THE PRODUCTION OF PERCHLORIC ACID

Thesis

by

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I.

I N T R O D U C T I O N .

Due to the fact that perchloric acid resembles sulfuric acid in many respects without having many of the disadvantages of use possessed by the latter, the devising of a cheaper means of producing it would be well warranted by its increased use in both analytical and industrial work. The present work was undertaken with the above idea in view and consisted in studying quantitatively the reaction taking place between nitric oxide (NO), nitric acid, and ammonium perchlorate.

Anhydrous perchloric acid is an unstable compound, decomposing spontaneously after a few weeks even when kept in the dark. It is a violently reacting oxidizing agent for many organic substances but aqueous solutions of the acid are not affected by light and are not active oxidizing agents.

Perchloric acid solutions (60% strength being the standard commercial form of the acid) are strong, monobasic solutions which are stable up to the 60% strength and have high boiling points. The salts which the acid forms are nearly all soluble, the potassium, rubidium, caesium and thallium perchlorates being the only ones which are only slightly soluble. This would recommend it over sulfuric acid in many cases where insoluble salts of

the latter prevent its use or cause it to seriously interfere on this account in analytical determinations. Also the difference in the solubilities of the potassium and sodium salts permits an easy separation of the perchlorates of these two metals.* The maximum boiling point of aqueous solutions at atmospheric pressure is 203° C., which corresponds to a constant boiling mixture having a perchloric acid content of 72.3%. Below 160° C. the distillate contains less than 1% of perchloric acid. Most perchlorates are deliquescent except ammonium,potassium, lead and mercury salts.

There have been a number of processes devised for the production of perchloric acid,some of which are only of theoretical importance,but the following methods are the ones which have been used to some extent commercially:

(a) The mixing of dry $NaClO_4$ or $KClO_4$ with H_2SO_4 and distilling the mixture under diminished pressure.† The distillation process is a troublesome and expensive one and redistillation must take place to remove the H_2SO_4 and obtain a pure acid - the product containing 88-98% $HClO_4$. HCl can be substituted for H_2SO_4,NaCl being precipitated from the solution. The HCl

* Compt. Rend.,13,1269.

† F.C.Mathers,J.A.C.S.,32,(1910),66-71;F.C.Mathers, Chem. Ztg.,37,363.

can then be distilled off from the filtrate and an approximately 95% $HClO_4$ acid obtained. However,there are small amounts of $NaClO_4$ still remaining which require distillation under reduced pressure to effect their removal.

(b) The electrolytic oxidation of HCl in dilute solution* is the method used in this country at the present time for commercial production. Howeverlthe resulting liquir contains HCl,chloric acids and chlorine in addition to the $HClO_4$. Also the acid obtained is quite dilute and must be concentrated for commercial use.

The above methods are expensive to operate due to the necessity of purification and concentration of the acid resulting from the reaction used,and the use of NH_4ClO_4 as a source of $HClO_4$ has been advocated as the best means of overcoming the above objections. NH_4ClO_4 can be obtained comparatively cheaply and when purified and the ammonium radical oxodized by oxides of nitrogen, there are no non-volatile impurities remaining in the product. All gases and volatile liquids can be easily distilled off at atmospheric pressure and any further concentration of the product can be accomplished at the same time although no such amount of concentration will be required as in (b) cited above.

* E.C.Walker,U.S. Patent 1271633.

H.M.Goodwin and E.C.Walker,Trans. A.E.S. 40.

Investigation of the possibilities of the above method is the object of the present work which is a continuation of the work begun at the Institute in 1921 by R. W. Stenzel and continued in the following year by A.W. Knight and in 1924 by V. A. Kalichevsky.

I I .

P R E V I O U S W O R K .

Only a few results have been published with regard to the investigation of the action of the oxides of nitrogen in the oxidation of ammonia and ammonium salts. Beeson and Rosset* did a considerable amount of work on this subject. In the case of NH_3 the dry gas was passed at -20° C. over solid NO_2 at the same temperature and, accompanied by the liberation of a large amount of heat, white fumes consisting chiefly of NO and NO_2 were given off. Ammonium nitrate and water were also formed.

When the ammonium salts were used, they were heated with the NO_2 in strongly sealed tubes at 100° C. With NH_4Cl a variety of products were formed due to the presence of the chlorine, but with NH_4NO_3 and $(NH_4)_2SO_4$ nitrogen was the only gas evolved, the reactions being

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

(1) $NH_4NO_3 + 2\ NO_2 = N_2 + 2\ HNO_3 + H_2O$

(2) $(NH_4)_2SO_4 + 4\ NO_2 = 2\ N_2 + 2\ HNO_3 + H_2SO_4 + 2\ H_2O$

Following out the above general idea, H. H. Willard† tried several methods of oxidizing NH_4ClO_4 in order to obtain $HClO_4$. A mixture of NO and NO_2 was produced by the action of H_2SO_4 on $NaNO_2$ and the gas was passed through a boiling NH_4ClO_4 solution. A second method consisted in allowing formic acid to run into a nitric acid solution of ammonium perchlorate, the oxides of nitrogen being produced by the reduction of the nitric acid, and acting on the ammonium perchlorate as they were formed in the solution. In both of the above methods the reaction was slow but some of the ammonium salt was oxidized.

The most successful method which he used consisted in allowing hydrochloric acid to drop slowly into a solution of HNO_3 and NH_4ClO_4. The reaction proceeded at a good rate and practically complete conversion of the ammonium perchlorate was obtained. From analyses, Willard formulated the following empirical equation

(2a) $34\ NH_4ClO_4 + 36\ HNO_3 + 8\ HCl = 34\ HClO_4 + 4Cl_2 + 35\ N_2O + 73\ H_2O$

The hydrochloric acid probably reduced the nitric acid which resulted in the formation of HNO_2 among other

† H. H. Willard, J.A.C.S., 34, (1912), 1480.

products and this was thought to be the agent acting upon the ammonium perchlorate. To show that chlorine did not enter into the reaction,he passed a stream of the gas through a solution of ammonium perchlorate and found no change.

