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POTASSIUM NITRATE FROM NITRIC ACID  
AND POTASSIUM CHLORIDE

by

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## ABSTRACT

This study was concerned with the development of a process for the production of potassium nitrate for use as a fertilizer material. The process uses KCl and 60%  $\text{HNO}_3$  as the starting materials and the intended co-product is  $\text{Cl}_2$ . From information in the literature it was decided to react the KCl directly with  $\text{HNO}_3$  simply by mixing the two rather than using some other scheme such as employing an organic solvent or vaporizing the  $\text{HNO}_3$  and using a gas-solid reaction. The work was carried out in equipment constructed of glass.

The analysis, by gas chromatography, of the gaseous products of the reaction mixed with air was studied. Both gas solid chromatography and gas liquid partition chromatography methods were examined. While none of the gas solid chromatographic methods gave encouraging results several gas liquid partition chromatography system results were encouraging. Air,  $\text{Cl}_2$  and  $\text{NOCl}$  were separated using a column packed with triacetin on non-acid washed Chromosorb P. This system was used to analyze the gases from a continuous reactor.

The reaction of KCl with 60%  $\text{HNO}_3$  was first studied in batch equipment. The reactor was kept in a constant temperature bath or in some studies the reaction products were heated to dryness with a flame. The gases were reacted with various reagents in absorbers and these reagents were later analyzed to find the nature of the gases evolved. The gases were found to be  $\text{Cl}_2$  and  $\text{NOCl}$ . The solid residues

were found to contain excessive amounts of chloride ions. For this reason, a batch reaction is not a satisfactory method to produce  $\text{KNO}_3$ .

To find if it were possible to fractionally crystallize  $\text{KNO}_3$  from aqueous nitric acid solutions containing  $\text{KCl}$  and  $\text{KNO}_3$  a study was made of the mutual solubility of these two salts in such solutions. The solubility studies were performed at 0, 16, 30, 45 and 60° C. and various acid-water ratios. Also a study of the solubility of  $\text{KNO}_3$  in solutions of 0.3 gm  $\text{HNO}_3$  per gm  $\text{H}_2\text{O}$  with controlled amounts of  $\text{KCl}$  was carried out at 30° C. These studies showed that the  $\text{KNO}_3$  solubility in such solutions changed markedly with temperature while the  $\text{KCl}$  solubility did not change very much over the range of temperature studied. Therefore, it was found that it was possible to fractionally crystallize  $\text{KNO}_3$  from aqueous nitric acid solutions containing  $\text{KCl}$  and  $\text{KNO}_3$ .

To demonstrate the final process, equipment was set up to continuously react  $\text{KCl}$  and  $\text{HNO}_3$ , withdraw liquid from the reactor, fractionally crystallize  $\text{KNO}_3$ , and continuously remove the gaseous products. This procedure produced solid  $\text{KNO}_3$  which contained no solid  $\text{KCl}$ . The only impurities in the  $\text{KNO}_3$  were from the mother liquor which adhered to the crystals. The reaction was found to proceed more rapidly as the temperature or the concentration of the reactants was increased.

## INTRODUCTION

There are three primary plant nutrients, nitrogen (N), phosphate ( $P_2O_5$ ) and potash ( $K_2O$ ). Plants need all three of these to grow properly. Numerous other elements are also needed in lesser amounts for satisfactory plant growth. However, the primary nutrients are depleted from almost all soils by continuous cropping. Then for satisfactory crop growth these nutrients must be replaced with naturally occurring or chemically produced fertilizer materials.

Approximately 93% of the  $K_2O$  applied as fertilizer in this country is applied as potassium chloride (KCl) (37). With the exception of specialized crops, one potash fertilizer is as effective as any other as a source of potash for the plant. Tobacco is one example of a crop sensitive to chlorides; quantities of  $K_2O$  in excess of 30 to 40 lb/acre as chloride are harmful to the tobacco burning quality (37).

