THE PRODUCTION OF NITROUS OXIDE BY CHLORIDE - CATALYSED DECOMPOSITION OF AMMONIUM NITRATE IN AQUEOUS SOLUTIONS

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ABSTRACT

Variables affecting the concentration of nitrogen and chlorine gases in nitrous oxide produced by chloride-catalysed decomposition of ammonium nitrate (AN) in aqueous, acid solutions have been studied by batch-scale experiments. A typical reaction mixture consisted of 300 g of AN, 300 ml of conc. nitric acid, 300 ml of water and 15 ml of conc. hydrochloric acid. The chlorine and nitrogen contents were found to be both between one and two per cent, when using mixtures of composition close to that given above, and operating at the boiling point. The rate of total gas evolution was reduced with the addition of ammonium sulphate and by substitution of sulphuric acid for the nitric acid.

A continuously operating bench-scale plant, to test the feasibility of the aqueous process as an alternative to the current industrial process (in which molten AN is decomposed at 250-260°) was constructed. Steady-state conditions were readily reached and a nitrous oxide production rate of 2,5-3 l min^{-1} (the theoretical) was achieved at the boiling point, using the typical mixture given above. The crude gas contained one to two per cent each of chlorine and nitrogen, and the chlorine was readily removed in a scrubber with a 5 per cent sodium hydroxide solution. The aqueous process was shown to be technically feasible; it was concluded that it offers a number of advantages over the current process including the possibility of using a cheaper grade AN (such as fertiliser grade), the absence of explosion hazards, and greater flexibility. These have been discussed in detail.

The kinetics of the aqueous process was studied by a batch procedure. The initial rate dependence of the evolution of nitrous oxide, chlorine and nitrogen on the concentrations of acid, nitrate, ammonium and chloride ions was investigated at 94,8°. The rate

dependence on temperature was also studied. The following empirical rate equations were found at 94, 8°:

$$\frac{dN_2O}{dt} = k_{N_2O}\left[H^+\right]^{3,72}\left[NO_3^-\right]^{4,21}\left[Cl^-\right]^{0,59}\left[NH_4^+\right]^{-1,66}$$

$$\frac{dCl_2}{dt} = k_{Cl_2}\left[H^+\right]^{3,54}\left[NO_3^-\right]^{3,47}\left[Cl^-\right]^{1,0}\left[NH_4^+\right]^{-1,64}$$

$$\frac{dN_2}{dt} = k_{N_2}\left[H^+\right]^{3,16}\left[NO_3^-\right]^{3,3}\left[Cl^-\right]^{1,3}\left[NH_4^+\right]^{-1,74}$$

These equations differ substantially from those derived for a reaction mechanism proposed by Keenan and Dimitriades for the chloride-catalysed thermal decomposition of AN in the melt. Their significance has been discussed.

CONTENTS

CHAPTER 1. INTRODUCTION

It was first shown by Smit[1-3] in 1964 that nitrous oxide may be produced by the thermal decomposition of ammonium nitrate in aqueous solution in the presence of a moderately high concentration of acid and a small amount of chloride ion. The reaction proceeds by the stoichiometric equation

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad \Delta H \approx -8,8 \text{ kcal mol}^{-1} \qquad (1.1)$$

which is the same as that for the current commercial process in which pure ammonium nitrate is decomposed in the melt at 250° - 260°.

On the basis of reactions reputedly undergone by *aqua regia*, Smit[2] concluded that nitrosyl chloride (NOCl), chlorine (Cl_2), nitrogen (N_2) and nitric oxide (NO) are simultaneously produced as impurities. The following reactions Smit[2] suggested as routes to these impurities:

$$3HCl + HNO_3 \rightarrow NOCl + Cl_2 + 2H_2O \qquad (1.2)$$

$$3Cl_2 + 2NH_4NO_3 \rightarrow N_2 + 2HNO_3 + 6HCl \qquad (1.3)$$

$$Cl_2 + NH_4NO_3 \rightarrow 2NO + 2HCl + H_2O \qquad (1.4)$$

The principal potential advantage of the aqueous process over the current commercial process for nitrous oxide, viz. ammonium nitrate pyrolysis in the melt, appeared to be the large saving that might be effected by substituting a lower grade ammonium nitrate (e.g. fertiliser grade) for the special, more expensive, nitrous oxide grade that is now used.

Although this potential was recognised early on, the original work was not followed up until recently, when fertiliser-grade ammonium nitrate, after an absence from the market of many years, once more became readily available.

In brief 4th-year research projects in this Department, two students, Mr D. J. Hennesy and Mr A. Ismail, carried out an empirical study of the effect of a number of parameters in the system on (a) the rate of N_2O production and (b) the Cl_2 content of the gas produced.

Their results seemed to confirm the potential of the aqueous process.

This report describes a more detailed investigation of the chloride-catalysed decomposition of ammonium nitrate in aqueous media. The object of the study was not only to gain an understanding of the important parameters affecting the rate of production of N_2O, as well as that of the impurities, but also to obtain kinetic data for the reactions. Since the ultimate aim was to develop the aqueous process as an alternative to the current melt process, the kinetic data were sought for their usefulness in the design of a prototype plant based on the aqueous process. It was also hoped that these data would shed light on the reactions involved, possibly leading to the unravelling of their mechanisms.

After initial batch-scale experiments, a laboratory bench-scale plant was constructed, and the aqueous process successfully tried out in continuous runs each of several hours' duration. The results of the bench-scale plant work permitted a rough assessment of the potential of the aqueous process. Steps are now being taken, in collaboration with a firm of chemical engineers, to construct a prototype industrial-size plant.

Experimental rate equations are reported for the production of nitrous oxide, chlorine and nitrogen. These indicate that the mechanisms of the reactions in this system are highly complex. Further experimental work would be required before complete mechanisms for the reactions can be postulated, and this has been regarded as falling outside the scope of the present study.

1.1. Thermal Decomposition of Ammonium Nitrate in the Melt

Pure ammonium nitrate (hereafter abbreviated to AN) melts at 169.6°. Small amounts of moisture as impurity markedly lowers the melting point.[4] AN undergoes slow sublimation even below its melting point and, as may be expected, the rate of sublimation increases sharply with rising temperature.

Even below the melting point, the dissociation of AN by the endothermic reaction:

$$NH_4NO_3 \rightarrow HNO_3 + NH_3 \quad \Delta H = +41,8 \text{ kcal mol}^{-1} \qquad (1.5)$$

becomes noticeable.[4] Upon raising the temperature in the melt, AN starts to decompose into nitrous oxide and steam according to the exothermic reaction (1.1), the reaction becoming significant at about 210° (ref. 4). At higher temperatures the following exothermic side-reactions become significant:[4]

$$2NH_4NO_3 \rightarrow N_2 + 2NO + 4H_2O \quad \Delta H \approx -6,9 \text{ kcal mol}^{-1} \qquad (1.6)$$

$$4NH_4NO_3 \rightarrow 3N_2 + 2NO_2 + 8H_2O \quad \Delta H = -24,5 \text{ kcal mol}^{-1} \qquad (1.7)$$

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O \quad \Delta H \approx -28,5 \text{ kcal mol}^{-1} \qquad (1.8)$$

The mechanism of AN decomposition in the melt according to the stoichiometric equation (1.1) is surprisingly poorly understood. Decomposition only sets in after an induction period, during which the melt becomes acidic by preferential loss of ammonia, owing to the greater rate of diffusion of ammonia over that of nitric acid (refs. 5-9).

The reaction is *first order*[7,10] with respect to AN. Wood and Wise[7] found that, when starting with pure AN, the initial rate of decomposition was also proportional to the concentration of nitric acid in the sample. They also showed conclusively that while the presence of (excess) ammonia in the melt or in the vapour phase above the melt inhibited decomposition, the presence of *free acid* in the melt was a prerequisite for the *onset* of decomposition. On the basis of their own and earlier data they postulated the following mechanism:

$$NH_4NO_3 \xrightarrow{\text{fast}} NH_3 + HNO_3 \qquad (1.9)$$

$$H^+ + NH_4NO_3 \xrightarrow{\text{slow}} NH_2NO_2 + H_3O^+ \qquad (1.10)$$

$$NH_2NO_2 \xrightarrow{\text{fast}} N_2O + H_2O \qquad (1.11)$$

They remarked that no definite conclusion could be drawn concerning the identity of the intermediate, although isotopic analysis[11] pointed to the formation of an *unsymmetrical* intermediate such as nitramide (NH_2NO_2). *Nitramide* now seems to be generally accepted as the *precursor* for nitrous oxide.

Various values have been reported for the activation energy for the thermal decomposition of pure AN - reaction 1.1 - viz.

34.5 kcal mol^{-1} (refs. 12 and 13), 31.4 kcal mol^{-1} (ref. 5), 39 kcal mol^{-1} (ref. 14), and the more recent value of 49.45 kcal mol^{-1} (ref. 10). These values are probably not directly comparable. The above values, other than the last quoted, are probably too low since no steps had been taken in those studies to purge the melt of HNO_3, known to autocatalyse the reaction.

Rate constants reported in the literature for N_2O evolution show a similar variation. Keenan's value[10] of 6.64×10^{-5} sec^{-1} at 250°, being lower than most of the others, is probably also the most reliable, for the reasons given in the foregoing paragraph.

1.2. Thermal Decomposition of Ammonium Nitrate in the Melt Catalysed by Chloride and Other Additives

It has been known for a considerable time that the presence of chloride in an AN melt catalyses its decomposition[6,15] and at the same time increases the N_2 content of the product gas, a N_2 content as high as 70 per cent having been reported.[15] The most extensive studies of this system have been those reported by Keenan and Dimitriades,[16] who proposed a detailed mechanism for the reactions leading to both N_2 and N_2O on the basis of their kinetic data.

Impurities such as Co, Cr, Mn, Ni, Cu and other halide ions catalyse the side reactions (1.6), (1.7) and (1.8). The presence of these impurities, as well as organic substances, also greatly increases the explosion hazards in both solid and molten AN.

CHAPTER 2. THE AQUEOUS PROCESS FOR N_2O PRODUCTION: BATCH EXPERIMENTS

2.1. Introduction

Smit's early work[1-3] indicated that, while high rates of N_2O evolution may be obtained over a wide range of experimental conditions, the gas contains up to a few per cent of Cl_2 and N_2 as impurities. While the Cl_2 could be readily removed from the product gas by a *suitable scrubbing step (e.g. with NaOH solution)*, it is desirable to find optimum conditions under which the rate of N_2O evolution is highest and the Cl_2 content at the same time the lowest. The presence of N_2 does not present a problem as such, inasmuch as it may be removed in the same way as in the current process (see chapter 5). Production of N_2 as impurity would only be of importance insofar as it affects the N_2O yield.

In preliminary work, the results of the 4th year students Hennesy and Ismail were confirmed. Thus when the reaction conditions were "severe", i.e. when the AN and/or acid and/or chloride ion concentration, as well as the temperature, was high and the amount of water in the system low, NO and NO_2 (and possibly also NOCl) were indeed produced as impurities, along with N_2 and Cl_2, the gas showing a brownish coloration. Under such conditions the highly concentrated HNO_3 and HCl in the mixture evidently tend to show the properties of aqua *regia*.

Higher N_2O evolution rates were found when the concentrations of AN, nitric acid and hydrochloric acid, as well as the temperature, were individually increased, although the effect of doubling the HCl concentration was unexpectedly low. The apparatus used in these preliminary experiments was similar to that used in the work described in the next section.

Addition of ammonium sulphate to the mixture had very little effect on the N_2O evolution rate, but led to a significant reduction in the Cl_2 content. Replacing nitric acid with an equivalent amount of sulphuric acid had the effect of reducing both the N_2O evolution rate and the Cl_2 content of the gas.

2.2 Quantitative Measurement of N_2 and Cl_2 Contents of N_2O Samples as a Function of Reaction Variables

The object of this series of experiments, as stated earlier, was to try to find conditions under which the Cl_2 (and N_2) content of the gas product is low, while at the same time a high rate of N_2O production is achieved. As an interesting side-line, more "severe" reaction conditions were also tried out to test the possibility of adapting the method for simultaneous production of N_2O and Cl_2.

2.2.1. Experimental

2.2.1.1. Reagents, Equipment and Analytical Methods

All chemicals except for nitric acid (commercial grade) were of Analar purity. The concentrated acids were standardised by appropriate dilution and titration with standard ca 0,1 M NaOH solution, using phenolphthalein as indicator. The nitrous oxide purging gas, supplied by African Oxygen Ltd., was of high purity (99,9% N_2O). The potassium iodide solution was 0,5 M in KI and was acidified with H_2SO_4.

The apparatus (Fig. 1) used to determine the nitrogen and chlorine content consisted of a 4-necked, 2-litre, Q/Q flask as reactor, fitted with a thermometer pocket reaching into the reactants, and a purging inlet tube, to which the N_2O cylinder was connected. A coil condenser was fitted at the top of the flask. As shown in Fig. 1, an adaptor was fitted which contained a tube connection to a U-tube manometer, a vent stopcock and a T-piece for connection to two trains of wash bottles containing the KI solution. Gas passing through the wash bottles was collected in a gas collection assembly consisting of an inverted 2-litre measuring cylinder filled with saturated potassium sulphate solution,

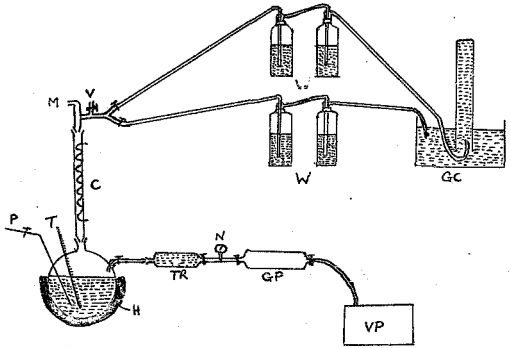

Fig. 1. Apparatus for determining the N_2 and Cl_2 contents of the N_2O product gas. H = heating mantle; T = thermometer, in mercury pocket; P = port for N_2O purge; TR = KOH trap; GP = gas pipette; VP = vacuum pump; W = train of wash bottles; C = condenser; GC = gas collection assembly; N = needle valve; M = to manometer; V = vent

as indicated in the figure. (Nitrous oxide is said to have a very low solubility in this medium).

Also connected to the reactor was a 150-ml glass vessel filled with KOH pellets. This served as a trap to absorb moisture and Cl_2 from the product gas. To the outlet side of this gas trap was connected, via a needle valve, a 250-ml gas pipette, which in turn was connected to a Speedivac E.S 38 vacuum pump. The reactor was heated by means of a 500-watt heating mantle of 3-litre capacity.

Analysis of the gas samples for N_2 was done in the laboratory of African Oxygen Ltd., using their routine gas chromatography method for N_2O samples. A Varian Aerograf (Series 1400) gas chromatograph was used. Molecular sieve 5A was the stationary phase. Argon was used as the carrier gas.

The Cl_2 content of the gas was found by titration of the iodine liberated in the KI solution contained in the two wash bottles with standard ca 0,1 N sodium thiosulphate. The method for calculation of the Cl_2 content of the product gas is described in Appendix A.

2.2.1.2. Procedure

Reaction mixtures containing varying quantities (tables 1 - 3) of AN, conc. nitric acid or sulphuric acid, conc. hydrochloric acid, ammonium chloride and water (as well as ammonium sulphate in some cases) were placed in the reactor flask. The apparatus was evacuated and N_2O from the cylinder passed through to displace the remaining air. The operation was repeated once more. Finally, the side arm containing the KOH trap and gas pipette was evacuated.

The reaction mixture was now heated at full load of the heating mantle to the temperature indicated in Tables 1 - 3. At the same time the valve V was used to vent gas slowly to the atmosphere at such a rate as to maintain a manometer pressure reading of about 5 cm above atmospheric (ca 625 mm of Hg).

The sample for N_2 analysis was collected as follows. After the mixture had reached the boiling point (except in the case of runs no 1 and no 13), product gas was slowly admitted into the KOH trap

TABLE 1. Cl_2 and N_2 impurity levels in gas obtained from different reaction mixtures. The mixture in each run also contained 300g of AN.

Run No.	Acid used,* and vol. in ml	HCl,* ml	H_2O, ml	Mixture temp, °C	Cl_2, %	N_2, %
1	HNO_3, 300	15	300	103	1, 37	0, 9
2	HNO_3, 300	15	300	110	1, 48	0, 95
3	H_2SO_4, 80	12	170	110	1, 64	1, 1
4	H_2SO_4, 80	12	170	110	1, 65	1, 12
5	HNO_3, 300	15	300	115	1, 57	0, 97
6	HNO_3, 200	15	200	103	1, 9	1, 3

TABLE 2. Cl_2 and N_2 impurity levels in gas obtained from different reaction mixtures; Influence of $(NH_4)_2SO_4$ additive.

Run No.	AN, g	HNO_3,* ml	HCl,* ml	H_2O, ml	$(NH_4)_2SO_4$, g	Mixture temp, °C	Cl_2, %	N_2, %	Rate
7	160	150	8	300	132	107	0, 5	1, 7	Slow
8	160	200	12	200	132	109	0, 42	1, 6	Slow
9	160	250	10	200	132	111	0, 55	1, 9	Fast
10	160	250	30	200	132	111	1, 1	2, 1	Fast

TABLE 3. Cl_2 and N_2 levels obtained under "severe" conditions. (Temperatures given are the boiling points of the mixtures, except in run 13).

Run No.	AN, g	HNO_3,* ml	H_2SO_4,* ml	HCl,* ml	H_2O, ml	NH_4Cl, g	Mixture temp, °C	N_2, %	Cl_2, %
11	300	50	-	200	300	-	102	8, 0	4, 8
12	300	50	-	200	100	-	108	12, 5	9, 7
13	300	50	-	200	100	-	98	11, 9	9, 45
14	250	-	50	100	100	50	110	14, 5	20, 5

* The acids used had the following concentrations: HNO_3, 11, 9M; HCl, 12, OM; H_2SO_4, 18M.

to reach the same pressure as in the reactor flask. After about 30 sec the needle valve N was slowly opened to admit gas into the gas pipette. The trap and gas pipette were now closed off from the reactor, and the gas pipette evacuated. The same procedure was repeated, finally allowing the gas in the gas pipette to reach the same pressure as in the reactor vessel. The gas pipette was now removed for subsequent analysis of its contents for N_2.

Simultaneously with the collection of the sample for N_2 analysis, product gas was allowed to pass through a train of wash bottles, to be collected in the measuring cylinder, until a known volume (usually 2 000 ml) had been collected. The wash bottle train was then isolated for subsequent determination of the free iodine liberated by the Cl_2, as described.

The volume of the gas collected in the measuring cylinder was read off after adjusting the cylinder until the height of liquid was the same inside and outside the cylinder. The atmospheric pressure and the temperature of the potassium sulphate solution were recorded.

2. 2. 1. 3. Results and Discussion

The results are given in Tables 1 - 3 and plotted in Figs. 2 and 3. In the absence of added $(NH_4)_2SO_4$ there is a roughly linear relationship between the N_2 content and the Cl_2 content. Table 2 and Fig. 2 show that while the Cl_2 percentage may be reduced by adding $(NH_4)_2SO_4$ to the mixture, the N_2 content actually increases.

The possibility of simultaneous production of N_2O and large percentages of Cl_2 was investigated by selecting more "severe" reaction conditions. Table 3 and Fig. 3 show that, as the Cl_2 content of the gas increases, so does the N_2 content. Although a Cl_2 content as high as 21 per cent was achieved by addition of ammonium chloride and using H_2SO_4 instead of HNO_3, the accompanying high N_2 content (and therefore the greatly reduced N_2O yield) would probably rule out the possibility of commercial application of such a system.

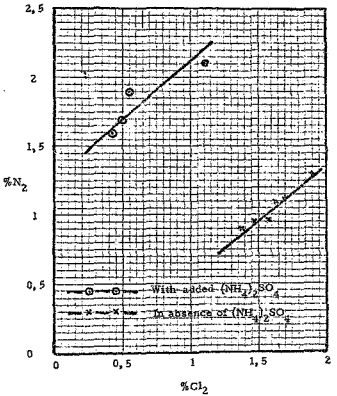

Fig. 2. Cl_2 and N_2 contents of nitrous oxide: influence of the addition of ammonium sulphate.

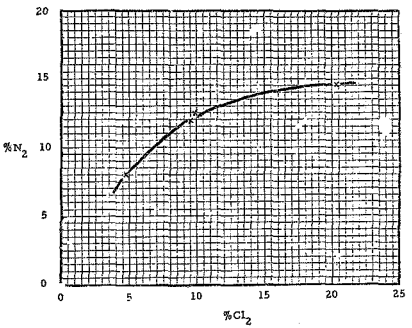

Fig. 3. Cl_2 and N_2 contents of the gas obtained under "severe" conditions.

CHAPTER 3. THE AQUEOUS PROCESS FOR N_2O PRODUCTION: BENCH-SCALE PILOT PLANT EXPERIMENTS

3.1. Introduction

The purpose of these experiments was to demonstrate the feasibility of the aqueous process as an alternative to the current process for N_2O production and to gain some insight into the problems that might be encountered in the operation of such a process.

The aqueous process differs in a number of important respects from the current melt process. Since water is one of the decomposition products of AN and, moreover, since AN would probably be fed into the reactor as an aqueous solution, water has to be removed continuously from the system, at least at the same rate as it is formed by reaction (1.1). Operation at, or close to, the boiling point of the solution is thus indicated. The vapour will, of course, also contain HNO_3 and HCl, which need to be returned to the mixture. Thus it is necessary to include a fractional distillation column so as to allow retention of the acids while achieving the desired rate of water removal.

HCl is slowly consumed in the inevitable formation of Cl_2. Moreover, since the water removed from the system would contain a small amount of acid (HCl, as well as HNO_3), provision would have to be made for the continuous replenishment of both HCl and HNO_3, if steady-state conditions are to be achieved.

Parameters controlling the efficiency of the process, yields and the levels of impurities could be investigated more simply in batch runs. For this reason a single reaction mixture, which was believed to be very close to the "best" (or optimum) composition, was chosen for all the experiments described in this chapter, except for those in which the operation of the fractionation column was

tested. This starting solution had the composition:

300 g of AN

300 ml of conc. HNO_3, 11,98 M

300 ml of water

15 ml of conc. HCl, 12,03 M

in a total volume of about 800 ml.

3.2. Experimental

3.2.1. Reagents and Analytical Methods

Solid nitrous oxide grade AN, manufactured by AE and CI Ltd., was kindly supplied by Union Liquid Air Ltd.. The fertiliser grade AN, as a 60% (w/w) solution, was obtained from the Sasol works. The acids were of Analar purity, except for the nitric acid (commercial grade). The sodium hydroxide was also a commercial grade product. The silica gel drying agent was activated by drying in an oven at 110° for two hours.

The chloride ion and total acid concentrations in the reactor were monitored by intermittently withdrawing a small sample into a tared weighing bottle, determining the mass of the sample, and titrating consecutively for acid (with standard NaOH solution, phenolphthalein as indicator) and chloride (Mohr's method) after suitable dilution. The bottoms product and condensate were analysed in the same way.

Samples of product gas were analysed for N_2 by gas chromatography as described in section 2.2.1.1. *Samples* of the crude gas, collected at a pressure slightly above atmospheric, were analysed for Cl_2 as follows: The gas pipette was immersed for 10 minutes in water of known *temperature*. A stopcock was then opened to adjust the pressure to atmospheric. A funnel was connected at one end, a suitable volume containing an excess of KI added, and the KI solution introduced into the gas pipette by chilling the pipette in ice water. After shaking to ensure complete reduction of the Cl_2, the liberated iodine was estimated by titration with standard thiosulphate solution.

starch indicator was added near the end point.

Efforts to analyse the crude gas product for Cl_2 by passing a known volume through a train of wash bottles containing acidified KI solution, as in the experiments described in section 2.2.1.1, were abandoned. This method resulted in a build-up of pressure in the reactor vessel, thus upsetting the steady-state conditions.

3.2.2. Design of the Bench Scale Process

The bench scale process was developed in collaboration with Mr A. Roukens de Lange, of the Department of Chemical Engineering, University of the Witwatersrand, who designed the fractionation column and worked out mass and heat balances for the whole system. (For details of Mr de Lange's calculations see Appendix B.)

3.2.2.1. The Reactor Vessel and Accessories

Experience with batch experiments indicated that the 800-ml reaction mixture chosen, the composition of which is given in Section 3.1, would at its boiling point initially give gas evolution at a rate equivalent to the consumption of about 8 g (i.e. 0,1 mole) of AN per minute. The design was thus based on a continuous feed rate to the reactor of 8 g of AN per minute.

