ANHYDROUS HYDRAZINE. II. ELECTROLYSIS OF A SOLUTION OF SODIUM HYDRAZIDE IN ANHYDROUS HYDRAZINE.[1]

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The hydrides of the elements in the second series, Groups V, VI, and VII of the Mendeléeff periodic table have, in so far as they have been studied from this point of view, been found; (1) to be very poor conductors of the electric current; (2) to act as solvents for certain inorganic salts; and (3) to behave as ionizing solvents. Ammonia, for example, has been extensively studied by Gore,[2] Cady,[3] Goodwin and Thompson,[4] Frenzel,[5] Franklin and Kraus,[6] and Franklin.[7]

Ostwald,[8] Hantzsch,[9] and West[10] have determined the conductivity of aqueous solutions of hydronitric acid. The action of the electric current upon ammonium trinitride in aqueous solution has been investigated by Hittorf.[11] Solutions of hydronitric acid and of sodium trinitride have been electrolyzed by Peratoner and Oddo[12] and by Sarvasy.[13] In 1909 Browne and Lundell[14] electrolyzed solutions of potassium trinitride in anhydrous hydronitric acid and have shown that, while the anhydrous acid is a very poor conductor of the electric current,[15] the solutions of potassium trinitride conduct the current very well indeed.

Calvert[16] found the specific conductivity of hydrogen peroxide to approach that of water. Franklin[17] has shown that hydrogen fluoride possesses strong solvent powers.

Cohen and de Bruyn[18] have shown that anhydrous hydrazine is a poor conductor of the electric current. De Bruyn[19] has determined the solu-

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[1] For the first article of this series see Hale and Shetterly, This Journal, **33**, 1071–6 (1911). The experimental work in this article was completed in January, 1912.

[2] *Proc. Roy. Soc. London*, **20**, 441 (1872); **21**, 140 (1873).

[3] *J. Phys. Chem.*, **1**, 707–13 (1896).

[4] *Physic. Rev.*, **8**, 38 (1899).

[5] *Z. Elektrochem.*, **6**, 477–80, 485–9, 492–500 (1900).

[6] *Am. Chem. J.*, **20**, 820–36 (1898); **23**, 277–313 (1900); **24**, 83 (1900); This Journal, **27**, 191–222 (1905).

[7] *Z. physik. Chem.*, **69**, 279 (1909); *Am. Chem. J.*, **47**, 285–317 (1912).

[8] See Curtius and Rodenhausen, *J. prakt. Chem.*, [2] **43**, 207 (1891).

[9] *Ber.*, **32**, 3066 (1899).

[10] *J. Chem. Soc.*, **77**, 705 (1900).

[11] *Z. physik. Chem.*, **10**, 593 (1892).

[12] *Gazz. chim. ital.*, **25**, II, 13 (1895); *Chem. Zentr.*, **1895**, II, 864.

[13] *J. Chem. Soc.*, **77**, 603 (1900).

[14] This Journal, **31**, 435–48 (1909).

[15] This fact has been corroborated in this laboratory by further work that has not yet been published on the conductivity of anhydrous hydronitric acid.

[16] Drude's *Ann. Physik.*, **1**, 483 (1900).

[17] See foot-note, This Journal, **27**, 821 (1905).

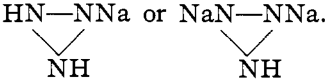
[18] *Proc. Accad. Wetenschappen*, **5**, 551–6 (1903); *J. Chem. Soc.*, **84**, II, 405 (1903).

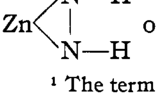
[19] *Rec. trav. chim.*, **15**, 174–84 (1896).

bilities of sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, and barium nitrate in anhydrous hydrazine at 12.5°.

The present paper contains the record of a series of experiments made upon the action of the electric current upon solutions of the hydrazo-base,[1] sodium hydrazide in anhydrous hydrazine. The results obtained have been described under the following headings: (1) preparation of sodium hydrazide, (*a*) preparation of anhydrous hydrazine, (*b*) action of anhydrous hydrazine upon sodium amide, (*c*) action of anhydrous hydrazine upon metallic sodium; (2) apparatus employed in the electrolysis; (3) general procedure; (4) details of experiments; (5) discussion of results; and (6) summary.

Preparation of Sodium Hydrazide.