From the results of Willard,just quoted,Stenzel* concluded that it might be possible to use N_2O_3,the anhydride of HNO_2,to act on ammonium perchlorate according to the reaction

(3) $2\ NH_4ClO_4 + N_2O_3 = 2\ N_2 + 2\ HClO_4 + 3\ H_2O$

This would leave no reaction products from which it would be necessary to purify the perchloric acid and hence would be an ideal reaction.

However,Stenzel found that the gas of the composition N_2O_3 did not act as such but instead as a mixture of NO and NO_2 and that the latter was the active consituent, the NO passing thrcugh the ammonium perchlorate solution practically unchanged. The following equations were used to explain the action of the NO_2

(4) $2\ NO_2 + H_2O = HNO_3 + HNO_2$

(5) $HNO_2 + NH_4ClO_4 = HClO_4 + N_2 + 2\ H_2O$

A combination of the above equations gives the same result

* R. W. Stenzel,Undergraduate Thesis,Calif. Inst. of Tech.,1921,"A Method for the Preparation of Perchloric Acid."

as obtained by Besson and Rosset for ammonium nitrate and ammonium sulphate

(6) $2\ NO_2 + NH_4ClO_4 = N_2 + HClO_4 + HNO_3 + H_2O$

The HNO_3 resulting from this reaction would not cause any serious inconvenience as it would be distilled off on concentrating the $HClO_4$.

Where Stenzel used hot aqueous solutions of ammonium perchlorate, he obtained from 77% to practically complete conversion. But in one case in which concentrated nitric acid was used as the solvent, the conversion was negligible.

Knight* continued the work of Stenzel and used a counter-current flow of gas and hot aqueous NH_4ClO_4 solution instead of just allowing the gas to bubble through the hot ammonium perchlorate solution. He used not only pure NO_2 gas but also mixtures of NO_2 with oxygen and NO, but found that the presence of the latter gases did not have any appreciable effect on the reaction. In each test which he made he found that more than twice as much HNO_3 as $HClO_4$ appeared in the product, and the equation

(7) $3\ NO_2 + H_2O = NO + 2\ HNO_3$

was used to account for this excess. The presence of oxygen increased the proportionate yield of nitric acid

* A. W. Knight, Undergraduate Thesis, Calif. Inst. of Tech., 1922, "Perchloric Acid from Ammonium Perchlorate and Oxides of Nitrogen."

in relation to $HClO_4$,due to the converting of NO to NO_2, while the presence of NO decreased it,as it would tend to prevent the reaction from taking place.

Kalichevsky† also worked with a counter flow system of ammonium perchlorate solution and NO_2 although he used a form of apparatus different than that of Knight. He found that a lower working temperature,less saturated ammonium perchlorate solution,and insufficient time of contact of NO_2 gas and solution,compared with Knight's experiments,favored the undesireable side reaction,(7). Hence he concluded that a longer contact of gas and solution would give a better conversion. Also,he drew the conclusion that since HNO_3 was formed by this side reaction,its presence (i. e.,the use of a dilute HNO_3 solution of ammonium perchlorate) would tend to prevent the reaction taking place. His results showed that at least up to a nitric acid concentration of about 8.5 N,the ratio of perchloric acid formed to HNO_3 formed became greater as the nitric acid concentration in the solution increased. He states that although Stenzel found that a high concentration of nitric acid practically prevented the formation of perchloric acid,this circumstance can be

† V. A. Kalichevsky,Undergraduate Thesis,Calif. Inst. of Tech.,1924,"Manufacturing of Perchloric Acid."

accounted for by the fact that nitric acid is formed with perchloric acid and too high an initial HNO_3 concentration would prevent the reaction taking place.

In view of the fact that the results obtained by Willard showed that the active agent in the NH_4ClO_4 oxidation was HNO_2, it was decided to try to use a gaseous reagent instead of HCl for the reduction of HNO_3, the decided advantage of the gas being that none of the reducing agent would remain in the product, as was the case with HCl. NO fitted the conditions very nicely not only with regard to the above requirements but also due to the fact that in the reaction

(8) $$NO + HNO_3 = HNO_2 + NO_2 ,$$

the NO_2 formed can be absorbed in a NaOH solution forming $NaNO_2$ and $NaNO_3$, both valuable by-products from a commercial standpoint.

III.

EXPERIMENTAL WORK.

As NO was the prime mover in the process, the first move was to obtain some method of producing it which provided a reasonably good control of the reagents used, and hence of the NO being evolved, and also a method which would give a gas of good quality. After consulting several reference works, the method finally selected consisted of the dropping of a concentrated aqueous solution of $NaNO_2$ into a solution of ferrous sulphate in a dilute sulphuric acid solution. The ferrous sulphate solution consisted of approximately 50 grams of $FeSO_4 \cdot 7H_2O$ in 200 cc. of water to which was added 10 cc. of concentrated H_2SO_4, so that the two reagents were present in the solution in the reaction flask in practically the quantities required by the equation

(9) $$2\ NaNO_2 + 2\ H_2SO_4 + 2\ FeSO_4 = Fe_2(SO_4)_3 + 2\ NO + Na_2SO_4 + 2\ H_2O$$

The $NaNO_2$ solution consisted of 65 grams of $NaNO_2$ per 100 cc. of water.

Several small batches of the above solutions were made up and runs made to see how good a control of the flow of NO gas could be obtained by control of the rate of adding $NaNO_2$, etc. The apparatus shown in Fig. 1 was used for these runs.