The apparatus is shown diagrammatically in Fig. 4. A 2-litre round-bottomed flask was used as the reactor. This was fitted with a thermometer pocket, inlet ports for the introduction of the various solutions, a port for connecting a manometer, an exit connection for the gas and vapour, as well as a sampling point and a level indicator loop. In the latter runs, six glass tubes of dimensions 15mm x 15mm were added to the solution to ensure smooth boiling.

From the top of the reactor flask, the vapour passed into the fractionation column via a 10mm i.d. glass tube, as shown in Fig. 4. Heating was done with a 500-watt heating mantle of 3-litre capacity, which also supported the reactor vessel. Peristaltic pumps of various makes were used as metering pumps.

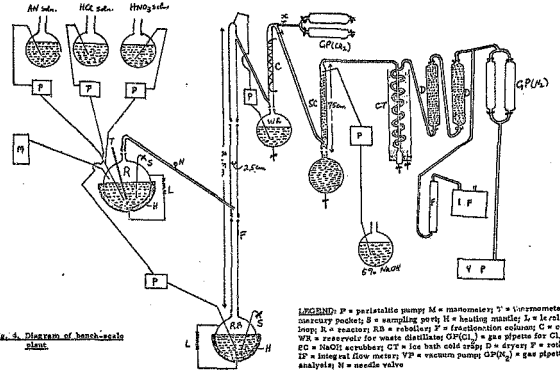

Fig. 4. Diagram of bench-scale plant

LEGEND: P = peristaltic pump; M = manometer; T = thermometer, in mercury pocket; S = sampling port; H = heating mantle; L = level indicator loop; R = reactor; RB = reboiler; F = fractionation column; C = condenser; WR = reservoir for waste distillate; GP(Cl_2) = gas pipette for Cl_2 analysis; SC = NaOH scrubber; CT = ice bath cold trap; D = dryer; F = rotameter; IF = integral flow meter; VP = vacuum pump; GP(N_2) = gas pipette for N_2 analysis; N = needle valve

3.2.2.2. The Fractionation Column

This consisted of a glass column, of internal diameter 25 mm, and was constructed in three sections, with a total length of 2,5 m. Ball and socket joints were used to connect the various sections of the column and other sections of the apparatus (Fig. 4). The packing of the column consisted of 6mm x 6mm glass Raschig rings, the total height of the packed bed being about 2,3 m. The bed was supported with a restriction made at the bottom end of the column. The entire length of the column was lagged with an inside layer of cotton wool, and aluminium foil on the outside.

The fractionation column was connected directly to a one-litre round-bottomed reboiler which was supported by a 300-watt, one-litre heating mantle. The reboiler was fitted with a level indicator loop (Fig. 4). Provision was also made for a sampling port and an exit tube for recycling bottoms product to the reactor.

3.2.2.3. The Remainder of the Bench-Scale Plant

From the top of the reflux column the vapour passed into a coil condenser (Fig. 4). The waste water condensate was collected in a flask fitted with an outlet drainage stopcock (used also for sampling) and an exit tube for recycling part of the condensate to the top of the fractionation column. The waste condensate building up in the collection flask was drained periodically, and always shortly before sampling.

Non-condensable gases then passed into the bottom of a NaOH scrubber column, of dimensions 2,5cm i.d. x 50cm, packed with Raschig rings of the same size as those used in the fractionation column. A 5 per cent NaOH solution was passed into the top of the scrubber for removing the Cl_2 impurity from the gas stream. To improve the efficiency of the scrubber, it was run under flooded conditions in all but the first of the series of full-scale experiments. The drainage stopcock of the receiver vessel was thus adjusted manually to give a drainage rate such as to balance the NaOH solut-

ion feed rate of about 5 ml per min, while maintaining the column in a fully flooded condition.

Gas emerging from the scrubber thereafter passed through an ice-bath cold trap, to remove most of the water vapour. Next in the train was a silica gel dryer, followed consecutively by a rotameter and, for full runs of the plant, an integral flowmeter. In the latter runs of these experiments the two dryers (Fig. 4) were used in series, with the second dryer packed with NaOH pellets. The NaOH pellets were introduced to remove traces of chlorine passing through the NaOH scrubber.

Provision was made, as shown in Fig. 4, for the collection of purified gas samples, for N_2 analysis, in evacuated gas pipettes, using a Speedivac E. S 35 vacuum pump, as well as for the direct collection of crude reactor gas, for Cl_2 analysis. In the latter case, gas was passed through a gas pipette until the air was considered to have been fully displaced. In the technique adopted the rate at which crude gas was allowed to escape into the gas pipette, was carefully controlled by means of the stopcock X in such a way as to ensure a more or less constant pressure in the reactor, as indicated by the manometer.

3. 2. 3. Procedure and Results

3. 2. 3. 1. Testing Reactor Operation

As a first step, the operation of the reactor was tested separately, omitting the fractionation column and remainder of the apparatus. Initially it was attempted to use an 80% (w/w) solution as the AN feed. However, this solution has to be kept hot (>100°) to prevent crystallisation. It was only with great difficulty that the formation of crystals in the tubes leading from the thermostatted reservoir via the peristaltic pump to the reactor could be prevented. To facilitate the matter, a 60% (w/w) AN solution was substituted. It was found that the system could readily handle this extra burden of water that needed to be evaporated. In all the experiments described in the following sections, the AN feed was a 60% solution. The AN solution (kept

at room temperature) was fed into the reactor at a rate of 10ml min^{-1}, which actually represented a feed rate of 7,62g min^{-1} of AN compared to that of 8g min^{-1} earlier decided upon. The heating mantle was operated at full load, and the vapour emerging from the reactor passed into a coil condenser, the condensate being collected in a reservoir for subsequent analysis. At the second attempt, reasonable "steady-state conditions" were achieved. The flow rates required were as follows: AN solution (fixed), 10ml min^{-1}; 6,0 M HCl, 2,5ml min^{-1}; 11,9 M HNO_3, 5,0ml min^{-1}; water, 8,7ml min^{-1}. (A dilute HCl solution was used since the concentrated liquid attacked the silicone rubber tubing of the peristaltic pump).

The rate of gas evolution initially rose to 3,5 l min^{-1} (at ambient temperature and pressure), then dropped to as low as 1,2 l min^{-1}, rising again to a value varying between 2,2 and 2,8 l min^{-1}. (The theoretical rate for steady-state conditions at a feed rate of 7,62g min^{-1} of AN is about 2,6 l min^{-1} at the ambient conditions.) The duration of the experiment was about $5\frac{1}{2}$ hours, about half an hour having been taken to heat the reactor solution to its boiling point. Gas evolution was first perceived when the reactor solution reached 78°.

Initially, when the mixture first reached its boiling point, the temperature rose to as high as 110,5°. This was accompanied (and apparently caused) by a rise in the pressure to 19cm of mercury above the ambient and (as shown in the foregoing paragraph) an unusually high rate of gas evolution. Afterwards, the temperature and manometer readings dropped and continued to fluctuate in the ranges 107,5° - 108,5° and 5 - 6 cm, respectively.

This pattern was repeated in all subsequent experiments: a rise in temperature, whether caused by changes in the composition of reactor solution or by a rise in pressure, always lead to an enhanced rate of gas evolution.

The slow rates reported above were caused by poor control of feed rates, leading to an increase in the volume of the reactor

solution or a drop in one or more of the reaction parameters such as HCl or HNO_3 concentration, as indicated by periodic analyses of the reactor solution for total acid and chloride.

Analysis of the distillate gave the following concentrations: HNO_3, 0,49 to 0,72 M; HCl, 0,037 to 0,091 M. Values towards the end of the run, when the system had achieved the closest approach to steady-state, were: HNO_3, 0,54 M; HCl, 0,091 M. Only one sample was analysed for Cl_2 and was found to contain 1,28 per cent (v/v). The calculation was made as before (Appendix A).

3.2.3.2. Testing Operation of Fractionation Column

In the first run, 1000 ml of an acid solution, 0,141 M in HCl and 1,18 M in HNO_3, was placed in the reactor vessel. These values represented averages of the concentrations of the distillate in runs with the reactor only (see foregoing paragraph). Five hundred millilitres of an acid solution 0,85 M in HCl and 7,50 M in HNO_3 was placed in the reboiler. These values were obtained by Mr de Lange in his mass-balance calculations. When the reboiler solution was heated to boiling in the start-up of this run, NO_2 fumes appeared. However, as the experiment proceeded, the NO_2 fumes disappeared, indicating that the reboiler solution was being diluted. At th start, pure water was placed in the condensate receiving vessel.

The unit was operated as a closed system, condensate being refluxed into the top of the column at the same rate as it was being collected in reservoir WR, and bottoms products being returned to the reactor at a rate to give a steady level in both reactor and reboiler.

Samples were periodically removed from the two vessels and analysed for total acid and HCl. At the end of the two-hour experiment the bottoms product had reached the steady analysis of 2,01 M in HNO_3 and 0,23 M in HCl. The concentrations in the reactor had, of course, risen at the same time, to accommodate the acid that had been removed from the reboiler.

Samples of condensate were also analysed periodically for total acidity. From an initial value of 0,102 M, it dropped to 0,093 M at the end of the run. These analyses give an indication of the efficiency of the fractionation column; from a reactor solution of total acidity 1,32 M, a distillate of acidity 0,10 M was obtained.

Subsequently, in the first run with the full bench-scale plant, a solution 2,01 M in HNO_3 and 0,23 M in HCl was used as charge in the reboiler. Thereafter the solution remaining in the reboiler was not changed from one full run to the next, although a check was, of course, kept on its composition, which fluctuated somewhat as the rate of reflux in these runs varied.

3.2.3.3. Full Runs with the Bench-Scale Plant

In the first series of runs the 60% (w/w) AN feed solution was made up from nitrous oxide grade AN. In the first run, HCl and HNO_3 were fed into the reactor by means of a single solution which was, by calculation, 3,93 M in HCl and 2,58 M in HNO_3. (This expedient was followed because of the lack of sufficient peristaltic pumps.) In this run, no glass tubes were used as "boiling stones" in the reactor. At the start of the experiment, 250 ml of pure water was placed in the WR flask (Fig. 4) as reflux liquid.

The start-up procedure was as follows. Heating of the reboiler solution (at full load of the heating mantle) was done until about two thirds the length of the fractionation column had been heated up by the vapour before starting heating of the reactor vessel. After about half an hour the reactor solution reached boiling point, and the metering pumps for AN solution, HCl/HNO_3 mixture, condensate and NaOH solution were started. Heating with both heating mantles was continued at full load throughout the experiment.

The run was of 8 hours' duration. The gas evolution rate reached the value of 3,8 l min^{-1} initially, as a boiling point of 109,0° and a pressure of 13 cm above atmospheric were recorded, but these values soon dropped, and about an hour after start-up (i.e.

after gas evolution for about half an hour), fairly steady conditions were achieved, with the gas evolution rate fluctuating between 2,5 and 2,8 l min^{-1}, the temperature between 106,7° and 108,0°, and the pressure between 8 and 9 cm. Analysis of the gas product gave Cl_2 values of between 0,84 and 1,5% (the latter value having been obtained apparently when the HNO_3 and HCl concentrations were simultaneously high compared to those of the starting reactor solution).

The condensate had a total acidity of only 0,019 to 0,04 M (the latter was obtained when acidities in the reactor were high), compared to a value of 0,10 M in the experiment with the fractionation column only. This five-fold improvement in fractionation column efficiency evidently resulted from the large non-condensable (largely N_2O) component in the vapour stream in the present run.

Gratifyingly, it was found easier to control the operation of the full bench-scale plant and approach steady-state conditions than had been the case in the experiment with the reactor alone. Operation of the system was controlled as follows. In the first instance the level in the reactor vessel was controlled by adjusting the pump rate of bottom product into the reactor. The level in the bottom products vessel was, in turn, controlled by adjusting the reflux rate of condensate to the top of the fractionation column. On the basis of analyses of the reactor solution, metering rates of the HCl/HNO_3 solution were adjusted. Analyses of the bottom product solution were recorded to assist judging the attainment of steady-state conditions.

The silica gel column used as dryer turned slightly yellowish green at the inlet side, probably by interaction with residual traces of Cl_2 not removed by the scrubber. The purified gas emerging at the far end of the bench-plant was shown to contain residual traces of Cl_2 at times, showing that the scrubber was not 100 per cent efficient.

In subsequent runs, the HCl and HNO_3 were added separately when a further peristaltic pump became available. Two constrictions were made in the vertical part of the level indicator of the reactor

to restrict oscillations of the liquid level in the loop, which made readings difficult. It was also at this stage that glass tubes (15mm x 15mm) were introduced into the reactor to promote smoother boiling, and that an integral rate meter was introduced into the train(Fig. 4).

Table 4 and Fig. 5 show the results of a 4-hour run with nitrous oxide grade AN using the bench-scale plant with all the modifications described above. (These are all incorporated in Fig. 4.) These data show clearly how the gas evolution rate varies with such parameters as temperature and pressure. The temperature (here the boiling point of the mixture) and the pressure are, of course, coupled. There does not appear to be a clearly evident relationship between rate of gas evolution and the concentrations of HCl and HNO_3. Clearly, the variation of reactor solution temperature was the predominant effect. Too few samples were taken for Cl_2 and N_2 analysis to allow even tentative conclusions about the dependence of their levels on the parameters mentioned, but the impression was gained that the Cl_2 concentration (and hence probably the N_2 content as well) increased with increasing rate of gas evolution. (It should be noted that the integral flow meter readings in Table 4 are in error by the amounts of gas that had bypassed it during gas sampling for N_2 and Cl_2 analysis.)

The above experiment was involuntarily terminated when the stopcock of the sampling port on the reactor accidentally popped out, and reactor solution was spilt on the heating mantle, putting out of action its top heating element. With the reduced heat output from the heating mantle, the reactor soon went out of control in the sense that the necessary rate of water evaporation could not be maintained despite the fact that the solution continued to boil. With the ensuing dilution of the reactor solution, the rate rapidly fell off.

In the next, 6-hour run a 60% (w/w) solution of AN of fertiliser grade was used instead of the nitrous oxide grade material. Slightly higher rates were observed (Table 5 and Fig. 6), possibly because of an error made in preparing the solution to the desired concentration.

TABLE 4. Results of a bench-scale run with nitrous oxide grade AN.

Time (min)	Temp °C	Manometer (cm of Hg)	Reactor level	Bottom product level	Rotameter, 1 min^{-1}	Integral rotameter 1 min^{-1}	Analysis of the reaction mixture			Analysis of the bottom product			%Cl_2 (v/v)	%N_2 (v/v)	Condensate analysis (N)
							Mass sample	NaOH titre/g	$AgNO_3$ titre/g	Mass sample	NaOH titre/g	$AgNO_3$ titre/g			
0	29	0	2,3	1,43	0	0	0,5862	37,12	1,77	0,7643	20,10	8,57			
25	107,0	8	2,3	1,43	2,5	2,77→7min	0,4934	33,74	1,70	0,7536	19,79	8,30			
40	107,2	7,5	2,28	1,41	2,2	2,77→27min	0,8166	35,63	1,74						0,012
55	108,2	9,0	2,28	1,39	2,0	2,33→42min	0,5987	34,99	1,70	1,1984	20,92	8,47	1,07		
70	108,5	9,5	2,30	1,32	3,2	2,27→53min	0,4236	37,41	1,93						0,017
85	108,5	10,3	2,31	1,32	3,4	2,78→72min	0,5729	36,72	1,95	0,[illegible]63	23,43	9,01			
100	108,0	9,5	2,33	1,32	3,0	3,46→87min	0,8468	37,08	1,91						0,022
115	107,4	8,0	2,31	1,32	2,5	3,0 →97min				0,3442	26,46	9,12	1,36		
130	107,9	8,5	2,30	1,41	2,6	2,89→110min	0,8927	37,02	1,94						0,020
145	107,7	9,2	2,30	1,43	2,8	2,66→125min	0,5824	37,29	1,99	0,6279	25,62	9,21			
160	107,2	9,5	2,30	1,40	3,0	2,71→148min	0,6237	37,83	1,97				1,41		0,024
175	108,3	10,0	2,30	1,40	2,8	2,75→162min				0,4007	25,74	9,18		1,8	
190	107,9	[illegible]2	2,30	1,21	2,6	2,95→180min	0,7905	39,21	1,63				1,38		0,029
205	108,0	10,0	2,30	1,29	2,8	3,07→199min	0,5137	39,40	1,58	0,3360	25,81	9,17			
220	108,0	10,0	2,30	1,42	3,1	2,56→217min	0,5099	40,04	1,67					1,8	

REMARKS

- Peristaltic pumps were started when the reaction mixture reached 80° and a flow rate of 1 1min^{-1} was observed.
- The rates of the pumps were finally adjusted at: AN, 10 ml min^{-1} (fixed); HNO_3, 0,4 ml min^{-1}; HCl, 0,8 ml min^{-1}; bottom product, 4 ml min^{-1}; H_2O reflux, 3,5 ml min^{-1}; NaOH, 5 ml min^{-1}.
- The concentrations of HCl and HNO_3 fed into the reactor were 3,04 and 2,55 N, respectively.

TABLE 5. Experimental data obtained in a bench-scale plant run with fertiliser grade AN.

Time (min)	Temp °C	Manometer (cm of Hg)	Reactor level	Bottom product level	Rotameter 1 min^{-1}	Integral rotameter 1 min^{-1}	Analysis of the reaction mixture			Analysis of the bottom product			Condensate analysis (N)	%Cl_2 (v/v)
							Mass sample	NaOH titre/g	$AgNO_3$ titre/g	Mass sample	NaOH titre/g	$AgNO_3$ titre/g		
0			2, 68	1, 78		3, 45→20min	0, 6257	35, 83	1, 95	0, 5432	37, 71	11, 41		
15	108, 7	13	2, 78	1, 80	3, 6	2, 86→18min	0, 4792	36, 56	2, 13	0, 6333	36, 94			
30	108, 3	12, 8	2, 8	1, 85	3, 5	2, 85→49min	0, 7172	38, 09	2, 41				0, 0363	
45	107, 5	12	2, 80	1, 85	3, 0	3, 25→53min	0, 4028	38, 48	2, 53					
60	107, 9	12	2, 72	1, 65	3, 1	2, 6 →68min	1, 1543	38, 64	2, 29				0, 0332	
75	107, 5	12	2, 80	1, 55	2, 7	2, 54→80min	0, 7705	38, 83	1, 82	0, 1057	22, 57	8, 61		1, 64
90	107, 9	10, 5	2, 78	1, 60	2, 5	3, 0 →88min	0, 7737	37, 91	1, 45				0, 0280	
105	108, 4	11	2, 80	1, 55	3, 0	2, 7 →98min	0, 9286	37, 87	1, 66	0, 8522	21, 01			
120	108, 7	12	2, 80	1, 55	3, 2	3, 0 →113min	0, 6672						0, 0371	
135	108, 6	12	2, 82	1, 50	3, 2	2, 7 →133min	0, 6525	37, 76	1, 56	0, 4235	23, 09	8, 47		1, 53
150	108, 2	11	2, 80	1, 64	3, 8	2, 93→249min								
165	108, 6	12	2, 80	1, 65	3, 2	3, 26→163min	1, 1264	37, 48	1, 60	0, 7954	24, 27			
180	108, 4	11, 6	2, 80	1, 62	2, 8	3, 26→173min	0, 8344	38, 03	1, 64				0, 0287	
195	108, 8	13	2, 80	1, 60	3, 7	3, 32→188min	0, 7780	38, 71	1, 63	0, 7457	24, 22	8, 93		1, 83
210	108, 5	12	2, 80	1, 50	3, 2	3, 21→208min	0, 6825	39, 74	1, 71				0, 0362	
225	108, 0	11	2, 80	1, 50	3, 1	3, 12→218min	0, 6799	39, 27	1, 71	0, 5743	24, 93			
240	108, 7	12	2, 80	1, 50	3, 2	2, 76→228min	0, 5894	38, 60	1, 78				0, 0369	
255	108, 4	11	2, 80	1, 55	3, 0	3, 34→238min	0, 7897	39, 47	1, 96	0, 4048	27, 64	9, 21		2, 00
270	108, 3	13	2, 80	1, 55	3, 2	3, 13→249min	1, 0302	39, 99	1, 96				0, 0372	
285	108, 7	15	2, 80	1, 55	3, 4	3, 0→261min	0, 7908	39, 87	1, 83	0, 7240	25, 96			

REMARKS

- Peristaltic pumps were started when the reaction mixture reached 80° and a flow rate of 1 l min^{-1} was measured.
- The rates of the pumps were finally adjusted at: AN, 10 ml min^{-1} (fixed); HNO_3, 0, 78 ml min^{-1}; HCl, 0, 82 ml min^{-1}; H_2O reflux, 4, 7 ml min^{-1}; Bottom product, 4 ml min^{-1}; NaOH, 5 ml min^{-1}.
- The concentrations of HCl and HNO_3 feeds were 3, 84 N and 2, 55 N, respectively.

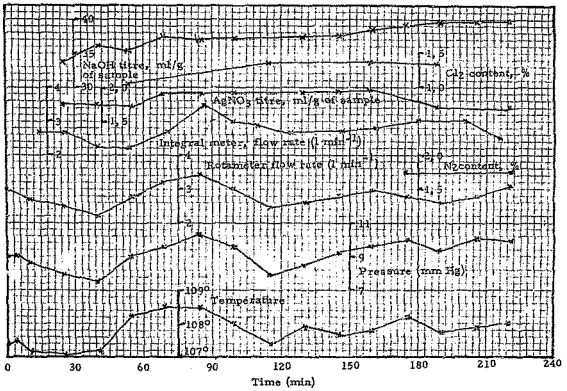

Fig. 5. Results of a bench-scale run with nitrous oxide grade AN.

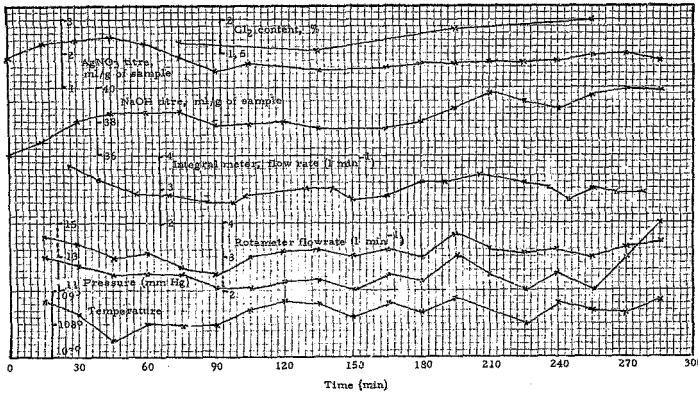

Fig. 6. Results of a bench-scale plant run with fertiliser grade AN.

(This was done in a rather crude way at the Sasol factory.) Another factor which may have affected the rate was the presence of colloidal rust particles, which were fortuitously introduced at Sasolburg when 88 per cent AN solution was drained from the production line through a rather rusty pipe that had to be bent for the purpose. The manometer readings, it is noted, are generally higher than those of Fig. 5.

Values for N_2 content of the gas product are not given for this run. Unfortunately, the detector of the gas chromatograph was defective at the time, giving spurious results.

In a 2-hour run with nitrous oxide grade AN the effect of pressure on the rate of product gas was tested. A needle valve (N) was introduced into the glass tube connecting the reactor vessel with the fractionation column (Fig. 4). It was found that by increasing the pressure in the reactor to 50 cm (above atmospheric) and thus increasing the boiling point of the mixture to 114, 1^{o}, a rate of product gas as high as 5,5 $lmin^{-1}$ was attained.

3.2.4. Discussion

Reasonable steady-state conditions were readily achieved in the bench-scale plant experiments, the fluctuations observed in the rate of N_2O evolution being mainly due to variations in the boiling point of the mixture, which were in turn caused by fluctuations in the pressure inside the reactor. The cause of the latter was not ascertained with certainty; we are inclined to ascribe this (except for the initial temperature rise at start-up) to fluctuations in the pressure drop along the flooded NaOH scrubber owing to variations in the level of liquid in the column, which was manually controlled.

Fractionation of the vapour is necessary to enable HCl and HNO_3 carried over with the water vapour to be returned to the reactor. Nitric acid does not appear to be consumed in either the formation of Cl_2 or of N_2, and losses of HNO_3 occur only as traces carried over into the distillate which goes to waste. Some HCl is

consumed in the formation of Cl_2, and the HCl in the reactor would thus have to be continuously replenished, albeit at a very slow flow rate. The product gas always contains up to a few per cent of both Cl_2 and N_2.

CHAPTER 4. KINETIC EXPERIMENTS

4.1. Introduction

From the experiments described in the foregoing Chapters it is clear that several factors influence the rate of production of N_2O and of the impurities Cl_2 and N_2 during chloride-catalysed decomposition of AN. The principal parameters affecting these rates have been shown in Chapter 2 to be the concentrations of AN, acid and chloride, as well as the temperature.

