PERCHLORIC ACID

from

AMMONIUM PERCHLORATE AND OXIDES OF NITROGEN

Thesis

by

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I. Introduction.

The object of this work was to study quantitatively the reaction between NO_2 and NH_4ClO_4, in which the latter is oxidized to $HClO_4$, with a view to determining the possibility of using this reaction as a commercial method for the production of perchloric acid.

While anhydrous perchloric acid is unstable and reacts violently as an oxidizing agent with many substances, such as charcoal, ether, and paper, its aqueous solutions are quite stable,[1] and are not active oxidizing agents, being reduced only by such substances as ferrous hydroxide and hyposulphurous acid.

Aqueous solutions of perchloric acid boil at a relatively high temperature, the maximum boiling point at atmospheric pressure being 203°C, and the composition of the constant-boiling solution obtained at this temperature being 72.3% $HClO_4$. Below 160°C the distillate contains less than 1% of $HClO_4$.

Perchloric acid solutions resemble those of sulphuric acid in many respects, and their stability and high boiling point indicate that they might be used commercially in some cases where sulphuric acid is now used, provided $HClO_4$ could be produced cheaply enough,

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1. Abegg, "Handbuch der Anorg. Chem.", IV,2, p.182.

on a large scale.

Furthermore, there are very few insoluble perchlorates, the exceptions being those of potassium, rubidium, caesium, and thallium. This fact would especially recommend the use of perchloric acid in cases in which the formation of insoluble sulphates prevents, or seriously interferes with, the use of sulphuric acid.

The cheap production of perchloric acid would also enable it to be used in the separation of potassium and sodium, and the analytical determination of the former. Its use for this purpose was suggested by Schlösing[1], who proposed to produce $HClO_4$ solutions by treating NH_4ClO_4 with aqua regia.

The principal methods which have been used for the commercial production of $HClO_4$ are:

(1) Mix dry $KClO_4$ and concentrated H_2SO_4 and distil under diminished pressure[2]. This distillation is troublesome and expensive, and if a pure product is desired it must be redistilled to remove H_2SO_4. The final product contains 88-98% $HClO_4$.

(2) Mix dry $NaClO_4$ and concentrated HCl.[2] NaCl is precipitated from the acid solution. Filter this off

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1. Compt. Rend., 73, p. 1269.

2. F. C. Mathers, Chem. Ztg., 37, p. 363.

and distil off the HCl from the filtrate. The product thus obtained contains about 95% $HClO_4$, but also contains a slight amount of $NaClO_4$, and in order to obtain the pure acid it must be distilled under diminished pressure.

(3) Electrolytic oxidation of HCl in dilute solution.[1] In addition to $HClO_4$, the resulting liquor contains in solution hydrochloric and chloric acids and chlorine. The product is also quite dilute and requires considerable concentration for commercial use.

Other methods have been used for laboratory preparation of perchloric acid,[2] but none of them seem to be adaptable to commercial production.

It does not seem to be possible to produce perchloric acid at a reasonable cost by any of the above methods, and as NH_4ClO_4 can be obtained fairly cheaply, it suggests itself as a possible source of cheap $HClO_4$. If pure NH_4ClO_4 is used and the ammonia can be completely removed by oxidation, for example with NO_2, there will be no non-volatile impurities left in the product. All the products of reaction will be either gases or volatile liquids which can be distilled off

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1. E. C. Walker, U. S. Pat. 1,271,633; and
   H. M. Goodwin and E. C. Walker, Trans. A.E.S. 40
2. Abegg,"Handbuch der Anorg. Chem." IV, 2, p.182.

at atmospheric pressure, thus avoiding the expensive and bothersome low-pressure distillation required in the other methods.

II. Previous Work.

Some study has been made of the oxidation of ammonia and ammonium salts by oxides of nitrogen. Besson and Rosset[1] passed a stream of dry NH_3 gas at -20°C over solid NO_2 at the same temperature. The reaction liberated a large amount of heat, and white fumes consisting chiefly of N_2 and NO were given off. Ammonium nitrate and water were also formed. They expressed the reaction by the equations

$$3NO_2 + 4NH_3 = 7N + 6H_2O$$

$$3NO_2 + 2NH_3 + H_2O = NO + 2NH_4NO_3.$$

They also oxidized NH_4Cl, NH_4NO_3, and $(NH_4)_2SO_4$ by heating with NO_2 at 100°C in strong sealed tubes. In the first case a variety of products were formed, due to the presence of chlorine, but in the other two cases the only gas evolved was nitrogen, and the reactions may be simply expressed by the equations

$$NH_4NO_3 + 2NO_2 = 2N + 2HNO_3 + H_2O$$

$$(NH_4)_2SO_4 + 4NO_2 = 4N + 2HNO_3 + H_2SO_4 + 2H_2O.$$

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

H. H. Willard[1] tried several methods of oxidizing NH_4ClO_4 to $HClO_4$. One of these consisted in generating a mixture of NO and NO_2 by the action of H_2SO_4 on $NaNO_2$, and passing the gas so obtained through boiling NH_4ClO_4 solution. Some oxidation occurred, but the reaction was slow. He also tried running formic acid into a solution of NH_4ClO_4 and HNO_3, whereby the latter was reduced to lower oxides of nitrogen which reacted with the ammonia and completely removed it from the solution, although the reaction was slow in this case also.