An alternate source of potassium is needed for tobacco and other chloride sensitive crops. Two forms of  $K_2O$  are immediately brought to mind, potassium sulfate ( $K_2SO_4$ ) and potassium nitrate ( $KNO_3$ ). Potassium sulfate is used to a limited extent while  $KNO_3$  has hardly been used at all. Presently one facility for producing  $KNO_3$  is known to exist in this country (33). However, little information has been divulged about the process (33). Additional work on the development of a process for the production of  $KNO_3$  seemed important.

The purpose of this investigation was to develop a  $KNO_3$  process.

Early in the work it was decided that KCl and nitric acid ( $\text{HNO}_3$ ) would be the reactants and that the most desirable co-product would be elemental chlorine ( $\text{Cl}_2$ ). Initially the KCl was reacted directly with  $\text{HNO}_3$  on a batch basis. However, the solid product contained too much KCl. Published solubility curves for KCl and  $\text{KNO}_3$  in water indicated that a fractional crystallization process for  $\text{KNO}_3$  might be possible and a study of the mutual solubility of  $\text{KNO}_3$  and KCl in aqueous  $\text{HNO}_3$  solutions tended to confirm this possibility. Following the solubility study a continuous fractional crystallization process for  $\text{KNO}_3$  was investigated using glass equipment.



## LITERATURE SURVEY

## History of Potassium Nitrate

Mehring et al. (30) gave a brief history of the supply of potassium nitrate ( $\text{KNO}_3$ ). The world supply was formerly derived from incrustations on the soils around heavily populated areas in tropical countries, notably, Ceylon, India, Egypt and Mexico. Its presence is due to the decomposition of organic matter by nitrifying organisms in soil containing soluble potassium compounds. Evaporation of soil moisture causes the salt to concentrate at the surface. When used as a source of  $\text{KNO}_3$  a thin layer of soil is scraped up at frequent intervals and extracted with boiling water. The yield of crude  $\text{KNO}_3$  is 2 to 8% of the weight of soil scrapings.

During the Crimean War the demand for  $\text{KNO}_3$  for the manufacture of gunpowder became so great that artificial saltpeter plantations were created. Garbage, animal refuse, and other decaying organic matter were mixed with limestone or old plaster, wetted with urine and allowed to ferment in piles protected from the rain. After complete decomposition, which required a year or two in northern Europe, the piles were mixed with hardwood ashes and the  $\text{KNO}_3$  extracted. The yield was about 5 kg of  $\text{KNO}_3$  per cubic meter. For many years European governments permitted their subjects to pay taxes with saltpeter ( $\text{KNO}_3$ ) and this practice was quite common among the peasants.

According to Russel (38) the use of  $\text{KNO}_3$  as a fertilizer was

first suggested by Glauber in 1656. Potassium nitrate was used by Home in the first pot experiments ever recorded and by Liebig and Lowes and Gilbert in their all important work (38). Mehring and his co-workers (30) report that in the middle 17th century Digby discussed the value of  $\text{KNO}_3$  in what is said to be the earliest record of actual use of artificial fertilizers as distinct from decaying organic matter.

#### Present Supply and Use of Potassium Nitrate

Kirk and Othmer (26) indicate that a small amount of  $\text{KNO}_3$  may presently come from natural deposits. However, they state that most of it is made by taking advantage of the solubility relationships in the system  $\text{KCl-NaNO}_3\text{-H}_2\text{O}$ . In aqueous solution, the solubilities of  $\text{KNO}_3$ , potassium chloride ( $\text{KCl}$ ), and sodium nitrate ( $\text{NaNO}_3$ ) increase markedly with temperature, while that of the fourth possible single salt of the system, sodium chloride, ( $\text{NaCl}$ ) changes little. Sodium nitrate and  $\text{KCl}$  are dissolved in hot water to form a concentrated solution. The solution is evaporated to just below the solubility limit of  $\text{KNO}_3$ . The  $\text{NaCl}$  crystals formed during the evaporation are removed and the solution cooled. Potassium nitrate is less soluble than either  $\text{NaNO}_3$  or  $\text{KCl}$ , and hence is obtained as the low-temperature crop.