This chapter describes a detailed investigation of the dependencies of N_2O, Cl_2 and N_2 evolution rates on the reaction parameters. Batch experiments were designed to obtain experimental rate equations for these gas evolution reactions with a view to selecting optimum conditions for an industrial-scale plant for N_2O production. At the same time it was hoped that the rate equations thus obtained would enable the elucidation of the mechanisms of the reactions involved.

The isolation method[17] was used. Several series of reaction mixtures, from which the chloride catalyst was omitted, were prepared. In each of these series, where possible, only one parameter at a time was varied. A known volume of such a mixture was placed in the reactor and heated in an oil bath to the desired temperature, whereupon the chloride catalyst was injected. Gases formed during the ensuing reaction were swept out of the reactor by means of helium sparge gas (passed through at a known rate). The concentrations of N_2O and Cl_2 in the product gas were measured continuously by passing the gas stream through the consecutive gas cells of a infrared spectrophotometer (for measuring N_2O) and a ultraviolet spectrophotometer (for measuring Cl_2). A 4-way stopcock was incorporated in the gas product line to enable intermittent injection of a gas sample

into a gas chromatograph for determination of the N_2 content.

Empirical rate equations for N_2O, Cl_2 and N_2 were obtained from the variations of the rates of evolution of the respective products as functions of the concentrations of chloride, nitrate and ammonium, and acidity.

The effect on the evolution rates of these gases of the concentrations of AN and HNO_3 (where two parameters vary at the same time) was also studied. These experiments were done for the purpose of obtaining data directly applicable to an industrial-scale plant (since in such a plant the real variables are likely to be $[NH_4NO_3]$ and $[FN[HNO_3]$ rather than $[NH_4^+]$, $[NO_3^-]$ and acid concentration separately) and also to check the rate data obtained for the individual variables for consistency.

It has not been possible to propose a plausible mechanism for the reactions in this system which would be in agreement with the high exponential dependence of the concentration terms in the rate equations. The mechanisms of these reactions are evidently very complex. They appear to be substantially different from those postulated by Keenan and Dimitriades[16] for chloride-catalysed decomposition of AN in the melt.

4.2. Experimental

4.2.1. Reagents and Equipment

Solid, nitrous oxide grade AN was used for all the experiments. Nitric acid and sulphuric acid were of commercial grade. The hydrochloric acid, ammonium sulphate, and the chloride, nitrate and sulphate of sodium were of Analar purity. Standard gas mixtures were prepared by Union Liquid Air Ltd.

The apparatus (Fig. 7) consisted of a 4-necked, 100-ml, round bottomed Q/Q flask as reactor, fitted with a thermometer pocket, an inlet port for the sparge gas and standard gases, and an injection point closed off with a rubber septum. The reactor was immersed in a silicone oil thermostat bath. The load in the heating element of the bath was controlled by means of a Variac transformer.

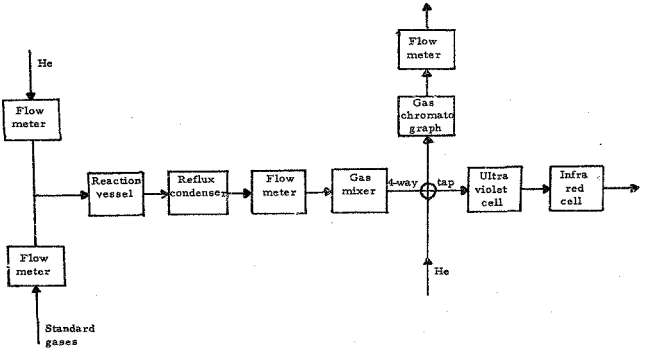

Fig. 7. Block diagram of the apparatus used in the kinetic experiments.

A reflux condenser was fitted to the top of the reactor. The condenser was connected to a gas mixing tube and a soap-film flow-meter. The 4-way tap allowed continuous flow in both the reactor off-gas stream and in the helium carrier gas stream to the gas chromatograph. In the reactor flow stream the 4-way tap was positioned between the gas mixing chamber and the ultraviolet cell in the reactor off-gas stream. In the gas chromatographic flow stream, the 4-way tap was positioned between the helium cylinder and gas chromatograph reference cell. By turning the cock rapidly through 160°, the same connections were again realised, but a reproducible volume (ca 2ml) of gas momentarily trapped in the bore of the cock carrying the gas from the reactor was thus introduced into the gas chromatograph.

The chlorine content of the gas stream was measured by the absorbance of Cl_2 at 330 nm in a gas cell, fitted with silica windows, with a Varian Techtron, model 635, recording spectrophotometer. The N_2O content was obtained from the transmittance (at 2080 cm^{-1}) through a second gas cell (fitted with polyethylene windows) in an Infragraph H 1200 infrared spectrophotometer. The N_2 content was determined with a Shandon UK-3 gas chromatograph. Helium at a rate of 25 ml min^{-1} was used as the carrier gas. A U-shaped column, ca 8 mm x 600 mm, packed with 60/80 molecular sieve 5A, lot number 10270 (supplied by Supelco, Inc.), as the stationary phase. All N_2 determinations were performed isothermally at room temperature.

4.2.2. Analytical Methods

For a study of the dependence of the evolution rates of N_2O, Cl_2 and N_2 as functions of the various concentration parameters, methods were required for quantitatively measuring the initial rates of production of the three gaseous products. This was done by sweeping out the reactor vessel with a sparge gas at a known and constant rate. The rates of production of N_2O, Cl_2 and N_2 could then be determined by measuring the individual concentrations of the three gases and

the total flow rate in the combined gas stream.

The N_2O concentration could readily be determined by measuring its absorption at one of the peaks in its infrared spectrum (Fig. 8). The peak at 2080 cm^{-1} was selected, and the Infragraph was adapted to record the percentage transmittance at this fixed wavenumber as a function of time. The percentage transmittance was minimised on the 2080 cm^{-1} peak to optimise the sensitivity of the spectrophotometer.

The Cl_2 concentration was conveniently measured from its absorbance at 330 nm in the ultraviolet region, where Cl_2 absorbs strongly (Fig. 9).

No convenient method was available for continuously measuring the N_2 concentration in the gas stream. It was thus necessary to resort to intermittent sampling and subsequent gas chromatographic determination. Chromatographic separation of N_2 from N_2O and Cl_2 was achieved under the conditions described in section 4.2.1, which also gave good resolution of N_2 and O_2 (Fig.10). The ability to detect O_2 provided an internal check on possible contamination of the gas stream with residual air.

4.2.3. Procedure

The dependence of N_2O, Cl_2 and N_2 evolution rates on the various concentration parameters was investigated by preparing in each series of experiments a number of reaction mixtures (Table 6), the composition of which was kept constant but for the parameter being varied. In the preparation of the mixture the source of chloride ions was omitted, and the mixture made up to 100 ml with distilled water. The mixture was transferred to the reactor vessel as quantitatively as possible and the apparatus assembled (Fig. 7), with the reactor immersed in the oil bath. The latter was heated to about 1° - 5° below the desired final temperature of 94.8°. Helium gas was passed through at a known and constant rate to expel all air from the system.

When the desired temperature had been reached, the chloride

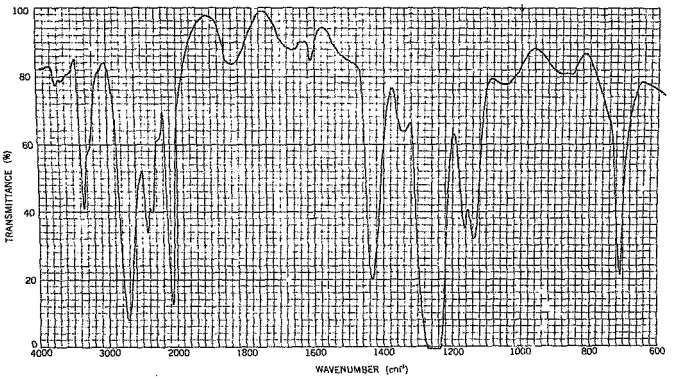

Fig. 8. Infrared spectrum of N_2O.

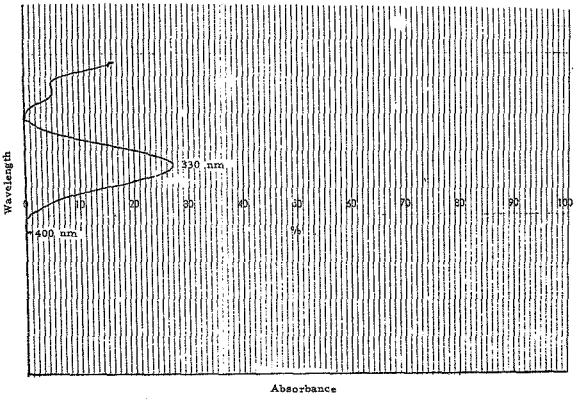

Fig. 9. Ultraviolet spectrum of Cl_2.

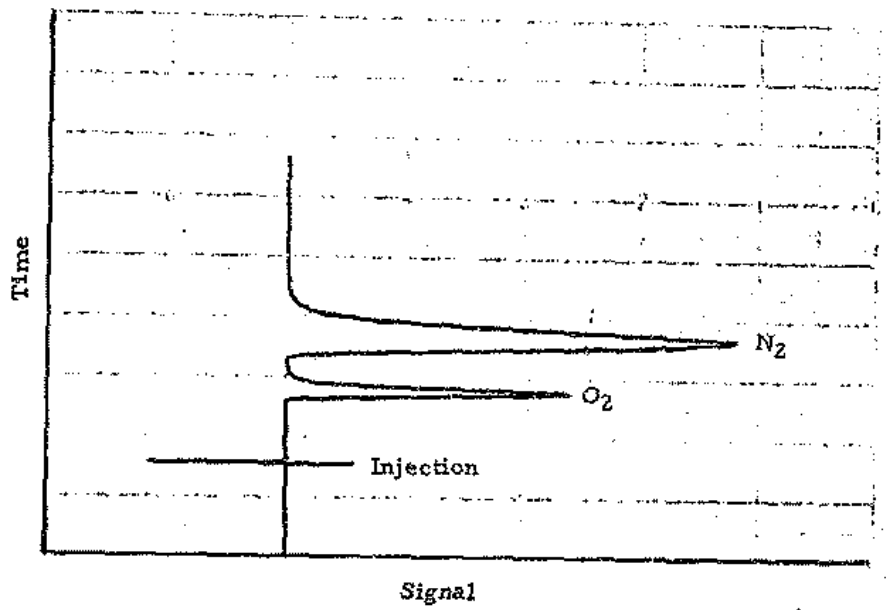

Fig. 10. Gas chromatogram showing separation of O_2 and N_2 in an air sample.

TABLE 6. Reaction mixtures used in kinetic experiments.
Each column lists the experimental conditions for a series of experiments in which the rates dependencies of evolution of the various gases were studied as a function of the parameter given at the top of the column. (x in each case signifies the appropriate varying quantity.)

$[H_3O^+]$	$[NO_3^-]$	$[Cl^-]$	$[NH_4NO_3]$	$[HNO_3]$	TEMP
45g NH_4NO_3 + x ml of H_2SO_4 12N ↓H_2O 100ml ↓ 94, 8° + 1, 5ml HCl 12N	30g NH_4NO_3 + 30ml HNO_3 12N + x g of $NaNO_3$ ↓H_2O 100ml ↓ 94, 8° + 1, 5ml HCl 12N	35g NH_4NO_3 + 35ml HNO_3 12N ↓H_2O 100ml ↓ 94, 8° + x g of NaCl	50ml H_2SO_4 12N + x g of NH_4NO_3 ↓H_2O 100ml ↓ 94, 8° + 1, 5ml HCl 12N	35g NH_4NO_3 + x ml of HNO_3 12N ↓H_2O 100ml ↓ 94, 8° + 1, 5ml HCl 12N	35g NH_4NO_3 + 35ml HNO_3 12N ↓H_2O 100ml ↓ Heat to desired temp + 1, 5ml HCl 12N

catalyst (in most experiments 1,5 ml of 12,0 M HCl) was injected by means of a hypodermic syringe. Injection of the catalyst immediately resulted in gas evolution from the reactor solution.

Because of the exothermic nature of the reaction (see equation 1.1), the temperature of the reaction mixture rapidly increased by a few degrees (the extent of the increase depending on the composition of the mixture), asymptotically approaching a maximum value. The temperature of the thermostat bath was at the same time adjusted upwards by means of the Variac control. By trial and error it was found possible to choose a starting temperature and to operate the Variac control in such a way that the temperature of both the reactor mixture and the bath asymptotically reached the desired reference temperature of 94,8° (arbitrarily chosen).

Helium sparge gas was passed through the reactor at a known rate controlled to within better than ± 3% throughout each run. Except for the first series, the product gases plus helium was passed through a flowmeter (to measure the total flow rate), the gas mixing tube, and then via the 4-way tap to the cells of the ultraviolet and infragraph spectrophotometers (Fig. 7). When a constant absorbance was recorded by the ultraviolet spectrophotometer, the first sample was introduced into the gas chromatograph for N_2 determination. (The ultraviolet spectrophotometer was found to be a more sensitive method of detection of steady state flow conditions.) Three to four samples were taken for N_2 determination in the course of each run.

The time, measured with a stop-watch, was periodically noted on the recorder tracings. Flow rates were checked at regular intervals by means of the flowmeters. A typical set of recorder tracings and a gas chromatogram are given in Figs. 11, 12 and 13. The theory of the measurements and methods of calibrating the instruments are discussed in the next sections.

4.2.4. Theory of Measurements

4.2.4.1. Determination of the N_2O Rate

In calibrating the infragraph spectrophotometer, two soap-film flowmeters

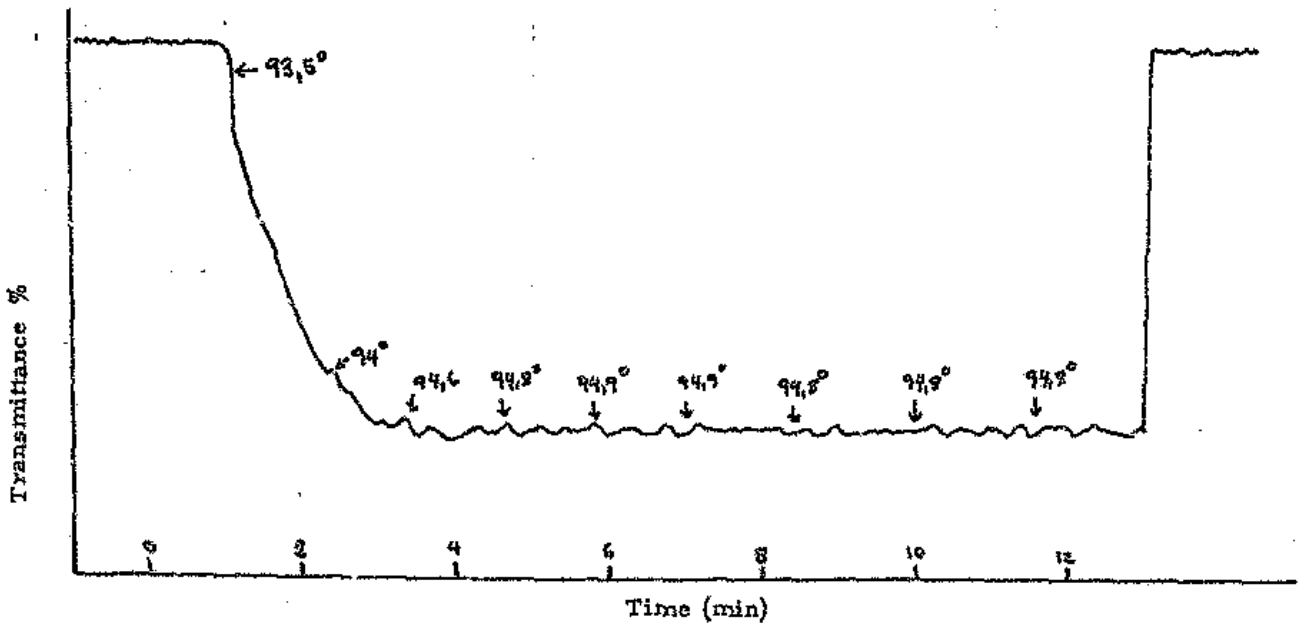

Fig. 11. Recorder tracing for N_2O.

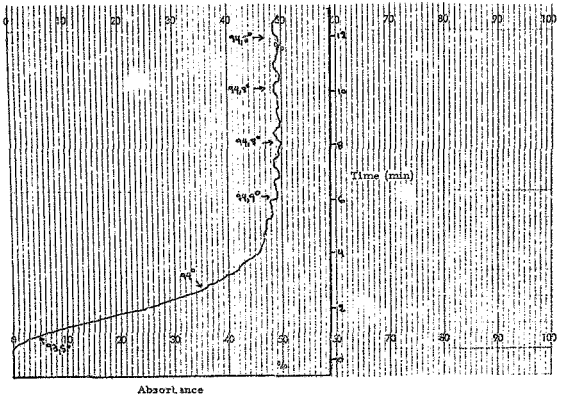

Fig. 12. Recorder tracing for Cl_2.

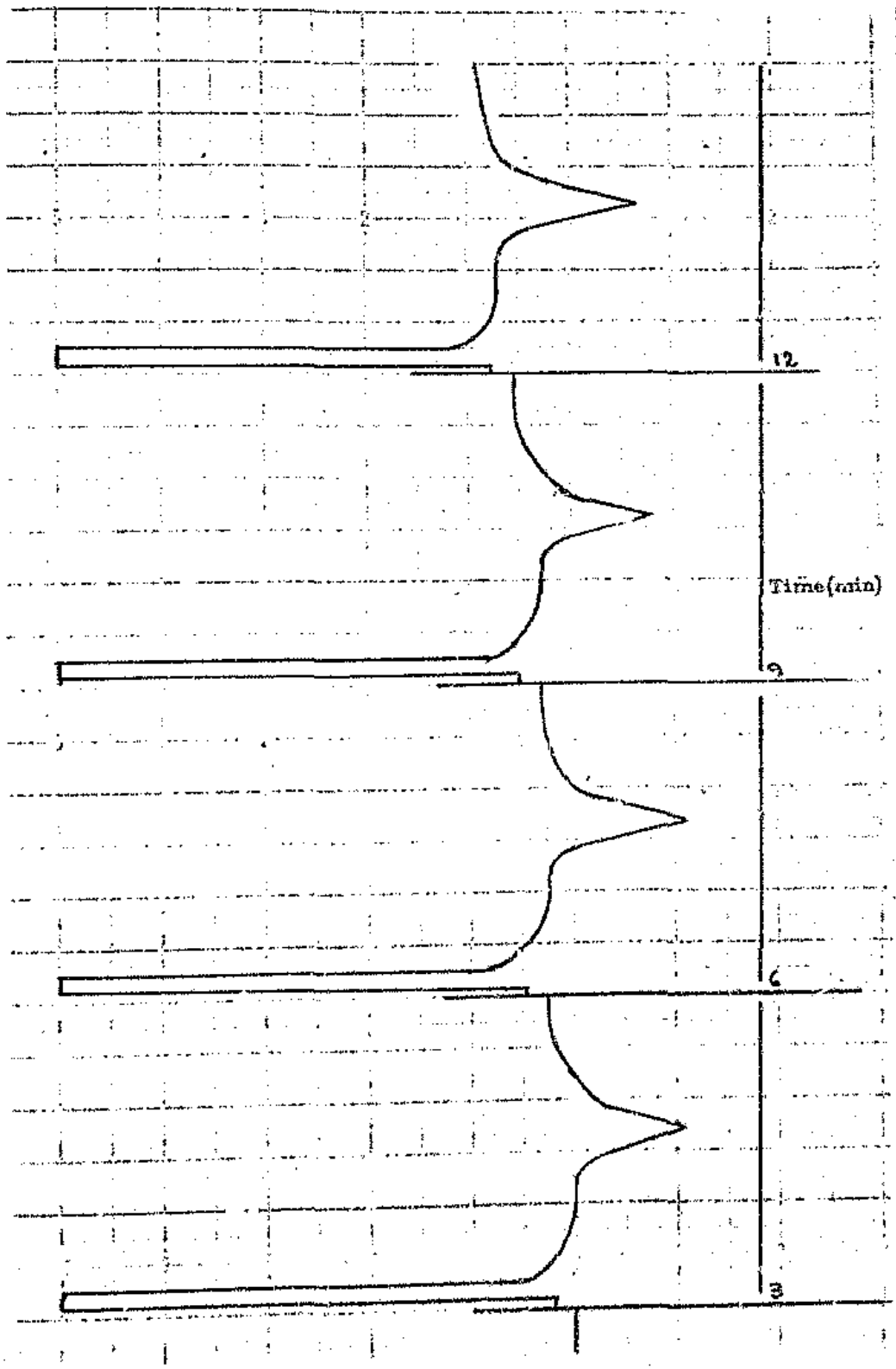

Fig. 13. Recorder tracing for N_2.

were used to measure the rates of pure N_2O (99.9%) and of helium sparge gas fed from cylinders into the reactor, which contained the solution and was kept at room temperature. When the air had been fully displaced the percentage transmittance recorded reached a constant value. By keeping the helium rate constant and varying the rate of N_2O from the cylinder, different concentrations, i.e. partial pressures, were established in the gas stream. Values of the transmittance were recorded corresponding to the different concentrations of N_2O. The transmittances recorded were converted into absorbances and these were plotted against the ratio of the partial pressure of the N_2O to the atmospheric pressure (i.e. the fraction of N_2O). This ratio was calculated from the flow rates of the N_2O and the He streams by the relationship

$$\frac{P_{N_2O}}{P_{atm}} = \frac{R_{N_2O}}{R_{N_2O} + R_{He}} \qquad (4.1)$$

where P_{N_2O} = partial pressure of N_2O

R_{N_2O} = rate of N_2O entering the reactor

R_{He} = rate of He entering the reactor

P_{atm} = barometric pressure.

The measured rates of the gases were always converted to S. T. P. Fig. 14 shows a typical calibration curve.

In the actual experimental run, the rate of flow of sparge gas, helium, was measured before entering the reactor, and was kept constant to within ± 3%. The total rate of gas flow was measured with a flowmeter located as shown in Fig. 7. The absorbance, calculated from the recorded transmittance, was then related to the fraction of N_2O by interpolation from the calibration curve. From the total flow rate of gases from the reactor, R_{total}, and the fraction of N_2O, the initial rate of production of N_2O was calculated by the equation

$$R_{N_2O} = \left[\frac{P_{N_2O}}{P_{atm}}\right] R_{total} \qquad (4.2)$$

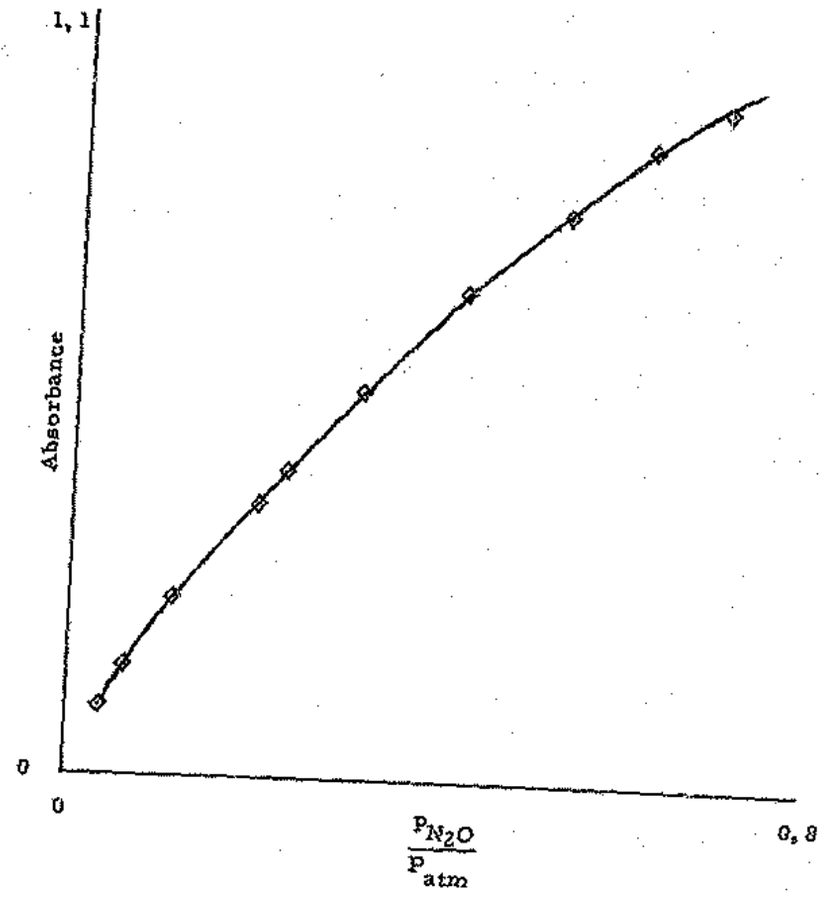

Fig. 14. Calibration graph for N_2O.