Better results were obtained by slowly dropping HCl into an aqueous solution of NH_4ClO_4 and HNO_3. Practically complete conversion was obtained and the reaction was fairly rapid. The excess HCl or HNO_3 was evaporated off. Willard suggests the following equation as explaining the reaction in this case

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

Stenzel[2] worked with a mixture of NO and NO_2 gases, in the hope that the NO present would combine with an equal molal amount of NO_2 to form N_2O_3 and

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1. J. A. C. S., 34 (1912), p.1480.
2. Thesis on "A Method for the Preparation of Perchloric Acid", Calif. Inst. of Tech., 1921.

that this N_2O_3 would then react according to the equation

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

He generated his gas mixture by slowly adding sodium nitrite solution to hot HNO_3 and bubbled the resulting mixture of NO_2 and NO through a hot solution of NH_4ClO_4. The gas generated in this manner only contained from 10 to 20% NO, so that if there was any appreciable tendency for the gases to act in the manner just described, there should have been little or no NO in the gas leaving the solution. Stenzel found, however, that the gas apparently acted entirely as a physical mixture of NO and NO_2 and that only the latter reacted to any extent, the NO largely passing through the solution without dissolving or reacting. This might be expected, as Thorpe[1] states that liquid N_2O_3 on contact with water forms NO and NO_2, of which only the latter dissolves in the water, so that there would probably be very little possibility of the reverse reaction taking place.

The action of NO_2 on the NH_4ClO_4 was explained by means of the equations

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

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

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1. Dict. of Applied Chem., III, p.686.

which may be combined to give

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

This corresponds exactly to the equation given by Besson and Rosset (loc. cit.) for the action of NO_2 on NH_4NO_3 and $(NH_4)_2SO_4$.

Stenzel obtained fairly good percentages of conversion to $HClO_4$ in some cases. The product, however, contained HNO_3, presumably formed as indicated in the above equation. It would therefore be necessary to remove this HNO_3 from the product, but this could readily be distilled off along with the water on concentrating.

III. Experimental Work.

A. Method and Apparatus.

The results of previous work indicated that in order to obtain the reaction

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

it would be necessary to generate the N_2O_3 right in the NH_4ClO_4 solution. This may have been one of the reactions obtained by Willard on dropping HCl into HNO_3 and NH_4ClO_4 solution. It is difficult to conceive of any practical method of accomplishing such a reaction as this, which could possibly be used on a large scale for the cheap production of perchloric acid.

It was therefore decided to make a quantitative

study of the reaction of gaseous NO_2 when bubbled through hot NH_4ClO_4 solution, even though this method would involve the subsequent removal of HNO_3 from the product by distillation.

In addition to pure NO_2, two gas mixtures were also tested, one of which contained some NO, and the other some O_2.

Several different forms of apparatus were tried for bubbling the gas through the solution, as it was desired to obtain as efficient absorption as possible. Simply bubbling through the solution in test tubes did not prove satisfactory, as the slight pressure due to the head of the liquid in the tubes caused leakage of NO_2 which was hard to prevent. Furthermore, it was desired to have the gas and liquid come in contact in a counter-current manner, so that the gas containing the highest concentration of NO_2 would continually come into contact with the solution containing the most $HClO_4$ and the least unconverted NH_4ClO_4.

The apparatus shown in Fig. 1 was therefore used. Except where otherwise noted, it was made entirely of glass, on account of the highly corrosive action of NO_2 on rubber tubing and corks. The part in which the absorption and reaction occurred consisted of an inclined

tube a about 14 inches long, having a number of bulges or pockets blown in the bottom, and corresponding indentations or projections downward from the top. At its upper end this tube was connected to the outer vertical tube b. A rubber stopper was fitted into the upper end of b and carried an inner vertical tube c. A piece of cloth was fastened over the lower end of this latter tube and the solid NH_4ClO_4 was placed therein, the cloth serving to hold back solid particles of the salt.

Water was allowed to drip slowly from the dropping funnel d onto the NH_4ClO_4 and dissolve it. The solution passed through the cloth, up around the outside of tube c, and down through a, collecting in each of the pockets in turn and then overflowing to the next. At the lower end the solution flowed out through tube e, which extended downward about an inch and then up again and was provided with a lip f to facilitate discharge. Tube e was broken and provided with a rubber connection e' to assist in assembling the apparatus. Liquid seals were thus formed at both the upper and lower ends of the absorption tube a, which permitted the solution to enter and leave this tube but prevented escape of the gas.