Lobry de Bruyn[2] subjected metallic sodium to the action of hydrazine hydrate and anhydrous hydrazine, respectively, and obtained in the first case, a substance to which he assigned the formula N_2H_5ONa, and in the second, the mono-sodium hydrazide. No analyses are given for either product, although it is stated that hydrogen and ammonia are evolved. Later Scandola[3] treated finely divided sodium, suspended in ether, with hydrazine hydrate and obtained a white explosive substance, soluble in alcohol and water, but insoluble in ether, petroleum ether and benzene; it decomposes at 58° and is combustible at higher temperatures when heated. No analyses were given. The conclusion was drawn that the substance is different from that obtained by de Bruyn[4] and may possibly have the formula  $\begin{array}{c} HN-NNa \\ \diagdown\;\diagup \\ NH \end{array}$ or $\begin{array}{c} NaN-NNa \\ \diagdown\;\diagup \\ NH \end{array}$.

Ebler and Schott[5] studied the action of hydrazine hydrate on zinc and found that in absence of air there was no action. In presence of air, however, the hydrazinated zinc salt of hydrazine carboxylic acid, $Zn(O.CO.NH.NH_2)_2.2N_2H_4$ was obtained and analyzed. In 1910 Ebler and Krause[6] prepared zinc hydrazide, to which they assigned the formula  $Zn\begin{array}{l} \diagup N-H \\ \quad\;| \\ \diagdown N-H \end{array}$ or $Zn:N.NH_2$, by the action of zinc ethyl or zinc diamide on

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[1] The term *hydrazo-base* for a metallic hydrazide and *hydrazo-acid* for an acid hydrazide are here suggested in order to follow the nomenclature used by Franklin in connection with the ammonia series of acids, bases, and salts. The behavior of the hydrazine series of acids, bases, and salts in anhydrous hydrazine is now under investigation in this laboratory and will be made the subject of a future communication.

[2] *Rec. trav. chim.*, 14, 85–88 (1895); 15, 174 (1896).

[3] *Estr. Boll. soc. med. Pavia,* 1910; *Chem. Zentr.*, 1910, II, 544.

[4] *Loc. cit.*

[5] *J. prakt. Chem.*, [2] 79, 72 (1909).

[6] *Ber.*, 43, 1690–5 (1910).

hydrazine in anhydrous ether. They suggest that they may possibly have obtained small amounts of $Zn(NH.NH_2)_2$ also. The investigators suggest these methods as generally applicable for the preparation of metallic hydrazides.

While preparing anhydrous hydrazine by treating hydrazine hydrate with sodium amide Stollé[1] found that when the sodium amide was present in excess he obtained sodium hydrazide in accordance with the equation[2] $N_2H_4 + NaNH_2 = NaN_2H_3 + NH_3$.

Preparation of Anhydrous Hydrazine.—The anhydrous hydrazine employed in the experimental work described in this paper was prepared by dehydrating hydrazine hydrate with barium oxide according to the method of de Bruyn[3] and using the very convenient apparatus described by Hale and Shetterly.[4] The apparatus was modified, however, to the extent of having the Vigreux distilling tube jacketed and cooled by running water so as to insure a most efficient condensation during the period of reflux.

Partially dehydrated hydrazine hydrate was boiled in this apparatus for about three hours with about a 50% excess of barium oxide. The water was then removed from the Vigreux condenser, and the hydrazine was distilled under reduced pressure, in an atmosphere of hydrogen, into the container. The product was found by analysis to contain 99.7% hydrazine.

The method used for the determination of hydrazine throughout the present research was that suggested by Rimini[5] and modified by Hale and Redfield.[6] Methylene blue was used as indicator in all of the iodine titrations. The hydrazine was kept in small glass-stoppered bottles, the stoppers of which were lubricated with a little of the anhydrous substance. By covering the stoppers and the necks of the bottles with tin foil and holding this tightly in place with rubber bands, circulation of air around the stopper was prevented and the amount of moisture working its way into the anhydrous hydrazine was reduced to a minimum.

Action of Anhydrous Hydrazine upon Sodium Amide.—The sodium amide used was obtained through the courtesy of the Synfleur Scientific Laboratories. On analysis it was found to be satisfactory for use in this piece of investigation.