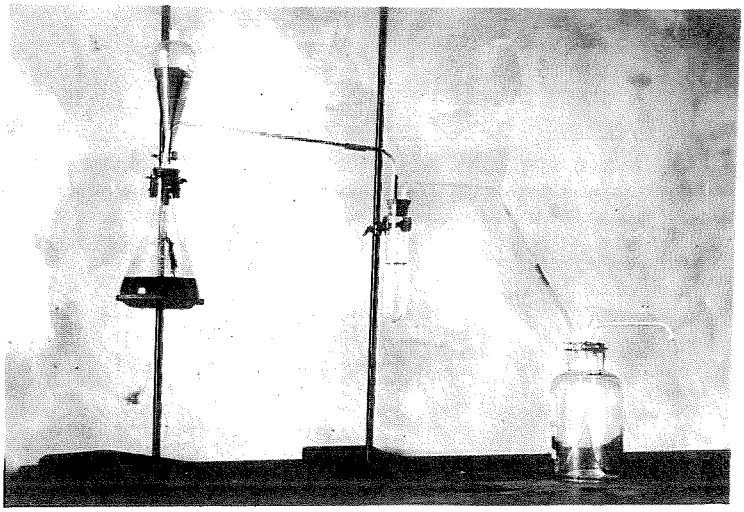

Fig. 1

A = Reaction flask containing $FeSO_4$-H_2SO_4 solution.
B = Dropping funnel for $NaNO_2$ solution.
C = Large test tube partly filled with water to observe rate of NO flow.

* * *

For a constant flow of $NaNO_2$ solution the rate of flow of NO was quite regular. A water bath, kept at about 60° C., was placed around (A) but did not appear to greatly hasten the rate of NO evolution for the same amount of $NaNO_2$ added. The $NaNO_2$ solution was allowed to flow down the side of the flask and the NO was uniformly evolved throughout the solution in (A) (using a very small stream of $NaNO_2$ solution). The cessation of

flow of NO into (C) came about 5 minutes after the flow of $NaNO_2$ solution was cut off,although a small evolution of gas continued in (A) for nearly half an hour afterward. However,this showed that a reasonably good control of the reagents could be maintained at ordinary temperatures without necessarily having to supply heat for the reaction flask from the outside. Commercial grade reagents were used in all three cases as any small amount of impurity contained in them did not affect the NO purity.

The next step consisted in determining how good a conversion of NH_4ClO_4 to $HClO_4$ could be obtained by the use of NO. For the first test the NO was simply allowed to pass through the NH_4ClO_4 solution by bubbling it from the end of a glass tube placed near the bottom of a 8" x 1 1/2" Pyrex test tube. As only a poor contact for the reaction could be maintained in this way between the gas and the solution,the apparatus was allowed to run from 1 1/2 to 1 3/4 hours,but at the end of that time tests showed that complete conversion of the NH_4ClO_4 had been obtained.

The method of making up the NH_4ClO_4 solution,which was the same in all subsequent runs,was as follows: 400 grams of recrystallized NH_4ClO_4 were dissolved in 1000 cc. of water by heating the mixture in a bath of boiling water,a nearly saturated solution of NH_4ClO_4 being thus obtained. From this hot solution portions were then

pipetted off for use in making the runs and one blank portion was also always drawn off so that the exact NH_4ClO_4 content of the solutions used for the runs could be later determined by analysis of the NH_3 content of this blank. To every 50 cc. of solution, approximately of the concentration given above, 30 cc. of 69-70% C.P. HNO_3 were added, these being the proportions between NH_4ClO_4 and HNO_3 which were used by Willard. After a run the acid was neutralized with 6 N NaOH, after the excess NO_2 contained in the solution had been driven off, and then the usual NH_3 analysis was made to determine the amount of NH_4ClO_4 conversion.

In this first test with NH_4ClO_4 and NO, (I), the apparatus arrangement shown in Fig. 1 was used and (C) was kept in a bath of boiling water throughout the run in order to keep the NH_4ClO_4 in solution. However, as only a poor contact had been made between gas and solution, a device on the order of a coffee percolator was next used (Fig. 2).

The rate of NO gas flow was at first faster than in Run I but slowed down to about the same rate towards the end. The run was continued until the evaporation of the water in the reaction vessel was such that crystals began to form rapidly and the run had to be stopped, after lasting about 25 minutes. About 1/2 the volume of the original reaction solution was lost by evaporation, the reac-

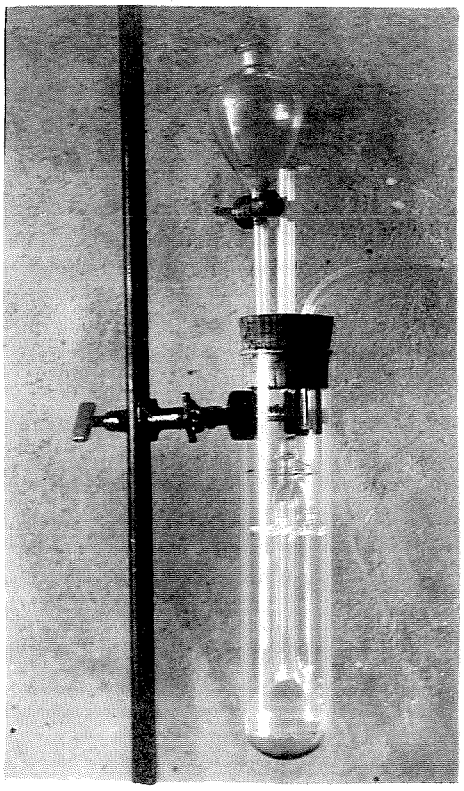

Fig. 2

tion tube being heated throughout the run by an open gas flame. However, only an 11.5% conversion of the NH_4ClO_4 was obtained so that another run (III) was made. In this a dropping funnel was attached to the reaction tube so that water could be run into the solution to replace that which was being constantly evaporated by percolation. This failed to appreciably increase the NH_4ClO_4 conversion (12.7%) so that the percolating device was abandoned. The failure of this apparatus was very probably due to the fact that the water vapor rising from the boiling solution formed a buffer or blanket above it which prevented a considerable proportion of the NO from reaching the main body of the solution so that a reaction could take place. The length of this run was 45 minutes.