The gas being tested was admitted through the

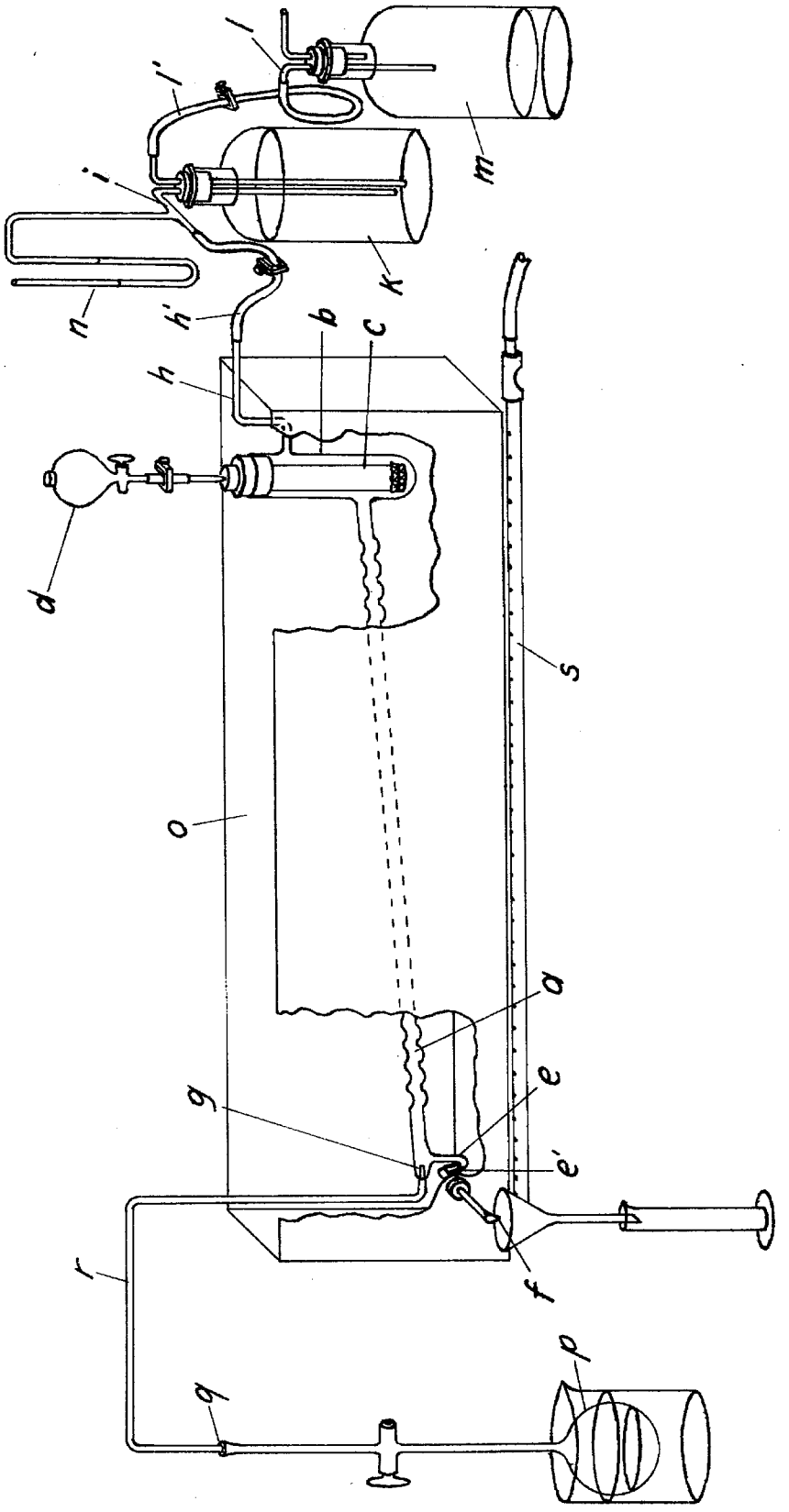

Fig. 1.

through the small opening or jet g at the lower end of a, and bubbled through the solution which was allowed to collect there. It then passed up through tubes a and b and out through the exit tube h. This was connected by a rubber tube h' (it being permissible to use rubber at this point, as well as for the stopper in the upper end of tube b, since all the NO_2 was apparently exhausted before reaching this point) to a tube i leading to a gas collecting bottle k, an ordinary 1 liter bottle being used for this purpose.

The inlet tube i extended down near the bottom of the bottle, which was filled with acidified potassium permanganate solution of known $KMnO_4$ content, so that the gas entering the bottle bubbled through this solution. A preliminary run gave evidence that a considerable amount of NO was contained in the colorless gas leaving the apparatus, since on collecting this gas over water and then admitting air to the collecting vessel a reddish-brown coloration was produced, indicating oxidation to NO_2. The purpose of the $KMnO_4$ was to remove this NO from the gas by oxidation to HNO_3.

The solution displaced from bottle k flowed through tubes l'and l into another bottle m, the rubber tubing l' being for the purpose of adjusting the rela-

tive heights of the two bottles. The outlet of l was lower than that of i by an amount sufficient to maintain a slight vacuum in the latter, and hence in tube a. The amount of this vacuum was observed by means of the manometer n containing paraffin oil.

The main portion of the apparatus was immersed in a water-bath in tank o, the outlet tube e extending through a rubber-stoppered opening in the side of this tank. A layer of paraffin oil was kept on top of the water-bath to cut down steaming and loss of water by evaporation. The water-bath was heated by means of a long perforated pipe burner s.

The means of producing the gas and admitting it to the absorption apparatus varied with the gas being tested and will be described separately for each test.

B. Test with Pure NO_2.

The NO_2 used in this test was prepared as follows, the apparatus being illustrated in Fig. 2. About 200 grams of pure $Pb(NO_3)_2$ were dried at 110°C for several hours and then placed in the 500cc. pyrex distilling flask. This was heated in a solder-bath to a sufficient temperature to give a moderate flow of deep reddish-brown gas, as indicated by the rate of bubbling through the paraffin oil in the U-tube. The condenser was kept

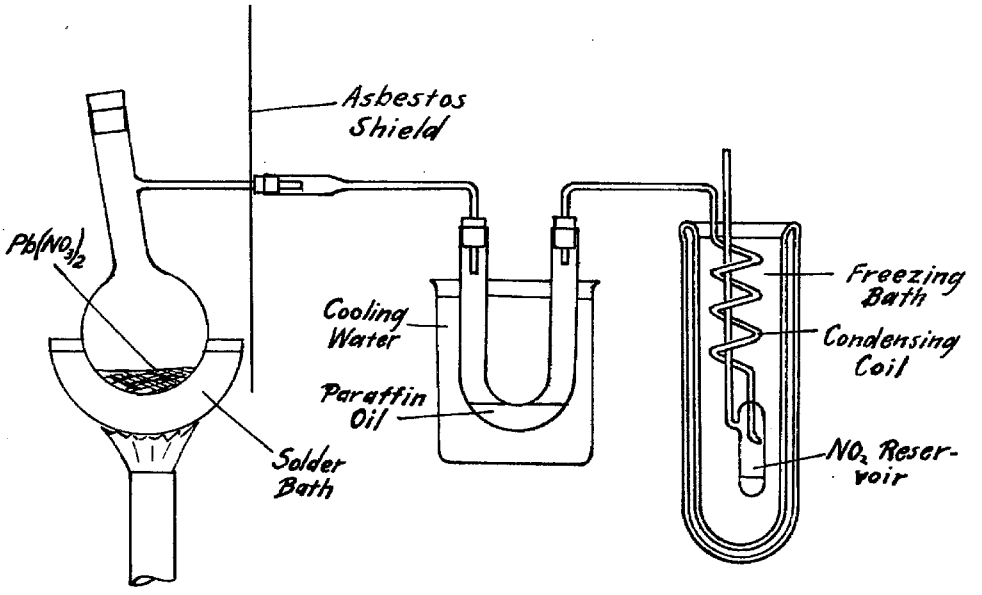

Fig. 2.

immersed in a bath whose temperature was approximately -15°C. For this purpose either a freezing mixture of ice and hydrochloric acid or an alcohol-liquid air solution was used. The rate of generation of the NO_2 was so regulated that a large part of it condensed in the condensing coil and collected in the reservoir at the bottom thereof.