As the result of preliminary experiments performed in this laboratory in 1909 by Dr. C. F. Hale it was found that a very explosive yellow compound was obtained by treatment of sodium amide with 96% hydrazine.

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[1] *J. prakt. Chem.*, [2] 83, 200 (1911).

[2] See Ebler and Krause, and Scandola, *loc. cit.*

[3] *Loc. cit.*

[4] THIS JOURNAL, 33, 1071–76 (1911).

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

[6] THIS JOURNAL, 33, 1353–62 (1911).

The reaction was conducted in an atmosphere of hydrogen and nitrogen, respectively. In every case the product exploded before it could be analyzed. In one instance, under reduced pressure, a somewhat bluish deposit, probably of metallic sodium, was formed upon the walls of the tube as a result of the explosion.

Experiments were first performed in order to determine the amount of ammonia liberated by the action of a weighed amount of sodium amide on an excess of anhydrous hydrazine. The apparatus employed was a glass-stoppered U-tube of special construction so arranged that the sodium amide and hydrazine could be brought into contact in an atmosphere of hydrogen (purified by bubbling through alkaline pyrogallol and sulfuric acid) and the liberated ammonia driven over and absorbed in sulfuric acid. Any hydrazine that may have been carried over into the absorbing liquid was oxidized by boiling with potassium iodate. The ammonia was determined by making the solution alkaline and distilling into an excess of standard acid.

It was found necessary to use the sodium amide in finely divided form, as otherwise it will react but slowly with the hydrazine on account of a protective coating of the sodium hydrazide which forms on the surface. Action began as soon as the materials were brought into contact with each other. Gas was given off, the powder became yellow, increased in bulk and eventually went into solution in the hydrazine. If the amount of hydrazine was not too great the solution was of an amber-yellow color. If, however, the hydrazine was present in excess of a certain amount, the solution became colorless. On standing, the yellow solution in general became colorless—in a few minutes in case a large excess of hydrazine was present, but only after a long time, several months in some cases, when a small excess was present.

In the three experiments performed 0.0571, 0.0484, and 0.0482 g. of sodium amide were treated, respectively, with a relatively large excess (about 8 cc.) of hydrazine. In the first two experiments, in which the reaction was conducted in an atmosphere of hydrogen, 0.0914 and 0.1024 g. of ammonia were obtained. By far the greater part of this ammonia was liberated during the first violent stage of the reaction. In the third experiment, in which the reaction took place in an atmosphere of pure dry ammonia and in which the evolved gases were collected in a Schiff nitrometer filled with dilute sulfuric acid, 20.8 cc. of nitrogen and 16.3 cc. of hydrogen were obtained.

From these experiments it is apparent that treatment of sodium amide with hydrazine results in the liberation of ammonia, nitrogen, and hydrogen. Since the amount of ammonia formed is far greater than that obtainable from the sodium amide it is possible that the initial hydrazinolysis of the sodium amide in accordance with the equation

$$NaNH_2 + N_2H_4 = NaN_2H_3 + NH_3$$

is followed by decomposition of a part of the excess of hydrazine with formation of ammonia, nitrogen, and hydrogen. This may be attributable to a secondary reaction between sodium hydrazide and hydrazine or to a catalytic decomposition such as that suggested by Tanatar.[1]

Action of Anhydrous Hydrazine on Metallic Sodium.—The action of anhydrous hydrazine on metallic sodium was studied in a preliminary way in a form of apparatus similar to that described by Browne and Houlehan[2] and used by them in studying the action of ammonium trinitride in liquid ammonia on certain metals. Small amounts of anhydrous hydrazine and sodium were brought together in approximately equivalent amounts. The hydrazine was weighed out in a Lunge-Rey weighing pipet and was introduced into the U-tube, which was immediately placed in a freezing mixture to freeze the hydrazine and prevent loss by fuming. The proper amount of sodium was then introduced into the pocket. The stopcocks were securely set in position and the U-tube was connected in the usual way with the Schiff nitrometer, filled with dilute sulfuric acid. A current of dry ammonia was now passed through the apparatus until the air was completely displaced, as indicated by the absence of bubbles of unabsorbable gas from the nitrometer. The freezing mixture was now removed and when the hydrazine had melted the sodium was brought into contact with it by jarring the apparatus slightly. The surface of the metal immediately became bright blue and soon after green in color. Gas was evolved and a yellow solid began to form and within a few minutes the whole mass assumed a light yellow color. A moment later and with scarcely any preliminary warning the material in one of the U-tubes exploded, completely wrecking the apparatus. Shortly afterward the other apparatus was destroyed by a similar explosion. Not enough gas was obtained in either case to warrant analysis with the apparatus at hand.