Potassium nitrate is used in the manufacture of some matches and in various pyrotechnics both of which make use of the oxidizing power of the nitrate. Other uses of  $\text{KNO}_3$  include the manufacture of certain

types of glass and ceramic glazes, meat curing, pickling, and in medicine. A mixture of 55%  $\text{KNO}_3$  and 45%  $\text{NaNO}_3$  melts at  $220^\circ \text{C}$ . and makes a convenient high-temperature liquid bath if contamination with organic materials is avoided (26).

#### Need for Potassium Nitrate as a Fertilizer Material

McCants (29) has written a review of the status of  $\text{KNO}_3$  as a possible fertilizer. While there is no difference between the chloride, sulfate and nitrate salts of potassium insofar as the potassium ion is concerned, there may be a difference on plant response due to the associated ion. For example, the use of  $\text{KCl}$  on a number of crops is restricted because of the adverse effect of excessive chlorine on crop quality. The most notable of these crops are potato and tobacco.

A number of experiments have been conducted in which the effects of  $\text{KCl}$  and potassium sulfate ( $\text{K}_2\text{SO}_4$ ) on the quality of potato tubers have been studied. Potassium nitrate was included in some of these studies. These studies have shown in general, that the chloride source of potassium as compared to the sulfate or nitrate source resulted in a decrease in the specific gravity, dry matter and starch content of the tubers. These effects are generally associated with a reduction in tuber quality. As a result of the effects of chlorides on quality of potatoes, in many of the commercial potato growing areas it is recommended that the potassium be added as the sulfate. However, when large amounts of fertilizer are used and the potassium is supplied as the

sulfate and ordinary superphosphate is used, the quantity of sulfate sulfur which is applied to the soil is in excess of that needed by the plants. While the effects of this excessive sulfate ion on the yield and quality of potato tubers has not been studied extensively, a tip burn associated with high sulfate ion in the presence of ammonium nitrogen has been reported (29).

McCants (29) further states that the effect of chlorine on the quality of tobacco has been reported by many investigators. The data show that generally as the percentage of chlorine in tobacco is increased, the green leaves frequently become thickened and brittle and roll upward at the leaf margins. When cured, the leaves are dull in appearance and soggy, and associated with this condition is a reduction in the duration of burn. This effect of chlorine on the burning characteristic of tobacco is so pronounced that there are laws in many states which regulate the maximum percentage of chlorine permissible in fertilizers for tobacco. Potassium, however, tends to improve leaf burning characteristics and consequently relatively high rates are generally used. These conflicting demands have resulted in the use of  $K_2SO_4$  and potassium magnesium sulfates. There are indications that excessive sulfate addition to tobacco may be undesirable (29).

Potassium nitrate may also be desirable in greenhouse production in that this type of fertilizer does not cause an accumulation of soluble salts in the soils.

K. D. Jacob claims that because of its high concentration of nutrients, low hygroscopicity, high solubility, and good storage

characteristics,  $\text{KNO}_3$  offers many advantages to the fertilizer manufacture (24). The claims he makes for  $\text{KNO}_3$  are that it:

1. mixes well with other materials simplifying processing of granular and non-granular fertilizers,
2. is chemically neutral and stable and therefore undergoes little or no chemical change in mixtures and does not contribute to loss of nitrogen during processing,
3. tends to reduce the hygroscopicity of mixtures, and thus favors maintenance of good mechanical condition,
4. is useful for the formulation of mixtures having either a neutral or an alkaline effect on the soil reaction as it is alkaline whereas  $\text{KCl}$  and  $\text{K}_2\text{SO}_4$  are neutral, and
5. has a low salt index and therefore reduces danger of seeding injury and plant burn.

#### Chlorine Demand

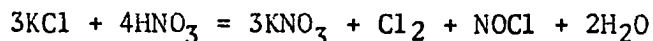
Elemental chlorine is a possible co-product for  $\text{KNO}_3$  when it is manufactured from  $\text{HNO}_3$  and  $\text{KCl}$ . Therefore, the status of  $\text{Cl}_2$  as an item of commerce is important.