As NO_2 rapidly destroys corks and rubber tubing, it was necessary to make as much as possible of the apparatus of glass, and where corks had to be used, to cover them with a coating of asbestos and sodium silicate. The corks used in this apparatus, as well as those used in other operations described later, were first well rolled, and then covered with two or three succes-

sive coats of the asbestos-sodium silicate mixture, made by grinding the two together in a mortar to form a smooth paste. After treatment in this manner, the corks stood up sufficiently to last throughout any one run.

The liquid NO_2 collected in the condenser was poured through a funnel, formed by drawing out a test tube and breaking it in the middle of the narrow portion, into the bulb p (shown attached to the absorption apparatus in Fig. 1). It was kept in this bulb until used, the glass stopcock being kept well greased and held in place by means of strong rubber bands.

Several preliminary tests were made of the action of this NO_2 on NH_4ClO_4 solution, using different types of apparatus and different methods of procedure, but in the final test the apparatus was as shown in Fig. 1 and the operation was briefly as follows.

The bulb p containing liquid NO_2 was connected by means of a ground glass joint at q to tube r leading to the jet g, the weight of the bulb and contents being taken before and after the test. About 10 gms. of recrystallized NH_4ClO_4 were placed in c, and water was run in until c and b were filled nearly to the level of the upper end of the inclined tube a. The water-bath was then heated to about 95°C.

Meanwhile, a known volume of standard $KMnO_4$ solution was placed in the gas collecting bottle k and diluted with water so as to completely fill this bottle and tubes l and l', the screw clamp on the latter being then shut to prevent flow of solution until the proper time.

When the water-bath reached the desired temperature, water was allowed to drop from funnel d at the rate of about 1 drop every 5 seconds, this rate of feed being afterward diminished as described later on. When the solution started to flow through the inclined tube a, the stopcock of bulb p was opened and NO_2 gas admitted to the apparatus. This bulb was in a beaker of water, and as the boiling-point of NO_2 is about 25-26°C, it was only necessary to warm this water very slightly in order to maintain a sufficiently rapid flow of gas.

The rubber tube h' was not connected to exit tube h until the brown NO_2 fumes reached jet g, when this connection was made and the screw clamp on l' was opened to regulate the flow of $KMnO_4$ solution so as to give the desired rate of flow of gas. The volume of air in the apparatus beyond jet g was therefore collected in bottle k along with the nitrogen, but as an equal volume of gaseous reaction products (largely nitrogen) was left in the apparatus at the end of the

test, these two errors practically balance each other.

By maintaining about a 1 inch difference in level in the oil manometer n the solution was caused to fill up about the lower fourth of the inclined reaction tube before overflowing through the outlet tube e, and this condition seemed to give the best results. The NO_2 therefore bubbled up through the solution in the lower part of the tube and then passed along in contact with the solution in the upper part. The solution product dripped from the end of the outlet tube through a funnel into a 10 cc. graduate, so that definite portions thereof could be collected and analyzed.

The first few 10 cc. portions of solution coming through had not had sufficient contact with the gas, and some NH_4ClO_4 crystallized out on cooling. This solution was therefore recirculated by returning it to the feed funnel d until steady conditions were obtained and no more NH_4ClO_4 crystallized out. The rate of feed of water from d was then decreased to about 1 drop every 7 seconds.

The rate of flow of $KMnO_4$ solution from bottle k and the temperature of the water surrounding the NO_2 bulb were so regulated that all the brown color disappeared from the gas slightly below the upper end of the reaction tube a.

The reaction was continued until the gas collecting bottle was nearly filled with gas. This bottle was then closed off and disconnected, and the water feed was stopped. The NO_2 bulb was closed off, disconnected, and weighed, the loss in weight giving the amount of NO_2 used.

The solution left in the lower end of a and in the outlet tube e was forced out by gently applying compressed air through r, the end of the gas exit tube h being closed off. The portions of solution collected, including that blown out as just described, were saved and analyzed separately as follows.

First, the total acidity was determined by titration with standard NaOH solution, using methyl red as indicator. Care was used not to go past the end-point, in order to prevent any possibility of loss of ammonia.

Second, the unconverted ammonia was determined by making the solution strongly alkaline, distilling off the ammonia from a Kjeldahl flask, and collecting it in a known volume of standard H_2SO_4, the excess of the latter being titrated against standard NaOH solution.

Third, the nitric acid formed in the reaction was determined by adding aluminum pellets to the alkaline solution remaining in the Kjeldahl flask, heating moderately for about 4 hours to reduce the nitrate to ammo-

nia, and then raising the temperature, distilling off the latter, and determining it by absorption in H_2SO_4 as before. The outlet of the condenser was kept dipping just below the surface of the H_2SO_4 solution in the receiving flask during this entire operation of reduction and distillation.

A check determination of both ammonia and nitrate, made in the above manner on a weighed amount of ammonium nitrate, gave an error of 0.7% in the ammonia and 1.8% in the nitrate. It may therefore be assumed that in these analyses the error in ammonia is not over 1% and in nitric acid not over 2%. The error in the total acid should be much less than this. The desired information was calculated from these analyses as described later under Calculation of Results.

