MANUFACTURING OF PERCHLORIC ACID.

Thesis

by

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CONTENTS.

INTRODUCTION.

The object of this research was to study quantitatively possibilities of a continuous process of production of perchloric acid from nitrogen peroxide and ammonium perchlorate. Perchloric acid has many properties which make it an important acid in industrial and analytical work and its use would be much greater if its cost of production could be lowered. It is a strong monobasic acid, stable in solutions (up to 60%), has a high boiling point. There are relatively few insoluble salts (potassium, rubidium, caesium, and thallium perchlorates are only slightly soluble) and the difference in solubilities of potassium and sodium perchlorates give an easy method of separation of these two metals in analytical work.

Anhydrous perchloric acid is a colorless, hygroscopic, volatile, mobile liquid, which fumes in air. On the skin it produces serious and painful wounds. Pure acid decomposes spontaneously even in the dark in a few weeks. It explodes when heated to 90°C. Solutions are much more stable and do not decompose either in darkness or in light if organic matter and reducing agents are absent. For specific gravities of solutions of perchloric acid see Table #1, the freezing and boiling points diagrams are given on the Figure #4. As it can be seen from these diagrams a constant

boiling solution has a composition of 72.3% of perchloric acid and a boiling point of 203°C at atmospheric pressure. Below 160°C the distillate contains less than 1% of perchloric acid. Pure perchloric acid freezes at -112°C (1) while its monohydrate freezes at 50°C. It boils at 39°C at 56 mm. pressure (2) and at 16°C at 18 mm. pressure (1). Specific heats of solutions of perchloric acid were determined by M.Berthelot (3). Most of perchlorates are deliquescent except ammonium, potassium, lead and mercury salts.

The following reactions are capable of producing larger or smaller quantities of perchloric acid:

1. Formation of perchloric acid by action of an acid on perchlorates.

This general method of obtaining acids is at present the most important one for production of perchloric acid. F.C.Mathers (4) distils potassium perchlorate with sulfuric acid and obtains a very concentrated perchloric acid (up to 98%). Potassium perchlorate may be substituted by sodium perchlorate and sulfuric acid by hydrochloric acid. In this

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(1) H.J.van Wijk. Zeit.Anorg.Ch.32,(1902),115.

(2) D.Varlander and R.von Schilling. Liebig's Ann.121, (1862),346.

(3) M.Berthelot. Compt.Rend.93,(1881),240,291.

(4) F.C.Mathers. J.Am.Chem.Soc.32,(1910),66-71.

case a 95% perchloric acid may be obtained. H.H.Willard (1) obtains perchloric acid by adding gradually hydrochloric acid in the mixture of ammonium perchlorate and dilute nitric acid and distilling the acid produced at 200 mm. pressure. Pure $HClO_4 \cdot 2H_2O$ is obtained, when the resulting distillate is bleached by air to remove chlorine and nitrous oxide formed during the process.

Purification of crude perchloric acid on commercial scale is performed in different ways depending upon the impurities contaminated with the acid. It involves a more or less complicated treatment. Thus addition of alkali-earth sulfides (like barium sulfide) is recommended in case if iron is present. The precipitate carries away also other impurities and sulfuric acid is then added to the solution to remove barium (2).

2. Electrolytic methods.

Perchloric acid can be obtained electrolytically from different materials like hydrochloric acid, chlorine or ClO_2. H.M.Goodwin and E.C.Walker (3) oxidize electrolytically HCl. Same method was worked out by E.C.Walker (4).

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(1) H.H.Willard. J.Am.Chem.Soc.34,(1912),1480-1485.

(2) Ger.Pat.262465.13 Nov.1912.

(3) Chem.Met.Eng.25,(1921),1093-1095.

(4) U.S.1271633, July 9,1918.

Sodium chlorate can be also oxidized electrolytically to sodium perchlorate [1] and the latter can be used as a starting material for manufacturing of perchloric acid. All these methods however are as yet of no commercial importance as sources of perchloric acid.

3. Decomposition of chloric acid and chlorates by heat.

The well known reaction of decomposition of chlorates by heat may be used for manufacturing of perchloric acid. Distillation of a mixture of fluosilicic acid and potassium chlorate is recommended as a commercial source of perchloric acid.

4. Oxidation processes involving ozone and photochemical reactions.

T.Fairley noticed that perchloric acid is produced when ozonized air is passed through a solution of hypochlorous acid or of a hypochlorite [2]. Oxygen activated by ultraviolet rays may be also used [3]. Decomposition of ClO_2 by light also yields perchloric acid. However all these processes are as yet of only theoretical importance.

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(1) Brit.Pat.125608 and 125609, Sept.5,1916.

(2) T.Fairley.B.A.Rep.57,(1874),58.

(3) C.W.Bennett and E.L.Mack. Trans.Am.Electrochem.Soc. 29,(1916),323.

5. Oxidation of ammonium perchlorate.

Possibilities of obtaining pure acids by oxidation of their ammonium salts with oxides of nitrogen in water solutions were pointed out by different observers. Yhe use of this method in relation to perchloric acid is the object of the present work which is a continuation of the work of other students in this Institute. Advantages of this method are that no non-volatile impurities are produced as nitric acid, the by-product of the reaction, can be easily distilled off with water at atmospheric pressure. Ammonium perchlorate is a cheap product and a continuous flow of nitrogen peroxide may be secured using the ammonia oxidation method for producing it.

PREVIOUS WORK ON THE OXIDATION OF AMMONIUM SALTS IN AQUEOUS SOLUTIONS.

Possibilities of oxidation of ammonia and ammonium salts by nitrogen peroxide were shown by Besson and Rosset [1] who succeeded to produce nitric and sulfuric acids by oxidation of the corresponding ammonium salts with nitrogen peroxide. They have also shown that in case of ammonium chloride a variety of products is obtained. In all cases nitric acid was formed as a by-product. The reactions were expressed by the equation:

$$NH_4Ac + 2NO_2 = N_2 + HNO_3 + HAc + H_2O$$

where Ac represents an acid radical.

This general method was tried by H.H.Willard with relation to perchloric acid [2]. He generated oxides of nitrogen (nitric oxide and nitrogen peroxide) by the action of sulfuric acid on sodium nitrite and passed them through a boiling solution of ammonium perchlorate. The reaction was slow although some ammonium perchlorate was oxidized to perchloric acid. Similar results were obtained when the oxides of nitrogen were generated directly in the ammonium

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(1) Compt.Rend. 142, (1906), 633.

(2) J.Am.Chem.Soc. 34, (1912), 1480.

perchlorate solution to which some nitric acid was added and formic acid run in. Better results were obtained by slowly dropping hydrochloric acid into a solution of ammonium perchlorate and nitric acid. Practically complete conversion was obtained and the reaction proceeded at a reasonable rate. Chlorine and nitrous oxide were evolved according to the following equation suggested by Willard as a possible explanation of the reactions involved:

$$34NH_4ClO_4 + 36HNO_3 + 8HCl = 34HClO_4 + 4Cl_2 + 35N_2O + 73H_2O$$

In case of direct oxidation of ammonium perchlorate with nitrogen oxides the most advantageous reaction is

$$2NH_4ClO_4 + N_2O_3 = 2N_2 + 2HClO_4 + 3H_2O$$

when no impurities are produced. Therefore this reaction attracted special attention of Stenzel (1) who found that nitrous anhydride acted not as a self-existent compound but as a mixture of nitric oxide and nitrogen peroxide, the latter being the only active constituent. The actual reactions studied by Stenzel probably were:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$HNO_2 + NH_4ClO_4 = N_2 + HClO_4 + 2H_2O$$

or combining them:

$$2NO_2 + NH_4ClO_4 = N_2 + HClO_4 + HNO_3 + H_2O$$

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(1) R.Stenzel. Undergraduate Thesis on "A Method for the Preparation of Perchloric Acid", Cal.Inst.of Tech.1921.