In July, 1962, it was stated that during the prior six months the demand for chlorine increased so sharply that processors were moving fast to fill orders (20). Expansions were in the works but the question was: Will the expansions planned be enough? The production of chlorine was then 4.9 million tons per year, which was 92% of capacity. A total requirement for 1967 of 6.3 million tons was predicted. It was also reported that there had long been concern that over capacity in caustic might accompany the chlorine growth. However, industry

spokesmen expected caustic use of about 6.6 million tons by 1967 and no serious overcapacity.

#### Reaction between Potassium Chloride and Nitric Acid

Mehring, Ross and Merz (30) have studied the reaction



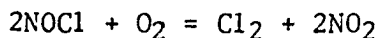
They found that under various conditions all of the KCl was converted to  $\text{KNO}_3$ . However, the chlorine and some nitrogen were evolved as mixtures of hydrochloric acid ( $\text{HCl}$ ) nitric acid ( $\text{HNO}_3$ ) chlorine, nitrosyl chloride ( $\text{NOCl}$ ) and water vapor. They found these mixtures difficult to separate.

Mirkin (32) also studied this reaction and found that it did not go to completion. He found yields on the basis of the nitrogen amounted to 45% almost independently of the concentration of the acid used. The yield based on the potassium fluctuated, depending on the strength of the acid, from 60 to 75%. The gases which were evolved were primarily  $\text{Cl}_2$  and  $\text{NOCl}$ .

Nikonova and Epshtein (19, 34) have calculated the free energy change for standard conditions, starting with crystalline KCl and liquid  $\text{HNO}_3$  and ending with solid  $\text{KNO}_3$  and all other products as gases, to be -5,563 cal/mole. They have calculated the heat of reaction to be 16,350 cal/mole under the same conditions.

## Patented Processes

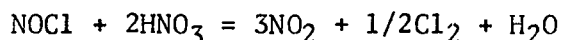
Kobe (27) describes a process shown in Figure 1 for the manufacture of  $\text{NaNO}_3$  and  $\text{Cl}_2$  which is used by the Solvay Process Company. Salt is fed into a reaction tower which contains a solution having at least 40% nitric acid at a temperature of about  $60^\circ \text{C}$ . At this temperature and concentration no hydrogen chloride is evolved. The solution from the reactor is withdrawn to a cooler where the temperature is reduced to  $30^\circ \text{C}$ . The  $\text{NaNO}_3$  that crystallizes out is filtered off and the filtrate returned to the reaction tower. The  $\text{HNO}_3$  concentration is maintained by bubbling  $\text{NO}_2$  into the reactor. The gas evolved from the reactor is mainly  $\text{NOCl}$  which passes to a condenser in which it is cooled to  $0^\circ \text{C}$ . to dry it. The moisture condensed out is returned to the reactor. If the amount of moisture in the gas is maintained below 0.1% the corrosion is greatly reduced. The dried  $\text{NOCl}$  is mixed with oxygen in the ratio of 2 to 1 and the mixture is passed into an oxidizer in which it is contacted at an elevated temperature with a catalyst. This reaction is



An alternate method is to liquify the  $\text{NOCl}$  and conduct the oxidation in the liquid phase at  $60^\circ \text{C}$ . and 400 psi.

This process with many possible changes is covered by patents issued to Beekhuis (3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14). These patents describe the process as outlined above except that different

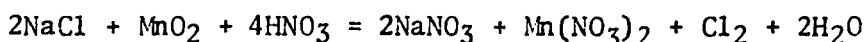
methods are used for oxidizing NOCl. In some cases it is oxidized in the liquid state at other times it is oxidized as a gas with air. One patent covers the oxidation of NOCl with HNO<sub>3</sub>. The reaction is



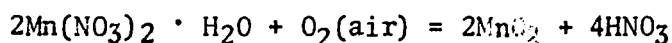
In this case at least some of the NO<sub>2</sub> must be absorbed in water to form HNO<sub>3</sub> and the resulting NO must subsequently be oxidized and absorbed. Some of Beekhuis's patents allow the use of HNO<sub>3</sub> in place of NO<sub>2</sub> and the removal of water.