The $KMnO_4$ solution remaining in the gas collecting bottle k was shaken for some time with the gas, to remove NO as thoroughly as possible. In order to ensure the presence of an excess of acid $KMnO_4$, fresh portions thereof were returned from the second bottle m by alternately applying pressure and suction to the latter. The remaining volume of gas, at atmospheric pressure, was marked on the bottle for subsequent measurement, the solution removed from the bottles, and the excess $KMnO_4$ titrated hot with freshly standardized $Na_2C_2O_4$ solution.

C. Test with $NO_2 + \frac{1}{4}O_2$.

The production of NO in the previous test represented the loss of a portion of the oxidizing power of part of the NO_2. It was thought that by using a mixture of NO_2 and O_2, this NO would be reconverted to NO_2 in the process and then react with more solution, thereby increasing the oxidation of NH_4ClO_4 per mol of NO_2 used.

The reaction obtained by heating lead nitrate may be written

$$\frac{1}{2}Pb(NO_3)_2 = \frac{1}{2}PbO + NO_2 + \frac{1}{4}O_2$$

which gives $\frac{1}{4}$mol of oxygen per mol of NO_2. This $\frac{1}{4}$ mol of O_2 would be capable of oxidizing $\frac{1}{2}$ mol of NO according to the equation

$$\frac{1}{2}NO + \frac{1}{4}O_2 = \frac{1}{2}NO_2$$

and since the NO obtained in the previous test represented only a little over a tenth of the NO_2 used, this proportion of O_2 should be more than sufficient to reoxidize all the NO produced.

A test was therefore made by simply heating lead nitrate and bubbling the gas so obtained directly through NH_4ClO_4 solution in the same manner as in the preceding test with pure NO_2. For this purpose a 500cc. pyrex flask t was connected to the gas inlet tube r of the apparatus illustrated in Fig. 1. This connection was made as shown in Fig. 3. The corks used were treated with

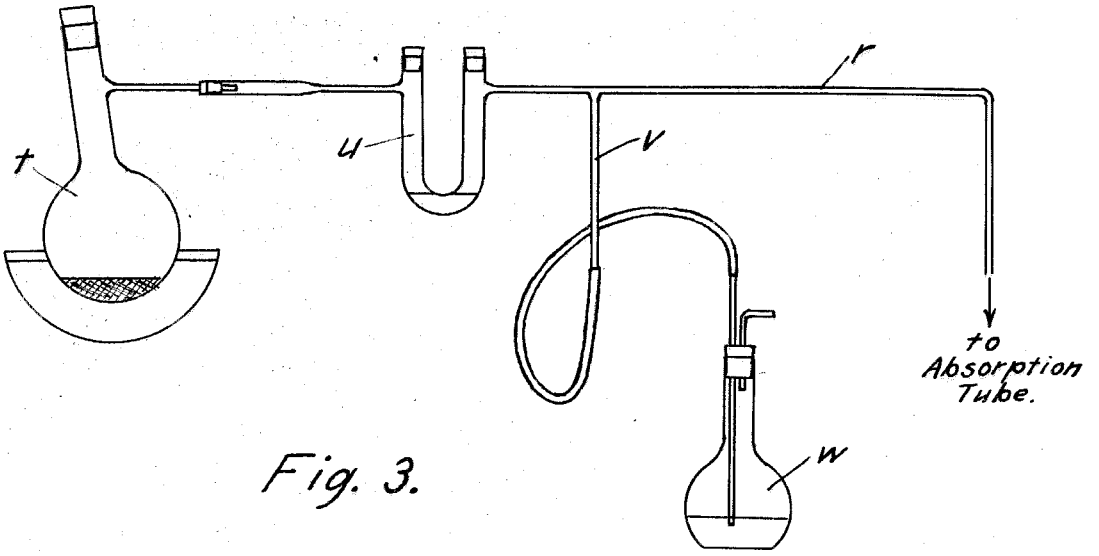

Fig. 3.

sodium silicate and asbestos as described under the preparation of pure NO_2. The U-tube u contained paraffin oil for the purpose of observing the rate of flow of the gas, especially before admitting this gas to the main apparatus. In order to obtain the desired rate of generation of gas before starting to bubble it through the solution, a side tube v was provided. By closing off the exit tube h, the gas was made to pass through this side tube and bubbled through a known volume of standard NaOH solution in flask w,

Fig. 4.

which absorbed the NO_2. The remainder of the apparatus and the method of producing the NH_4ClO_4 solution and of collecting the gaseous products over $KMnO_4$ solution were the same as before. The general appearance of the apparatus as used in this test is shown in Fig. 4.

A weighed amount of $Pb(NO_3)_2$ was placed in flask t at the start, and this was heated on a solder-bath until the reddish-brown gas mixture of NO_2 and O_2 was generated at the desired rate. The exit tube h was then opened and the side tube y closed off, thus causing the gas to bubble through the NH_4ClO_4 solution. This test was conducted in the same manner as the first one, except that water was fed in at a slightly faster rate, about 1 drop every 5 seconds, throughout the test. The rate of flow of gas was regulated by the temperature of the solder-bath.

After completion of the test, the residue in flask t was weighed to give a means of determining the NO_2 generated, and the excess NaOH in flask w was titrated against standard H_2SO_4. The other analyses, on both the gaseous products and the portions of solution product, were the same as in the preceding case.

D. Test with Mixed NO_2 and NO.

It was also desired to try a gas mixture similar

to the one used by Stenzel (loc. cit.); that is, one in which a certain percentage of NO was present, in order to see if any evidence could be obtained as to whether or not any portion of such a mixture would react as N_2O_3, and whether better conversion of NH_4ClO_4 could be obtained with this mixture than with pure NO_2.