Return was then made to the idea of allowing the

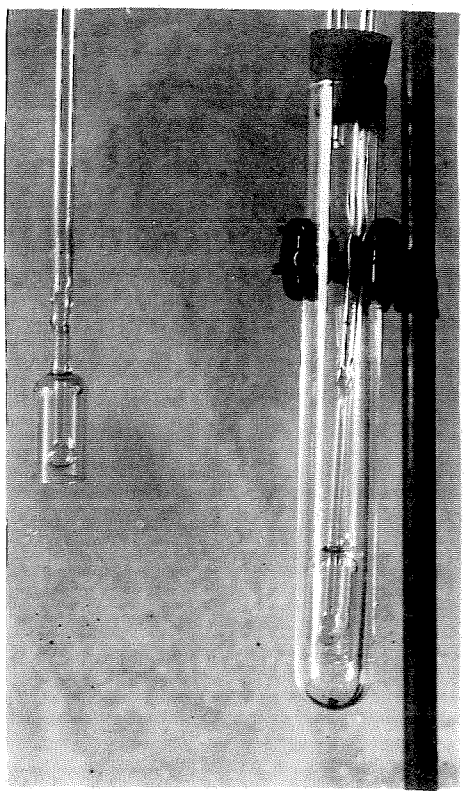

Fig. 3

NO to bubble through the NH_4ClO_4 solution. The apparatus was again practically the same as that used in Run I,(D) being disconnected. Instead of using a straight tube for the gas inlet,one was used whose outlet was arranged so as to break up the incoming gas stream into small bubbles and also spread it over a larger cross section of the reaction tube. (See Fig. 3). The NO was allowed to flow in at about the same rate as in Run I and the reaction was allowed to continue for 35 minutes. Analysis showed that 97.6% of the NH_4ClO_4 had been converted. It was then evident that the NO had to form its contact with the NH_4ClO_4 solution by means of a bubbling device in order to get good conversion of the ammonium salt,and in the following runs the same type of bubbling device was used.

A method of obtaining good conversion of the NH_4ClO_4

having been found, the next problem was to determine how much NO was being passed through unused and also what the exit gases from the reaction tube were. As a beginning the apparatus shown in Fig. 4 was set up. The NaOH solu-

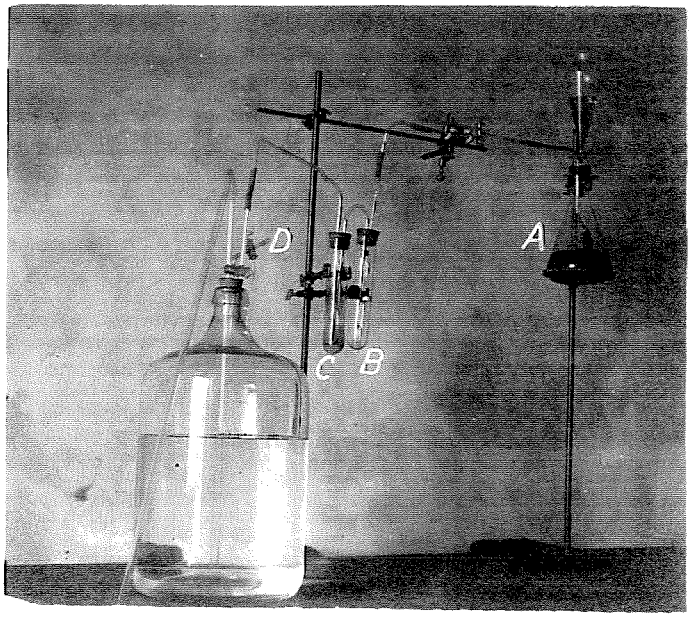

Fig. 4

A = NO generator.
B = Reaction tube containing NH_4ClO_4-HNO_3 solution.
C = Tube containing NaOH solution to absorb NO_2.
D = Connection for small mercury-filled U-tube manometer.

* * *

tion (6 N) in (C) was used to absorb the NO_2 coming from the reaction flask, the reaction being

(10) $2\ NO_2 + 2\ NaOH = NaNO_2 + NaNO_3 + H_2O$.

The large 20 liter bottle was filled with water and the gas was drawn through the system by letting the water out through the siphon, the U-tube partly filled with mercury being used to determine how fast to let out the water. After the run the NaOH solution was titrated against standard acid to obtain the amount of NO_2 formed during the run. To determine the amount of excess NO, water was forced back into the bottle and the gas allowed to bubble through an approximately 0.1 N solution of $KMnO_4$ acidified with H_2SO_4. Calculations were made on the basis of the equation

(11) $$5\ NO + 3\ MnO_4^- + 9\ H^+ = 3\ Mn^{++} + 5\ HNO_3 + 2\ H_2O$$

The results (See Tabulation of Results) of this run, (V), allowed in no way for the amounts of gas absorbed by the water in the bottle nor were they very accurate as to the amount of excess NO. Nevertheless, they did show that there was a large excess of the latter being used, that NO_2 was one of the products of the reaction, and that there were also other gases given off by the reaction because the rubber connections used were sufficiently tight to prevent the amount of air leaking in such as would compensate for the remaining gas volume difference. Also air coming into the bottle would be easily noticed because the oxygen would immediately form NO_2 with the NO

present, and could be detected by the color.

Two possible equations for the reaction were devised:

(12) $NO + NO_3^- + NH_4^+ = 2\ H_2O + N_2 + NO_2$

(13) $4\ NO + 2\ H^+ + 4\ NO_3^- + 2\ NH_4^+ = 4\ NO_2 + 3\ N_2O + 5\ H_2O$

Another run (VI) was started using practically the same apparatus as in (V) except that two smaller test tubes (8" x 1") were used instead of the one large one. The manipulation in this run was begun the same as in (V).