Fogler claims that the process uses HNO<sub>3</sub> rather than NO<sub>2</sub> (22). In his diagram of the process no liquid is returned to the reaction tower from the filter. Thus the reaction tower is a once through reactor. However, he claims virtually complete conversion of NaCl. A mole ratio of about 1 to 1.7-1.9 NaCl to HNO<sub>3</sub> is used (22). The vessels for the reaction are constructed of acid-resistant brick and chrome-iron alloys.

Miller (31) reports carrying out the following reaction in a slurry



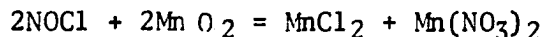
The chlorine is recovered from the overhead gases and the slurry is cooled and filtered to remove the nitrates. Following the filtration the solution is returned to the reaction vessel and the solid nitrates are heated to above 200° C. and contacted with air to oxidize the manganese nitrate.



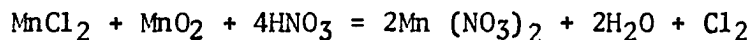


The acid is recovered by suitable means and the  $\text{NaNO}_3$  is leached from the manganese dioxide ( $\text{MnO}_2$ ) with a hot solution from which it may be recovered by cooling.  $\text{MnO}_2$  is returned to the reaction vessel.

Miller also mentions that the  $\text{MnO}_2$  may be kept separate from the reaction vessel and reacted with the  $\text{NOCl}$  in the off gases as follows:



It is then necessary to react the resulting  $\text{MnCl}_2$  with  $\text{HNO}_3$  and more  $\text{MnO}_2$  as follows:



The resulting  $\text{Mn}(\text{NO}_3)_2$  is treated as it was in the above case.

Stengel has been issued several patents covering a process for the manufacture of  $\text{KNO}_3$  (43, 44, 45). Two of these patents relate to processes for separating  $\text{HCl}$  and  $\text{HNO}_3$  while the other (44) relates to a process for production of  $\text{KNO}_3$ . In his process a bed of  $\text{KCl}$  is maintained at a temperature above the melting point of  $\text{KNO}_3$ ,  $333^\circ \text{C}$ . The vapors evolved by heating  $\text{HNO}_3$  are passed through the bed and the  $\text{KNO}_3$  formed melts and flows from the reactor. Since the  $\text{KNO}_3$  leaves the surface of the  $\text{KCl}$  as it is formed the reaction is allowed to go to completion rather than only partially as is usually the case in reacting solid  $\text{KCl}$  in the absence of water and the separation problem is reduced. Stengel preferred to use dilute nitric acid, less than 35% by weight, because this reduced the output of noncondensable gases such as the nitrogen oxides.

Two different processes for producing  $\text{KNO}_3$  using an organic

solvent have been patented (1, 28). Baniel and Blumberg (1) use a solvent mixture consisting of water, an organic solvent and the acid. The solvent mixture is so constituted that the salts are insoluble in it. The following is part of the first example given: "The reaction liquor is a homogeneous solution composed of 77 ml of 60% by weight aqueous  $\text{HNO}_3$  and 50 ml of water made up with isoamyl alcohol to 1000 ml. The acidity of this solution is 1.0N calculated on its total volume. This liquor is contacted in a countercurrent manner with 56 gm of finely ground solid KCl. The conditions, in particular the rate of flow of the liquor and the total time of contact, are so chosen that virtually all the KCl is converted to  $\text{KNO}_3$  by one single passage of the liquor. The solid end product, therefore, consists of  $\text{KNO}_3$  of a degree of purity of 98% or even higher. The solvent may be treated in one of several ways: (a) The solvent phase is mixed with one half its volume of benzene. The water and acid content of the solvent phase is separated as a bottom layer and can be drained off the solvent mixture. (b) The solvent phase is extracted with aqueous chloride brine whereby  $\text{HNO}_3$  is preferentially extracted."