The experiment was repeated in a modified manner so as to eliminate the possibility of an explosion. The same kind of apparatus was employed, but a large excess of hydrazine was used and, as soon as there was evidence of the formation of the yellow solid, ammonia was condensed on the reacting mass by means of solid carbon dioxide and alcohol. The mass then became blue, owing to the solution of sodium in ammonia. The freezing mixture was removed and, as soon as the tube warmed up and the ammonia evaporated, the mass became white and shortly afterward regained the yellow color. Ammonia was again condensed on the mass and again allowed to evaporate. This operation was repeated three times, and the reacting mixture was allowed to stand for about three weeks. At the end of this time the current of ammonia was again turned on in order to carry over any gas that might have collected in the U-tube. The gas was no sooner turned on, however, than the U-tube was completely

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[1] *Z. physik. Chem.*, 40, 475–80 (1902); 41, 37–42 (1902); see also Purgotti and Zanichelli, *Gazz. chim. ital.*, 34, 1, 57–87 (1904).

[2] THIS JOURNAL, 33, 1742–52 (1911).

demolished by a terrific explosion. Analysis of the gas collected in the nitrometer gave 0.2 cc. of hydrogen and 19.3 cc. of nitrogen. Further experiments carried out under somewhat different conditions confirmed the observation that both hydrogen and nitrogen, the former in relatively small amounts, were liberated during the reaction between sodium and hydrazine in the presence of ammonia. It is probable that interaction between the sodium and hydrazine first takes place with formation of sodium hydrazide and liberation of nascent hydrogen in accordance with the equation

$$Na + N_2H_4 = NaN_2H_3 + H.$$

That hydrogen is not evolved as gas, except in relatively small amounts, is probably to be explained by the reducing action on hydrazine. The presence of a large proportion of nitrogen in the evolved gases may be attributed either to the liberation of this gas as the result of some secondary reaction that occurs during the reduction of hydrazine, or to the catalytic decomposition of hydrazine; in the author's opinion, however, it is probably due to the ammonolysis of sodium hydrazide with formation of sodium amide, ammonia, and nitrogen. This reaction would be analogous to the hydrolysis of sodium peroxide with formation of sodium hydroxide and oxygen.

The extremely explosive character of the products obtained by the interaction of hydrazine with sodium amide and sodium was found to preclude the possibility of obtaining exact analytical data concerning their composition, without the use of unusual methods. Some evidence has been obtained of the existence not only of the primary sodium hydrazide, NaN_2H_3, but also of the secondary sodium hydrazide, $Na_2N_2H_2$. Until further work has been done, however, no more definite statement can be made concerning these substances.

Apparatus Employed in the Electrolysis.

Because of the corrosive action of hydrazine upon rubber or cork it was necessary to construct the apparatus used in the electrolysis entirely of glass. Since the oxygen of the air acts on hydrazine it was also necessary that provision should be made to carry on the electrolysis in an atmosphere of some inert gas and yet prevent this gas from contaminating the resulting gaseous products. The apparatus employed is shown in Fig. 1. It consisted of cell A containing the inner tubes B and B′ reaching nearly to the bottoms of the two arms. In these inner tubes the two platinum electrodes C and C′ were suspended by platinum wires as shown in the figure. The inner tubes B and B′ communicated, by means of capillary tubes and the two-way stopcocks D and D′ either with the air or through the four-way stopcocks F and F′, with the Hempel burets E and E′ filled with mercury. Each arm of the cell A could be connected, through the two-way stopcocks G and G′, either with a suction pump or with a source of pure dry nitrogen. The capillary stopcocks H and H′, respectively, permitted the introduction of the electrolyte from the graduated glass-stoppered mixing tube K, and the drawing off of samples at the conclusion of the experiment. The whole apparatus was supported by suitable clamps and, with the exception of the two leveling tubes, was rigidly mounted upon a wooden base. The stopcocks, lubricated with a small amount of anhydrous hydrazine, were securely wired in place.