The final product of the reaction contained a certain amount of nitric acid as would be expected from the reactions expressed by the equations given above. Stenzel found likewise that in case strong nitric acid was used as a solvent for ammonium perchlorate no reaction took place.

The work of A.Knight (1) was the continuation of the work of Stenzel. He tried not only the pure nitrogen peroxide as an oxidizing agent for ammonium perchlorate but its mixture with oxygen and nitric oxide as well. No advantage was found in using mixtures of these gases instead of pure nitrogen peroxide. In every case over twice as much nitric acid as perchloric acid was found in the product. It was also found that the presence of nitric oxide is of some value in reducing the production of nitric acid and the presence of oxygen increases its yield. As part of nitrogen peroxide was reduced to nitric oxide the following side reaction probably took place:

$$3NO_2 + H_2O = NO + 2HNO_3$$

This reaction likewise explains why an excess of nitric acid was produced.

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(1) A.Knight. Undergraduate Thesis. "Perchloric Acid from Ammonium Perchlorate and Oxides of Nitrogen". Cal. Inst.of Tech.1922.

From the previous works done it was evident that high temperature favored the reaction of oxidation of ammonium ion by increasing considerably its rate. The time of contact should be also as long as possible. High temperature was also advantageous due to the rapid increase in solubility of ammonium perchlorate with the temperature. The maintenance of these conditions was attempted as far as possible during the experiment performed. The process was also made continuous in order to obtain different data at varying rates of flow of the gas through the liquid.

EXPERIMENTAL PART.

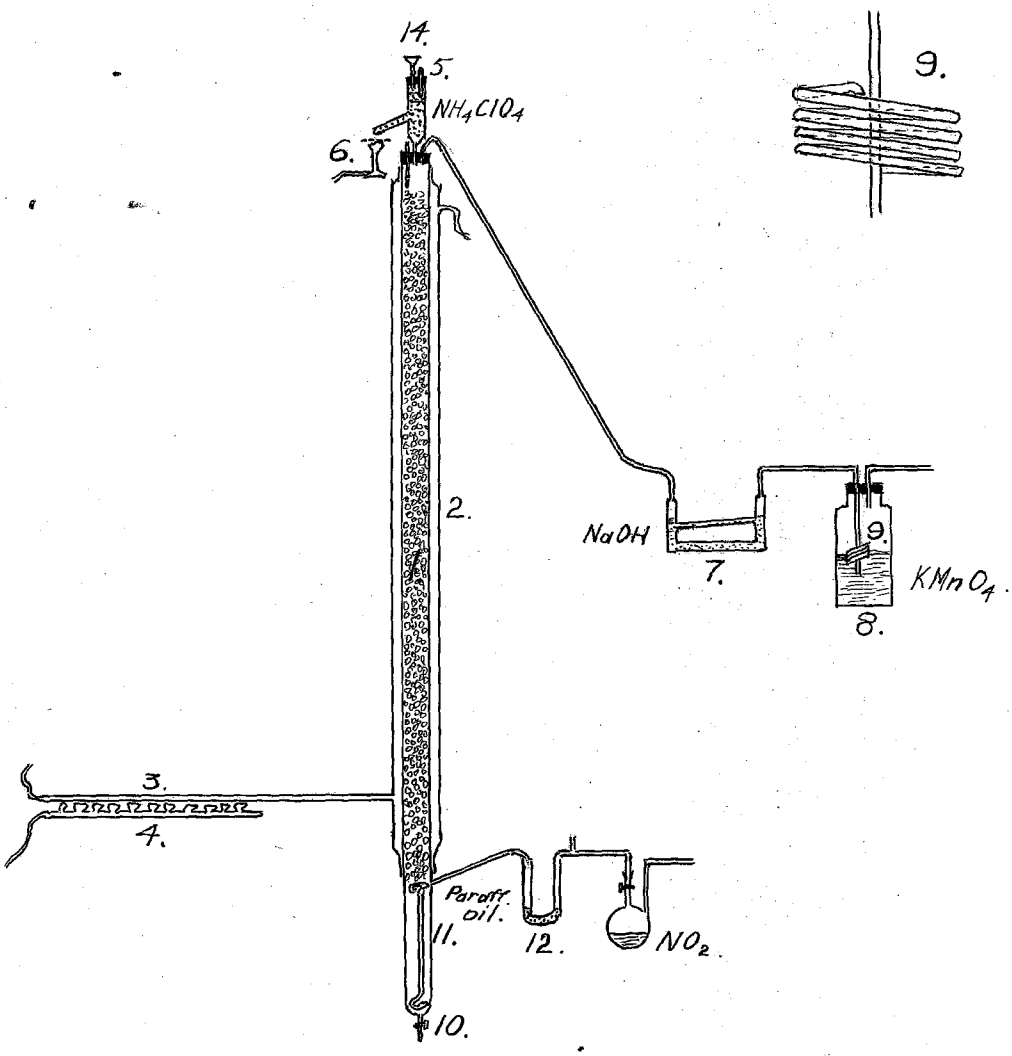
A.

Description of the Apparatus.

A sketch of the apparatus actually used in the experiments performed is given in Figure #1. The apparatus consisted of five feet of glass pipe (1) 25 mm. in diameter. The pipe was filled with glass beads which were supported by means of a glass rod (11). This glass rod was about one foot long and allowed about 100 c.c. open space at the bottom of the column where the samples were collected. This glass column was surrounded by a jacket about 45 mm. in diameter through which a stream of hot water circulated to keep the temperature inside as close as possible to the boiling point of water. The water was fed in through the pipe 3 and heated by means of a burner 4. The corresponding part of the water-feed tubing was replaced by a brass pipe. Due to large heat losses from the apparatus the temperature of the water at the upper end of the jacket could not be maintained higher than 80°C. Nitrogen peroxide obtained as described below, was kept in the flask 13. The flask was connected with the apparatus by means of a ground glass joint. The stopcock in the neck of this flask allowed the supply of the gas to be cut off if necessary. The flow of the gas was

FIGURE NO 1.

Sketch of the Apparatus for Manufacturing of Perchloric Acid in the Experiments Performed.



regulated by immersing the flask in the water and by regulating the temperature of this water. The U-tube (12) was filled with paraffin oil to allow to count the number of bubbles of nitrogen peroxide entering the main column.

The hot ammonium perchlorate solution was supplied at the top of the glass column by means of a glass container 5 of about 150 c.c. capacity. The solution was kept close to its boiling point by heating the branch-tube with a gas-burner 6. The hot solution was introduced into the glass container 5 through the funnel 14. The glass container 5 was connected with the main column through a very short rubber tube and the stream of the solution was regulated with a clamp.

The exit gases were passed first through an absorption apparatus 7 with a measured quantity of standardized sodium hydroxide solution to remove the excess of nitrogen peroxide, and through the absorption apparatus 8 which contained a measured quantity of standardized potassium permanganate solution to remove nitrogen oxide evolved during the reaction. The apparatus 7 was replaced by a simple absorption bottle as nitrogen peroxide is very easily absorbed by alkalies. The construction of the absorption apparatus 8 is clear from the sketch. 9 represents the same apparatus using larger scale.

To enable the regulation of the temperature one thermometer was inserted at the top of the glass container 5 and another at the top of the column 1.