Stenzel had found that the gas generated by slowly forcing sodium nitrite solution into hot HNO_3 did not have a constant composition, due to dilution of the nitric acid, not only by the water added in the $NaNO_2$ solution but also by the water produced in the reaction.

Other means of generating such a gas mixture were therefore investigated, and the method finally adopted consisted in adding pellets of As_2O_3 to hot concentrated HNO_3. If the As_2O_3 was added in powdered form it was not readily and uniformly wetted by the acid, and the generation of gas was slow and uneven. By compressing it into pellets, however, and dropping these into the acid at regular intervals, much better results were obtained.. The pellets used were made in a small pellet press and weighed about $2\frac{1}{2}$ to 3 gms. each. The nitric acid was heated on an oil-bath to 110-120°C.

The gas generated in this manner varied somewhat in composition. Analyses of this gas were made as follows. An evacuated bulb was connected to a tube lead-

ing from the generating vessel, and the bulb allowed to fill with gas. It was then closed off and disconnected and a known volume of standard NaOH solution was forced in and shaken. The brown color disappeared and a partial vacuum was created inside the bulb. Hydrogen gas was admitted to equalize the pressure, and the solution was then drawn out, care being taken not to lose any of the unabsorbed NO gas remaining in the bulb nor to admit any air. The excess NaOH in this solution was titrated against standard H_2SO_4. The reactions which may be involved in this step are

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

$$3NO_2 + 2NaOH = 2NaNO_3 + NO + H_2O$$

$$NO_2 + NO + 2NaOH = 2NaNO_2 + H_2O .$$

Let A = number of mols of NaOH consumed.

B = " " " " $NaNO_2$ produced

C = " " " " NO remaining in bulb

x = " " " " NO_2 in gas sample

y = " " " " NO in gas sample.

Then

(1) $x + 3y = 2B + 3C$ since the reducing power of the NO_2 and NO together at the start must be equal to that of the NO and $NaNO_2$ together at the end;

(2) $x + y = A + C$ since all the NO_2 and NO are final-

ly in the form of either Na salts or of free NO gas.

From (1) and (2)

(3) $y = B + C - \frac{1}{2}A$

(4) $x = (3/2)A - B$

A is determined by the H_2SO_4 titration described above.

B is determined by adding the neutral solution resulting from this titration to an excess of acidified $KMnO_4$ solution, and then titrating the excess $KMnO_4$ against $Na_2C_2O_4$ solution. The reaction in this case is

$$5NaNO_2 + 2KMnO_4 + 6H^+ = 5NaNO_3 + 2K^+ + 2Mn^{++} + 3H_2O .$$

If E = number of mols of $KMnO_4$ used in this reaction, then

(5) $B = (5/2)E$.

C is then determined by forcing acidified $KMnO_4$ solution into the sampling bulb, shaking to absorb and oxidize the remaining NO, then drawing out the solution and titrating the excess $KMnO_4$ as before. This reaction is

$$5NO + 3KMnO_4 + 9H^+ = 3K^+ + 3Mn^{++} + 5HNO_3 + 2H_2O .$$

If D = number of mols of $KMnO_4$ consumed, then

(6) $C = (5/3)D$.

By combining equations (3), (4), (5), and (6)

$$y = \frac{5E - A}{2} + \frac{5D}{3}, \text{ and } x = \frac{3A - 5E}{2}$$

Three analyses made in this way at different times, of mixed gases generated as described above, gave the following results:

	$\%NO_2$	%NO
1.	84.3	15.7
2.	86.1	13.9
3.	77.4	22.6

It may therefore be assumed that the average composition of the gas used in the following test was from 80 to 85% NO_2 and from 20 to 15% NO.

For the test using this gas mixture generated by As_2O_3 and HNO_3 the connections were substantially the same as in the preceding test, the general arrangement of the apparatus being as shown in Fig. 5. As shown in Fig. 6, however, a short tube x was inserted in the cork of the pyrex flask t for the purpose of adding the As_2O_3 pellets. This tube was in turn closed by a cork, which was removed each time a pellet was added. Some gas was

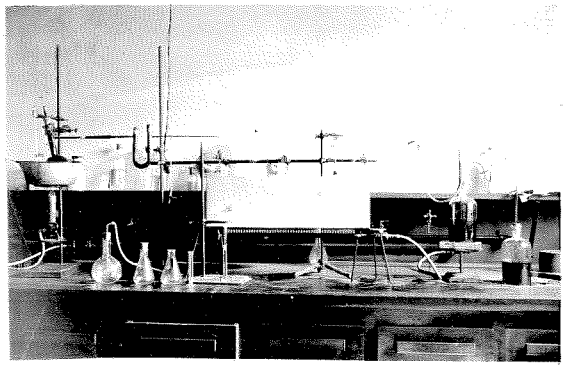

Fig. 5.

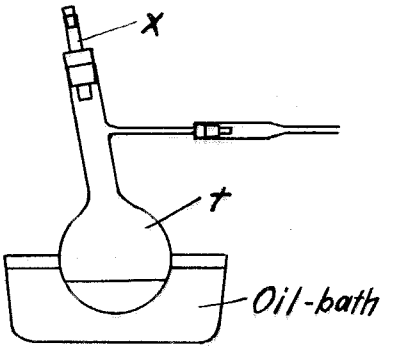

Fig. 6.

thus lost, and for this and other reasons no determination was made in this case of the amount of NO_2 used. Aside from this the operation and analyses were substantially the same as in the preceding test.

IV. Results.

A. Methods of Calculation.

In the solutions resulting from these tests, the only positive ions are assumed to be NH_4^+ and H^+, and the only negative ones NO_3^- and ClO_4^-. The amount of NO_2^- ion should be negligible since the reaction between HNO_2 and NH_4ClO_4 is said to be quite rapid and complete. If any nitrite was present, however, it was determined together with the nitrate and included in the latter and did not lead to an error in any of the other quantities.