However, soon after turning the NO into the system and starting the siphon for suction, a vacuum very quickly built up in the system, going to about 2 inches of mercury. The NO stream was cut off and the remainder of the system opened up so as to return it to atmospheric pressure. The same procedure was repeated and the same result obtained, so that it was concluded that the gas or gases resulting from the reaction with the NH_4ClO_4 were being absorbed in the water in the bottle as fast or nearly as fast as they were being produced. (This of course excludes NO_2 which was being absorbed in the NaOH solution.)

The NO was again allowed to run into the system, but this time the siphon was closed. A vacuum was gradually built up but not nearly as fast as before and finally steadied itself, remaining at from 3/4" to 1". After running for about 5 minutes or so, the vacuum began to

gradually decrease and then the siphon was opened and a very small stream of water allowed to flow out, just sufficient to maintain a small vacuum so as to permit the gas to come through the system.

The radical difference in results between this run and (V) showed that the assumption made after (V) was completed, that the gas which resulted from the conversion of NH_4ClO_4 was N_2, was an erroneous one. N_2 is only very slightly soluble in water while N_2O is very soluble. There was practically none - if any - NO which passed through the two reaction tubes unchanged and hence would be contained in the water bottle receiver. This was shown by the fact that there was no perceptible brown coloration of the gases in the bottle when air was let in to equalize the pressure. Hence N_2O was the only other possibility, and its solubility in water fitted in with the conditions observed. However, this did not mean that N_2 might not also be one of the products of reaction.

Analysis of the two NH_4ClO_4 solutions and the NaOH absorbing solution was deemed unnecessary because no definite results could be obtained as to the N_2O formed, nor could the latter be determined by volume because of its absorption by the water.

The original idea of Run VII was to get the gas, minus NO and NO_2, into the bottle by first partially evacuating the air from it (air instead of water being used

to fill it for this run) and then permitting the pressure to be built up by allowing the gases to enter. Water was then to be run in, part of the N_2O present dissolving in it, and from the resulting partial pressure of the gases the amount of N_2O could be obtained as well as the amount of N_2 if the latter were present, the solubilities of the two gases in water being known and decidedly different. However, the pressure connections separated when the bottle was being shaken up with some water in it so that this part of the original plan had to be abandoned. Analyses were made of the solutions and the results are given in Tabulation of Results, Table I.

The apparatus used was the same as in (VI) except for the addition of the tube containing the $KMnO_4$ solution after the NaOH tube and the addition of a good sized manometer tube in place of the small U-tube of (V) and (VI).

Run VIII was made in the same manner as (VII) but a part of the manometer tubing broke while the bottle was being shaken so that the entire run was discarded as no information additional to that of (VII) could have been obtained by making the analyses. In (IX) and subsequent runs, two two-way stopcocks were placed in the tubing connecting the manometer and the bottle so that the two could be entirely separated during the shaking

of the bottle and prevent any further breaking of pressure connections during this operation.

In (IX) the same procedure and arrangement was used as in (VIII) and data on the absorption of gas by the water in the bottle were obtained. However, the volume of water used was so small that only a small pressure difference was obtained due to the gas solubility. The value obtained for the latter should therefore be considered as only qualitatively rather than quantitatively indicating a solubility. Due to faulty manipulation of the apparatus towards the latter part of the run, a small quantity of the $KMnO_4$ solution was sucked back into the NaOH solution and also a few drops of the solution from the reaction tubes were blown over. The extent of this contamination of the NaOH, although appreciable, was not large enough to seriously affect the results of the run as a whole, especially considering the questionable quantitative gas solubility results.

As Runs IX and X were completely analyzed before any calculations were made on either one and the quantities of water used for dissolving the gas were similar, the gas solubility data of (X) cannot be considered to be of any more value than that of (IX). A small amount of $KMnO_4$ again sucked back and contaminated the NaOH solution as in (IX). The rate of passing the gas through the system was about the same as in (IX). Analytical results for

all runs are given in Tabulation of Results,Table I.

Since (IX) and (X) were so unsatisfactory in regard to quantitative gas solubility data,it was decided to take several gas solubility measurements in (XI) and use larger volumes of water. To get an idea of the quantity of HNO_3 which was disappearing during the reaction, the total acidity of the reaction mixture was to be determined and from the NH_4ClO_4 conversion and the amount of HNO_3 originally taken,the desired data could be obtained.

Also there arose the question as to how much of the NO_2 formed might remain in the perchlorate solution after the reaction had stopped. To determine this the solution was boiled,compressed air being run through at the same time,and the air and vapor passed through an NaOH solution. However,analysis showed that the amount of such NO_2 was not appreciable.

A sufficient pressure difference was obtained with the 3 1/2 liters of water used to obtain what was believed to be reasonable solubility data. The value for volumes of gas absorbed per volume of water seemed to indicate that the gas which had been drawn into the bottle was a mixture of N_2O and N_2,(See Tabulation of Results,Table I,and Gas Solubilities),nitrogen being in greater quantity.

On account of the solution from reaction tube #1 overflowing somewhat into #2 when the gas was coming

through at too rapid a rate,a separate determination of the amounts of conversion in each tube could not be made. Also,when the vacuum in the bottle had been reduced to a value of 261 mm. it was impossible to draw any more NO through the system. This phenomenon may be accounted for by the considerable amount of pressure required to bubble the gas through the various solutions.

In order to prevent contamination of the NaOH solution and consequent decrease in the perchlorate or $KMnO_4$ solutions,a trap was placed between the NaOH and each of these two solutions. The trap consisted simply of an ordinary 8" x 1" test tube having the inlet and outlet gas tubes projecting only a slight distance below the bottom of the stopper. The devices served their purpose admirably and were worth much more than the time spent in altering the apparatus to get them in. The apparatus used in XI was the same as that used in the remaining two runs and is shown in Fig. 5.