Rubber connections were avoided as far as possible owing to corrosive action of nitrogen peroxide. Only glass joints were used along the passage of nitrogen peroxide up to its entrance in the main column 1. At the top of this column a rubber stopper was used previously covered with a mixture of asbestos and water glass to protect it from corrosion. Absorption vessels were connected through glass tubing joined together by means of very short pieces of rubber tubing as nitrogen peroxide in this part of the apparatus could be present only in very small concentrations.

B.

Preparation of Nitrogen Peroxide.

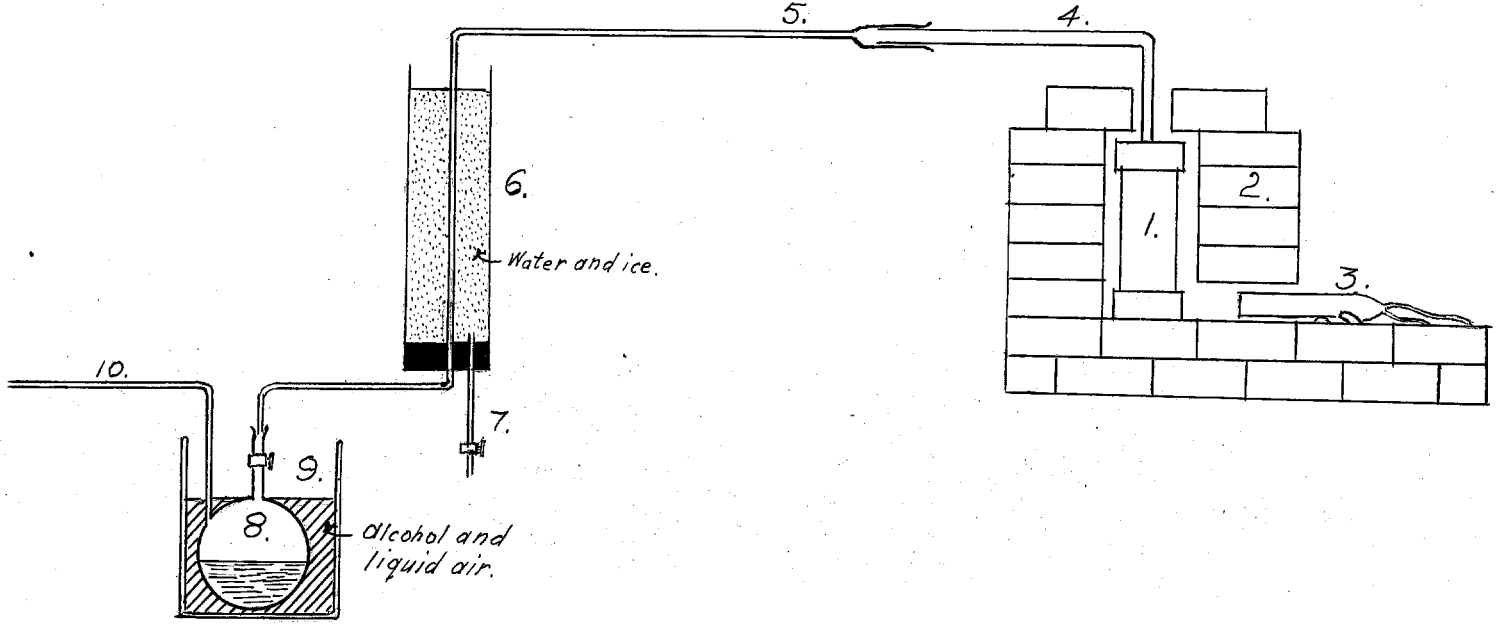
Nitrogen peroxide for the experiment was obtained by decomposition of lead nitrate according to the equation:

$$Pb(NO_3)_2 = PbO + \frac{1}{2}O_2 + 2NO_2$$

As the reaction proceeds at a high temperature when even Pyrex glass begins to soften the process was carried on in a cast iron container. Apparatus used in the experiment is shown in Figure #2 on next page. (1) represents the cast iron container. It was made of a 2-1/2 inch

FIGURE NO 2.

Sketch of the Apparatus for Manufacturing of Nitrogen Peroxide.



iron pipe seven inches long. Two caps were screwed on the ends of the pipe. In the upper cap a 1/4 inch pipe was screwed (4). This pipe was connected with a 6 mm. glass pipe through a glass reducer (5). In the refrigerator (6) the gases were precooled with a misture of ice and water. The gases then passed over to the flask 8, immersed in a mixture of alcohol and liquid air. The temperature was kept 30°C below zero. 9 represents a vacuum flask to prevent rapid heating of the cooling mixture by the surroundings. Pipe 10 conducted any uncondensed nitrogen peroxide and the oxygen evolved during the reaction to the outside air.

The joint between pipes 4 and 5 (iron and glass respectively) was made with a mixture of asbestos and sodium silicate. Pipe 4 was connected with the cap of 1 with litharge-glycerine mixture. The threads at the top and bottom of the pipe 1 were coated with a mixture of litharge and oil so they could be easily removed after the experiment to clean them out and to introduce new quantities of lead nitrate if the experiment should be repeated.

The volume of the iron container 1 was calculated as follows. Theoretical yield of nitrogen peroxide from lead nitrate is 27.7% by weight. Making an allowance for side- reactions and mechanical losses it was assumed

that the yield would be about 20%. For one run of the perchloric acid apparatus including five samples of about 100 c.c. each, 0.4 lbs. of nitrogen peroxide are required corresponding to 2 lbs. of lead nitrate. As the specific gravity of lead nitrate is 4.5, the two pounds of it would occupy about 200 c.c. or 12.2 cu.in. The iron container was made about twice that volume.

The iron container 1 was surrounded by a brick oven 2 which was heated through a small opening at the bottom by the burner 3. The flame was regulated to ensure a uniform flow of the gas which condensed in 8. About 500 c.c. of alcohol and two liters of liquid air were required for one run. When all lead nitrate was decomposed the stop-cock of the flask 8 (450 c.c. capacity) was closed, pipe 10 was sealed and the whole flask was disconnected from the remaining part of the apparatus, a simple thing to do as it was connected with the pipe 5 by means of a ground glass joint.

C.

Actual Tests.

The first run was made using ammonium perchlorate solution saturated at 80°C. The run was unsuccessful as ammonium perchlorate began to crystallize out at the top of the apparatus and it was impossible to re-

dissolve it by heating the solution with the burner 6. Therefore in the second run the apparatus was first preheated by passing through it hot water and then by displacing the water with the ammonium perchlorate solution. The solution used this time was saturated at 70°C. Six samples were collected at intervals of ten minutes each. This run was more successful than the first one but the following defects were found in the apparatus:

a. Ammonium perchlorate crystallized out at the bottom of the column and clogged up the stop-cock 10 through which the samples were collected. Every time the sample was taken the stop-cock should be cleaned and this inevitably resulted in losses of the liquid collected and in the ammonium perchlorate which crystallized out. This was an evidence that only a comparatively small amount of ammonium perchlorate was oxidized to perchloric acid or in other words that the contact between the solution and the gas was too short although the solution was introduced at a very slow rate (about one drop in two seconds during the most part of the experiment).

b. Under the conditions of the experiment no nitrogen peroxide fumes were seen above the middle of the column although the flow of the gas was very rapid (more than

four bubbles per second). At that rate the evolution of nitric oxide was so rapid that it was not sufficiently absorbed by the potassium permanganate solution and a small brownish fume could be seen coming off from the potassium permanganate absorption apparatus.

c. The glass tubing leading from the top of the main column to the absorption apparatus was clogged up at the end of the experiment with the ammonium perchlorate solution and the crystals of the salt increased the resistance to the passage of the gases to such an extent that it was impossible to force the solution from container 5 into the main column. At that moment the experiment was stopped. This clogging up of the glass tubing was due to the very rapid passage of the gas through the absorption column so that this gas carried along some of the solution into the exit tubing where the salt crystallized out.