Of these four ions, NH_4+, H^+, and NO_3^- were determined as has been described, and the ClO_4^- content was calculated by difference. Subtracting from this total perchlorate the unconverted ammonia gave the amount of NH_4ClO_4 converted to $HClO_4$ (or this could be calculated by subtracting the NO_3^- from the total acid or H^+ content).

The percentage conversion was taken as the ratio of $HClO_4$ produced to the total ClO_4^- content.

The mols of N_2 produced were calculated from the volume of gas left in the gas collecting bottle after absorption of the NO, on the assumption that 1 mol = 22.4 liters under standard conditions, correction being made for temperature and pressure.

The NO formed was calculated from the mols of $KMnO_4$ used up in the absorption from the gas in the gas collecting bottle, the reaction being

$$5NO + 3KMnO_4 + 9H^+ = 5HNO_3 + 3K^+ + 3Mn^{++} + 2H_2O .$$

As previously stated, in the first test the mols of NO_2 were simply calculated from the difference in the weight of the NO_2 bulb before and after the test. In the second test the mols of NO_2 formed were calculated from the loss in weight of the $Pb(NO_3)_2$ in the generating flask. If w_1 = weight of $Pb(NO_3)_2$ at the start

w_2 = " " residue in flask at the end

M_1 = molecular weight of $Pb(NO_3)_2$

M_2 = " " " PbO

and N = number of mols of NO_2 produced,

it may be seen from the reaction

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

that $N = 2 \times \frac{W_1 - w_2}{M_1 - M_2}$.

From this was subtracted the number of mols of NO_2 absorbed in the NaOH solution through which the gas was passed before starting to pass it through the apparatus.

There was also a considerable amount of NO_2 gas left in the apparatus at the end of this test. This volume was estimated to be approximately 650 - 700 cc. or .029 to .031 mols. Since the figure obtained previous to making this correction was 0.229 mols (by subtracting that absorbed in the NaOH from that generated from the $Pb(NO_3)_2$), the number of mols of NO_2 actually used was taken to be approximately 0.20.

As stated before, the amount of NO_2 used in the third test was not determined.

In order to get some idea of the total NH_4ClO_4 converted to $HClO_4$ in each test, and of the total HNO_3 formed along with it, the sums of each of these two constituents in all the portions of product collected from each test were taken. These figures do not represent the total amounts of these substances formed during the test, however, for in each case about the first 30 - 40 cc. of solution leaving the apparatus had to be returned before steady conditions could be secured, and not all of this solution came through again. In order to determine total $HClO_4$ and total HNO_3 produced, the solution remaining in the feed funnel and in the lower end of tube b should also have been analyzed. This was not done, however, as it was principally desired to determine the percentage con-

version in each portion of product, and the relation between $HClO_4$ and HNO_3 in the product.

B. Tabulation of Results.

Test No. 1.

Gas used - Pure NO_2

Total time of run - 2 hrs. 20 min.

Time of collecting product - 55 min.

Volume collected - 18.5 cc.

Average temperature - 94.5°C

Portion of Product		Total Acid (equiv)	NH_4ClO_4 unconverted (mols)	HNO_3 (mols)	NH_4ClO_4 converted to $HClO_4$ (mols)	Percentage Conversion
No.	Vol.					
1	10cc.	0.0383	0.0108	0.0302	0.0081	42.8%
2	8.5"	0.0415	0.0050	0.0273	0.0142	74.0%

Total NO_2 used = 0.1481 mols

* " $HClO_4$ collected = 0.0223 "

* " HNO_3 " = 0.0575 "

" N2 produced = 0.0470 "

" NO " = 0.0155 "

* These figures and the corresponding ones in other tests do not represent total amounts formed, as explained

under Calculation of Results.

Test No. 2.

Gas used - $NO_2 + \frac{1}{4}O_2$

Total time of run - 2 hrs. 35 min.

Time of collecting product - 1 hr.

Volume collected - 35 cc.

Average temperature - 97.5° C

Portion of Product		Total Acid (equiv)	NH_4ClO_4 unconverted (mols)	HNO_3 (mols)	NH_4ClO_4 converted to $HClO_4$ (mols)	Percentage Conversion
No.	Vol.					
1	10cc	0.0188	0.0142	0.0154	0.0034	19.3%
2	10cc	0.0198	0.0127	0.0146	0.0052	29.1%
3	15cc	0.0544	0.0121	0.0411	0.0133	52.4%

Total NO_2 used = 0.20 mols(approx)

* " $HClO_4$ collected = 0.0219 "

* " HNO_3 " = 0.0711 "

" N_2 produced = 0.0363 "

" NO " = none (too small to determine)

* See footnote under Test No. 1.

Test No. 3.

Gas used - NO_2 and NO

Total time of run - 1 hr. 52 min.

Time of collecting product - 42 min.

Volume collected - 26.5 cc.

Average temperature - 96° C

Portion of Product		Total Acid (equiv)	NH_4ClO_4 unconverted (mols)	HNO_3 (mols)	NH_4ClO_4 converted to $HClO_4$ (mols)	Percentage Conversion
No.	Vol.					
1	10 cc	0.0201	0.0095	0.0145	0.0056	37.1%
2	10 cc	0.0348	0.0099	0.0225	0.0123	55.5%
3	6.5cc	0.0201	0.0059	0.0136	0.0065	52.5%

Total NO_2 used not determined

* " $HClO_4$ collected = 0.0244 mols

* " HNO_3 " = 0.0506 "

" N_2 produced = 0.0300 "

" NO " = 0.0232 "

* See footnote under Test No. 1.