4.2.4.2. Determination of the Cl_2 and N_2 Rates

Standard gases of 0.87% (v/v) Cl_2 in N_2O and 1.8% (v/v) N_2 in N_2O were used for calibrating the ultraviolet spectrophotometer and the gas chromatograph for Cl_2 and N_2, respectively. As before, helium at a constant rate was passed through the reactor together with one of the standard gases at varying flow rates. Calibration graphs were constructed relating absorbance in the UV (for Cl_2) and gas chromatographic peak height (for N_2) against the ratio of the fraction of Cl_2 (or N_2) in the gas stream to the Cl_2 (or N_2) in the standard gas (Figs. 15 and 16) as follows

$$F_{Cl_2} = \left[\frac{R_{Cl_2 - N_2O}}{R_{Cl_2 - N_2O} + R_{He}}\right] (F_{Cl_2})_{Std} \qquad (4.3)$$

$$F_{N_2} = \left[\frac{R_{N_2 - N_2O}}{R_{N_2 - N_2O} + R_{He}}\right] (F_{N_2})_{Std} \qquad (4.4)$$

where $R_{Cl_2 - N_2O}$ and $R_{N_2 - N_2O}$ are the flow rates of the standard gases Cl_2 and N_2, F_{Cl_2} and F_{N_2} are the mole fractions of Cl_2 and N_2 in the gas stream, and $(F_{Cl_2})_{Std}$ and $(F_{N_2})_{Std}$ are the mole fractions of Cl_2 and N_2 in the standard samples.

Although the quantitative relationship of peak area to amount of N_2 (partial pressure of N_2 in a constant volume) is linear over a wider range of conditions, the relationship of peak height to amount of N_2 was adequate for our purposes and much more convenient.

In the experimental runs, calibration graphs for N_2 were always determined immediately before the actual series of runs, to allow for day to day variations in operating conditions of the gas chromatograph. On the other hand, the calibration curves for Cl_2 and N_2O were not subject to variations in ambient temperature and pressure, and thus a single calibration curve (which was checked periodically) could be used throughout the entire kinetics study.

The initial rates (at S. T. P.) for Cl_2 and N_2 were determined from the equations

$$\frac{dCl_2}{dt} = \left[\frac{R_{Cl_2 - N_2O}}{R_{Cl_2 - N_2O} + R_{He}}\right] (F_{Cl_2})_{Std} \; R_{total} \; \frac{P_e}{P_c} \qquad (4.5)$$

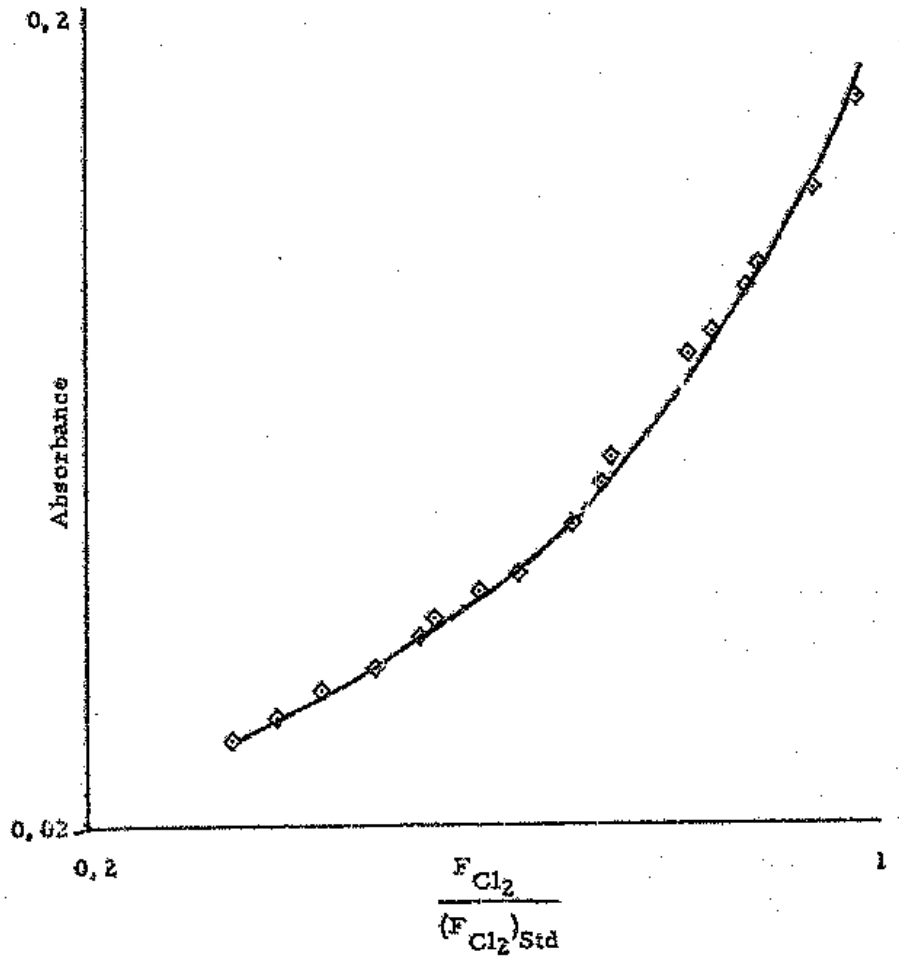

Fig. 15. Calibration graph for Cl_2.

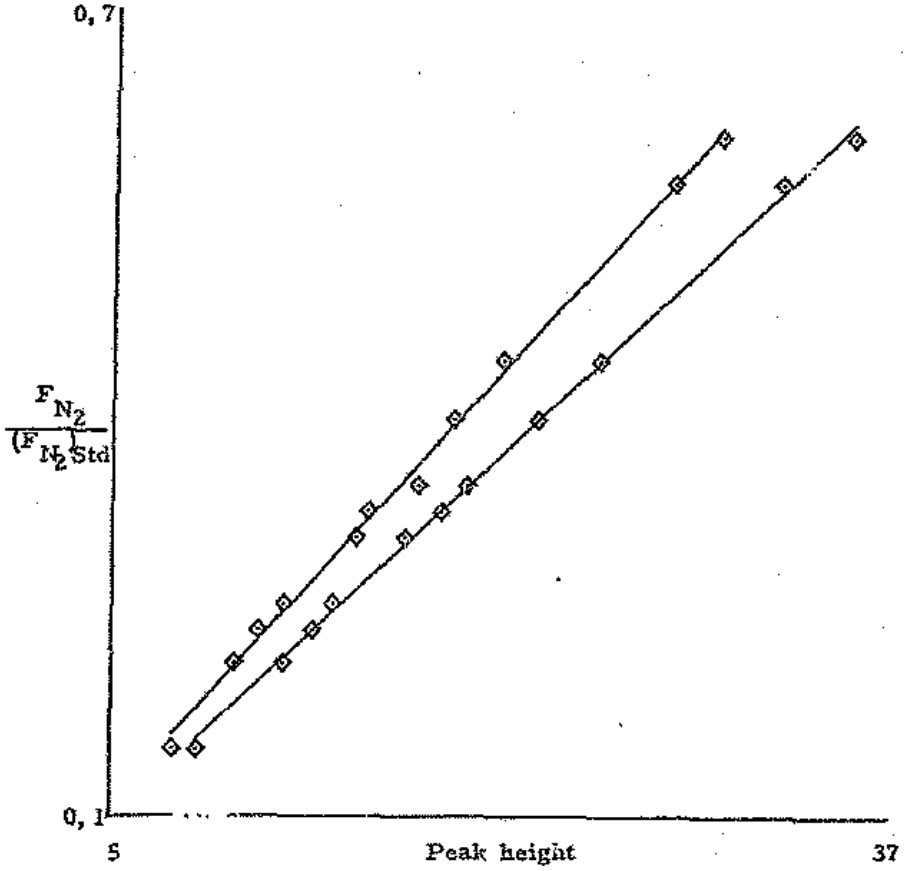

Fig. 16 Calibration graphs for N_2 for different volumes of gas samples (i. e. both bores of the stopcock).

$$\frac{dN_2}{dt} = \left[\frac{R_{N_2 - N_2O}}{R_{N_2 - N_2O} + R_{He}}\right] (F_{N_2})_{Std}\, R_{total} \qquad (4.6)$$

where dCl_2/dt, dN_2/dt are the initial rates of Cl_2 and N_2 in ml l^{-1}, reapectively. R_{total} is the total flow rate measured in the system, P_e and P_c the barometric pressure at the time of the experimental run and at the time of when the calibration graph was determined, respectively, and $(F_{Cl_2})_{Std}$ and $(F_{N_2})_{Std}$ the mole fractions of Cl_2 and N_2 in the standard samples. The quantities $R_{Cl_2 - N_2O}/(R_{Cl_2 - N_2O} + R_{He})$ and $R_{N_2 - N_2O}/(R_{N_2 - N_2O} + R_{He})$ were calculated from the calibration graphs.

The derivation of equations (4.5) and (4.6) is given in Appendix C.

4.3. Results

For a study of the initial rates of production of N_2O, Cl_2 and N_2 as a function of the concentrations of acid, nitrate, chloride and ammonium ions, it was desired in each series of experiments to vary the concentration of only one of the components which affected the rate of product evolution at a time. To this end, the following compounds were used as variables:

H_2SO_4 where $[H^+]$ was varied
$NaNO_3$ where $[NO_3^-]$ was varied
NaCl where $[Cl^-]$ was varied
$(NH_4)_2SO_4$ where $[NH_4^+]$ was varied

In these experiments either SO_4^{2-} or Na^+ are thus introduced as foreign ions, and it was necessary to verify the assumption that their presence had no influence (or a negligible one) on the reactions in the system.

The influence of the presence of Na^+ and SO_4^{2-} on the rates of production of N_2O with a typical reaction mixture was studied by including 20 g of Na_2SO_4, (which was near the maximum amount that could be dissolved) in 101.5 ml of reaction mixture. Table 7 shows that the presence of Na_2SO_4 had no significant effect on the rates up to the maximum concentration of Na_2SO_4 tested.

In the course of a series of experimental runs the rate of sparge gas helium was adjusted to ensure that the instruments were operating in their most sensitive regions. To check whether the rate of sparge gas flow had any influence on the observed rates of production of N_2O, Cl_2 and N_2, a series of experiments was carried out in which varying rates of sparge gas was used with reaction mixtures of fixed composition. Table 8 shows that the measurement of rate is independent of the sparge gas rate.

4.3.1. Determination of the Exponents of the Concentration Terms in the Rate Equation

The rate of product (N_2O, Cl_2 or N_2) evolution was found to be highly dependent upon the concentrations of H^+, NO_3^-, Cl^- and NH_4^+ in the reaction mixture. The exponent of each of the concentration terms which appear in the expression for rate of production of either N_2O, Cl_2 or N_2 was determined from the slope of the straight line obtained when the logarithm of the experimentally determined rate of gas evolution was plotted against the logarithm of the concentration of the component which was varied. The validity of this treatment is shown below.

Consider the expression

$$R = k' C_1^x \qquad (4.7)$$

where R is the rate of product evolution, k' is a pseudo-constant which incorporates the rate constant and each of the concentrations and their respective exponents of the components which have been held constant in the experiments, C_1 is the concentration of the component which is varied and x is the exponential dependence of the rate on the concentration of that component.

By taking the logarithm of each side of equation (4.7) we have:

$$\log R = \log k' + x \log C_1 \qquad (4.8)$$

Since $\log k'$ is a constant, a plot of $\log R$ versus $\log C_1$ should have a slope of x.

In this study the value of x was determined in each case for

TABLE 7. The effect of Na_2SO_4 on the rate of N_2O evolution.

Mixture 1	R_{N_2O} (mol sec^{-1}) x 10^{-5}	Mixture 2	R_{N_2O} (mol sec^{-1}) x 10^{-5}
35 g NH_4NO_3 + 40 ml HNO_3 12N $\downarrow H_2O$ 100 ml solution $\downarrow$ 94, 8° + 1, 5 ml HCl 12N	5, 85	35 g NH_4NO_3 + 40 ml HNO_3 12N + 20 g Na_2SO_4 $\downarrow H_2O$ 100 ml solution $\downarrow$ 94, 8° + 1, 5 ml HCl 12N	5, 78

TABLE 8. The effect of varying rates of helium on the rates of N_2O, Cl_2 and N_2 production.

Mixture	Rate of He (ml/sec)	Rate of N_2O (mol sec^{-1}) x 10^{-6}	Rate of Cl_2 (mol sec^{-1}) x 10^{-8}	Rate of N_2 (mol sec^{-1}) x 10^{-8}
30g NH_4NO_3	1, 99	20, 4	34, 3	21, 7
30ml HNO_3 12N	3, 11	21, 0	35, 0	21, 9
+	1, 5	19, 8	34, 7	21, 1
11g $NaNO_3$ $\downarrow H_2O$ 100ml solution $\downarrow$ 94, 8° 1, 5ml HCl 12N				

the straight-line plots obtained by doing a least squares fit, with a 95% confidence limit, on a Hewlett-Packard "Calculator".

4. 3. 2. Rate Dependencies on Acid Concentration

The exponential dependence of the rates of evolution of N_2O, Cl_2 and N_2 on the acidity, $[H^+]$, was determined by the method described in section 4. 3. 1. H_2SO_4 was used as variable instead of HNO_3, to ensure that only one parameter, H^+, would indeed be varied in the series. The acidity (Table 9) was varied over the concentration range 3, 36 to 8, 15 M.

The results are given in Figs. 17, 18 and 19. Exponents of 3, 72 (for N_2O), 3, 54 (for Cl_2) and 3, 16 (for N_2) were obtained.

It is to be noted that in this series of experiments the apparatus did not incorporate a flow meter for measuring the flow rate of the gas mixture issuing from the reactor. Instead, the gas was assumed to contain only helium (the flow of which into the reactor was measured) and N_2O (the rate of production of which was obtained from the Infragraph recording). Although the partial pressures of N_2O, Cl_2 and N_2 were accurately measured, the total flow rate of reaction product and helium sparge gas had to be determined indirectly from the measured helium flow rate and the calculated partial pressure of N_2O. Although we are confident of the relative values of the rates determined in this series of experiments, we would not place too great a confidence in the absolute values that were determined.

4. 3. 3. Rate Dependencies on Nitrate Concentration

The amounts of sodium nitrate added were such as to give a variation in total nitrate concentration in the reaction mixtures over the range 7, 24 to 9, 55 M (Table 10). The results are plotted in Figs. 20, 21 and 22. The exponential dependencies of the rates of production of N_2O, Cl_2 and N_2 on nitrate concentration were found to be 4, 21 (for N_2O), 4, 47 (for Cl_2) and 3, 30 (for N_2).

TABLE 9. Rates of N_2O, Cl_2 and N_2 evolution as a function of acid concentration.

$C_{NO_3^-}$ = 5,542 mol l^{-1}, $C_{NH_4^+}$ = 5,542 mol l^{-1}, C_{Cl^-} = 0,177 mol l^{-1} and T = 24,5°

C_{H^+} mol l^{-1}	Measured rate of He (ml sec^{-1})	Calculated total flow rate (ml sec^{-1})	Calculated values from calibration curves: R_{N_2O}	R_{Cl_2}	R_{N_2}	Calculated rate of N_2O (mol sec^{-1}) x 10^6	Calculated rate of Cl_2 (mol sec^{-1}) x 10^6	Calculated rate of N_2 (mol sec^{-1}) 10^3	k_{N_2O} x10^9	k_{Cl_2} x10^9	k_{N_2} x10^9
			R_{N_2O}/R_{N_2O+Ne}	R_{Cl_2}/Std	R_{N_2}/Std						
8,15	1,47	3,00	0,510			68,3			0,981		
7,62	1,47	2,87	0,485			62,1			0,114		
7,09	1,48	2,47	0,400	0,750	0,230	44,1	60,5	45,7	0,106	0,145	0,613
6,50	1,51	2,11	0,285	0,514	0,170	26,8	42,3	28,9	0,866	0,133	0,490
5,03	1,54	2,00	0,230	0,400	0,135	20,5	31,0	21,7	0,904	0,132	0,487
5,49	1,56	1,93	0,195	0,300	0,107	16,8	22,5	16,6	0,104	0,133	0,498
4,96	1,58	1,83	0,135	0,220	0,078	11,0	15,6	11,5	0,998	0,132	0,476
4,43	1,62	1,79	0,095	0,150		7,59	10,4		0,105	0,131	
3,90	1,64	1,76	0,068	0,095		5,34	6,5		0,118	0,129	
3,36	1,53	1,57	0,028		0,029	1,96		3,6	0,730		0,508

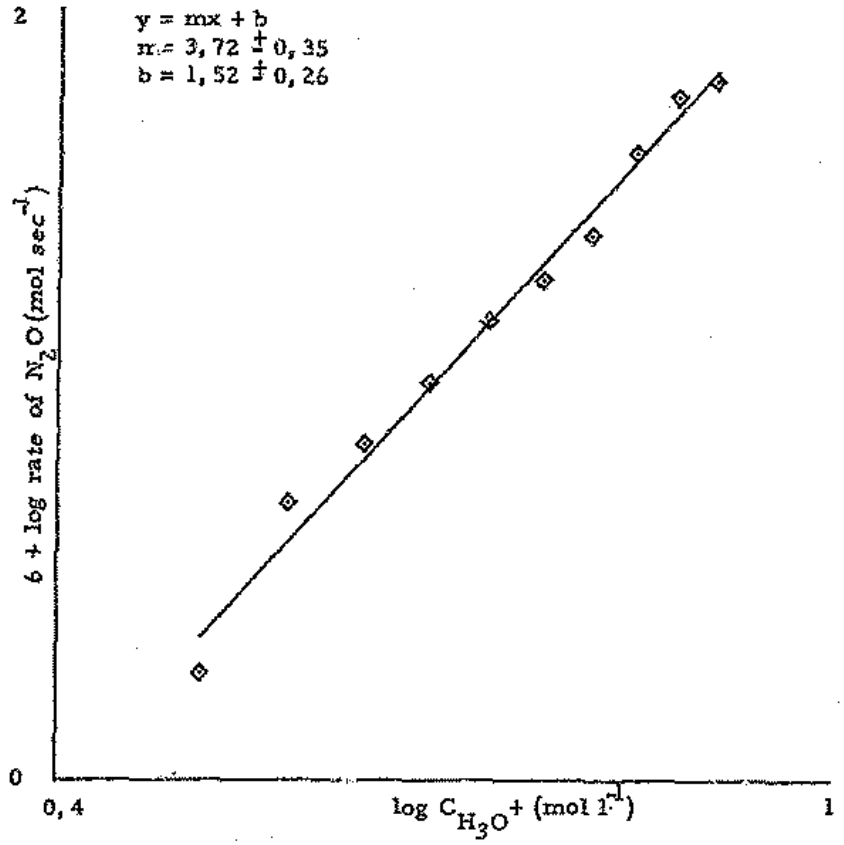

Fig. 17. Determination of the exponential dependence of the rate of N_2O on the acid concentration.

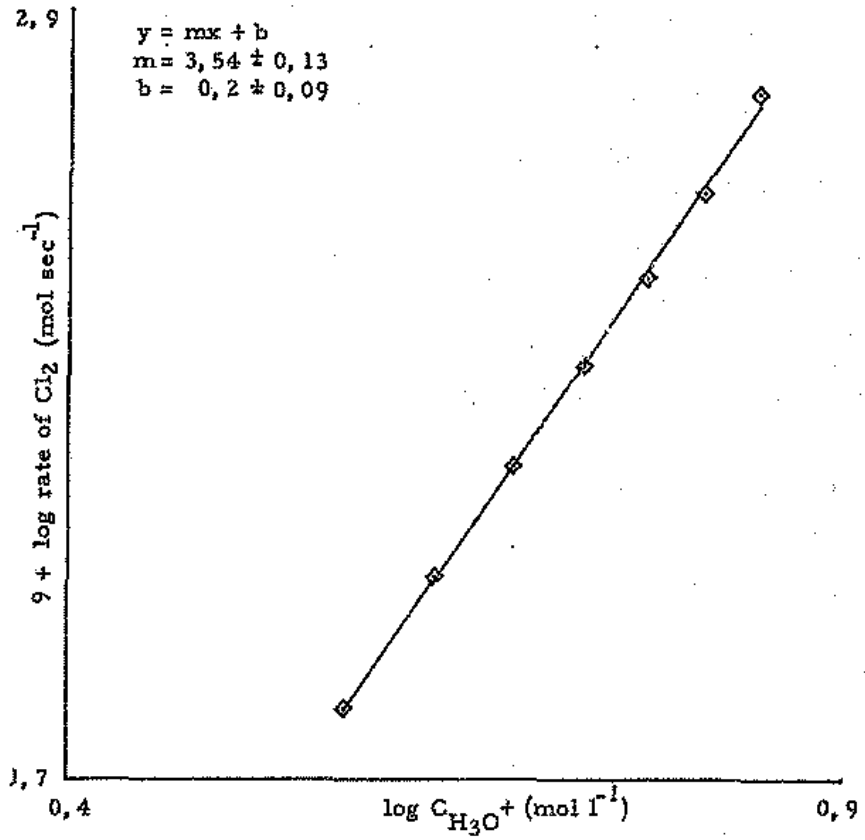

Fig. 18. Determination of the exponential dependence of the rate of Cl_2 on the acid concentration.

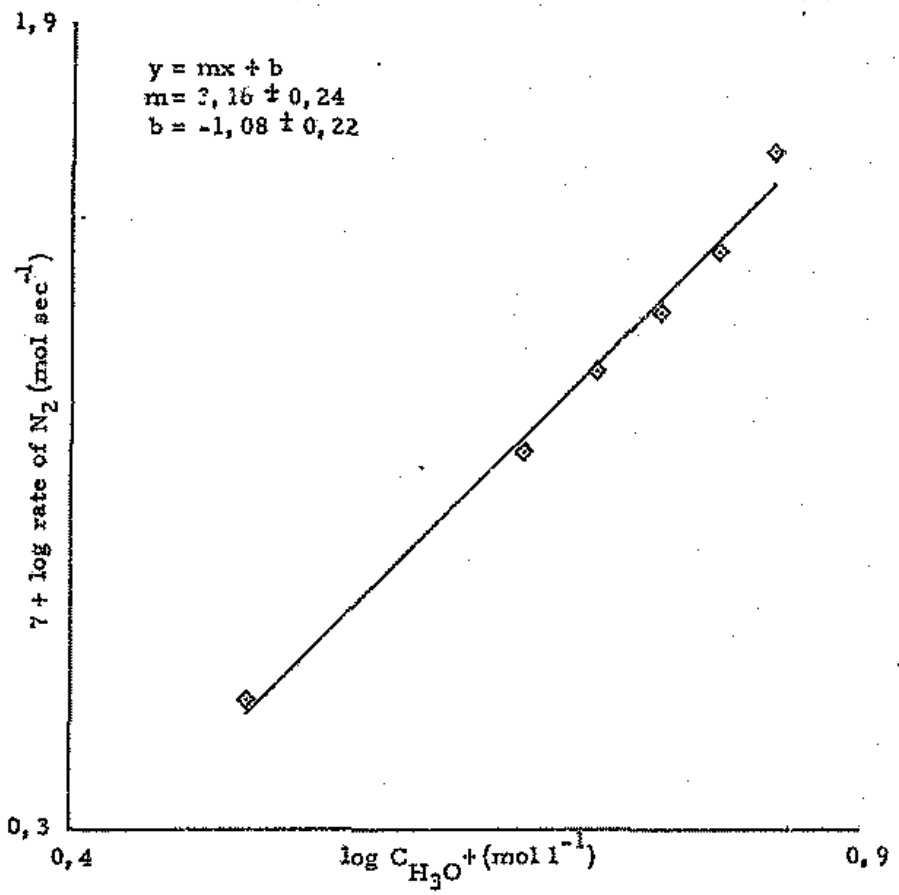

Fig. 19. Determination of the exponential dependence of the rate of N_2 on the acid concentration.

TABLE 10. Rates of N_2O, Cl_2 and N_2 evolution as a function of the nitrate concentration.