Since the solubility data for (XI) was based on only one quantity of water and also in order to check the analytical data on HNO_3 and NO_2,Run XII was made,starting with approximately the same quantities of HNO_3 and NH_4ClO_4 and also making the initial and final pressures in the bottle nearly the same. 2,3 1/2,and 5 liter portions of water were used for obtaining gas solubility data.

With the exception of the relation of mols of

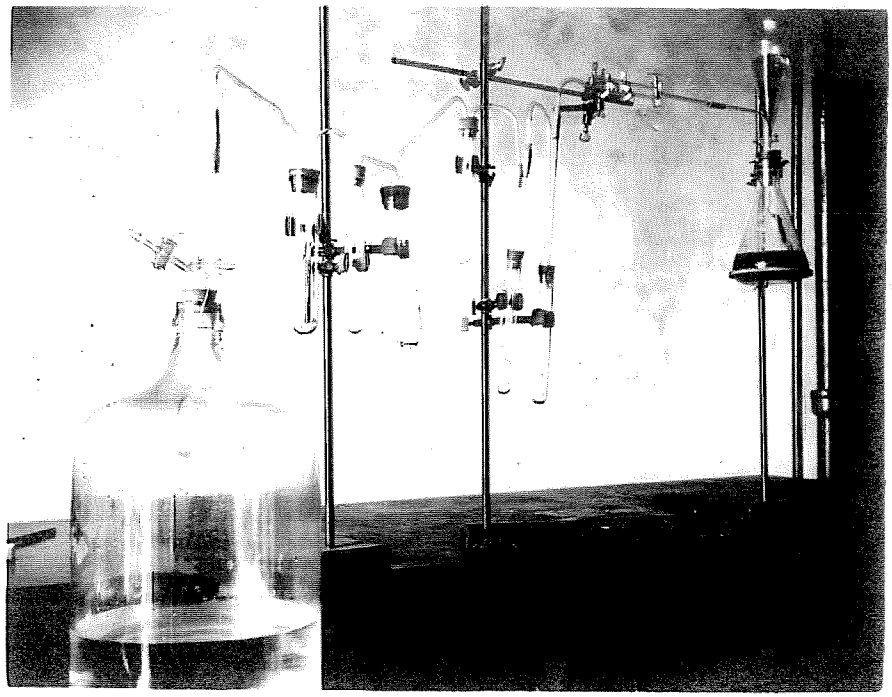

Fig. 5

A = NO generator.
B = Two reaction tubes containing NH_4ClO_4-HNO_3 solution.
C and E = Traps or catch-alls.
D = Tube containing NaOH absorbing solution.
F = Tube containing $KMnO_4$ absorbing solution.
G = Two-way stopcock connection for manometer.

* * *

NH_4ClO_4 converted per mol of HNO_3 used, the values obtained in this run differed widely from those of (XI). Because of this variation (XIII) was made to try to obtain some kind of a check on either (XI) or (XII).

At the start of the run the rate of bubbling of the gas through the NaOH solution was adjusted so that it was

approximately the same as during the larger part of (XII). When the vacuum had reached about 320 mm. the rate of bubbling was decidedly decreased and after 15 or 20 minutes completely stopped although there was considerable pressure in the generator - shown by NO bubbling vigorously through the $NaNO_2$ solution when the stopcock of the dropping funnel was slightly opened. The large bottle and the generator were disconnected from the remainder of the system and the vacuum broken through the tubes. It was then discovered that the lower end of reaction tube #1 had become clogged with crystals. After cleaning these out the system was connected again and proceeded satisfactorily to the end of the run. However,crystals again formed but not so as to interfere with the run any further,although the rate of bubbling was again slow towards the end.

A comparison of results of these last three runs is given in Table II of Tabulation of Results.

IV.

METHODS OF CALCULATION.

Data to illustrate methods all taken from Run XII.

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A.- Amount of Conversion of NH_4ClO_4 to $HClO_4$.

cc. of NH_4ClO_4 solution used for blank	25 cc.
cc. of NH_4ClO_4 solution used for reaction tubes	50 cc.
cc. of HCl (2.01 N) used to absorb ammonia from blank	35 cc.
cc. of HCl (2.01 N) used to absorb ammonia from reaction tubes	50 cc.
cc. of NaOH (0.4984 N) to back titrate HCl used with blank	21.3 cc.
cc. of NaOH (0.4984 N) to back titrate HCl used with reaction tubes	206.5 cc.

$2(.035 \times 2.01 - .0213 \times .4984) - (.05 \times 2.01 - .2065 \times .4984) =$ 0.1194 m. of NH_4ClO_4 converted.

B.- Decrease in HNO_3 Concentration During Run.

cc. of HNO_3 (0.229 m. of HNO_3 per 15 cc. of acid) used in reaction tubes	30 cc.
cc. of solution from reaction tubes after run	253 cc.
" " " " " " " " used to determine acid concentration	10 cc.
cc. of NaOH (0.4984 N) used to titrate 10 cc. portion of acid	37.2 cc.
Mols of $HClO_4$ formed during run (from A)	0.1194 m.

$2 \times 0.229 = 0.458$ m. of HNO_3 placed in reaction tubes.

$\frac{253}{10} \times 0.372 \times 0.4984 = 0.469$ m. = H^+ concentration in reaction tubes at end of run.

$0.469 - 0.1194 = 0.3496$ m. = final HNO_3 concentration in reaction tubes.

$0.458 - 0.3496 = 0.1084$ m. of HNO_3 used during run.

C.- Determination of NO_2 in Exit Gases from Reaction Tubes.

Volume of NaOH (5.53 N) used	75 cc.
" to which absorbing solution was diluted after run	250 cc.
Volume of diluted absorbing solution used for making titration	10 cc.
Volume of HCl (2.01 N) used to titrate 10 cc. portion of NaOH	5 cc.

$(5.53 \times .075) - \frac{250}{10} \times .005 \times 2.01 = .164$ m. of NO_2 absorbed in NaOH solution.

Note: Calculations made on the basis of Equation (10).