The following suggestions can be made for the subsequent runs:

a. To decrease the rate of flow of ammonium perchlorate solution to a still greater extent and at the same time to increase the flow of nitrogen peroxide so as to keep the entire column full with brown fumes. The bottom of the column not inclosed in hot water jacket should be also heated. This can be done by immersing it in hot

water bath removing it for a short time when the samples are taken, or by making an arrangement similar to that used in the nitrogen peroxide manufacturing (Figure #2).

b. To introduce a second absorption apparatus for nitric oxide or to replace the one used by a more efficient one. As this inevitably leads to a larger resistance to the passage of the gas, the container 5 at the top of the main column must be made somewhat higher to ensure more pressure. Another way to solve this problem is evidently to decrease the rate of flow of nitrogen peroxide.

c. To raise the gas exit tube much above the glass beads.

As these suggestions are to a certain extent contradictory the following conclusion must be made concerning the regulation of the passage of the gas and the flow of the solution. It would be best to decrease the flow of the ammonium perchlorate solution from the top of the column and to regulate the flow of nitrogen peroxide so that it reaches the top of the main column and nitrogen oxide is at the same time completely absorbed by the potassium permanganate solution. This regulation is a very difficult one as it is hard to control the flow of the solution in the way it was done. The size of the appara-

tus makes it difficult to control simultaneously at different points. Some changes in the design of the apparatus must therefore be done. It is also desirable to increase the concentration of the salt in the solution, hardly to be done under the present conditions. The whole column should be covered with some insulating material to diminish heat losses. Windows should be made in several places to enable the control of the flow of the gases.

The analysis of the samples collected was made and the amount of nitric oxide evolved was measured.

D.

Methods of Analysis.

Total acidity of the solutions was first determined. Ammonia was driven off by boiling with sodium hydroxide solution. Nitric acid was then determined by reducing it to ammonia with nascent hydrogen.

After ammonia was driven out with sodium hydroxide every sample was diluted to 100 c.c. A known volume (usually 10 c.c.) was then introduced into a Kjeldal flask, where the following substances were added: 100 g. zinc, 50 g. iron fillings, and 40 c.c. 40% sodium hydroxide solution with 50 c.c. of water. The Kjeldal flask was dipped in the measured amount of standard sulfuric

acid solution. The whole apparatus was carefully sealed to prevent leakage. The mixture was allowed to stand for one hour in the cold and then about half of the water present was distilled off and the amount of ammonia determined by titrating back the standard acid solution.

Amount of ammonium perchlorate was determined from its solubility at 70°C in water. It was impossible to determine it in a different way as much of it crystallized out in the apparatus while cooling.

E.

Conclusions.

The following conclusions can be drawn from the data obtained (See Appendix #1):

1. Lower temperature of the experiment, less saturated solution with respect to ammonium perchlorate, and insufficient time of contact of nitrogen peroxide with the solution as compared with Knight's experiments favored the undesirable side-reactions. A larger amount of nitric oxide was therefore evolved per unit amount of nitrogen peroxide used, a relatively larger amount of nitric acid being produced, and the percent conversion of ammonium perchlorate being small.

2. Longer contact of the solution with nitrogen peroxide undoubtedly favors greater conversion of ammonium perchlorate into perchloric acid.

3. It is likely that the solution of ammonium perchlorate in dilute nitric acid will give somewhat better results since the results shown in Appendix #1 indicate that as the nitric acid concentration increases up to at least 8 normal the relative rate of formation of perchloric acid compared to that of nitric acid becomes greater. On the other hand Stenzel found that a very high concentration of nitric acid was not favorable to the formation of perchloric acid. This might be explained by the fact that nitric acid is formed in the same reaction as the perchloric acid and high concentration of nitric acid would tend to retard this reaction.

APPENDIX #1.

Experimental Data.

Amount of NO_2 used:

Weight of the NO_2 bulb	295.82 g.(1)
1 st weighing of the bulb	293.43 "
2 nd " " " "	230.92 "
Weight of NO_2 used	62.51 "

Analysis of the $KMnO_4$ solution:

Total volume of $KMnO_4$ solution (0.4701 N)	1557.0 c.c.
" " " " $FeSO_4$ " " (0.4206 N)	440.5 "
Equivalents of $KMnO_4$ reduced	0.5467
Mols of NO absorbed	0.1822
" " NO_2 used during the run	1.3586
" " NO per 1 mol of NO_2	0.132

Analysis of the samples:

	Volume collected. c.c.	Time of the run. hrs.min.	NaOH used c.c.	Normality in H*.	Mols of acid present.
I	14.2	2.10-2.20	39.76	1.693	0.02404
II	27.4	2.20-2.30	234.40	5.172	0.14172
III	18.3	2.30-2.40	259.80	8.583	0.15708
IV	28.9	2.40-2.50	182.00	3.807	0.11004
V	11.0	2.50-3.00	121.60	6.684	0.07352
VI	2.4	3.00-3.10	40.00	10.077	0.02418

	Volume of H_2SO_4. c.c.	Volume of NaOH for neutralliz. c.c.	Volume of the sample (2)	Mols of HNO_3 present.
I	100	60.94	50	0.0226
II	100	58.60	10	0.127
III	50	16.80	10	0.139
IV	50	21.40	10	0.0956
V	50	29.10	10	0.0648
VI	50	33.80	10	0.0204

	Normality in HNO_3	Normality in $HClO_4$	Ratio of HNO_3 to $HClO_4$	Normality in NH_4ClO_4 (3)	%% conversion of NH_4ClO_4
I	1.591	0.102	15.6:1	3.702	2.8
II	4.635	0.537	8.6:1	3.702	14.5
III	7.592	0.991	7.7:1	3.702	26.8
IV	3.308	0.499	6.6:1	3.702	13.5
V	5.891	0.792	7.4:1	3.702	21.4
VI	8.517	1.560	5.4:1	3.702	42.1

(1) 2.39 g. were lost in trial run.
(2) Every sample was diluted to 100 c.c.
(3) Solubility of NH_4ClO_4 at 70°C is 435 g. per liter (See Figure #5).

APPENDIX #2.

ESTIMATE OF THE POSSIBLE MANUFACTURING COST OF PERCHLORIC ACID.

The plant for manufacturing perchloric acid by oxidation of the ammonium ion in ammonium perchlorate solution by means of nitrogen peroxide, in its general features can be compared with a plant for the production of nitric acid by the ammonia oxidation method. Additional apparatus needed are suitable devices for the concentration of the acid produced and for the distillation of the nitric acid, the by-product of the process. Therefore as the basis on which the estimate is made, the construction and operating cost of the United States Nitrate Plant #2, where the ammonia oxidation method of production of nitric acid is used, was taken into consideration.

The United States Nitrate Plant #2 was built during the war when the prices were much higher than at present. Therefore a 60% reduction was made on the corresponding data of the construction cost of the plant as suggested in the report of the Nitrate Division (1) but a 25% allowance was made for the additional expenses as the plant

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(1) Report #2041 on the Fixation and Utilization of Nitrogen. Nitrate Division. Ordnance Office War Department. 1922.

for manufacturing perchloric acid requires somewhat more complicated apparatus as was already mentioned.

All the data concerning the construction and operating cost were calculated on the basis per one ton of 60% perchloric acid produced. It was also considered that each mol of nitrogen peroxide will produce only 0.15 mols of perchloric acid, as was found in the experiments performed by Mr.Knight.