$C_{H^+} = 3,547$ mol l^{-1}, $C_{Cl^-} = 0,177$ mol l^{-1}, $C_{NH_4^+} = 3,695$ mol l^{-1} and $T = 94,8^{\circ}$

$C_{NO_3^-}$ mol l^{-1}	Measured rate of He (ml sec^{-1})	Measured total flow rate (ml sec^{-1})	Calculated values from calibration graphs			Calculated rate of N_2O (mol sec^{-1}) x10 ^{6}	Calculated rate of Cl_2 (mol sec^{-1}) x10 ^{8}	Calculated rate of N_2 (mol sec^{-1}) x10 ^{8}	k_{N_2O} x10 ^{9}	k_{Cl_2} x10 ^{9}	k_{N_2} x10 ^{9}
			R_{N_2O} / $R_{N_2O}+R_{He}$	F_{Cl_2} / $(F_{Cl_2})_{Std}$	F_{N_2} / $(F_{N_2})_{Std}$						
9,557	2,35	3,18	0,253	0,440	0,132	35,9	53,6	33,3	0,565	0,116	0,327
9,212	2,33	3,15	0,213	0,418	0,125	28,7	50,5	31,2	0,524	0,124	0,345
8,857	2,05	2,64	0,196	0,410	0,120	22,1	41,6	25,2	0,451	0,117	0,318
8,512	1,99	2,49	0,184	0,360	0,110	20,4	34,3	21,7	0,518	0,111	0,312
8,167	1,91	2,39	0,174	0,308	0,102	18,5	28,3	19,4	0,552	0,105	0,320
7,813	1,88	2,26	0,143	0,302	0,096	14,4	26,2	17,2	0,520	0,114	0,328
7,408	1,86	2,18	0,125	0,290	0,088	12,1	24,3	15,2	0,535	0,123	0,336
7,241	2,28	2,47	0,113	0,280		11,4	19,8		0,537	0,112	

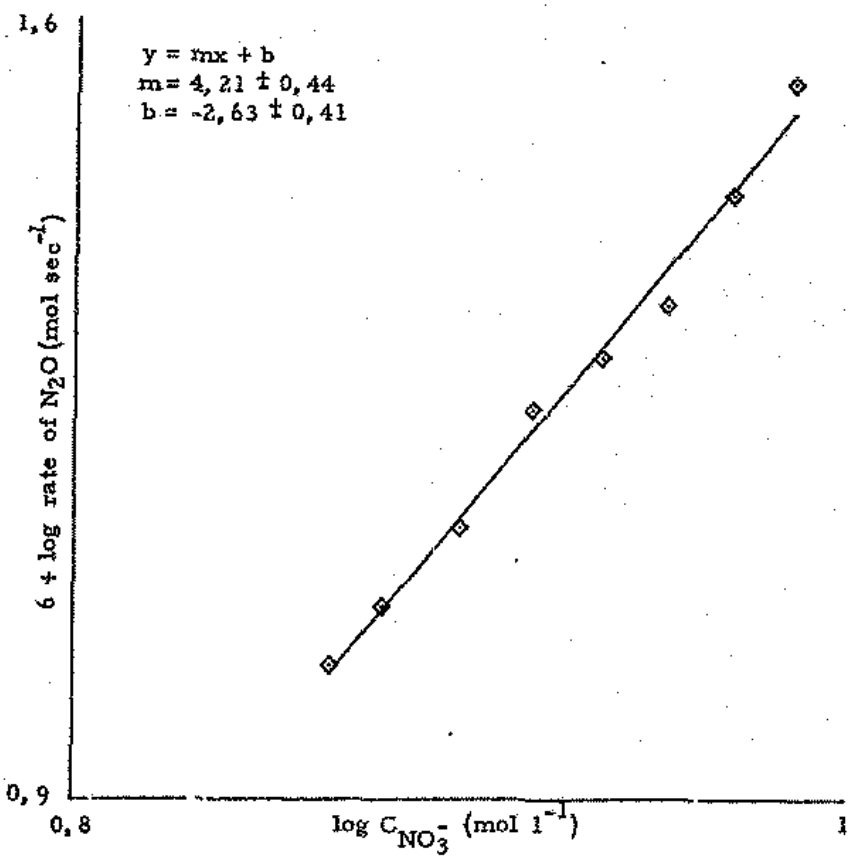

Fig. 20. Determination of the exponential dependence of the rate of N_2O on the nitrate concentration.

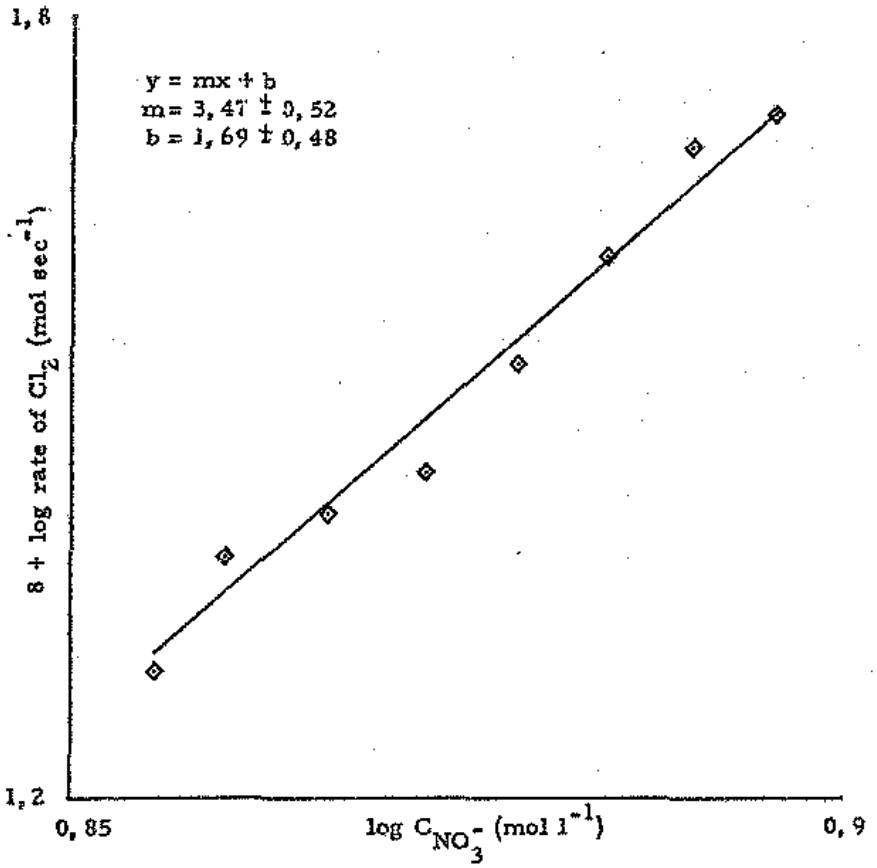

Fig. 21. Determination of the exponential dependence of the rate of Cl_2 on the nitrate concentration.

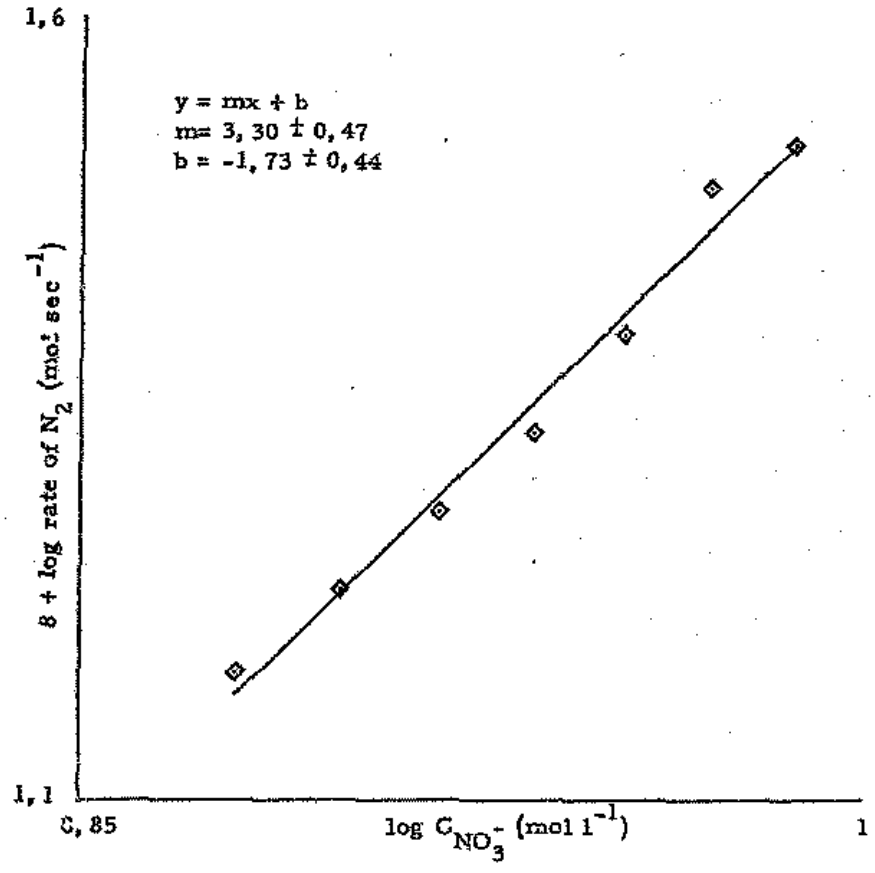

Fig. 22. Determination of the exponential dependence of the rate of N_2 on the nitrate concentration.

4. 3. 4. Rate Dependencies on Chloride Concentration

The chloride concentration was varied over the range 0, 12 to 0, 60 M. In each run the chloride was injected into the hot reaction mixture in the form of NaCl solution. This resulted in a variation of the final volume of the reaction mixture by up to 3, 5%. To obtain straight line plots in a treatment of the experimental data according to section 4. 3. 1 , it was necessary to apply a correction to the logarithm of the measured rate in each case. These corrections were as follows:

$$-\log \left[\frac{101,5}{100+v}\right]^{6,27} \quad \text{(for the case of } N_2O\text{)}$$

$$-\log \left[\frac{101,5}{100+v}\right]^{5,37} \quad \text{(for the case of } Cl_2\text{)}$$

$$-\log \left[\frac{101,5}{100+v}\right]^{4,72} \quad \text{(for the case of } N_2\text{)}$$

where v is the volume of the NaCl solution injected and 6, 27, 5, 37 and 4, 72 are the values calculated from equations (4. 11), (4. 12) and (4. 13) (section 4. 3. 8.) by adding the exponents of $\left[H^+\right]$ and $\left[NO_3^-\right]$ and substracting the exponent of $\left[NH_4^+\right]$ in each case.

The results are reported in Table 11 and Figs. 23, 24 and 25. Exponents of 0, 59 (for N_2O), 1, 0 (for Cl_2) and 1, 3 (for N_2) were obtained.

4. 3. 5. Rate Dependencies on AN and Nitric Acid Concentration

In order to determine the effect of AN and of HNO_3 on the rate of production of N_2O, Cl_2 and N_2, two series of experiments were run in which the AN concentration was varied from 1, 25 to 7, 50 M and the HNO_3 acid concentration covered the range 2, 4 to 6, 6 M. These results are shown in Tables 12 and 13. In addition to providing valuable data for an industrial scale pilot plant, these data provide an experimental check on the validity of the empirical rate expressions developed in this study (section 4. 3. 8). Treatment of these data according to the method which was outlined in section 4. 3. 1 would be meaningless since in these experiments two parameters were varied simultaneously and, moreover, by varying relative amounts.

TABLE 11. Rates of N_2O, Cl_2 and N_2 evolution as a function of the chloride concentration.

$C_{H^+} = 4,15$ mol l^{-1}, $C_{NO_3^-} = 8,49$ mol l^{-1}, $C_{NH_4^+} = 4,332$ mol l^{-1} and $T = 94,8^\circ$

C_{Cl^-} mol l^{-1}	Measured rate of He (ml sec^{-1})	Measured total flow rate (ml sec^{-1})	Calculated values from calibration graphs			Calculated rate of N_2O (mol sec^{-1}) x10 ^{6}	Calculated rate of Cl_2 (mol sec^{-1}) x10 ^{8}	Calculated rate of N_2 (mol sec^{-1}) x10 ^{8}	k_{N_2O} x10^9	k_{Cl_2} x10^{10}	k_{N_2} x10^9
			$\frac{R_{N_2O}}{R_{N_2O}+R_{He}}$	$\frac{F_{Cl_2}}{(F_{Cl_2})_{Std}}$	$\frac{F_{N_2}}{(F_{N_2})_{Std}}$						
0,119	1,59	2,04	0,225	0,324	0,100	20,4	25,4	10,25	0,505	0,911	0,199
0,117	1,41	1,99	0,265	0,450	0,165	23,5	34,6	26,26	0,475	0,854	0,311
0,235	1,52	2,23	0,290	0,540	0,180	28,8	46,5	32,06	0,485	0,888	0,209
0,293	1,39	2,23	0,310	0,725	0,205	30,8	62,4	36,51	0,444	0,984	0,236
0,350	1,50	2,43	0,330	0,670	0,230	35,8	62,3	44,69	0,481	0,840	0,234
0,400	1,40	2,40	0,345	0,870		36,9	80,6		0,485	0,965	
0,461	1,44	2,53	0,358	0,830	0,325	40,4	81,1	65,72	0,477	0,878	0,252
0,517	1,40	2,53		0,960			93,8			0,928	
0,571	1,42	2,72	0,370	0,990		44,9	103,7		0,505	0,944	

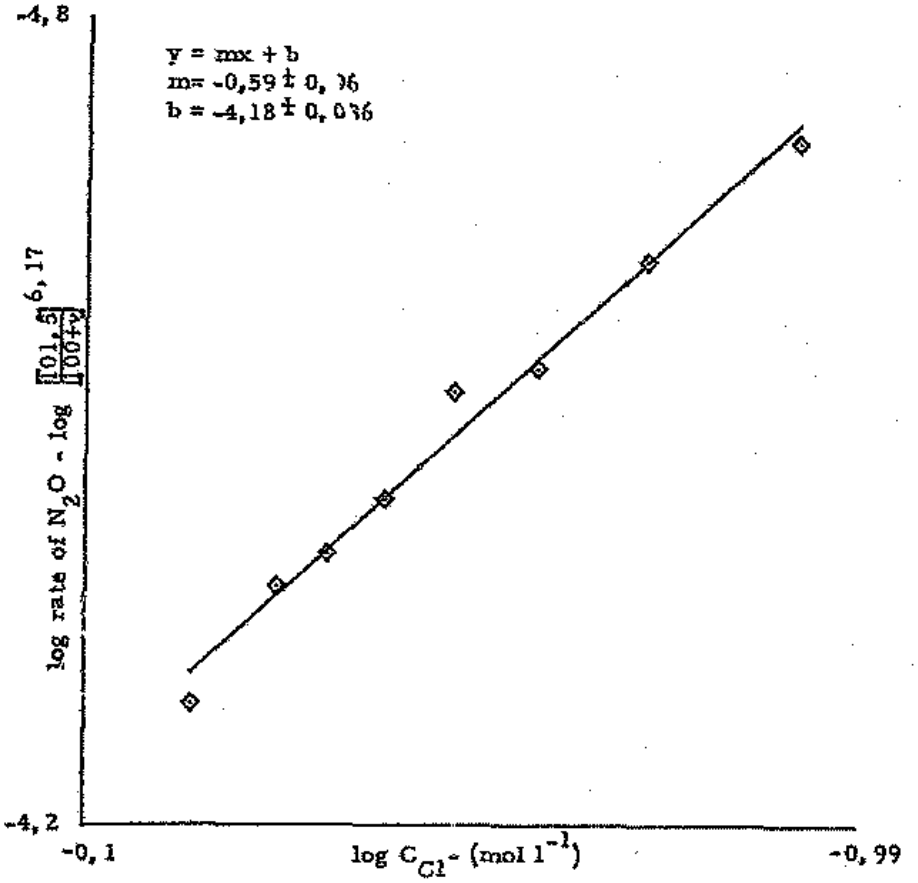

Fig. 23. Determination of the exponential dependence of the rate of N_2O on the chloride concentration.

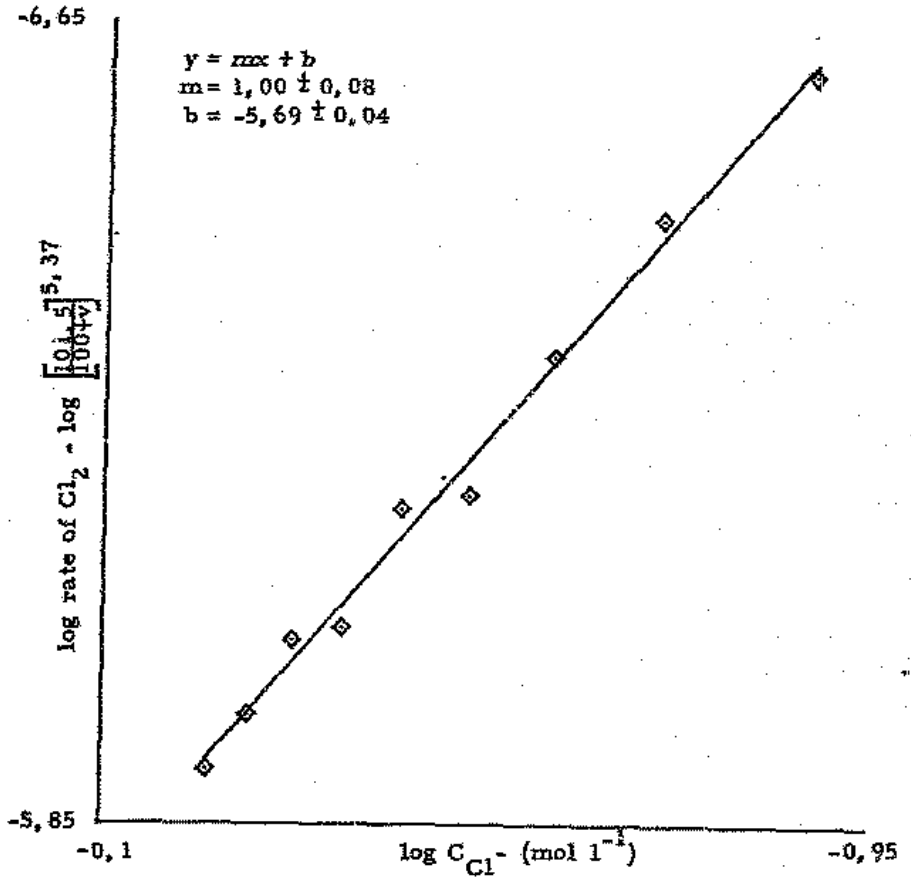

Fig. 24. Determination of the exponential dependence of the rate of Cl_2 on the chloride concentration.

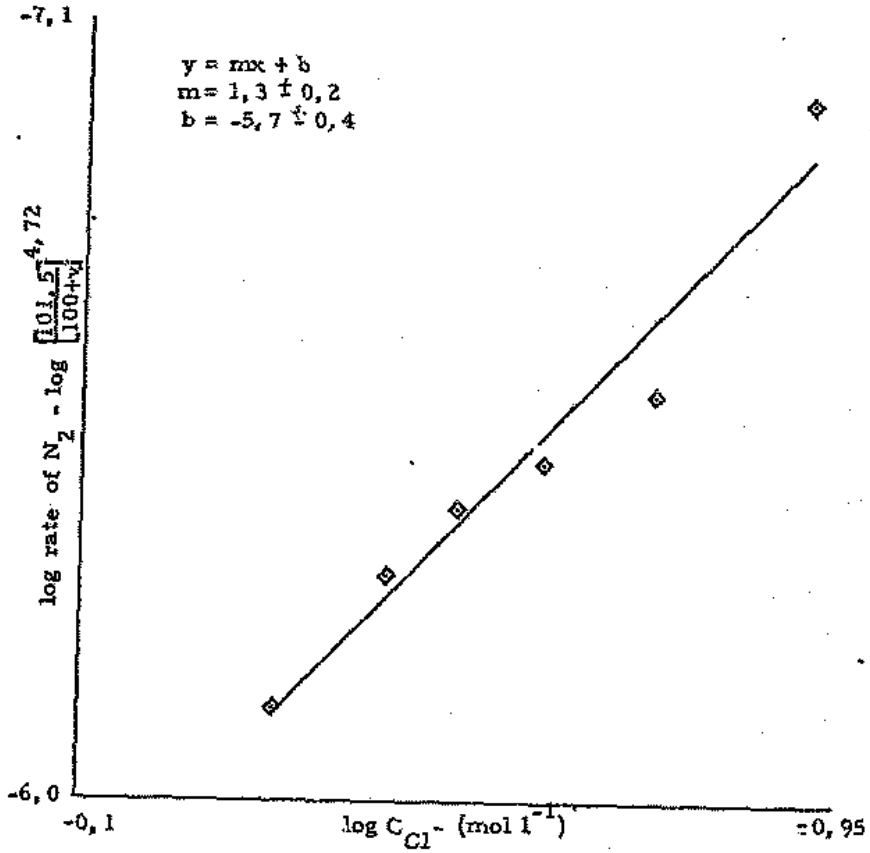

Fig. 25. Determination of the exponential dependence of the rate of N_2 on the chloride concentration.

TABLE 12. Rates of N_2O, Cl_2 and N_2 evolution as a function of the HNO_3 concentration.

$C_{Cl^-} = 0,177$ mol l^{-1}, $C_{NH_4^+} = 4,31$ mol l^{-1} and $T = 94,8^{\circ}$

C_{H^+} ml l^{-1}	$C_{NO_3^-}$ ml l^{-1}	Measured rate of He (ml sec^{-1})	Measured total flow rate (ml sec^{-1})	Calculated values from calibration graphs			Calculated rate of N_2O (mol sec^{-1}) x10^5	Calculated rate of Cl_2 (mol sec^{-1}) x10^8	Calculated rate of N_2 (mol sec^{-1}) x10^8	k_{N_2O} x10^9	k_{Cl_2} x10^{10}	k_{N_2} x10^9
				R_{N_2O} / $R_{N_2O}{}^{+R}{}_{He}$	F_{Cl_2} / $(F_{Cl_2})_{Std}$	F_{N_2} / $(F_{N_2})_{Std}$						
2,552	6,675	2,18	2,27	0,035		0,032	0,35		5,8	1,15		0,689
3,133	7,266	2,17	2,36	0,080	0,135	0,055	0,84	12,31	10,3	0,893	1,37	0,486
3,724	7,857	2,17	2,51	0,130	0,220	0,088	1,4	21,4	17,6	0,566	0,987	0,371
4,315	8,448	2,16	2,81	0,228	0,370	0,123	2,8	40,2	27,5	0,471	0,855	0,266
4,906	9,039	2,16	3,27	0,295	0,550	0,195	4,3	69,6	50,1	0,321	0,744	0,282
5,498	9,631	2,87	5,75	0,280	0,630	0,182	7,1	140	83,6	0,297	0,803	0,262
6,098	10,222	6,03	8,63	0,270	0,770	0,245	10,4	257	168	0,212	0,835	0,315
6,680	10,813	6,03	10,5	0,345	0,930	0,330	16,1	379	276	0,169	0,729	0,321

TABLE 13. Rates of N_2O, Cl_2 and N_2 evolution as a function of the NH_4NO_3 concentration.

$C_{H^+} = 5,91$ mol l^{-1} and $C_{Cl^-} = 0,177$ mol l^{-1}

$C_{NH_4NO_3}$ (mol l^{-1})	Measured rate of He (ml sec^{-1})	Measured total flow rate (ml sec^{-1})	Calculated values from calibration graphs			Calculated rate of N_2O (mol sec^{-1}) x10 ^{6}	Calculated rate of Cl_2 (mol sec^{-1}) x10 ^{8}	Calculated rate of N_2 (mol sec^{-1}) x10 ^{8}	k_{N_2O} x10 ^{8}	k_{Cl_2} x10 ^{9}	k_{N_2} x10 ^{9}
			R_{N_2O}	F_{Cl_2}	F_{N_2}						
			$R_{N_2O}+R_{He}$	$(F_{Cl_2})_{Std}$	$(F_{N_2})_{Std}$						
7,50	3,24	5,26	0,365	0,550	0,160	85,7	112,0	67,4	0,188	0,301	1,03
6,25	3,21	4,41	0,247	0,450	0,135	48,6	76,8	47,6	0,170	0,289	0,964
5,62	3,21	3,99	0,200	0,400	0,128	35,6	61,8	40,8	0,170	0,282	0,975
5,00	3,21	3,87	0,165	0,375	0,114	28,5	56,1	35,2	0,181	0,317	1,01
3,75	3,21	3,57	0,090	0,250	0,090	14,3	34,6	25,7	0,189	0,331	1,15
2,50	3,21	3,35	0,030	0,135	0,042	4,49	16,2	11,2	0,165	0,325	0,947
1,25	1,42	1,47	0,010	0,070		0,66	4,0		0,141	0,288	

In the series in which $[NH_4NO_3]$ was varied, for instance, $[NH_4^+]$ was determined only by the AN concentration, whereas the nitric acid component also contributed to the $[NO_3^-]$.