D.Determination of Unused NO in Exit Gases.

Weight of $KMnO_4$ (The amount of water in which the $KMnO_4$ was dissolved preliminary to the run was not measured but was from 85 - 100 cc.)	3.888 gm.
Volume of diluted $KMnO_4$ solution after run	250 cc.
Weight of sodium oxalate	0.5615 gm.
Volume of diluted $KMnO_4$ solution required to titrate $Na_2C_2O_4$	17.65 cc.

Equation used for calculations:-

$$5\ Na_2C_2O_4 + 2\ KMnO_4 + 8\ H_2SO_4 = 10\ CO_2 + K_2SO_4 + 2\ MnSO_4 + 5\ Na_2SO_4 + 8\ H_2O$$

Molecular weight of $KMnO_4$ = 158
" " " $Na_2C_2O_4$ = 134

Equation (11) also used in calculations.

$0.5615 \times \frac{2 \times 158}{5 \times 134} \times \frac{250}{17.65} = 3.755$ gm. of $KMnO_4$ unused.

$3.888 - 3.755 = 0.133$ gm. of $KMnO_4$ reacted with NO.

$\frac{0.133}{158} \times \frac{5}{3} = 0.0014$ m. of NO absorbed by $KMnO_4$ solution.

E.- Mols of Gas Collected in Bottle During Run.

Volume of bottle	19560 cc.
Pressure in bottle before run	345 mm.
" " " after run	490 mm.
Temperature of room	24° C.

$\frac{19560}{22400} \times \frac{273}{297} \times \frac{345}{760} = 0.3645$ m. of air in bottle at start of run.

$\frac{490}{345} \times .3645 = 0.5175$ m. of gas and air in bottle at end of run.

$.5175 - .3645 = 0.153$ m. of gas let into bottle.

F.- Determination of Aqueous Solubility of Gases Collected in Bottle.

Volume of bottle	19560 cc.
Barometric pressure	746 mm.
Room temperature	24° C.
Pressure in bottle before run	345 mm.
Pressure in bottle after run	490 mm.
Volume of water let into bottle	3.5 l.
Pressure after letting water in	594 mm.
Pressure after shaking water	594 mm.

$\frac{19560}{16060} \times 490 = 597$ mm. = pressure which would result if gas volume were decreased by 3.5 liters without any solution of gas.

594 mm. = pressure actually obtained.

$\frac{597 - 594}{760} \times \frac{273}{297} \times \frac{16060}{22400} = 0.0026$ m. of gas dissolved.

$\frac{.0026 \times 22400}{3500} = 0.01665$ volumes (S.C.) of gas absorbed per volume of water.

TABULATION OF RESULTS.

TABLE I.

Run No.	I	II	III	IV	V	VII	IX	X	XI	XII	XIII
1. Mols of NH_4ClO_4 taken	.1225	.14	.1394	.1256	.1358	.0627(1) .0627(2)	.0643(1) .0643(2)	.0592(1) .0592(2)	.1211	.1194	.127
2. Mols of NH_4ClO_4 converted	.1223	.016	.0179	.1226	.0472	.0621(1) .0568(2)	.0298(1) .0208(2)	.0129(1) .0136(2)	.083	.1194	.1046
3. Mols of HNO_3 taken	29 cc. 69-70%	30 cc. 69-70%	Same	Same	Same	15cc. in each	Same as (VII)	Same as (VII)	.458	.458	.464
4. Total H^+ at end of run									.469	.469	.499
5. $HClO_4$ conc. (from 1)	.1223	.016	.0179	.1226	.0472	.1189	.0506	.0265	.083	.1194	.1046
6. Final HNO_3 conc. (4 - 5)									.386	.3496	.3944
7. HNO_3 used (3 - 6)									.072	.1084	.0696
8. Mols of NO_2 formed					.0728	.102	.066	.021	.066	.164	.09
9. Mols of gas let into bottle						.188	.113	.16	.149	.153	.145
10. Mols of gas absorbed by H_2O. V=H_2O volume							V = 1 l. .00298	V=1/2 l. .00102 V=1 1/2 l. .00578	V=3.5 l. .019	V=3.5 l. .0026 V=5 l. .0039	V=2 l. .00377 V=3.5 l. .00431 V=5 l. .00625
11. Volumes of gas (S.C.) absorbed by 1 volume of water. t = room temp.							t = 26.5° .0667	t= 27° .0456 .0863	t = 25° .1217	t=23.5° .01665 .0176	t=25.5° .0422 .0276 .028
12. Mols of unused NO							.01045	.0063	.02315	.0014	.01085

For Notes see page 30

Table I.(Continued)

Notes

Run I.- Contact of gas and solution by straight tube bubbling. Length of run,1 1/2 - 1 3/4 hours.

Runs II & III.- Percolator used. Time:II = 25 minutes, III = 45 minutes.

Run IV.- Bell-shaped bubbler used - same type as used in all remaining runs. Time = 35 minutes.

Run V.- First run for exit gas analysis.

Run VI.- Due to the apparent presence of N_2O in exit gases no analyses were made.

Run VII.- Broken pressure connection. No gas solubility data obtained. Number following data in 1 and 2 indicates the number of the reaction tube, tube #1 being nearest the NO generator. Same notation is used in Runs IX and X.

Run VIII.- Run discarded. Broken pressure connection.

TABLE II.

Giving a summary of Runs XI,XII,and XIII showing comparative results on the basis of 1 mol of NH_4ClO_4 converted.