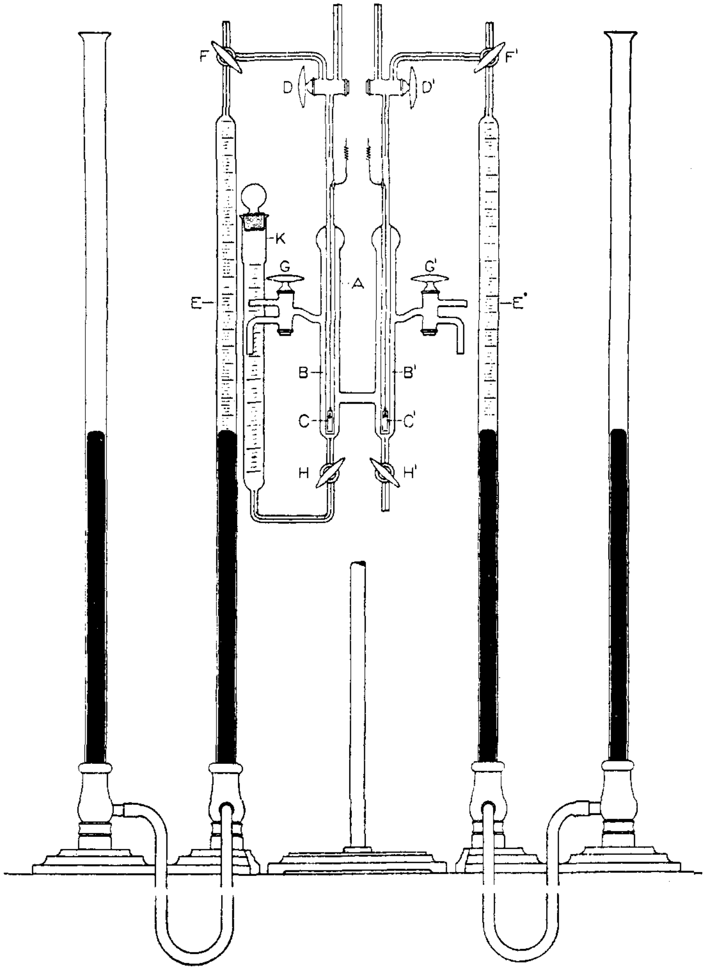

Fig. 1.

General Procedure.

The cell was thoroughly cleaned and dried, and the air was displaced by dry nitrogen. The proper amount of anhydrous hydrazine was then introduced into K and a slow stream of nitrogen allowed to bubble through it by opening either G or G′ and properly adjusting H. The nitrogen was allowed to escape from K around the glass stopper, which was kept from fitting tightly by means of a fine platinum wire. In the experiments in which sodium amide was used a weighed amount of this substance was introduced directly into the hydrazine. When metallic sodium was employed, ordinary glass tubing was drawn out to small diameter and cut into approximately 10 mm. lengths. These were weighed, molten sodium was drawn up into them, and they were again weighed. A tube was then placed on a flat surface, crushed by means of a pestle and the resulting sodium wire with the crushed glass adhering was then quickly introduced into the hydrazine in the mixing tube. This operation was repeated until sufficient sodium was in solution. This gave a means of employing small amounts of sodium with a clean surface while the adhering particles of glass prevented too violent a reaction. When sodium amide is used it must be introduced a little at a time, otherwise frothing will result and the stopper will be forced out, with consequent loss of hydrazine. The nitrogen which was kept bubbling through the liquid served to prevent the oxidation at the surface and also stirred the liquid, giving a homogeneous solution.

The stopcock H was now closed, the cell was partially evacuated, H was opened and the solution was slowly sucked over into A. While passing from the mixing tube into the cell the solution was filtered through glass wool, which had previously been placed in the bottom of the mixing tube. When sufficient solution had been introduced into the cell, H was closed, D and D′ were opened to the air, and nitrogen was admitted at G or G′ under pressure sufficient to force the solution up into B and B′ until they were completely filled. D and D′ were then closed, the supply of nitrogen was shut off and G and G′ were opened to the air a moment to allow the pressures and the levels of the columns of liquid in the cell arms to equalize themselves. A milliameter and a copper coulometer were connected in series with the cell and a voltmeter was shunted across the cell terminals. The voltmeter was in circuit for a few seconds only at the time of each reading, so that the total amount of current passing through it was negligible in any one experiment. During an experiment the gaseous products of the electrolysis that accumulated in B and B′ were from time to time drawn over into the burets by proper manipulation of the stopcocks D, D′, F, and F′. The gases were analyzed by transferring them from E and E′ to a water-jacketed Hempel buret containing mercury, on the surface of which were a few millimeters of water. Any hydrazine vapor or ammonia was removed by absorption in a pipet containing dilute sulfuric acid. In order to detect possible leakage of air into the apparatus, oxygen was determined by absorption in alkaline pyrogallol. Hydrogen was determined with palladium black and the nitrogen was obtained by difference. The palladium tube was filled with nitrogen each time before use which obviated the necessity of correcting for the contraction due to the presence of oxygen.