Under the operation cost were included the cost of power, compressed air, miscellaneous supplies and repair parts, labor and superintendance. Other expenses include interest, depreciation, obsolescence, insurance, and taxes, and were taken to be 15% of the construction cost of the plant. The price of ammonia gas was taken as $600 a ton, which corresponds to the present market price of the gas. In the Nitrate Plant #2 where ammonia gas was also manufactured, its cost per ton was only $211.30. Therefore the price of perchloric acid can be lowered if the same plant produces also ammonia gas. The cost of ammonium perchlorate was taken as $400 per ton (20¢ a pound), which likewise corresponds to its present market price. The cost of 36°Bé (52.8%) nitric acid was taken as $90 per ton.

As the yield of perchloric acid in the experiments of Mr. Knight should be considered exceedingly small another estimate was made on the supposition that the yield of perchloric acid would be 50% larger. This procedure is justified by the fact that Mr. Knight could not collect all the acid produced during his experiments, as part of the acid inevitably adhered to the different parts of the apparatus; its amount in all probability was not very far from 50% of the total yield if the small laboratory scale of the experiment is taken into consideration as well as the small volume of the liquid collected in comparison with the size of the apparatus used. In both cases it was considered that 90% of the ammonia was converted into nitric oxide and 95% of the nitric oxide into nitrogen peroxide, as can be expected from an average plant producing nitrogen peroxide by ammonia oxidation process. Commercial ammonium perchlorate was considered to be 97% pure. It was also assumed that 95% of it is converted into perchloric acid as can be expected if a sufficiently long absorption tower is built.

According to Mr. Knight's data about 0.105 mol of nitric oxide was produced per each mol of nitrogen peroxide used. Here is another possible source of economy which was not considered in the estimation of the total cost of manufacturing perchloric acid as this cost was calculated for the

most unfavorable conditions. This large quantity of nitric oxide can be evidently converted into nitrogen peroxide and used again in the process.

According to the figures given below the cost of one pound of perchloric acid manufactured by this process must be about 30-35 cents all expenses included as well as the interest on the invested capital. The present cost of perchloric acid is $3.00 a pound or about ten times as great. It is interesting to note that due to the large molecular weight of perchloric acid large variations in the amounts of nitrogen peroxide used influence only to a very small extent the final cost of the product.

Manufacturing Cost of One Ton of 60% Perchloric Acid.

		I.		II.
Construction cost		$258		$258
Operating cost ..		$ 23		$ 23
Other expenses ..		$ 39		$ 39
Ammonia used	0.795 ton	$477	0.530 ton	$318
NH_4ClO_4 used	0.797 "	$319	0.797 "	$319
HNO_3 collected ..	1.850 "	$167	1.230 "	$111
$HClO_4$ produced ..	1.000 "	$691	1.000 "	$588

Cost of perchloric acid per pound - 30-35¢.

The first column corresponds to the data of Mr.Knight's experiment, the second column takes into consideration a possible 50% increase in yield of the acid for the same quantity of nitrogen peroxide used. Construction and operating expenses in both cases were considered to be the same although they will be also less. In any case they are negligible as compared with the cost of the products involved in the process.

APPENDIX #3.

PROJECT OF AN APPARATUS FOR CONTINUOUS PRODUCTION OF PERCHLORIC ACID ON A SEMI-COMMERCIAL SCALE.

The apparatus for the manufacture of perchloric acid by the process in question must consist of a suitable device for producing a continuous flow of nitrogen peroxide and an absorption tower where the nitrogen peroxide meets a stream of hot ammonium perchlorate solution. The most convenient method for manufacturing nitrogen peroxide seems to be the one by which the gas is produced by catalytic oxidation of ammonia. Nitrogen peroxide can also be obtained by passing an electric arc through the mixture of nitrogen and oxygen but the apparatus is more complicated and the production of nitrogen peroxide is more expensive.

The catalytic oxidation of ammonia has for a long time attracted the attention of chemists and, in connection with the manufacturing of nitric acid, was well developed during the Great War. The essential features of this method are as follows.

A mixture of ammonia gas (about 10% by volume) (1)

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(1) With electrically heated gauzes high oxygen content is especially advantageous. Rep.#2041.Nitrate Div. Ordn.Office.War Dept.(1922),182.

and air is passed continuously through a catalyst. Platinum is usually used as a catalyst but other catalysts may be also used (1). It is desirable to increase the oxygen concentration but only to a certain extent as the mixture is liable to explode unless some changes in the design of the catalyst are made (2). The following reactions take place:

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$4NH_3 + 3O_2 = 4N_2 + 6H_2O$$

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(1) Chem.Weekblad IX,(1912),47-58, suggests Cu, Ni, FeO_2, and Pt as catalysts.

U.S.1458969. A layer of metallized asbestos and separate layers of oxides of copper, iron, and rareearths are used as catalyzers.

Different catalyzers are also suggested in the following articles: J.Knox.Fixation of Atmospheric Nitrogen. Chemical Monographs. 4,1914,57-60; E.Décarrière. Compt.rend. 177,(1923),186-188. The Catalytic Oxidation of Ammonia by Air in Contact with pure Palladium.

(2) J.Ind.and Eng.Chem.XII,(1920),15-16.

Brit.Pat.181486. The concentration of the catalyst gradually increases in the direction of the gas flow. In this way mixtures containing up to 40% of ammonia may be treated without explosion.

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad (1)$$

As the second and the third reactions are undesirable, it is important to reduce their effect as much as possible. An excess of oxygen is therefore desirable as the second reaction is proportional to the third power and the first reaction to the fifth power of oxygen concentration.

Nitric oxide thus obtained must be oxidized further to nitrogen peroxide. Activated carbon used as a catalyst, increases the speed of the reaction fourteen times but the problem of its utilization is a very difficult one as the concentration of nitric oxide over 10% can hardly be used as carbon begins to burn. Carbon also loses the properties of a catalyst when it becomes wet with steam. The problem was however solved a short time

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(1) Other theoretically possible reactions are:

$$4NH_3 + 8O_2 = 4HNO_3 + 4H_2O$$

$$4NH_3 + 7O_2 = 4NO_2 + 6H_2O$$

$$2NO_2 = 2NO + O_2$$

These reactions are prevented by the high temperature of the process.

$$2NO = N_2 + O_2$$

Proceeds only to a negligible extent at the temperature of the process. (J.Ind.and Eng.Chem.XII,(1920),6).

ago by A.A.Noyes and C.L.Burdick. A mixture containing nitric oxide and oxygen and obtained by oxidizing ammonia (or by oxidizing atmospheric nitrogen) is subjected to catalytic oxidation in the presence of a carboniferous catalyst, e.g. charcoal from coconnut and cohune nut (1).

If the source of ammonia gas does not give a product of sufficient degree of purity, as happens when coke oven ammonia is used, the gas must be washed with a solution of sodium hydroxide. Phosphines are especially to be avoided due to their action on platinum. Ammonia is then mixed in a definite proportion (about 10% by volume) with air in a chamber and then the mixture of the gases is passed through the catalyst.

As the platinum catalyst is the type which is best worked out it alone will be considered here. There are two different types of platinum catalyst in use - electrically heated platinum gauze or a multi-layer platinum gauze which works without requiring any outside energy. Both of these methods have approximately the same efficiency, which is a 90% conversion of ammonia into nitric oxide, but while working on a small scale the electrically

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(1) U.S. 1433969.

Rep.#2041. Nitrate Div.Ordn.Office.War Dept.(1922), 183.

heated gauze is more advisable as the apparatus is less expensive and the preheating of gases is not necessary. Therefore only the electrically heated gauze will be discussed here.