4.3.6. Rate Dependencies on Ammonium Concentration

The effect of ammonium concentration on the rates of N_2O, Cl_2 and N_2 was not determined directly by the addition of varying quantities of $(NH_4)_2SO_4$. Because of the low solubility of $(NH_4)_2SO_4$ in the reaction mixture only two experimental points were obtained. For the reaction mixture in which $[H^+]$ was 4,2 M, $[NO_3^-]$ 4,375 M, $[Cl^-]$ 0,18 M and T = 94,8°, addition of 20 g of $(NH_4)_2SO_4$ reduced the rate of evolution of N_2O from $6,917 \times 10^{-6}$ mol sec^{-1} to $2,054 \times 10^{-6}$ mol sec^{-1}. This reduction in measured rate was surprising, since Keenan and Dimitriades's mechanism[16] suggests that the rate of N_2O should increase with increasing $[NH_4^+]$. Because $[NH_4^+]$ in our experiment varied only over a small range, little significance could be attached to this result. We therefore attempted to obtain the exponential dependence of the rate on ammonium concentration by an indirect method. Since we had already established the exponential dependence of the rates on the nitrate concentration, we utilized this result, and the influence of AN concentration on the rate, to determine the ammonium exponential dependence.

Consider the rate equation

$$R = k'' C_{NO_3^-}^{x} \; C_{NH_4^+}^{y} \qquad (4.9)$$

where R is the rate of product gas (N_2O, Cl_2 or N_2), k'' incorporates the rate constant and all other concentration terms which are constant, x the exponential dependence of the rate on the NO_3^- concentration, C the concentration of AN, and y the exponential dependence of the rate on the ammonium concentration.

Equation (4.9) may be written as

$$\log R - x \log C_{NO_3^-} = \log k'' + y \log C_{NH_4^+} \qquad (4.10)$$

By using the appropriate exponential dependencies of the rates of production of N_2O, Cl_2 or N_2 on NO_3^- concentration (see section 4.3.3), the

exponential dependencies of the rates of production of N_2O, Cl_2 and N_2 on the NH_4^+ concentration were determined from a plot of $\left[\log R - x \log C_{NO_3^-}\right]$ versus $\left[\log C_{NH_4^+}\right]$. The results are plotted in Figs. 26, 27 and 28 giving exponents of -1, 66, -1, 64 and -1, 74 for the rates of N_2O, Cl_2 and N_2, respectively.

4. 3. 7. The Effect of Temperature on the Rates of N_2O, Cl_2 and N_2 Production

The effect of temperature on the rates of the product gases was determined in the range 78, 3° to 100°, Table 14. Arrhenius plots for the rates of N_2O, Cl_2 and N_2 evolution are given in Figs. 29, 30 and 31. As may be seen, these plots are linear in all three cases.

4. 3. 8. Empirical Equations and Rate Constants

Combination of the results from the preceding sections give the following empirical rate expressions:

$$\frac{dN_2O}{dt} = k_{N_2O}\left[H^+\right]^{3,72}\left[NO_3^-\right]^{4,21}\left[Cl^-\right]^{0,59}\left[NH_4^+\right]^{-1,66} \qquad (4.11)$$

$$\frac{dCl_2}{dt} = k_{Cl_2}\left[H^+\right]^{3,54}\left[NO_3^-\right]^{3,47}\left[Cl^-\right]^{1,0}\left[NH_4^+\right]^{-1,64} \qquad (4.12)$$

$$\frac{dN_2}{dt} = k_{N_2}\left[H^+\right]^{3,16}\left[NO_3^-\right]^{3,3}\left[Cl^-\right]^{1,3}\left[NH_4^+\right]^{-1,74} \qquad (4.13)$$

Determination of the empirical rate constants in equation (4, 11), (4, 12) and (4, 13) for the experimental data yielded values which appeared consistent for any given series of experiments except that in which the HNO_3 concentration was varied (see calculated values of the rate constants in Tables 9, 10, 11, 12, and 13).

The units of the rate constants are such that the rate will be in units of mol sec^{-1} when the concentrations are expressed in units of mol l^{-1}. When the several series of experiments are compared, the agreement is considerably less good than the case within a single series. The average values of the empirical rate constant for the several series of experiments are shown in Table 15. The values

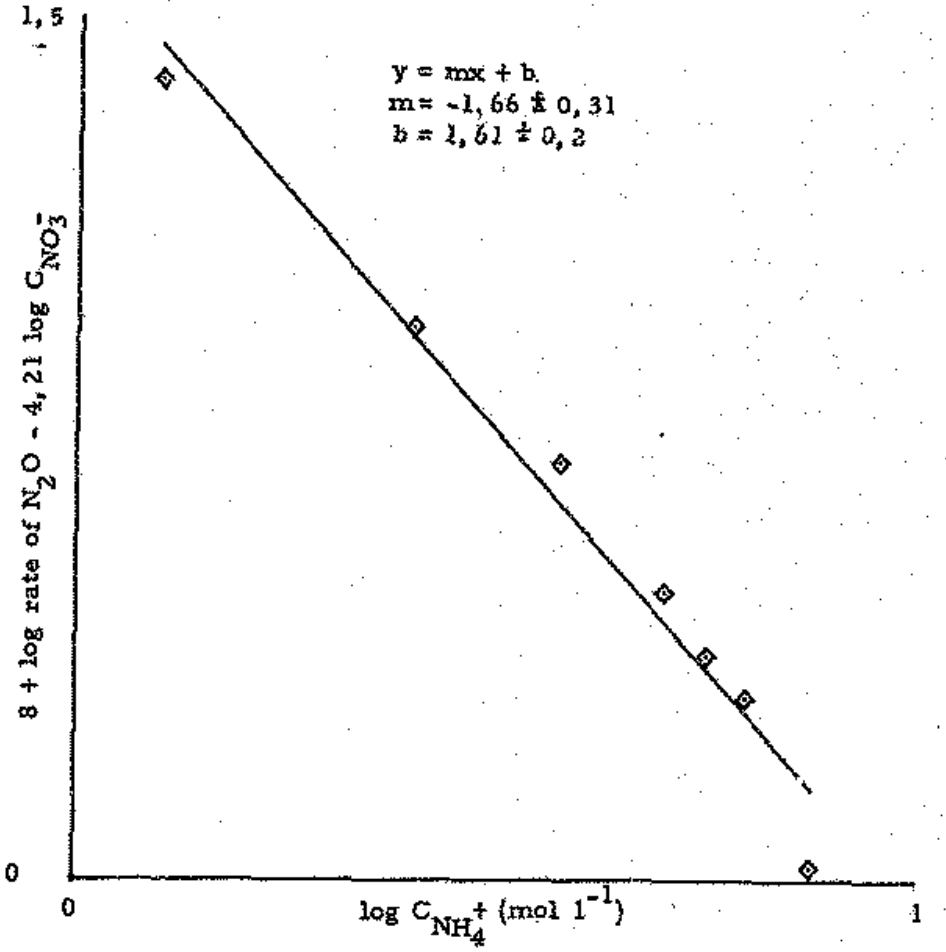

Fig. 26. Determination of the exponential dependence of the rate of N_2O on the ammonium concentration.

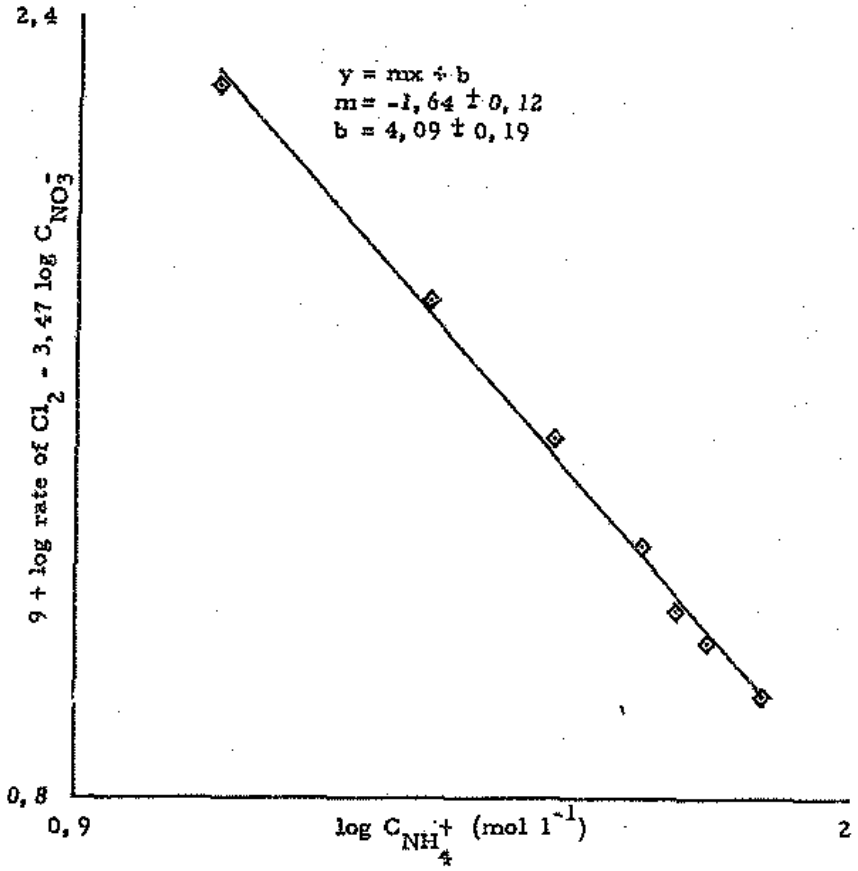

Fig. 27. Determination of the exponential dependence of the rate of Cl_2 on the ammonium concentration.

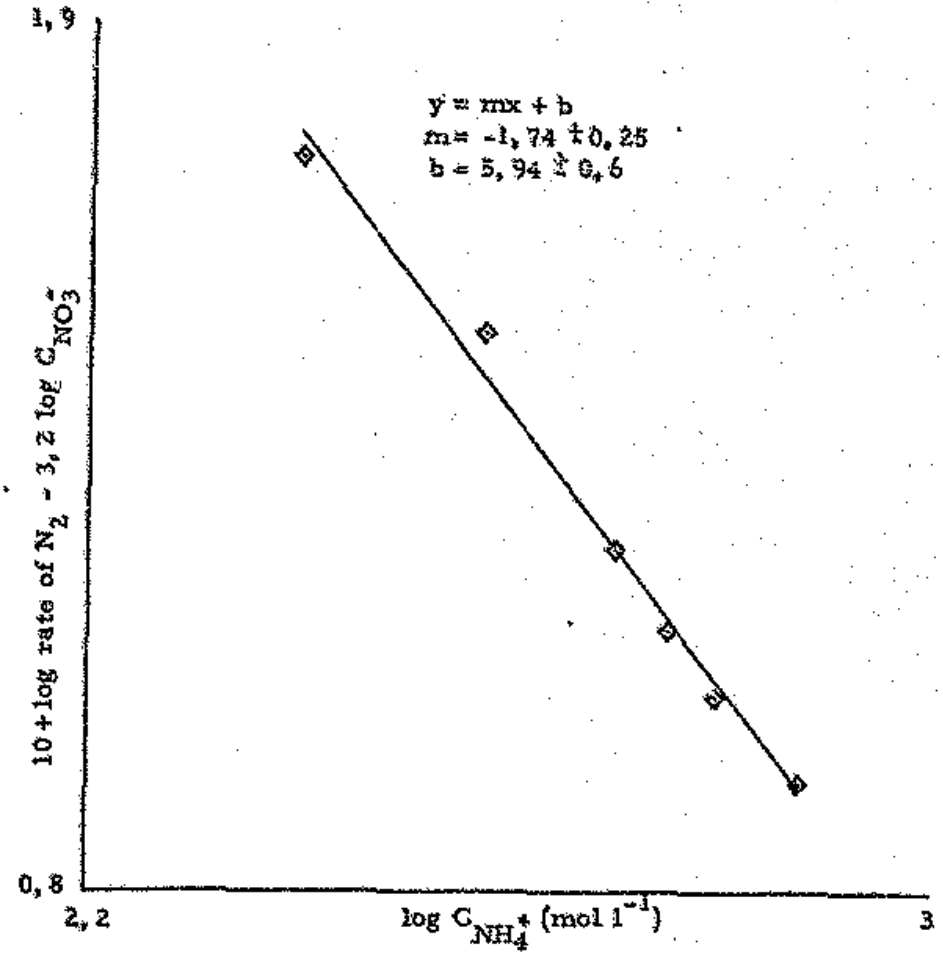

Fig. 28. Determination of the exponential dependence of the rate of N_2 on the ammonium concentration.

TABLE 14. The effect of temperature on the rates of N_2O, Cl_2 and N_2 evolution.

$C_{H^+} = 4,15$ mol l^{-1}, $C_{NO_3^-} = 8,43$ mol l^{-1}, $C_{NH_4^+} = 4,32$ mol l^{-1}, $C_{Cl^-} = 0,18$ mol l^{-1} and $T = 94,8^{\circ}$

Temp $^{\circ}C$	Temp (T)	$\frac{1}{T}10^3$	Measured rate of He (ml sec^{-1})	Measured total flow rate (ml sec^{-1})	Calculated values from calibration graphs			Calculated rate of N_2O (mol sec^{-1}) x10 ^{6}	Calculated rate of Cl_2 (mol sec^{-1}) x10 ^{8}	Calculated rate of N_2 (mol sec^{-1}) x10 ^{8}
					R_{N_2O}	F_{Cl_2}	F_{N_2}			
					$\frac{R_{N_2O}}{R_{N_2O}+R_{He}}$	$\frac{(F_{Cl_2})}{Std}$	$\frac{(F_{N_2})}{Std}$			
100,0	373	2,68	3,12	4,42	0,297	0,660	0,233	58,6	112	81,9
98,0	371	2,69	3,12	4,18	0,260	0,536	0,148	48,6	86,2	49,2
95,5	368,5	2,71	3,07	3,93	0,216	0,370	0,108	37,9	55,9	35,7
92,4	365,4	2,73	3,04	3,77	0,200	0,260	0,076	33,7	37,7	22,8
89,8	362,8	2,75	1,77	2,23	0,198	0,235	0,087	19,7	20,2	15,4
87,6	360,6	2,77	1,56	1,91	0,185	0,195	0,068	15,7	14,3	10,3
83,4	356,4	2,80	1,56	1,80	0,118	0,130		9,4	9,0	
78,3	351,3	2,84	1,56	1,67	0,063	0,085		4,7	5,4	

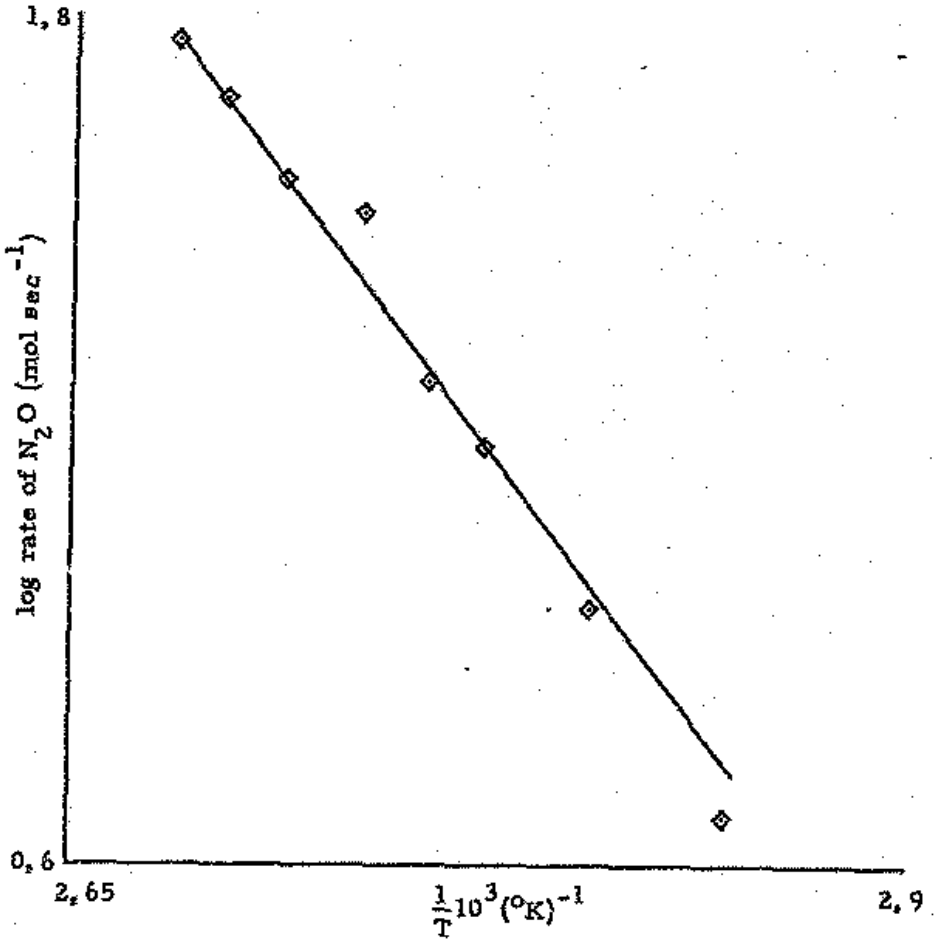

Fig. 29. The effect of temperature on the rate of N_2O evolution.

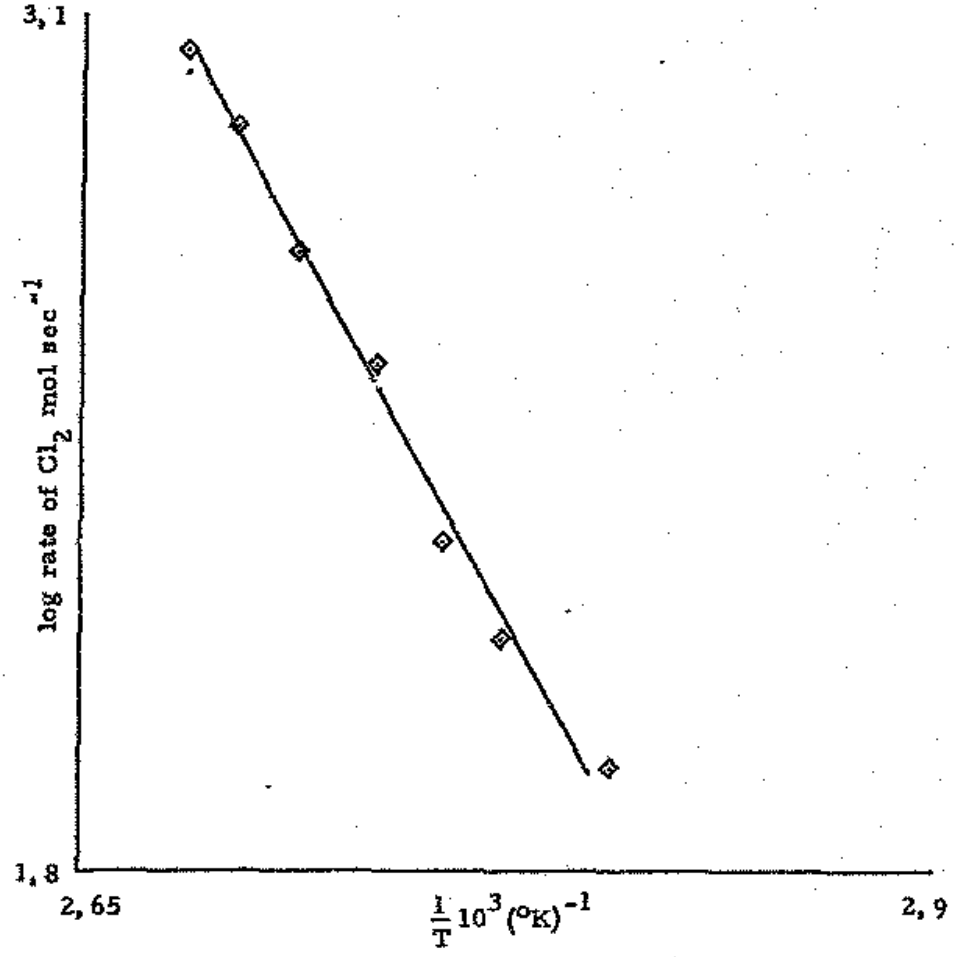

Fig. 30. The effect of temperature on the rate of Cl_2 evolution.

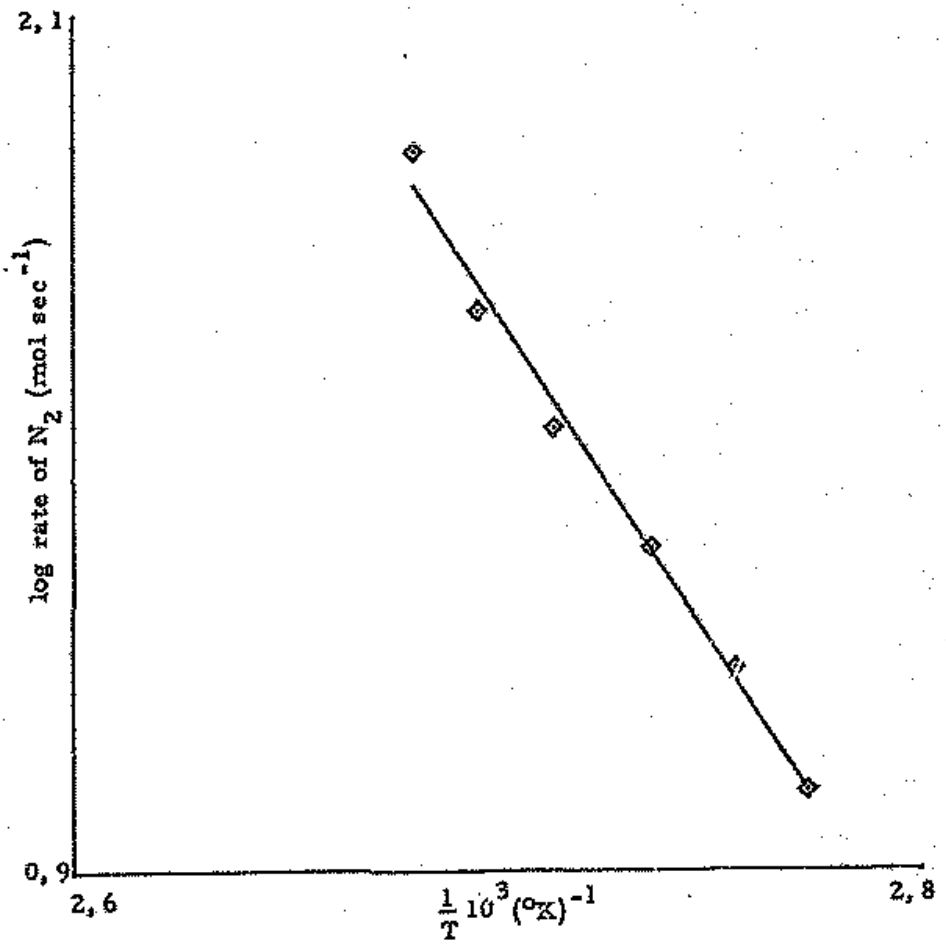

Fig. 31. The effect of temperature on the rate of N_2 evolution.

TABLE 15. Average values of the rate constants

Series variation of	k_{N_2O} x10^{9}	k_{Cl_2} x10^{10}	k_{N_2} x10^{9}
H^+	0, 996	1, 33	0, 513
NO_3^-	0, 530	1, 15	0, 327
Cl^-	0, 482	0, 911	0, 250
AN	1, 72	2, 58	1, 01
HNO_3	0, 507	0, 903	0, 376

for those series in which H^+ and AN concentrations were varied seem somewhat inconsistent with the average values obtained from the series in which the concentrations of NO_3^- and Cl^- were varied. For the series in which the H^+ concentration was varied, the inconsistency could be due to the deficiency in the experimental method used, noted in section 4. 3. 2. For the case in which [AN] was varied, no explanation for the inconsistency can be offered.

The "best" average values for the empirical rate constants (disregarding the values for the series in which H^+ and AN concentration were varied) were calculated to be: k_{N_2O} 0, 506 x 10^{-9}, k_{Cl_2} 0, 999 x 10^{-10} and k_{N_2} 0, 323 x 10^{-9}.

4. 4. Discussion

From the experimental data obtained it is clear that increasing the acidity and nitrate and chloride concentrations, substantially increases the rates of N_2O, Cl_2 and N_2 evolution, whereas increasing the ammonium concentration has the opposite effect for all the gases.

The unexpectedly high exponents which appear in the empirical equations (4. 11, 4. 12 and 4. 13) could be due to a number of factors, such as variations in the water activity of the mixture when varying the concentration parameters, pre-equilibrium, etc. Changes in water activity in the reaction mixture when varying the concentration of the parameter being studied could possibly account for some part of the

high exponential dependencies, although addition of up to 20 g of Na_2SO_4 had no significant effect on the rates of N_2O, Cl_2 and N_2. The high exponential dependencies of the terms in the rate expressions could also be due to a series of pre-equilibrium steps, the combination of which would give rise to the high exponents that were found in the empirical rate expressions.