Details of Experiments.

Experiment 1.—After electrolysis for about five hours the solution, which was colorless at the outset, became yellow in the neighborhood of the cathode. The circuit was now broken and the solutions in the two arms of the cell were thoroughly mixed, with the result that the yellow color disappeared. After three hours of further electrolysis the cathode solution again became yellow and it was allowed to remain so until the end of the experiment. A small amount of a yellowish solid seemed to be deposited on the cathode. During the electrolysis, the total duration of which was eleven hours and thirty-five minutes, the current dropped from 9.5 to 2.9 milliamperes and the voltage rose from 89 to 107 volts.

Experiment 2.—In order to ascertain whether the yellow color that appeared in the cathode tube during the preceding experiment could be transferred to the opposite side of the cell, the solution obtained during the previous experiment was subjected to further electrolysis for a period of twelve hours with the direction of the current reversed. The yellow solution which was now in the anode tube gradually became colorless while the colorless solution in the cathode tube assumed the usual yellow color. During this experiment which was essentially a continuation of Expt. 1 the current fell from 3 to 1.2 milliamperes and the voltage increased from 90 to 102 volts.

Experiment 3.—The solution in this experiment was the same as that used in Expt. 2. It was thoroughly stirred at the outset, however, by means of the current of nitrogen. During the adjustment of the level of the mercury in the buret connected with the cathode tube, a few drops of mercury accidentally passed over through the inner tube and came into contact with the electrode, spreading over the whole surface in a peculiar manner. The electrolysis was, therefore, conducted virtually with a mercury cathode. The usual evolution of gas at the cathode did not take place. The surface of the mercury soon darkened, became purple, and was finally covered with a mass of purplish needle-like crystals which showed a brownish color at the lower end of the electrode. If this material was a sodium amalgam it gave no evidence of any chemical action even after the electrolysis had been discontinued, but stood in contact with the electrolyte apparently unchanged for several days. Gas was evolved as usual from the anode throughout the experiment which covered a period of about nine hours. The usual yellow color appeared in the neighborhood of the cathode. Toward the middle of the experiment the current dropped from 4 to 1 milliampere and from 102 to 92 volts.

Experiment 4.—The electrolyte employed in the previous experiment was thoroughly stirred, without, however, disturbing the crystals on the cathode. The direction of the current was now reversed thus making the electrode holding the purplish crystals the anode and the clean platinum electrode the cathode. At the beginning of the experiment no gas was evolved at the anode but the crystals underwent a gradual disintegration and in a short time gave place to liquid mercury which adhered to the electrode. As soon as this transformation was complete gas was evolved at the anode while the mercury soon became tarnished to a brassy yellow color which faded out gradually when the circuit was broken and left the mercury surface bright and clean. The solution in the neighborhood of the cathode became yellow as before. The gases were not analyzed.

Experiment 5.—After the conclusion of Expt. 4 the electrolyte was thoroughly stirred until it became colorless. The mercury electrode was made the anode. As soon as the electrolysis started the clean mercury surface became tarnished as in Expt. 4. The solution in the cathode tube became yellow. The current varied from 4.8 to 1.7 milliamperes and the voltage increased from 100 to 102 volts during the progress of the experiment.

Experiment 6.—The contents of the cell were removed and the cell and electrodes were thoroughly cleaned and dried. The electrolyte used had, at the outset, a deep yellow color. The duration of the electrolysis was six hours and twenty-two minutes. At the end of the first half-hour the solution in the inner anode tube had become colorless. An hour later the whole solution in the anode compartment had lost its yellow color while that in the cathode compartment became deep yellow in color. The current dropped from 5.6 to 3.1 milliamperes and the voltage increased from 99 to 105 volts during the experiment.