According to the latest work done the most advisable platinum catalyst is made in the form of a gauze or net. It is impracticable to use wires of much less than 0.0020 inches or more than 0.0030 inches in diameter. In the first case the wire is liable to break and in the second case a large percent of the platinum has no catalytic effect. The best gauze is considered to be the one which is made of a wire containing about 0.1% of iridium and approximately 0.0026 inches in diameter. The presence of iridium is desirable as it secures sufficient ductility and tensile strength of the wire (1). There should be 100-120 mesh per linear inch, although some consider that 80 mesh is sufficient (2). The Frank and Caro catalyst which is probably the most suitable for the purpose of the experiment, consists of a single platinum gauze made up of 0.0026 inch diameter wire and has 80 meshes per linear inch. The gauze is welded to silver terminals and heated

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(1) J.Ind.and Eng.Chem.XII,(1920),12.

(2) J.Ind.and Eng.Chem.XI,(1919),544-545.

Chem.and Met.Eng.XXII,(1920),125.

by electric energy to 650-700°C. This type of apparatus usually consists of an aluminium frame and a rectangular catalyst 15.75" by 23.5". The flow of the ammonia-air mixture goes up through the electrically heated gauze just described. This platinum gauze weighs about 2.89 oz. and such an apparatus oxidizes 176 lbs. of ammonia per day with 90-92% efficiency (1). The size of the apparatus for the semi-commercial scale experiment must be certainly reduced according to the desired output of the perchloric acid. For this calculation it is important to remember that 1 oz. of platinum can oxidize efficiently about 0.025-0.035 lbs. of ammonia gas per minute (2). If the rate of flow of the gas is increased the efficienty of the apparatus decreases.

It is important to take into consideration that an excessively large contact surface and a low gas velocity at any temperature above 600°C favor the ammonia decomposition reaction and the catalytic decomposition reaction of nitric oxide into nitrogen and oxygen, which must be certainly avoided. Influence of poisons such as naphthalene, soluble tar, phosphine etc. can also be minimized by using high oxygen concentrations with simultaneous

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(1) Chem.and Met.Eng.XXII,(1920),125.

(2) Chem.and Met.Eng.XXII,(1920),129.

high gas and catalyst temperature and minimum time of catalyst contact (1).

The mixing chamber for air and ammonia and the catalyst holder on the ammonia-air side should preferably have a silica lining. The cylinder itself must be made of nickel steel as pure nickel is not so economical. It must be remembered that nickel, aluminium, and silica are the only suitable materials to use for the construction of the chamber as they do not decompose ammonia at red heat (2). Aluminium is less advantageous as it is a very good heat conductor (3), but for the experimental purposes it can be used as it is much less expensive and easier to work with.

According to the experiences of the Sheffield Experiment Station (4) the catalyst chamber should be 20 inches high and 1 square foot in cross-section. It should be built of cast iron and lined with enameled terra-cotta blocks. The air-ammonia mixture enters at the top through aluminium piping and a platinum gauze is stretched across the bottom being clamped to the nickel frame so that it can be easily removed. Electric current must be supplied

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(1) J.Ind.and Eng.Chem.XII,(1920),120-122.

(2) Rep.#2041.Nitrate Div.Ordn.Off.War Dept.(1922),183.

(3) J.Ind.and Eng.Chem.XII,(1920),126.

(4) Chem.and Met.Eng.XXVII,(1922),699.

up to 350 amperes. The hot nitrous gases from the oxidizer are cooled in cast iron pipes and finally in Duriron if it is desired that they leave the apparatus at room temperature. Two kinds of platinum gauzes were used. The electrically heated gauze was 13 x 27 inches, 80 mesh, made of 0.0030 inch diameter wire, and had a flat rectangular shape, weighing 5.20 oz. The cylindrical four-layer gauze was 13 x 114 inches, also 80 mesh, 0.0026 inch diameter wire, and weighed 16.50 oz. (1). In further calculations these data were taken as a basis as they are in all probability the most reliable although they somewhat differ from the data previously given for the Frank and Caro catalyst.

The striking interdependence of oxygen concentration, temperature of the reaction and contact surface upon the speed of the reaction must be remembered (2). These factors cannot be predicted and must be determined experimentally. However it is important to notice that the gauze temperature in all probability will be about 790-870°C or even higher in order that maximum efficiency can be obtained (3).

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(1) Rep.#2041.Nitrate Div.Ordn.Off.War Dept.(1922),184.

(2) J.Ind.and Eng.Chem.XII,(1920),125.
Chem.and Met.Eng.XXII,(1920),128-129.

(3) J.Ind.and Eng.Chem.XXII,(1920),120.

The nitric oxide produced must be cooled to about 50°C and at that temperature mixed with air just sufficient to oxidize it to nitrogen peroxide. After 100 seconds 92% of nitric oxide is converted into nitrogen peroxide (1).

Table #2 contains different data which refer to a gauze of one inch square. Calculations were based upon the data of the Sheffield Experimental Station, if they differed from other data found in the literature. A 10% mixture of ammonia by volume with air was considered and the equations of the reactions assumed to be:

$$10NH_3 + 2.8H_2O + 18.3O_2 + 68.9N_2 = 10NO + 17.8H_2O + 68.9N_2 + 5.8O_2$$

$$10NO + 17.8H_2O + 68.9N_2 + 5.8O_2 = 10NO_2 + 17.8H_2O + 68.9N_2 + 0.8O_2$$

For each gram-molecular weight of ammonia 211750 calories are evolved during the first reaction. It was also assumed that 90% of the ammonia was converted into nitric oxide, 95% of the nitric oxide into nitrogen peroxide, and 95% of the ammonium perchlorate into perchloric acid. A saturated solution of ammonium perchlorate at 100°C contains 570 grams of the salt per liter of solution (see Figure #5).

It was assumed that for the experimental purposes a 4 x 5 inches platinum gauze would yield a sufficient amount of nitrogen peroxide for the use in the process. Data of the Table #3 refer to the 20 square inches of electrically