In all the experimental runs the acidity was calculated as hydrogen ions (H^+), although it is difficult to know what the actual chemical species are in these extremely concentrated solutions. This assumption was also made for convenience sake. Complete dissociation of sulphuric acid in all experiments was assumed. This might also be an additional reason for the inconsistent average values for the rate constants obtained when the H^+ concentration was varied.

The linearity of the Arrhenius plots suggests, although it is no proof, that the rate expression consists of a single term, i.e. a single mechanistic pathway is predominately responsible for the formation of the reaction products. The activation energies for the formation of the three components are 30, 57 kcal mol^{-1} (for N_2O), 37, 80 kcal mol^{-1} (for Cl_2) and 41, 92 kcal mol^{-1} (for N_2).

Finally these empirical rate expressions obtained from our data seem to differ substantially from those derived from Keenan's and Dimitriades mechanism[16] for the chloride-catalysed decomposition of AN in the melt.

CHAPTER 5. DISCUSSION

5.1. Review and Discussion of Experimental Results

In Chapters 2 and 3 it has been shown that N_2O may be produced with an aqueous solution of AN containing a relatively high concentration of acid, and chloride ions as catalyst. Nitric acid has been generally used as the source of acid, but sulphuric acid may also be used. N_2 and Cl_2 are produced as impurities, and, in general, the higher the rate of N_2O production, the higher is the level of impurities in the product gas. The reaction may be carried out below 100°, but in a commercial process the boiling point of the mixture, which would fall in the range of 104°-115°, would probably be more appropriate, since under these conditions it would be possible to continuously volatilise all the water introduced as solvent and formed as a reaction product in the pyrolysis of AN. Increasing the temperature in the reactor by as much as 3-4° (by imposing an elevated pressure) resulted in almost a doubling in the rate of N_2O evolution. This points to a need for careful control of pressure in the reactor.

The N_2O content of the product gas was found to be ~95% and the Cl_2 and N_2 contents both about 1-2%. A single scrubbing stage (with NaOH solution) is required to remove the Cl_2. This would, of course, lead to a small loss of N_2O owing to its solubility in the scrubbing solution.

5.2. Comparison of Kinetic Results of this Study with those for Chloride-Catalysed Decomposition of AN in the Melt

Keenan and Dimitriades[16] studied the kinetics of AN in the melt, in which Cl_2 and N_2 (the latter in relatively large proportion) are

also produced as impurities. They found that chloride added to an AN melt catalysed both the reactions leading to N_2O and those in which N_2 is formed. Because of experimental limitations their study did not embrace a complete examination of the kinetics of the system. Nevertheless, using a steady-state treatment, they were able to postulate detailed mechanisms for the reactions in the system. These included several steps in which, amongst other intermediates, chlorine atoms and other free radicals are involved. Their experimental results were consistent with the postulated mechanism, and evidence was adduced in subsequent work[18, 19] in support of the mechanism.

Keenan and Dimitriades did not derive complete rate equations for their postulated mechanism, nor did they arrive at experimental rate equations. In the melt, the concentrations of ammonium and nitrate ions do not vary sufficiently to allow reliable correlations to be made. This is not the case for studies of the aqueous system.

In Appendix D, we have carried out derivations of the rate equations based on the Keenan-Dimitriades mechanism. The following expressions were found:

$$\frac{dN_2O}{dt} = d(H_3O^+)(NO_3^-)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}} \qquad (5.1)$$

$$\frac{dCl_2}{dt} = e(H_3O^+)^2(NO_3^-)(Cl^-) - f(NH_4^+)(Cl_2) / (H_3O^+) \qquad (5.2)$$

$$\frac{dN_2}{dt} = g\left[(H_2O)(Cl_2)/(H_3O^+)\right](NH_4^+) + h\,(H_2O)(NO_3^-)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}} \qquad (5.3)$$

where d, e, f, g and h are composite rate constants (see Appendix D).

A comparison of the above set of theoretical rate equations with the empirical rate equations (4.11), (4.12) and (4.13) for N_2O, Cl_2 and N_2, respectively, obtained in this study leads to the following conclusion: either the mechanisms are radically different for the two systems, viz. chloride-catalysed decomposition of AN in the melt, and chloride-catalysed decomposition in strong-acid aqueous

medium; or Keenan and Dimitriades's postulated mechanism is in error. This statement is, of course, based on the assumption that the high empirical exponents in the concentration terms for acid and nitrate obtained in the present study are real, and not due to water-activity effects, etc.

Perhaps the only firm conclusion that may be drawn is that the reaction mechanisms in both systems are highly complex, not only because of the apparent succession of reaction steps, but also because of the obvious difficulties in attempting a physico-chemical interpretation of the kinetic results.

5.3. Present Commercial Method of Producing Nitrous Oxide

Nitrous oxide is now produced commercially by the thermal decomposition of AN (equation 1.1) in the melt at 250°-260°. If solid AN is used as raw material, the plant consists of two interconnected pots, in the first of which the AN is melted and heated to about 200°, and a second in which the melt is further heated to produce decomposition. In other versions the AN is fed into the reactor in the form of a hot, concentrated aqueous solution (usually about 88 per cent). During the reaction, some AN is lost as fumes and partly as NH_3. The raw gas emerging from the reactor contains, apart from N_2O, N_2, fumes of AN, some ammonia, several parts per million of higher oxides of nitrogen (i.e. NO and NO_2, usually designated NO_x) and traces of O_2. These impurities are eliminated as follows.

The raw gas first passes through a dilute sulphuric acid scrubber, which removes the AN fumes and NH_3. The higher oxides of nitrogen are thereafter scrubbed out with a NaOH solution containing a small amount of $KMnO_4$. The reaction between NO/NO_2 and the NaOH solution is relatively slow, and removal of these impurities is improved by the presence of the permanganate, which oxidises the nitrite to nitrate. It should be noted that NO_x is poisonous, and the N_2O product gas, if it is to be suitable for medical purposes, has to meet a stringent specification regarding the presence

of NO_x.

Following compression of the gas and cooling, which eliminates most of the water vapour, the gas is passed through dryer columns (packed with either activated alumina or molecular sieve 5A). These columns also remove residual traces of NO/NO_2.

The N_2 and traces of O_2 are finally eliminated by bleeding off these non condensable gases after liquefaction of the N_2O.

5.4. Economic Feasibility of the Aqueous Process

The results of the bench-scale plant experiments clearly show that the aqueous process for the production of N_2O is technically feasible, and thus a tentative assesment of its economic feasibility is warranted.

The aqueous process appears to offer a number of advantages over the current process.

(a) The Use of a Cheaper Grade Ammonium Nitrate

A special, high-specification grade, solid AN is currently required for the production of N_2O. In the U.S.A., solid material must meet the following specifications:[4]

NH_4NO_3 (dry basis)	: 99,95% minimum
Chloride	: 0,0002% maximum
Ether extractable matter	: 0,01% maximum
Acidity (as HNO_3)	: 0,025% maximum

Moisture content (<0,3%) has to be sufficiently low[4] to minimise caking of the salt.

The material is locally supplied to the two N_2O producers at R 87 a ton by AE and CI Ltd., Modderfontein. We understand that the price is to be raised to R 111 per ton, when present constracts expire.

Fertiliser grade AN, on the other hand, is available from three sources, AE and CI Ltd., Fisons (at Milnerton, Cape Town) and Sasol (at Sasolburg), and a fourth plant, that of Fedmis Ltd., is shortly to come into operation at Sasolburg. At present, this grade of AN is transported in special road tankers as a hot, 88% (w/w)

solution. Prices range between R 50 and R 56 a ton of AN. Under South African conditions a changeover to the fertiliser grade AN would thus produce a saving of about 35 to 40 per cent in the cost of the principal raw material for N_2O production. The cost of the AN constitutes about 40 per cent of the over all production costs of N_2O for a small plant, and somewhat higher for a larger one.[20]

It should be noted that two of the items listed in the above specification for solid AN, viz. ' ride and HNO_3, are important additives in the aqueous process. Ether extractable matter (i.e. organic impurities) have to be absent because they would give rise to the production of N_2 and NO/NO_2, and particularly because of the explosion hazard associated with their presence. The latter consideration does not apply to the aqueous process.

Although chromium is a particularly undesirable material[4] in nitrous oxide grade AN, as would also be Co, Mn, Ni and Cu and apparently also Fe (see below), no limits for metallic elements are set in the American specification.[4] The build-up of such impurities in the AN melt necessitates periodic interruption of plant operation to allow drainage of the reactor and replacement of the AN with fresh, pure material.[21] In South Africa, such forced interruptions are caused by the build-up of Fe in the melt.

Fertiliser grade AN is considerably cheaper than the nitrous oxide grade material, but this does not imply that the cheaper grade product is necessarily of materially lower purity. Both are manufactured by the same process, from a gaseous starting material (NH_3), and the impurities would be expected to derive mainly from corrosion products of process equipment, and from impurities introduced via water and the air.

While the effects of impurities that may be expected to build up in the reactor solution have not been studied for the aqueous system, it is not expected that their presence in the fertiliser grade material would be at such levels as to necessitate interruption of plant operation at greater frequency than is required in the current

melt process.

In the aqueous process such reactor clean-out operation would also be expected to be simpler and of much shorter duration.

(b) Absence of Explosion Hazard

Explosions may be caused in AN melts by the presence of excessive levels of certain impurities and/or if the temperature is allowed to go too high. As a result, modern N_2O plants are equipped with fairly extensive safety devices, and plant operation practice has to follow directions rather closely. No such limitations apply to the aqueous process, and safety equipment could be dispensed with altogether.

In practice, the operation of an N_2O plant is not as hazardous as the foregoing statements might seem to imply. Additives to the AN, such as phosphates and pyrophosphates, are claimed to ensure that the AN decomposition reaction proceeds smoothly and to prevent the reaction from tending to the explosive region.[2] The main "explosion hazard" would seem to arise during plant start-up, if the AN had been allowed to solidify in the reactor during the previous shut-down. If the reactor is heated too strongly before the AN is fully melted, the decomposition reaction could set in and dangerous pressures, perhaps leading to an explosion, built up below a residual crust of solid AN.

Such hazards do not, of course, arise in the aqueous process, in which start-up and shut-down operations would, as a result, be simpler. Start-up should also take less time, the time to heat the mixture to its boiling point, compared to a period of about five hours in a small plant based on the melt process.

(c) Higher Yields

In the present study, reactor yields were not measured directly, but were of the order ~95 per cent, a figure similar to the maximum achieved in the current process. Loss of AN by sublimation is an important source of losses in the melt process; losses of this kind are not possible in the aqueous process. Further losses occur in the gas purification stages. Since only a single scrubbing stage is

required in the aqueous process, an overall yield higher by an estimated 5 per cent may be expected for the aqueous process.

This small expected improvement in yield has been estimated by comparison with the best yields achieved with the melt process. In practice, yields in South Africa and elsewhere are on average substantially lower than 95 per cent. This is mainly due to difficulties arising from the presence of Fe as impurity to above the specification limit of 3 p. p. m. (in South Africa) for the nitrous oxide grade AN. The Fe, which accumulates in the reactor, apparently catalyses side reactions leading to NO/NO_2, which, as pointed out earlier, is scrubbed out with some difficulty. As a result, interruption in production, with drainage of the reactor and recharging with fresh AN, occurs rather frequently. This down-time adds considerably to production costs and, naturally, lowers yields.

(d) Greater Flexibility

For the current process the rate of N_2O production per unit volume of melt is more or less fixed. The production rate may be pushed up marginally by operating at a slightly higher temperature, but this occurs at the expense of a higher NO/NO_2 content. In the aqueous process, the rate for a given volume of reactor solution may be increased by increasing the "severity" of conditions in the solution, e. g. by raising the operating pressure (and hence the temperature of the boiling solution), or by increasing the concentrations of AN, acid and/or chloride. Indications are that such increases in the N_2O production rate will be achieved only at the expense of purity of the crude N_2O, and hence the yield. Increased concentrations of Cl_2 in the crude N_2O should, however, present few problems since Cl_2, unlike NO/NO_2, is readily scrubbed out with NaOH solution, the reaction between Cl_2 and NaOH being instantaneous and the rate of Cl_2 removal being determined solely by mass transfer considerations.

In a situation where demand for N_2O is steadily rising the ability to raise the production rate of a plant without the need

for structural modification might prove to be an important advantage, even if this is to be achieved at the cost of a somewhat higher Cl_2/N_2 content of the crude gas, and hence of slightly lower yield. (The additional cost of removing the large amounts of Cl_2 would probably be compensated for by the increased production of saleable NaOCl.)

5.4.1. Other Considerations

The most important disadvantage of the aqueous process is the high corrosiveness of the reactor liquid, the vapour to be fractionated, as well as the gas stream (up to the point where Cl_2 has been removed). This should, however, not prove to be an insurmountable difficulty since suitable vessels and other equipment made of glass or glass-lined steel are now fairly readily available.

The quantities of HNO_3 and HCl consumed in the aqueous process would be small and would only make a small contribution to overall process costs. Larger quantities of NaOH would probably be used in comparison with that used in the melt process, but these costs should be more than offset by the credit accruing from sales of the NaOCl by-product, formed in the scrubber.

5.5 Conclusion

The feasibility of an aqueous process for the production of N_2O has been demonstrated by batch and bench-scale plant experiments. In the latter a production rate of about 2,5 to 3 l min^{-1} of gas was maintained for several hours in a 2-litre reactor containing 800 ml of reacting solution. Variations in the temperature (i.e. the boiling point) of the mixture, brought on by fluctuations in the pressure in the reactor (a few centimeters of Hg above atmospheric), had a pronounced effect on the rate of N_2O evolution.

The crude gas contains 1-2 per cent each of Cl_2 and N_2, and it was shown that the former is readily removed by scrubbing with a 5% NaOH solution. The N_2 impurity may be removed after lique-

faction of the product gas, as in the current commercial process. Reasonably steady-state conditions were readily obtained, but for smooth running of a production plant, provision for pressure control in the reactor must be provided.

The main advantage of the aqueous process over the current melt process is the fact that cheaper, fertiliser grade AN may be substituted for the special nitrous oxide grade material now used. Other advantages expected include greater flexibility, the possibility of dispensing with elaborate safety devices and practices, and an improved yield. A reduction of about 20 to 30 per cent in N_2O production costs is conservatively estimated, if the aqueous process is to replace the current melt process in South Africa. It should also be noted that scale-up of the bench-scale plant by a factor of about 50 to 100 would give a plant of dimensions (and N_2O production capacity) similar to those of the N_2O plants now used in South Africa.

APPENDIX A

Method for the Calculation of Cl_2 Content of Product Gas

The volume of gas collected in the measuring cylinder was converted to S. T. P. using the formula

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where P_1, V_1 and T_1 are the atmospheric pressure, the volume collected and temperature of the K_2SO_4 solution, respectively. P_2 and T_2 are the standard pressure and temperature, respectively, and V_2 the volume of gas at S. T. P.

No correction was applied for water vapour pressure, since the value for air above saturated K_2SO_4 solution was not available. Corrections were also not made for the N_2 content of the gas which, for the sake of simplicity and bearing in mind the semi-quantitative nature of the results, was assumed to contain only N_2O. Both of these errors are to some extent compensated for by the finite solubility of N_2O in the K_2SO_4 solution.

The quantity of Cl_2 in the gas was calculated from the equation

$$V_{Cl_2} = \frac{t \cdot N}{1000} \cdot \frac{22400}{2}$$

where V_{Cl_2} = volume of Cl_2 in mls, and

t = thiosulphate titre of normality N

The Cl_2 content, expressed as volume per cent, is thus given by:

$$\text{Percentage } Cl_2 = \frac{V_{Cl_2}}{V_2} \cdot 100$$

APPENDIX B

Design of Bench Scale Plant for N_2O Production

B. 1. The Reaction System

We shall not concern ourselves with the reaction mechanism but simply assume that the reactions occurring in the reactor are

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \qquad \text{(b. 1)}$$

$$NH_4NO_3 + 2HCl \rightarrow N_2 + Cl_2 + 3H_2O \qquad \text{(b. 2)}$$

The reactor will be assumed to operate at steady-state conditions. A fraction a = 0, 02 of the AN will be assumed to react by reaction (b. 2).

B. 2. Mass Balance over Reactor - Distillation Column System

Basis: 1 mole AN (≡ 80g) per hour entering the reactor

IN : 1 mole AN = 80g

2a moles HCl = 1, 46g

H_2O associated with AN and HCl solutions:

Assume 80% (w/w) AN solution, 20% HCl solution.

Mass H_2O entering = 20 + 1, 46 x 4 = 25, 84g

Moles H_2O entering = $m = \frac{25,84}{18}$ = 1, 437 moles

OUT : 1 - a = 0, 98 moles N_2O = 43, 1g N_2O

2 + a + m moles H_2O = 2, 02 + 1, 437 = 3, 457 moles = 62, 2g H_2O

a = 0, 02 moles N_2 = 0, 56g N_2

a = 0, 02 moles Cl_2 = 1, 42g Cl_2

Overall mass balance:

IN : 80 + 1, 46 + 25, 84 = 107, 3g

OUT : 43, 1 + 62, 2 + 0, 56 + 1, 42 = 107, 3g

All material out leaves in distillate product stream.

B. 3. Boil up Rate in the Reactor

A minimum quantity of vapour must be obtained from the reactor. This vapour will automatically contain all the N_2O, Cl_2 and N_2

produced in the reaction. Sufficient water must be boiled off to give a distillate stream of 2 + a + m= 62, 2g H_2O per mole AN fed to reactor, as well as the water present in the bottoms product of the column which is returned to the reactor. The quantity of water in this stream depends on the operating conditions of the distillation column (to be considered next). The maximum possible acid concentration in the bottoms sets the minimum boil-up rate per mole AN fed to the reactor. The maximum boil-up rate is not theoretically limited.

B. 4. Vapour-Liquid Equilibrium Data

At this stage we are concerned not with the physical . e of the column but with the problems of reflux ratio, reboil rate, stream compositions, etc.

In order to carry out a design we need to have vapour-liquid equilibrium data for the system H_2O - HCl - HNO_3. The other gases, *i. e. N_2O, Cl_2 and N_2 are so volatile that their presence in the liquid* mixture need not be considered. They merely increase the total gas flow rate through the column.

We do not have data on vapour-liquid equilibrium, nor on enthalpy-composition for the ternary system H_2O - HNO_3 - HCl. Data are only available on the two binary systems H_2O – HNO_3 and H_2O - HCl.

Without ternary data one can only get a very rough approximation as the system is extremely non-ideal and assumptions involving ideality are worthless.

A very rough idea may be obtained, however, by looking at the two systems H_2O - HNO_3 and H_2O - HCl separately. From data in Perry[22] the following calculations have been done:

% w/w HNO_3	x_{HNO_3}	T* °C	p_{HNO_3} mm Hg	p_{H_2O} mm Hg	P_T mm Hg	y_{HNO_3}
20	0, 0667	95	1, 37	555	556, 4	0, 00246
		105	2, 50	800	802, 5	0, 00311

% w/w HNO_3	x_{HNO_3}	T* °C	P_{HNO_3} mm Hg	P_{H_2O} mm Hg	P_T mm Hg	y_{HNO_3}
		100	1, 07	675	676, 9	0, 00276
30	0, 109	100	6, 05	580	586, 0	0, 01033
		105	7, 90	690	698	0, 0113
40	0, 160	105	20, 0	573	593	0, 0337
		110	25, 7	688	714	0, 0360
		115	32, 5	810	842	0, 0385
50	0, 222	110	54, 5	560	605	0, 0902
		115	67	665	742	0, 0902
		120	84	785	869	0, 0966
60	0, 300	110	103	417	520	0, 198
		115	126	495	621	0, 203
		120	156	590	746	0, 209
70	0, 400	115	262	330	592	0, 442
		120	312	393	705	0, 442
		125	372	469	841	0, 442

% w/w HCl	x_{HCl}	T °C	P_{HCl} mm Hg	P_{H_2O} mm Hg	P_T mm Hg	y_{HCl}
6	0, 03054	100	0, 92	715	716	0, 001288
		110	1, 78	888	890	0, 002000
10	0, 0520	100	2, 9	677	680	0, 00427
		110	5, 4	960	965	0, 00560
14	0, 0743	100	9, 0	625	634	0, 01420
		110	16, 0	892	908	0, 01760
18	0, 0979	100	28, 0	550	578	0, 0485
		110	48, 0	783	831	0, 0578

* Symbols used in this table and in the text are defined at the end of this Appendix.

Although y_{HCl} and y_{HNO_3} vary with pressure and temperature, plotting approximate interpolated values for a pressure of 700mm Hg gives a good enough idea. Both systems are roughly plotted on the accompanying graph (Fig. B. 1), as y_{H_2O} versus x_{H_2O}. From this graph azeotropic points appear beyond which one cannot go. The azeotropic point for the ternary mixture represents the limit in our case. We are not interested in obtaining a very concentrated mixture of acids and we shall take a lower limit of $x_{H_2O} = 0,800$, as the maximum acid concentration giving the least boil-up rate requirements in the reactor. A rough idea of the possible range of behaviour of the acid mixture is obtained by making the two extreme assumptions, i.e that it behaves either as a binary HNO_3 - H_2O mixture or as a binary HCl - H_2O mixture. In the former case we should be able to work to the HNO_3 - H_2O azeotropic composition, but in the latter case only to the HCl - H_2O azeotropic composition point. The behaviour is likely to lie closer to the former since the HCl is only present in a fairly low proportion (normally $<$10 mole % of the HNO_3 concentration). The choice of $x_{H_2O} = 0,8$ as the lower limit therefore seems reasonable. Any higher reactor boil-up rate will not only give a higher value of x_{H_2O} in the bottoms product but will also require fewer stages. For the purposes of design of the number of stages we therefore take the extreme case ($x_{H_2O} = 0,800$) and we shall assume that the HCl present behaves as pure HNO_3, so that the H_2O - HNO_3 equilibrium relationship may be used. This is a somewhat hazardous assumption but probably compensated for by the generous value of $x_{H_2O} = 0,800$. Also, operation will normally be at a boil-up rate higher than the minimum giving $x_{H_2O} > 0,800$.

B. 5. Distillation Column; *Operating Conditions*

We shall consider the case of a specific (N_2O free) vapour composition which, from previous batch experimental work, appears to be realistic. Actual prediction of vapour composition leaving the reactor is even more complex than indicated by vapour-liquid equilibrium predictions for the acid mixture because of the presence of AN. The

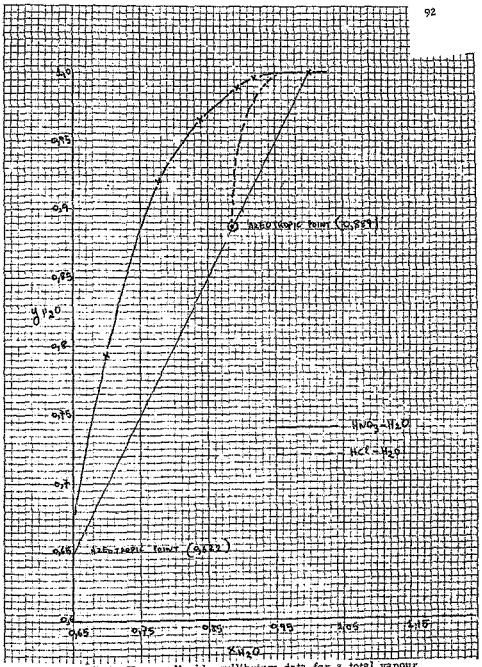

Fig. B. 1. Vapour-liquid equilibrium data for a total vapour pressure of 700 mm Hg.

experimental composition to be used is a vapour which, when condensed, gives an aqueous solution of 0,5 M HNO_3, 0,06 M HCl. This is equivalent to a vapour composition 98,95% H_2O, 0,94% HNO_3, 0,11% HCl.

The liquid from which this vapour is obtained has the approximate composition: 300g AN, 300ml conc. HNO_3, 300ml H_2O, 15ml conc. HCl. This reacts at a boiling point in the range 107° - 109° at a total pressure of about 700mm Hg.

Consider a mass balance over the column.

N_2O, Cl_2 and N_2 pass straight out at the top and do not concern us now.

Let 100 moles N_2O free vapour enter. The composition of this vapour is as above.

The liquid distillate may be assumed to be pure water.

The bottoms has the composition $x_{H_2O} = 0,80$ and contains all the HCl and HNO_3 in the distillation column feed, i.e. 0,111 mole HCl and 0,939 mole HNO_3. Hence the number of moles of water in bottoms is

$$\frac{0,80}{0,20} \times 1,05 = 4,20.$$

This water is returned to the reactor.

