-tubes were filled with an aqueous solution of potassium iodide, and the cell was cooled with the aid of liquid air to a temperature of about  $-80^{\circ}$ . A fairly rapid current of dry air was now drawn over the hydronitric acid and through the test-tubes in order to test for the presence of any volatile oxidizing agent formed during the experiment, and the circuit was closed. For about one-half hour the electrolysis proceeded without accident. At the end of this time, however, since it became necessary to make a slight adjustment of one part of the accessory apparatus, the passage of the current was discontinued. No sooner had the cell been barely touched with the hand of the operator, than a frightful explosion took place which completely demolished the apparatus and shattered two window-panes at a distance of about two meters from the cell.

*Experiment 11.*—Thirteen grams of potassium trinitride were used in the generator, and about 0.2 gram in the cell. An exact duplicate of the apparatus described in the preceding experiment was used, and the same conditions were chosen. Mercury was placed in the test-tubes instead of the solution of potassium iodide, and the tubes were cooled to a temperature in the neighborhood of the freezing point of mercury. The electrolysis proceeded without mishap for about four hours, at the end of which time the cell exploded as before, but this time without any apparent cause. The temperature throughout the experiment was held at  $-80^{\circ}$ , and moreover, at the time of the explosion part of the hydronitric acid was in the solid state.

It has been found by repeated experiments performed during the course of the present research that hydronitric acid at room temperature or even at its boiling point may be subjected to considerable mechanical disturbance without great danger of explosion. Fairly rapid currents

of air have many times been blown through the liquid, and the cell has been subjected to a series of light shocks, without causing any explosion. That the substance after electrolysis at  $-80^{\circ}$  should be so extremely sensitive to shock, seems to point toward the possible accumulation in the cell of a very explosive compound, perhaps a polymer of nitrogen, during the electrolysis.

### Summary.

In the present investigation it has been shown that

1. Hydronitric acid, like hydrazine and ammonia, in the pure, anhydrous condition offers a remarkably high resistance to the electric current.
2. The introduction of dry potassium trinitride very greatly increases the conductivity of the anhydrous acid.
3. When a solution of potassium trinitride in hydronitric acid is electrolyzed, the ratio of nitrogen to hydrogen evolved is approximately 3:1, but is somewhat lower under certain conditions. Appreciable amounts of ammonia are obtained during the electrolysis, but no hydrazine is formed.
4. Certain peculiar phenomena are observed in connection with the electrolytic experiments, which may perhaps be explained on the assumption that traces of ozone are formed, but which might possibly be attributed to the formation of small amounts of nitrine, a polymeric modification of nitrogen.

Further work along several different lines suggested by these experiments is now in progress in this laboratory.

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(CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.<sup>1</sup>)

## A NEW METHOD OF MEASURING THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES. (PRELIMINARY COMMUNICATION.)

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No property of a substance is more characteristic of its intimate physical condition than its vapor pressure. The vapor pressure of a single liquid

<sup>1</sup> The study outlined in this communication was begun at New York University in 1906. In the following year one of us (M. A. R.) was called to assume charge of the Department of Chemistry in Clark University. Since then the method here proposed has been employed in the Clark University laboratories in determining iso-