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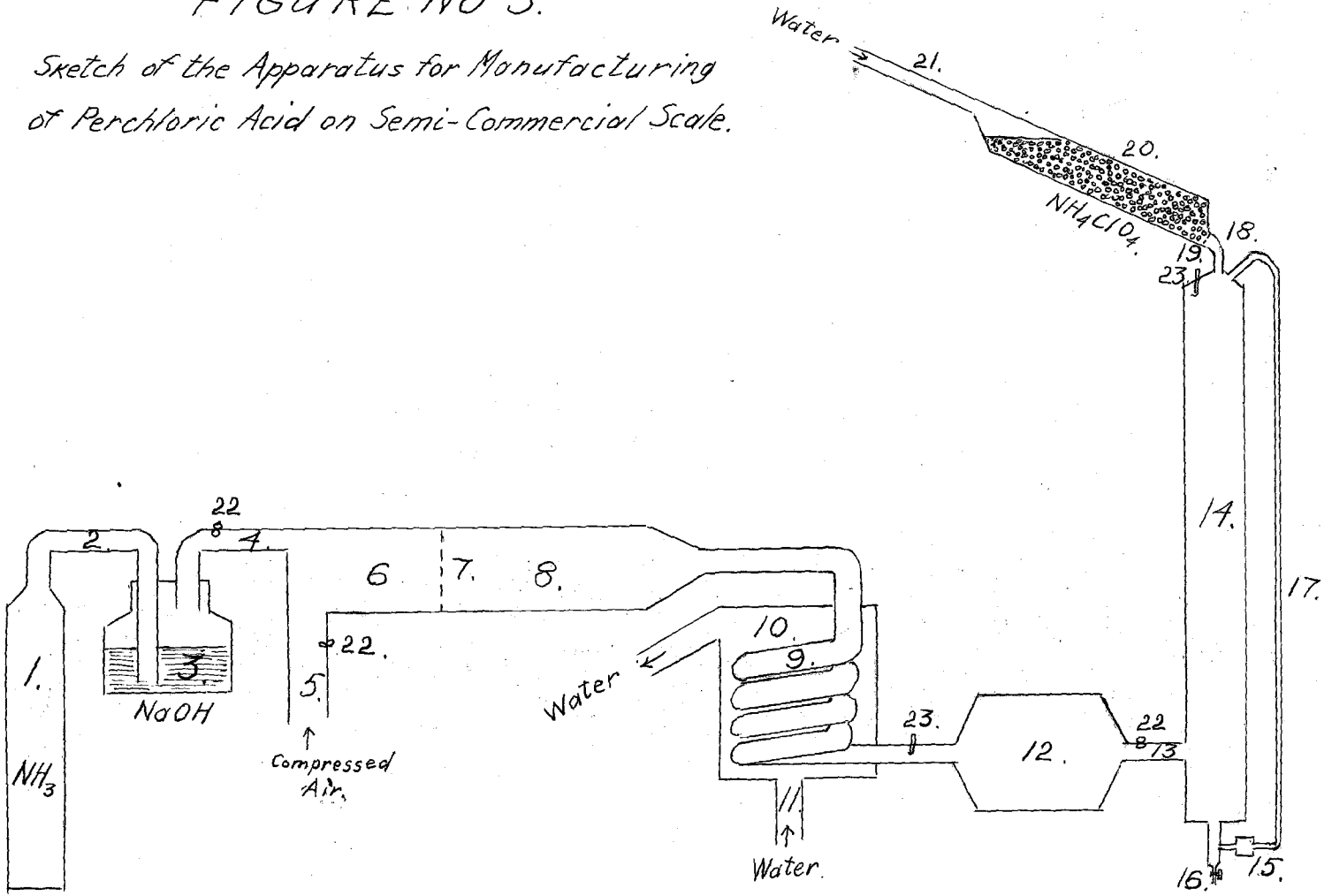
(1) Compt.rend. CLXVIII, (1919), 235-237.

heated platinum gauze and to one minute time. The temperature of the substances involved in the process was taken as 20°C unless special remarks are made. One pound-mol of gas occupies at that temperature 664,000 cubic inches, 1 liter is equal 0.264 gallon, and the molal heat capacities of the gases were assumed to be $7.68+0.0007T$, where T is the absolute temperature in degrees Kelvin.

Apparatus shown in Figure #3 consists of the tank with ammonia gas (1), which is connected by a pipe 3/4 inch in diameter with a tank containing sodium hydroxide solution to wash the gas before it enters the mixing chamber. Pipes (2) and (4) are of the same diameter and as their cross-section area is 0.44 sq.inch the velocity of the gas in this part of the apparatus will be about 48.5 ft. per minute. The washing tank (3) must be made of lye-resisting material, probably iron. Pipe (5) is 2 inches in diameter and carries compressed air with a velocity of about 62 ft. per minute as the cross-section area of the pipe is 3.14 sq.inches and the volume of the air admitted is nine times the volume of the ammonia gas. Mixing chamber (6) is made of aluminium pipe 5 inches in diameter. Its cross-section area is 19.6 sq.inches and the velocity of the gases increases from 16 ft. to 42 ft. per minute as the gases become hotter from the heat introduced from the platinum gauze. Platinum gauze

FIGURE NO 3.

Sketch of the Apparatus for Manufacturing of Perchloric Acid on Semi-Commercial Scale.



(7), 20 sq.inches in area, catalyzes the reaction and the gases then enter the 5 inch pipe (8) made of cast iron which conducts the mixture to the cooler (9). Cold water enters the cooler jacket (10) through the pipe (11) at a rate of approximately 1.12 gallons per minute, and leaves it through a pipe at the top of the tank. The pipe which conducts the gases, cooled to 50-60°C, to the large chamber (12) must be 2.5 inches in diameter having a cross-section area of 4.9 square inches and giving a velocity of 62 feet per minute. Chamber (12)made of cast iron must be of about 6,000 cubic inches capacity to allow the gases to remain there during 100-120 seconds until the reaction between nitric oxide and oxygen is almost complete. Nitrogen peroxide produced passes through pipe (13) to the absorption tower (14) where it meets the stream of hot saturated solution of ammonium perchlorate which enters the tower at the top. The temperature of the tower must be kept at 95-100°C as this temperature gives the best results. Therefore the whole column must be surrounded by a steam jacket. The solution of ammonium perchlorate must be returned by means of the pump (15) and pipe (17) to the absorption tower until the process is complete. Then the solution must be run out through the cock (16). At the top of the tower a suitable device must be attached to obtain a saturated solution of ammo-

nium perchlorate at about 100°C, which must be filtered before it enters the absorption tower if the commercial salt contains insoluble impurities. (23) indicates positions of thermometers and (22) positions of the gas-flow meters. The temperature of the gauze can be controlled by measuring its resistance.

TABLE #1.

Specific Gravities of $HClO_4$ Solutions.

% $HClO_4$	Specific Gravity. 20°C.	50°C.
100.00	1.7676	1.7078
94.67	1.8089	1.7531
84.81	-	1.7756
75.59	1.7386	1.7023
60.38	1.5353	1.5007
39.75	1.2901	1.2649

(H.J.van Wijk.Zeit.Anorg.Ch.32,(1902),115).

Specific Gravities at 20°C.

Sp.Gravity.	%$HClO_4$
1.05	8.48
1.10	16.00
1.15	22.64
1.20	29.26
1.25	34.95
1.30	40.10
1.35	44.81
1.40	49.23
1.45	53.31
1.50	57.06
1.55	60.78
1.60	64.50
1.65	68.26
1.67	69.77

(K.van Emster.Zeit.Anorg.Ch.52,(1907),270).

TABLE #2.

Data Corresponding to One Square Inch Platinum Gauze and One Minute Time.

Weight of 0.0030 in. gauze	0.01482 oz.
" " " 0.0026 " " "	0.01113 "
" " " ammonia	0.000334 lb.
" " " nitric oxide produced	0.000530 "
" " " nitrogen peroxide formed	0.000773 "
" " " air in 10% ammonia mixture	0.005109 "
" " " " " nitric oxide mixture	0.001275 "
Volume of the gases passing the gauze at 800° C. and 1 atmosphere	420 cu.in.
Rate of flow through the gauze (0.030 lb. of ammonia gas per minute per oz. of platinum)	35 ft/min.
Volume of the gases in nitric oxide-air mixture at 60°C	140 cu.in.
Volume of the reaction chamber for the nitric oxide-air mixture (120 sec)	300 " "
Weight of ammonium perchlorate converted	0.000292 lb.
" " " perchloric acid produced	0.000252 "
Volume of ammonium perchlorate solution	0.015 cu.in. 0.25 cu.cm.
Cost of the gauze ($116 per oz. of platinum plus work)	$1.50