Table Showing Comparative Results of Tests 1, 2, and 3

Test No.	Gas Used	Rate of Flow of Gas cc./min.	Maximum Percent. Conversion	Mols of Products Collected						
				Per Mol of NO_2 Used				Per Mol of $HClO_4$ Collected *		
				* $HClO_4$	* HNO_3	N_2	NO	HNO_3	N_2	NO
1	Pure NO_2	20.8	74.0%	0.151	0.388	0.317	0.105	2.58	2.10	0.69
2	NO_2 + $\frac{1}{4}O_2$	35.0	52.4%	0.109	0.356	0.181	none	3.24	1.66	none
3	NO_2 and NO	37.8	55.5%	-	-	-	-	2.07	1.25	1.05

* See footnote under results of Test No. 1.

V. Discussion.

A. Conversion.

The best percentage conversion was obtained in the first test, using pure NO_2, but this may have been due to the slower rate of flow in this case. The flow should have been kept the same in all the tests in order to obtain comparative figures on conversion.

In each case the conversion increased as the test progressed. This may have been due to steadier conditions, or to the fact that some of the solution that had been recirculated came through the absorption tube for the second time.

B. Utilization of NO_2.

It is impossible to make accurate deductions in regard to this point, due to the fact that not all the $HClO_4$ and HNO_3 formed were determined. It would appear from the preceding table that NO_2 alone reacted more efficiently than when O_2 was present, but this cannot be stated positively.

C. Production of NO.

The presence of O_2 in the second test apparently eliminated the production of NO, but as far as can be seen from the results, did not increase the conversion of NH_4ClO_4 nor the efficieny of utilization of the NO_2, as was hoped.

The fact that more NO was produced in the third test than in the first indicates that at least a portion of the NO in the mixed gases passed through without reacting, as was also found to be the case by Stenzel.

This production of NO is objectionable since it means that the oxidizing power of the NO_2 is not completely utilized.

D. Production of HNO_3.

In each test, over twice as much HNO_3 as $HClO_4$ was found in the product, indicating that the reaction must not take place entirely according to the equation

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

but that some other reaction must occur which results in the production of a greater proportion of HNO_3.

It may also be seen that the ratio of HNO_3 to $HClO_4$ was greatest in the test with $NO_2 + \frac{1}{4}O_2$ and least in that with mixed NO_2 and NO. The presence of NO is therefore apparently of some value in reducing the production of HNO_3.

The formation of HNO_3 is objectionable because it means that part of the NO_2 is oxidized instead of reduced and because it must be removed from the product.

E. Production of N_2.

The number of mols of N_2 formed is in each case

somewhat greater than the $HClO_4$ collected. This fact indicates either that a considerable portion of the $HClO_4$ formed was left in the unanalyzed portion of solution remaining in the apparatus at the end of each test, or else that some reaction which produces N_2 but does not produce $HClO_4$ takes place. In test 1, due to the small amount of solution taken for analysis, a larger proportion of the solution was left in the apparatus and not analyzed for $HClO_4$, which may account for the extra large relative amount of N_2 produced in this case, on the basis of $HClO_4$ collected.

F. Probable Reactions.

The principal reaction is probably that given as the theoretical one, which may be broken up into the two equations

(1) $2NO_2 + H_2O = HNO_3 + HNO_2$

(2) $HNO_2 + NH_4ClO_4 = HClO_4 + N_2 + 2H_2O$.

Instead of the NO_2 all reacting in this manner, some of it may react according to equation

(3) $3NO_2 + H_2O = NO + 2HNO_3$,

which would account for the formation of both NO and HNO_3. The relation between $HClO_4$ and HNO_3 produced is therefore not fixed as indicated by equations (1) and (2), but depends on the relative extents to which this reaction and the reaction of equation (3) take place.

The presence of NO, as in Test 3, would tend to prevent reaction (3) from taking place provided it is reversible, and would therefore decrease the production of HNO_3, as was actually found to be the case.

The presence of O_2 on the other hand, as in Test 2, would remove the NO formed and consequently cause reaction (3) to take place to a greater extent, thereby increasing the production of HNO_3, as was also found to be the case.

G. Suggested Improvements in Method.

It would be very desirable to analyze all the solution involved in each test, in order to determine the relative efficiency of $HClO_4$ production on the basis of NO_2 used in the different cases. For this reason the solution left in the apparatus at the end of the test should also be analyzed.

In order to have a uniform concentration of ClO_4^- in the solution at all times, it would be better to prepare a hot NH_4ClO_4 solution of definite concentration outside the apparatus and then feed this solution in, rather than dropping water onto NH_4ClO_4 and producing the solution in the apparatus as was done in the above tests. The method used, beside giving a varying concentration of total ClO_4^- ion, required that the first part of the product be recirculated, as it

was otherwise impossible to place enough $HClO_4$ in the dissolving tube to last throughout a test.

Slower rates of solution flow through the apparatus, or a more efficient absorption system, should be tried in order to obtain higher percentages of conversion..

Some means should also be devised for determining the amount of gas used in the case of mixed NO_2 and NO, so that the comparative efficiency of utilization of the NO_2 in the three cases could be calculated.

VI. Summary.

The reaction between NO_2 and NH_4ClO_4 in solution was studied by subjecting a slow stream of hot NH_4ClO_4 solution to the action of a stream of gas containing NO_2, in a continuous counter-current system.

The main reactions involved are probably

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

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

The second reaction is disadvantageous, as it wastes NO_2 and produces excessive HNO_3.

The effects of admixture of O_2 and of NO with the NO_2 were also tested, neither of which had a very marked effect.

The maximum conversion of NH_4ClO_4 to $HClO_4$ obtained

under the conditions used was 74% at the minimum rate of solution flow, but this could undoubtedly be increased by the use of a more efficient absorption system.

As a commercial method for the production of perchloric acid this reaction has the advantage that no non-volatile impurities are formed as is the case in the methods now used. The chief disadvantage is the production of a large amount of HNO_3, but this could readily be distilled off together with water at atmospheric pressure.