Experiment 7.—The electrolyte used in the preceding experiment was thoroughly stirred, with the result that it became entirely colorless. A few drops of mercury were introduced into the anode compartment so as to coat the electrode as in Expt. 3. As before, no evolution of gas was observed at the cathode during the electrolysis, but a crystalline solid similar in appearance to that previously obtained was deposited on the electrode. At the conclusion of the experiment, which lasted for ten hours and twenty-two minutes, the solution in the cathode tube had become very yellow in color. The current fell from 3.1 to 1.1 milliamperes and from 105 to 101 volts during the course of the experiment.

Experiment 8.—The mercury remaining on the electrode from the preceding experiment was removed with nitric acid, leaving the platinum clean and bright, and the cell was thoroughly cleaned and dried. The new solution employed in this case was intensely yellow and showed a much lower resistance than the electrolytes previously used. The electrolysis was continued for one hour, during which period a vigorous evolution of gas was observed at both electrodes. A blue deposit, probably consisting of either metallic sodium or an addition product of sodium with hydrazine, was at once formed on the cathode. This remained only for a short time, however, after the circuit was broken, quickly dissolving in the electrolyte with evolution of gas. Throughout the entire cell the solution remained yellow during the experiment. The current dropped from 115 to 105 milliamperes and from 85 to 80 volts.

Experiment 9.—During the preparation of the electrolyte used in this experiment a yellow solid was at first formed, which subsequently dissolved yielding a dark yellow solution. In the course of the electrolysis, which was continued for a period of one and one-half hours, a slight blue deposit was formed on the cathode. Small portions of this deposit appeared to be continuously projected from the surface of the cathode, subsequently dissolving with appreciable evolution of gas. The whole solution remained yellow. and at the end of the experiment a very slight deposit of a dull black color remained on the cathode. This deposit seemed to dissolve very slowly in the electrolyte with evolution of small amounts of gas. The current increased from 50 to 58 milliamperes while the voltage remained practically constant at 38 volts.

Experiment 10.—The electrolyte used in Expt. 9 was thoroughly stirred and was subjected to further electrolysis for a period of thirteen and one-half hours. In this case the blue deposit was not formed on the cathode but the black substance appeared as before. After the circuit was broken this material gradually disappeared with slow evolution of gas. The whole solution remained yellow throughout the experiment. The current was held practically constant at 7 milliamperes and 5.5 volts.

Experiment 11.—The solution used in the last two experiments was again electrolyzed, after it had been thoroughly stirred, for a period of fourteen hours and thirty-five minutes. The current was held practically constant at 8.5 milliamperes and 6 volts. Similar phenomena to those described under Expt. 10 were noted.

Experiment 12.—The same solution was thoroughly stirred and was electrolyzed for two hours and five minutes. Although the current density was somewhat higher than in Expt. 11 the same phenomena were noted and no blue deposit was formed. The current was nearly constant at 25 milliamperes and at 16 volts.

Experiment 13.—The conditions prevailing in Expt. 12 were duplicated as nearly as possible. The phenomena noted were similar in every particular to those described under the preceding experiments. The current averaged 24 milliamperes and 17 volts.

Further details of the experiments are summarized in Table I.

TABLE I.—RESULTS OBTAINED IN ELECTROLYTIC EXPERIMENTS.

Number of Expt.	$NaNH_2$ or Na used. Grams.	N_2H_4 used. Cc.	Copper on coulometer cathode.	Gas evolved at anode.		Ratio Cu : N (anode).	Gas evolved at cathode.	
				Nitrogen. Cc.	Hydrogen. Cc.		Nitrogen. Cc.	Hydrogen. Cc.
1	$NaNH_2$ 0.3	40	0.0605 g.	16.2	0.7	1 : 1.5	2.6	2.4
2	$NaNH_2$ 0.3	40	0.0950 g.	20.0	2.2	1 : 1.2	14.4	13.1
3	$NaNH_2$ 0.3	40	0.0244 g.	4.8	0.0	1 : 1.1	....	....
4	$NaNH_2$ 0.3	40	....	....	....	......	....	....
5	$NaNH_2$ 0.3	40	0.0232 g.	4.6	0.8	1 : 1.3	....	....
6	Na 0.1	40	0.0304 g.	5.9	0.5	1 : 1.1	1.1	5.4
7	Na 0.1	40	0.0201 g.	4.6	0.4	1 : 1.2	....	....
8	Na 0.5	35	0.0890 g.	23.3	14.2	1 : 1.5	8.3	12.6
9	Na 1.0	33	0.0999 g.	39.2	4.3	1 : 2.2	7.3	7.4
10	Na 1.0	33	0.1004 g.	36.6	6.2	1 : 2.1	13.1	23.8
11	Na 1.0	33	0.1291 g.	56.9	10.8	1 : 2.5	2.4	32.0
12	Na 1.0	33	0.0592 g.	27.2	4.4	1 : 2.6	1.9	13.8
13	Na 1.0	33	0.0665 g.	30.9	2.9	1 : 2.6	2.4	15.5