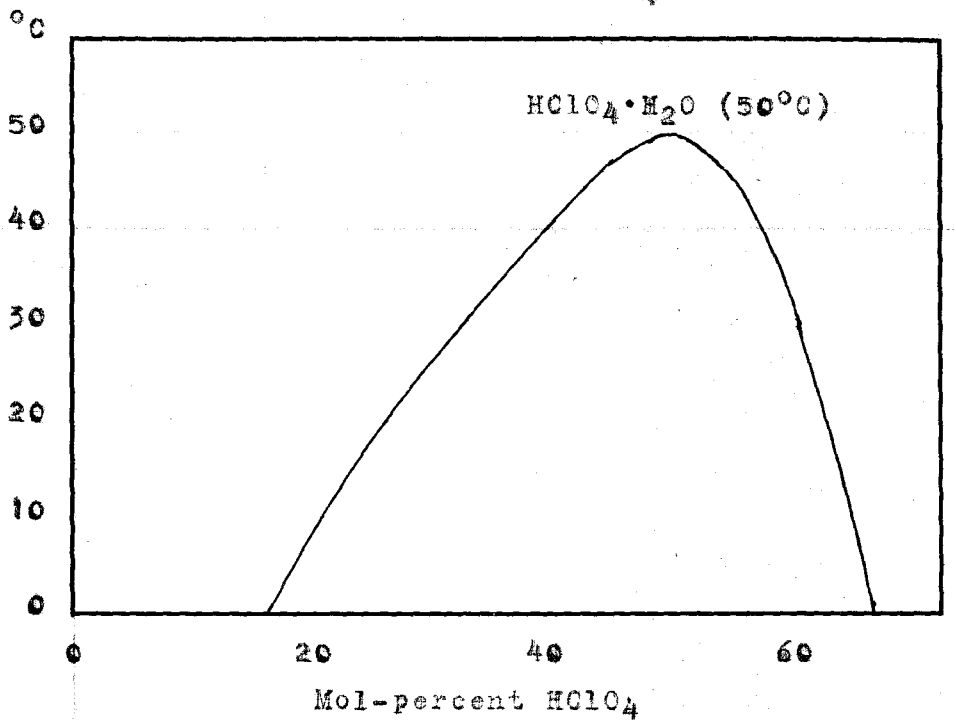
TABLE #3.

Data Corresponding to 20 Square Inches Gauze and One Minute Time.

Weight of ammonia gas	0.00668 lb.
" " " air from pipe (5)	0.10300 "
Volume of ammonia gas	261 cu.in.
Total volume of gases in (6)	2610 " "
" " " " " " " at 800°C at the gauze	9800 " "
" " " " " " " at 60°C after cooling	3000 " "
Volume of ammonium perchlorate solution ..	0.30 " "
Heat consumed by the cooler	677 B.T.U.
	170000 cal.
Cold water supply for the cooler	1.12 gallons
	4.25 liters.

FIGURE #4.

a) Freezing Points of $HClO_4$ Solutions.



b) Boiling Points of $HClO_4$ Solutions.

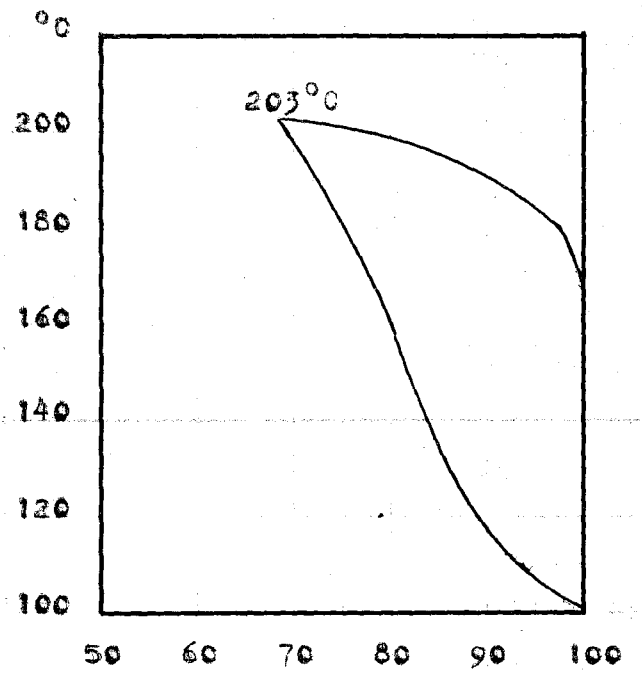
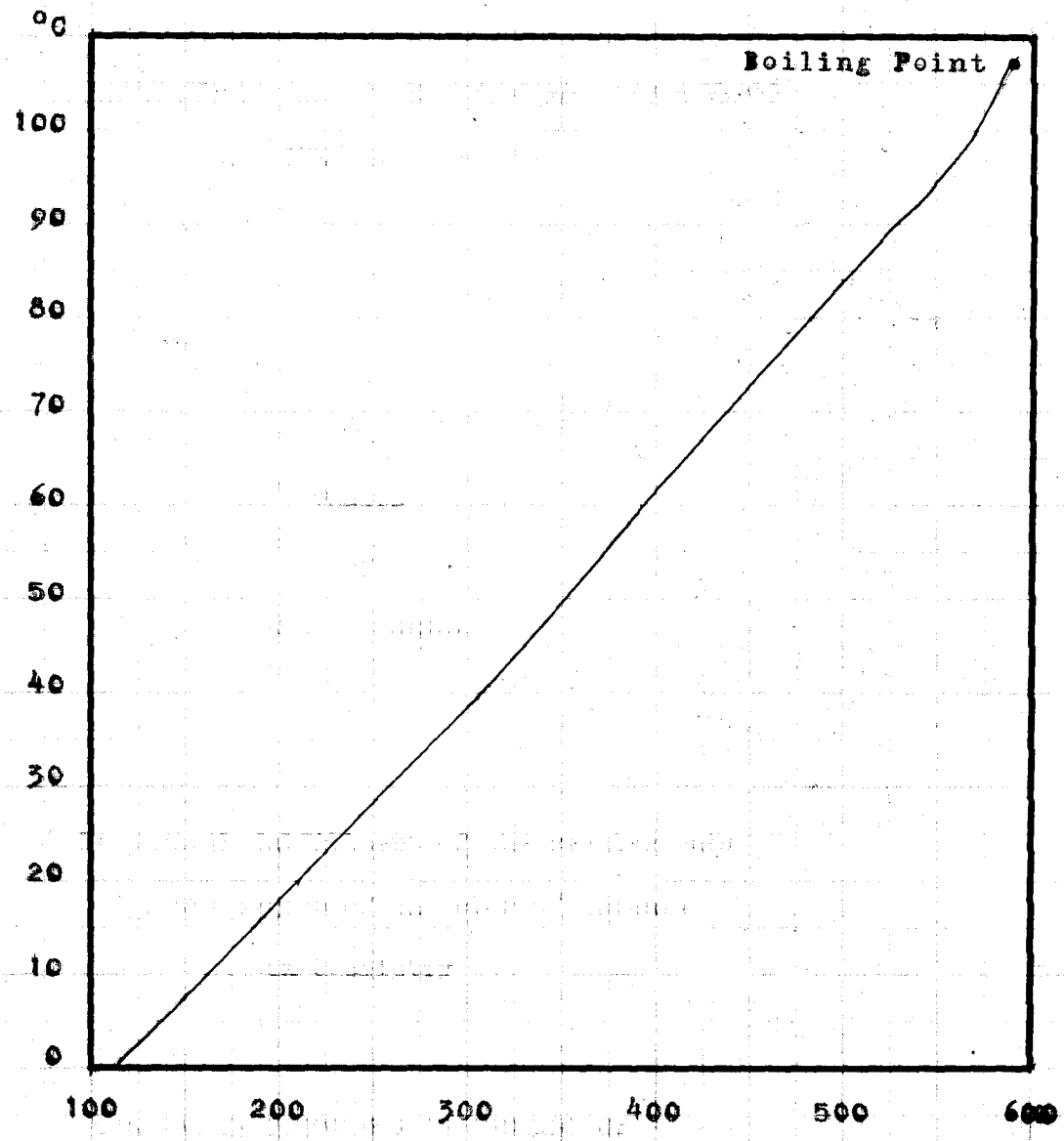


FIGURE #5.

Solubility of Ammonium Perchlorate in Water.



(Tables Annuelles de Constantes et Données Numérique. 1, 379).