Run No.	XI	XII	XIII
NH_4ClO_4 converted	1	1	1
HNO_3 used	0.868	0.908	0.666
NO_2 formed	0.795	1.373	0.861
Gas let into bottle	1.8	1.28	1.39
Volumes of gas (S.C.) absorbed per volume of water	0.1217	0.01665 0.0176	0.0276 0.028
Unused NO	0.279	0.017	0.104

G A S S O L U B I L I T I E S

I. Nitrous Oxide (N_2O) in Water.*

1 volume of water at t° C. and 760 mm. absorbs V volumes of N_2O, reduced to 0° C. and 760 mm.

t°	V	t°	V
0	1.3052	19	.6888
5	1.0954	20	.6700
10	.9196	21	.6525
15	.7778	22	.6364
16	.7535	23	.6216
17	.7306	24	.6082
18	.7090	25	.5961

1 volume of water absorbs $(1.30521 - .045362t + .0006843t^2)$ volumes of N_2O at t° C. and 760 mm. (Bunsen)

* Comey, "A Dictionary of Chemical Solubilities.")

II. Solubility of Oxygen of the Air in Water.†

t°	5.2°	5.65°	14.78°	24.8°
Solubility	8.856	8.744	7.08	5.762

Solubility is given in cc. of oxygen per 1000 cc. of water saturated with air at 760 mm.

III. Nitrogen in Water.†

Volume of nitrogen (S. C.) which is absorbed by 1 volume of water when the barometer indicates 760 mm.

t°	V	t°	V
0	.0233	20	.0151
5	.0206	25	.0139
10	.0183	30	.0128
15	.0165		

† Seidell, "Solubilities of Inorganic and Organic Substances."

V.

CONCLUSIONS.

The two possible equations for the reaction taking place which were given above,((12) and (13),Part III),were considered to be evolved as follows:

$$NO + HNO_3 = HNO_2 + NO_2$$

$$HNO_2 + NH_4^+ = 2\ H_2O + N_2 + H^+$$

(12) $$NO + NO_3^- + NH_4^+ = 2\ H_2O + N_2 + NO_2$$

$$4\ NO + 4\ H^+ + 4\ NO_3^- = 4\ HNO_2 + 4\ NO_2$$

$$4\ HNO_2 + 2\ NH_4^+ = 3\ N_2O + 5\ H_2O + 2\ H^+$$

(13) $$4\ NO + 2\ H^+ + 4\ NO_3^- + 2\ NH_4^+ = 4\ NO_2 + 3\ N_2O + 5\ H_2O$$

Although (XI) apparently indicated that (13) represented the reaction,there was no check obtained on the volume of gas absorbed (Tabulation of Results,Table II) and hence the value obtained can not be taken as representing the actual case to any degree of certainty.

Furthermore,(XII) and (XIII) check one another to the extent of showing that only a small volume of gas was absorbed and the magnitude of the data obtained would also tend to show that the gases drawn into the bottle consisted principally of N_2 with the possibility of only a small amount of N_2O.

Such a conclusion would lead to the adoption of (12) as representing the conditions with the possibility

of (13) taking place slightly. However, the last assumption depends on the accuracy of the solubility data and this cannot be considered as being definite as such a conclusion would demand.

Another circumstance which is not compatible with either equation is the considerable excess of NO_2 above that demanded by (12). To account for this it was considered that the side reaction

(14) $\quad 2\ NO + 2\ HNO_3 = H_2O + NO + NO_2$

took place. This would give a resultant NO_2 content in the exit gases of 1 1/2 times that which would otherwise be obtained. Since (XII) went to completion while (XIII) did not and proportionately more HNO_3 was used and NO_2 formed in (XII) than in (XIII), it could be inferred that the nearer completion the reaction became, the greater the extent to which (14) took place. This might also be borne out by the fact that in (XII) the unused NO was small while in (XIII) it was several times as great.

As far as arriving at any definite result as to the nature and quantities of the exit gases from the reaction, the results can only be taken in a qualitative sense. Preference should be given to those from (XII) and (XIII) as the technique and operating conditions were best in those.

It is deemed inadvisable to attempt the use of this method of determination for any further investigation of

the exit gases because of the wide limits of error involved in it, so that another method of attack should be taken. Due to the varying results obtained in these runs, it might be that the technique of the run is a determining factor in the products obtained.

Besides making a satisfactory determination of the exit gases, further work should involve a means for the utilization of the valuable oxides of nitrogen given off; whether or not (in a batch process) the reaction is to be carried to completion or, if not, the best point at which to stop it and get out the $HClO_4$ formed, and (in a continious process) the point during the process at which the $HClO_4$ solution is to be drawn off and the acid separated.

Further work on the production of $HClO_4$ by the process used in this experimentation should be encouraged because complete conversion of the ammonium salt can be obtained and the resulting solution contains only nitric acid as an impurity and this can be boiled off at the same time as concentration of the $HClO_4$ takes place. All non-volatile impurities with attendant requirements of possible difficult removal are thus obviated and this removes the main point of objection of existing processes.

The idea for the use of NO instead of HCl to form the HNO_2 for the reaction was due to the suggestion of Dr. Arthur A. Noyes, at whose request work on the problem of perchloric acid production was originally begun in 1921,

and the experimental work was carried out under the direction of Dr. W. N. Lacey.

V I .

S U M M A R Y .

The reaction between NO and a nitric acid solution of ammonium perchlorate was studied from the following standpoints:

(1) To determine the maximum conversion of NH_4ClO_4 possible and the type of apparatus best adapted for effecting it.

(2) To determine the nature and amounts of the exit gases from the reaction and their quantitative relation to the NO and HNO_3 entering the system.

Two types of apparatus for effecting contact between NO and the NH_4ClO_4 solution were used - a percolator spray and a bubbling device. The first was unsatisfactory because of the blanket of vapor formed above the boiling solution which allowed only a small portion of the latter to come in contact with the NO, resulting in poor conversion. The bubbler gave good conversion for a reasonable time of contact of gas and solution, and the better the gas stream was broken up during the bubbling, decidedly the better the conversion. By the use of the bubbler, complete conversion of the NH_4ClO_4 to $HClO_4$ was obtained

without any difficulty.

At first the exit gases appeared to consist of N_2O and NO_2 but later runs indicated that nitrogen was also present and in some cases predominant, N_2O being present in only small quantity if at all.