Discussion of Results.

Among the numerous ionic species that might be assumed to be present in a solution of sodium hydrazide in anhydrous hydrazine are Na^+, $N_2H_3^-$, $N_2H_2^{=}$, $N_2H^{\equiv}$, and $N_2^{==}$. That Na^+ is present as ion is indicated by the appearance of the blue cathode deposit noted in several experiments. This indication is further confirmed by the results obtained during the electrolysis of the solutions with a mercury cathode.

The sodium liberated would, of course, act upon the solvent with formation of sodium hydrazide and evolution of hydrogen, at least part of which reacts with hydrazine to form ammonia. On the basis of this explanation it is not surprising to find that the volume of hydrogen liberated at the cathode is distinctly lower than that required for the theoretical ratio Cu : 2H. The liberation of nitrogen at the cathode may be explained as a result of the action of sodium upon hydrazine as already described in connection with the preliminary study of this reaction, that is, as a result of ammonolysis of the sodium hydrazide.

It seems reasonable to suppose that the principal anion present in the electrolyte is $N_2H_3^-$. This ion in anhydrous hydrazine would be analogous to the OH^- ion in water and to the NH_2^- ion in liquid ammonia. Assuming for the present that no condensation products are formed at the anode it is probable that four $N_2H_3^-$ ions would react with liberation of one molecule of nitrogen gas and regeneration of three molecules of hydrazine, or it may be that the $N_2H_3^-$ ions discharge upon hydrazine molecules with formation of $N_2H_2^{=}$, or $N_2H^{\equiv}$ ions which then react yielding as before nitrogen gas and hydrazine. Any of these three sorts of ions might still further be considered to discharge upon hydrazine yielding the ion $N_2^{==}$ which, finally discharging on the anode, would be directly converted into nitrogen gas. In any event one atom of nitrogen would be liberated at the anode for each atom of copper deposited on the coulometer cathode.

This theoretical ratio Cu : N is approximately realized in the first eight experiments in which the concentration of the electrolyte with respect to sodium hydrazide is relatively low. The excess of nitrogen found as well as the presence of hydrogen is probably to be accounted for either by the failure of the regeneration of hydrazine to take place quantitatively or by the slight catalytic decomposition of the solvent.

In Expts. 9 to 13, inclusive, in which the concentration was distinctly higher, the ratio of copper to nitrogen was much lower, averaging 1 : 2.4. This points to more extensive decomposition either of the discharged anions or of the solvent under these conditions.

Summary.

In the present investigation it has been shown that:

(1) Sodium derivatives of hydrazine may be prepared by the action of anhydrous hydrazine upon either metallic sodium or sodium amide.

(2) Solutions of sodium hydrazide in anhydrous hydrazine readily conduct the current, yielding in general nitrogen and hydrogen at both anode and cathode. For each gram atom of copper deposited on the coulometer cathode from 1.1 to 1.5 g. atoms of nitrogen gas were liberated at the anode when the electrolyte was rather dilute. With a more highly concentrated solution, however, the ratio Cu : N varied from 1 : 2.1 to 1 : 2.6.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out with his coöperation.

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THE SOLUBILITY OF CERTAIN DIFFICULTLY SOLUBLE SILVER SALTS.

BY A. THIEL.

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In an article of the above title in THIS JOURNAL, **30,** 68 (1908), which has only recently come to my attention, A. E. Hill describes several determinations of the ratio of the solubilities AgCl, AgBr, AgI and AgCNS.