The number of moles of water removed in the distillate is

98,95 - 4,20 = 94,75.

The number of moles of H_2O which must be removed per mole AN fed is

$2 + a + m = 2 + 0,02 + 1,437 = 3,457$ moles.

Number of moles H_2O removed per mole N_2O produced is

$$\frac{2 + a + m}{1 - a} = \frac{3,457}{0,98} = 3,524.$$

94,75 moles H_2O must therefore have a maximum of

94,75/3,524 = 26,90 moles N_2O coming off with it.

Reverting to the basis of 1 mole AN feed to the reactor, the molar vapour composition for the minimum boil-up rate will be:

0,98 moles N_2O, 0,02 moles Cl_2, 0,02 moles N_2,

$\frac{98,95}{26,90} \times 0,98 = 3,604$ moles H_2O,

$0,939 \times \frac{0,98}{26,90} = 0,0342$ moles HNO_3, and

$0,111 \times \frac{0,98}{26,90} = 0,00404$ moles HCl.

Distillate product will be:

3,457 moles H_2O, 0,98 moles N_2O, 0,02 moles Cl_2 and N_2, respectively.

Bottoms product returned will be:

0,0342 moles HNO_3, 0,00404 moles HCl,

$\frac{80}{20} \times (0,0342 + 0,00404) = 0,153$ moles H_2O.

Water balance: IN = 3,604

OUT = 3,457 + 0,1530 = 3,610.

We shall design for a maximum feed rate of 480 g/h of AN, corresponding to a maximum of 0,100 mol min^{-1} of N_2O or 2,24 litres min^{-1} at S. T. P.. The system must also be capable of coping with a production rate very much less than this.

Mass and energy balances for the system at this AN feed rate, with a minimum reactor boil-up rate, a reflux ratio of 0,25 and a selectivity parameter a = 0,02 are shown in Fig. B. 2.

B. 6. Number of Theoretical Equilibrium Stages Required

In order to achieve the least number of theoretical stages, feed should enter at a point in the distillation column where the composition most closely matches the feed composition.

To determine the number of theoretical stages and the heat load required, we carry out a *Ponchon-Savarit* construction on an enthalpy-concentration diagram. The enthalpy data for the HNO_3-H_2O system obtained from data in Perry[22] will be used. As the quantity of HCl is only about 10% of that of HNO_3, we shall assume this assumption will not give serious problems. The following data are obtained from this chart:

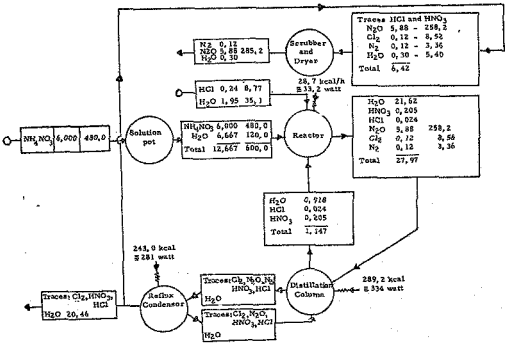

Fig. B.2. Material balance for N_2O process
Conditions: 98% conversion of AN to N_2O
Minimum heat addition to reactor for H_2O product removal
Reflux ratio of 0.25
Basis: 6 mole AN feed/h
1st value: flow rate in mole/h
2nd value: flow rate in g/h

Conc % w/w	x_{HNO_3}	h Btu./lb at 32°F	C_p B.t.u./lb °F	T_{bp} 0°C 760 mm	H_{sl} Btu./lb	h_{sv} B.t.u./lb	H_{sl} Btu./lb mole	H_{sv} B.t.u./lb mole
0	0,00	0	1,0	100	212	1150	3820	20,700
10	0,0320	-22	0,91	101	172	1151	3330	20,720
20	0,0667	-42	0,83	103	112	1152	2358	20,770
30	0,109	-60	0,73	108	82	1154	1877	21,170
40	0,160	-74	0,67	112	61	1155	1537	22,460
50	0,222	-55	0,66	116	53	1155	1485	25,180

P.S. construction has been carried out for the case of a reflux ratio $1,5 \times R_{min} = 0,733$ assuming feed to enter the bottom of the column (see Fig. 3):

$$\frac{B}{F} = \frac{33100 - 20700}{-\Delta h_B + 20700} = \frac{1,147}{21,85}$$

$\Delta h_B = -215500$ B.t.u./lb mole.

Heat input in reboiler is $\frac{215500 + 1500}{1000 \times 1,8} \times 1,147 = 138,2$ kcal/h.

Heat removed in condenser is

$$\frac{33100 - 3800}{1000 \times 1,8} \times 20,46 = 333,4 \text{ kcal/h}$$

The number of equilibrium stages required is 4, of which one represents the reboiler. Even better operation can be achieved if feed is entered 2 stages from the top.

Vapour and liquid rate will be a maximum at the top of the column. Here we have

$$V = \frac{33100 - 3800}{20700 - 3800} \times 20,46 = 35,5 \text{ mol/h}$$

To this we must add the non-condensable gases whose total flow rate is 6,42 mol/h.

Hence total vapour flow rate

$V_{tot} = 35,5 + 6,4 = 41,9$ mol/h

Allowing for a 25% increase due to higher production rate or higher reflux,

$V_{max} \approx 52,4$ mol/h

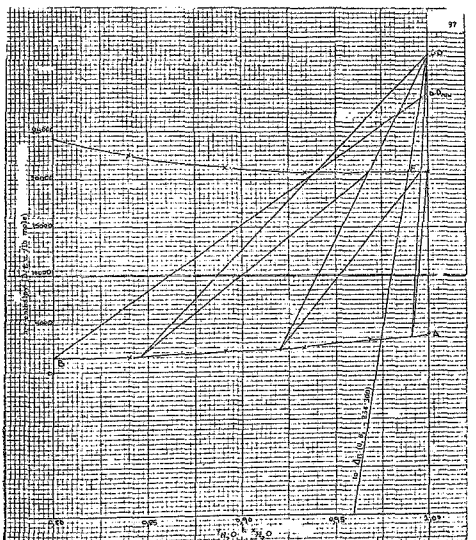

Fig. B. 3. PONCHON-SAVARIT construction for feed entering column at bottom as vapour.

Liquid rate will be

$L = 35,5 - 20,46 \simeq 15,0$ mol/h

$L_{max} = 15,0 \times 1,25 = 18,8$ mol/h

If feed rate is less than 6,0 mole AN/h the liquid rate will be higher if the reboil rate is kept constant.

By maintaining a constant boil-up rate in the reboiler, irrespective of the load on the column, the vapour rate should not vary with loading, but the liquid rate will increase significantly as a much larger reflux ratio will be required. Thus we need not be concerned about large fluctuations in column loading.

Let us now look at the type of packing to be used. We shall follow the procedure given by Morris and Jackson.[23]

Volumetric gas rate is

$41,9 \times 22,4 \times \frac{373}{273} = 1282$ l/h.

(This assumes operation at 1 atm pressure.)

Volumetric liquid rate is $\frac{15,0 \times 18 \times 1}{1000} = 0,270$ l/h

(This may be slightly higher near the bottom because of measuring molecular weight but the effect will be insignificant.)

$$\phi = \left[\frac{\rho_{H_2O}}{\rho_{g(\text{air at Rtp})}}\right]^{\frac{1}{2}} = \left(\frac{18}{29} \times \frac{293}{373}\right)^{\frac{1}{2}} = 0,697$$

$$\frac{V_g}{V_l} \times \phi = \frac{1282 \times 0,697}{0,270} = 330$$

This indicates a packing greater than 3" for operation at the minimum wetting rate (M.W.R.) of 0,85 ft^3/h ft. This is clearly impractical on this scale and we shall have to content ourselves with operation well below the M.W.R. and make allowances for it.

Let us assume we are going to use 1/4" rings. Assume a wetting rate of 0,22 ft^3/h ft. This should give a packing effectiveness of roughly 50%.

$$L = \frac{V_l}{S}$$

S for 1/4" packing is 240 ft^2/ft^3

$V_l = 0,22 \times 240 = 52,6$ ft^3/ft^2 h

$52,6 \times 0,3044 = 16,02$ $m^3/h\ m^2$.

Hence area of column required is:

$$\frac{0,270 \times 10000}{1000 \times 16,02} = 0,169 \text{ cm}^2$$

This is unrealistic. The liquid rates are so low that a packed column clearly is not a satisfactory method for performing the distillation.

Assuming an area of 10 cm^2, the gas flooding rate is:

$$\frac{S}{\epsilon^3} = \frac{768}{0,3044} = 2520 \text{ m}^2/\text{m}^3$$

The liquid rate

$$V_l = \frac{0,270 \times 10000}{10 \times 1000} = 0,270 \text{ m}^3/\text{h m}^2$$

$$x = 2,5^{0,2} \approx 2,5 \times 0,00284^{0,2} = 2,5 \times 0,491 = 1,23$$

$$x\frac{S}{\epsilon^3} = 1,23 \times 2530 = 3,100$$

$$YV_{gf} = 3000 \text{ m}^3/\text{h m}^2$$

$$Y = 28,8 \times \left(\frac{5,9 \times 10^{-4}}{1}\right)^{\frac{1}{2}} = 0,7$$

$$V_{gf} \approx \frac{3000}{0,7} = 4290 \text{ m}^3/\text{h m}^2$$

The actual rate is about 1282 $m^3/h\ m^2$.

A cross sectional area of about 2,5 cm^2 would be better than 10 cm^2,

i. e. D= 1,78 cm

The wetting rate is about 0,0074 x M. W. R. and effectiveness will be considerably less than 10%.

The height equivalent to a theoretical state

(HETP) for 1/4" rings is 20 x 0,135 = 3 ft

For 3 stages the column height is about 9 ft (very rough estimate)

B. 7. Heat Requirements for the Reactor

For the reactor at steady state:

$$\Delta H = Q - W_s - \Delta KE - \Delta PE$$

Therefore

$$\Delta H \simeq Q$$

A process enthalpy balance may be calculated by assuming the following path:

1. Hot, concentrate[illegible]^0, 80%) AN solution mixed with a large

quantity of water at 25° and cooled to 25°

2. Cold concentrated (25°, 20%) HCl, mixed with a large quantity of water at 25° and cooled to 25°
3. AN and HCl solutions mixed and reacted at 25°, water and other products in gaseous form.
4. *Product gases heated to* T_{exit} *of about* 110°
5. Water of dilution removed at 25°
6. Water of solution of AN and HCl heated to T_{exit} and vaporised
7. A quantity of solution with composition equal to that of the bottoms product of the distillation column with the same composition is vaporised.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 = Q$$

ΔH_1: Heat of dilution of AN is likely to be fairly small (although heat of solution is significant). We must find data on NH_4NO_3 for this and we shall ignore this for the time being.

ΔH_2: Heat of solution of 20% HCl is about 190 B.t.u./lb. 1 lb of 20% mixture = 0,00548 + 0,0445 = 0,0500 moles. For 0,04 moles in a 20% HCl solution, $\Delta H_2 = -190 \times \frac{0,04}{0,00548} \times 0,252 = -350$ cal

ΔH_3: In dilute solution at 25°, for the reaction

NH_4NO_3 (aq) $\rightarrow N_2O$ (g) + H_2O (g)

$\Delta H_{R_1} = 19,55 + 2(-57,80) + 80,89 = -15,16$ kcal/mole

For the reaction

NH_4NO_3 (aq) + 2HCl (aq) $\rightarrow N_2 + Cl_2 + 3H_2O$

$\Delta H_{R_2} = -3 \times 57,80 - (-80,8\ g) - 2(-22,063) = -48,39$ kcal/mole

Therefore

$$\Delta H_3 = -15,16 \times (1-a) + (-48,39)a$$
$$= -15,16 - 33,23\ a \text{ kcal/mol AN}$$

For a = 0,02

$\Delta H_3 = -15,82$ kcal/mol AN

H_4: No heat capacity data on H_2O are immediately available. Assume that for N_2O, Cl_2 + N_2 Cp = 0,25 (same as air)

Therefore

$$\Delta H_4 = (110 - 25) \times 0,25 \times (43,1 + 0,56 + 1,42) + \frac{2,02 \times 18}{1,8} \times$$
$$\times (1157,0 - 1092,2) = 960 + 1328 = 2288 \text{ cal/mol AN}$$

$\Delta H_5 = 0$

$\Delta H_6 = \frac{25.84}{118} \times (1157 - 38) = 16,07$ kcal/mol AN

ΔH_7: This can be found from the enthalpy concentration diagram

$\Delta H_7 = 0,1912 \times \frac{23,500}{118} = 2,500$ cal/mol AN

Hence for the entire reactor process for a feed of 1 mole AN

$\Delta H = Q = 0 - 0,35 - 15,82 + 2,29 + 16,07 + 2,50$

$Q = 4,79$ kcal/ mole AN fed.

This term is the minimum heat required. If maximum heat is added this will cause more of the acid solution to be evaporated.

B. 8. Absorption Column for Trace Cl_2 Removal

Again absorption column design is difficult because of low flow rates, but approximately the same size of column as for the distillation column should be adequate. A NaOH solution rate of about 4 l/h should be satisfactory.

B. 9. Note on N_2O Process System Design

The process used to produce N_2O in the laboratory was designed using a distillation column with its own reboiler and recycle of bottoms product to the reactor. In retrospect a simpler system could have been designed in which the distillation column would have been mounted over the reactor with vapour entering at the bottom of the column and reflux liquor running directly from the column back into the reactor. Such a system would have been possible because of the large difference in composition between vapour leaving the reactor and the liquid in equilibrium with this vapour. Failure to use such a system gave rise to some unnecessary operating difficulties but conclusions drawn from the actual experimental set-up are not materially affected as a result.

List of Symbols

a = Fraction of AN reacted to form by-products

m = Moles H_2O entering the reactor

T = Temperature

P_{HNO_3} = Partial pressure of nitric acid in vapour

P_{H_2O} = Partial pressure of water in vapour

P_T = Total pressure

y_{HNO_3} = Mole fraction of nitric acid in vapour

y_{HCl} = Mole fraction of hydrochloric acid in vapour

y_{H_2O} = Mole fraction of water in vapour

x_{HNO_3} = Mole fraction of nitric acid in liquid

x_{HCl} = Mole fraction of hydrochloric acid in liquid

x_{H_2O} = Mole fraction of water in liquid

P_{HCl} = Partial pressure of hydrochloric acid in vapour

h = Enthalpy (B. t. u. /lb)

H = Enthalpy (B. t. u. /lb mole)

H_{sv} = Enthalpy of saturated vapour

H_{sl} = Enthalpy of saturated liquid

C_p = Specific heat at constant pressure

B = Bottom products rate

F = Feed rate

V = Vapour rate

L = Liquid rate

Δh_B = Delta point in the Ponchon-Savarit construction

Q = Quantity of heat transfered

KE = Kinetic energy

PE = Potential energy

APPENDIX C

The Derivation of Equations for Calculating the Rates of Chlorine and Nitrogen

From Beer's law, we have $A = abc$ (c. 1)

where A = absorbance, a = absorptivity for the substance, b = thickness of the cell, and c = concentration.

From the ideal gas law, $F_{Cl_2} PV = nRT$ (c. 2)

where $c = \frac{n}{V}$ (c. 3)

Combining (c. 2) and (c. 3), $c = F_{Cl_2} \frac{P}{RT}$ (c. 4)

where F_{Cl_2} = mole fraction of Cl_2 and P = Barometric pressure

$F_{Cl_2} P = P_{Cl_2}$ (c. 5)

where P_{Cl_2} = partial pressure of Cl_2.

Thus we can relate the absorbance of the gas cell to the fraction of Cl_2 in the gas

$$A = \left[\frac{abP}{RT}\right] F_{Cl_2} \quad \text{(c. 6)}$$

For the calibration run we can relate the fraction of Cl_2 in the gas stream to the fraction of Cl_2 in the standard cylinder by the flow rates of the standard gas and the sparge gas

$$F_{Cl_2} = (F_{Cl_2})_{Std} \left[\frac{R_{Cl_2 - N_2O}}{R_{Cl_2 - N_2O} + R_{He}}\right] \quad \text{(c. 7)}$$

where $R_{Cl_2 - N_2O}$ is the flow rate of standard gas, R_{He} is the flow rate of helium and $(F_{Cl_2})_{Std}$ is the mole fraction of Cl_2 in the standard cylinder. Calibration runs of absorbance versus the ratio of the fraction of Cl_2 in the gas stream to the Cl_2 in the standard gas were constructed.

In the experimental runs the mole fraction of Cl_2 in the combined exhaust from the reaction vessel is calculated from

$$R_{Cl_2} = (R_{Cl_2 - N_2O} + R_{He}) F_{Cl_2} \frac{P_e}{P_c} \text{ mls sec}^{-1} \quad \text{(c. 8)}$$

where R_{Cl_2} is the flow rate of Cl_2 production, $(R_{Cl_2 - N_2O} + R_{He})$ is the measured total flow rate in the system, and P_e, P_c are the

barometric pressures at the time of the experimental run and at the time when the calibration graph was determined, respectively.

The rate of N_2 production in the gas cell is obtained by an analogous procedure. Instead of Beer's law applying, the peak height of the N_2 peak in the gas chromatogram is proportional to the amount of N_2 in our gas sample. Since we had constant volume samples, the peak height from our procedure is directly proportional to the concentration of N_2 in the gas stream.

APPENDIX D

The Mechanism for the Chloride-Catalysed Decomposition of Ammonium Nitrate in the melt proposed by Keenan and Dimitriades

According to the Keenan-Dimitriades mechanism,[16] the excess HNO_3 in an AN melt which has become acidic by preferential loss of NH_3 from the partially dissociated AN, undergoes the following autoprotolysis and ionic self-dehydration reactions:

$$2HNO_3 \rightarrow H_2NO_3^+ + NO_3^- \quad \text{(autoprotolysis)} \qquad \text{(d. 1)}$$

and $$H_2NO_3^+ \rightarrow NO_2^+ + H_2O \quad \text{(self-dehydration)} \qquad \text{(d. 2)}$$

by analogy with the case of $HNO_3 - H_2SO_4$ mixed acid systems, where such reactions have been experimentally verified by Hughes et al.[24] Keenan and Dimitriades assert that such reactions are feasible for the chloride-containing AN melt because of the high temperature (185° in their study) and the low water content of the melt.

Chloride ions are oxidised by the nitronium ions (NO_2^+) to chlorine atoms:

$$NO_2^+ + Cl^- \rightarrow NO_2 + Cl \qquad \text{(d. 3)}$$

a radical mechanism deduced by Keenan and Dimitriades from the square-root dependence of the N_2O rate on the chloride concentration they had found experimentally.

The chlorine atoms now react with NH_4^+ (present in high concentration) by the hydrogen abstraction reaction

$$Cl + NH_4^+ \rightarrow NH_3^+ + HCl \qquad \text{(d. 4)}$$

thus being reduced back to chloride and completing the catalyst cycle. The NH_3^+ radical is formed on the wall of the 'solvent cage' which contains the NO_2 resulting from reaction (d. 3). By the reaction

$$NH_3^+ + NO_2 \rightarrow \left[O_2NNH_3^+\right] \xrightarrow{\text{fast}} N_2O + H_3O^+ \qquad \text{(d. 5)}$$

these two radicals combine to form N_2O via the intermediate nitramide, written in equation (d. 5) as the nitrammonium ion. They state that these radical processes are expected to be of low activation energy, thus explaining the high reaction rate.

For radicals which escape after the initial cage reaction (d. 3) alternative reaction paths are postulated to explain the formation of Cl_2 and N_2. Chlorine is formed by recombination of chlorine atoms:

$$Cl + Cl \rightarrow Cl_2 \qquad (d.\ 6)$$

Part of the Cl_2 escapes by volatilisation, but most of it reacts in the melt with NH_3 to produce N_2, according to Keenan and Dimitriades, "probably by fast reactions through a series of chloramine-type intermediates which need not be specified for the present kinetics". The reactions proposed are given by the equation:

$$Cl + NH_3 \rightarrow [NH_2Cl] \rightarrow N_2 + HCl \qquad (d.\ 7)$$

A second reaction path proposed for the formation of N_2 is by NO_2 radical recombination and self-ionisation (i.e. dis[illegible]n):

$$NO_2 + NO_2 \rightarrow NO^+ + NO_3^-$$

The NO^+ now oxidises a Cl^- ion to a chlorine atom:

$$NO^+ + Cl^- \rightarrow NO + Cl \qquad (d.\ 9)$$

followed by hydrogen abstraction by the chlorine atom from an NH_3 molecule in the cage wall:

$$Cl + NH_3 \rightarrow NH_2 + HCl \qquad (d.\ 10)$$

whereby the chlorine cycle is completed to Cl^-. The NH_2 radical then combines with the NO radical already present in the cage [from reaction (d. 9)] to produce nitrosamine, a known unstable precursor for N_2, thus:

$$NH_2 + NO \rightarrow [NH_2NO] \rightarrow N_2 + H_2O \qquad (d.\ 11)$$

Keenan and Dimitriades then proceeded, by steady-state treatments, to calculate rate equations for N_2 and N_2O evolution. For the rate of N_2 production, after making some simplifying assumptions, they deduced the equation

$$\frac{dN_2}{dt} = k_7 K_h \left[\frac{(H_2O)(Cl_2)}{(H_3O^+)}\right](NH_4^+) + k_{10} K_h \left[k_3/k_6\right]^{\frac{1}{2}} \times (H_2O)(NO_3^-)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}} \qquad (d.\ 12)$$

where k_7, k_{10}, etc., represent rate constant for reactions (d. 7), (d. 10), etc., respectively, and K_h is the equilibrium constant for the hydrolysis reaction

$$NH_4^+ + H_2O = H_3O^+ + NH_3 \qquad \text{(d. 13)}$$

In equation (d. 12), (H_3O^+) and (NO_2^+) are both measures of acidity, which has a constant, steady-state value in these melts, as pointed out earlier (see Section I. 1). The same applies for (H_2O). Keenan and Dimitriades argued that the (Cl_2) in their melts was probably also constant. If rates are compared for runs at a point where (NH_4^+) is the same for all runs, equation (d. 12) simplifies to

$$\frac{dN2}{dt} = a + b(Cl^-)^{\frac{1}{2}}$$

(where a and b are composite constants), in agreement with their experimental findings.

Keenan and Dimitriades did not succeed in obtaining an experimental rate law for N_2O evolution, but derived the following rate law for the postulated mechanism:

$$\frac{dN_2O}{dt} = k_4(k_3/k_6)^{\frac{1}{2}}(NO_2^+)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}} \qquad \text{(d. 14)}$$

and since

$$(NO_2^+) = k_1k_2(HNO_3)^2/(NO_3^-)$$

$$= \left[k_1k_2/K_a^2\right](H_3O^+)^2(NO_3^-) \qquad \text{(d. 15)}$$

we have that

$$\frac{dN_2O}{dt} = \left[k_4(k_3k_1k_2/k_6)^{\frac{1}{2}}/K_a\right]\left[(H_3O^+)(NO_3^-)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}}\right]$$

$$= c \times (H_3O^+)(NO_3^-)^{\frac{1}{2}}(NH_4^+)(Cl^-)^{\frac{1}{2}} \qquad \text{(d. 16)}$$

where c is a composite constant and K_a the acidity constant of HNO_3.

It could be argued that since (H_3O^+) is constant, and if rates were compared at a point where the AN concentrations are the same, the N_2O rate should be proportional to $(Cl^-)^{\frac{1}{2}}$. However, Keenan and Dimitriades found no correlation between the N_2O rate and chloride ion concentration in their experiments. They explain this by pointing out that whereas equation (d. 12) for N_2 has an acidity factor in both the numerator and the denominator of the dominant term, no such cancellation occurs in equations (d. 14) or (d. 16) for N_2O. They suggest that the lack of correlation of experimental N_2O rates with chloride concentration may have been due to a very much greater

sensitivity of this reaction to small variation in acid concentration, and proceed to adduce experimental evidence in support of this view.

The authors did not obtain a rate equation, whether experimental or theoretical, for the rate of Cl_2 formation. This rate for their postulated mechanism is given by

$$\begin{aligned}\frac{dCl_2}{dt} &= k_6(Cl)^2 - k_7(Cl_2)(NH_3) \\ &= k_3(NO_2^+)(Cl^-) - k_7K_h(NH_4^+)(Cl_2)/(H_3O^+) \\ &= k_3k_1k_2(H_3O^+)^2(NO_3^-)(Cl^-) - k_7K_h(NH_4^+)(Cl_2)/(H_3O^+) \\ &= f(H_3O^+)^2(NO_3^-)(Cl^-) - g(NH_4^+)(Cl_2)/(H_3O^+) \qquad \text{(d. 17)}\end{aligned}$$

where f and g are composite constants.

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