Lovell (28) dissolved  $\text{NO}_2$  in a halogenated hydrocarbon such as carbon tetrachloride and then suspended KCl in the solution. Water in an amount equivalent to about 3% of the chloride increases the reaction rate. However, at 20-28° C. only about 55% of the KCl is converted to  $\text{KNO}_3$  in 90 minutes. In four hours 88.5% is converted. No mention is made of possible recovery of the  $\text{NOCl}$  released.

## Production of Potassium Nitrate at Vicksburg

The Southwest Potash Division of American Metal Climax began production of fertilizer grade  $\text{KNO}_3$  in its Vicksburg, Mississippi plant in the fall of 1963 (36). Although the plant was completed in the spring of 1962 a series of engineering difficulties delayed high level production. Company officials said the difficulties involved equipment and corrosion in unexpected areas. While the capacity of the plant has not been released it is reported to have cost \$7 million (25) and alternatively \$8 million (36).

Reportedly the plant is designed to turn out  $\text{KNO}_3$  and chlorine (from  $\text{KCl}$  and dilute  $\text{HNO}_3$ ) (25). However, until its patent position is entirely settled, the company will divulge little information about the process, nor will it reveal the capacity of the plant (36).

## Analysis

E. L. Nelson presented a method for determining the total nitrogen in materials containing nitrate (33). Wolf and Schier (49) have developed a conventional analysis for mixtures of  $\text{NOCl}$ ,  $\text{NO}_2$  and  $\text{Cl}_2$ . Details on these procedures are in Appendix A and Appendix B.

## Gas Chromatography

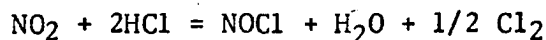
Horton has had some success in separating the oxides of nitrogens on a dry silica gel column, partly at ambient temperatures and partly

at elevated temperatures.<sup>1</sup> He claims to have also separated NOCl, N<sub>2</sub>O, and Cl<sub>2</sub>. His results are at best semiquantitative.

Others have separated N<sub>2</sub> and NO on silica gel columns both at elevated and dry ice temperature (2, 39).

NO and NO<sub>2</sub> have been separated on Ballantine glass spheres (41). The 0.02 mm spheres were cleaned with chromic acid, washed and then heated to 300° C. for 3 hours. The spheres were then placed in a column 4 mm i.d. by 4 feet long and conditioned with NO and NO<sub>2</sub> for 2 days. The separation was carried out at -25° C.

The products of the reaction



have been separated by gas-liquid partition chromatography (46). The separation was carried out at room temperature, using a 12 foot column of Celite 545 and dimethyl phthalate (50% by weight) with hydrogen as the carrier gas. The column would not separate NO<sub>2</sub> from the products of the above reaction so an excess of HCl was used.

Isbell separated various gases with a column containing 25% triacetin on non-acid washed -30 + 60 mesh Chromosorb P (Fisher Scientific Co.) (23). The column was 8 feet long by 5 mm i.d. copper tubing. The helium carrier gas was supplied at 18 psi and 108 ml/min measured at atmospheric pressure. Some of the retention times he found, in minutes, were CO<sub>2</sub>, 0.54; Cl<sub>2</sub>, 0.80; (CN)<sub>2</sub>, 1.02; NO, 0.48

---

<sup>1</sup>A. D. Horton, Oak Ridge National Laboratory Oak Ridge, Tennessee. Separation of the oxides and chlorides of nitrogen. Private communication. 1962.

and  $O_2$ , 0.48.

Runge separated various inorganic gases using a column packed with Aroclor 1232 on Haloport F (37). The following table gives retention times for various gases in a column 9 m by 6 mm i.d. filled with Aroclor 1232 on Haloport F in ratio 1:20. The carrier gas was 200 ml  $H_2$ /min and the temperature was 22° C.

Table 1. Retention time of various gases relative to air

Gas	Time, sec
Air	0
CO	0
CO <sub>2</sub>	12
HCl	36
HCN	147
(CN) <sub>2</sub>	89
Cl <sub>2</sub>	213
ClCN	426
COCl <sub>2</sub>	518
NOCl	323
SO <sub>2</sub>	253

Unfortunately the NOCl was dissolved in CCl<sub>4</sub> which gave the long retention time.

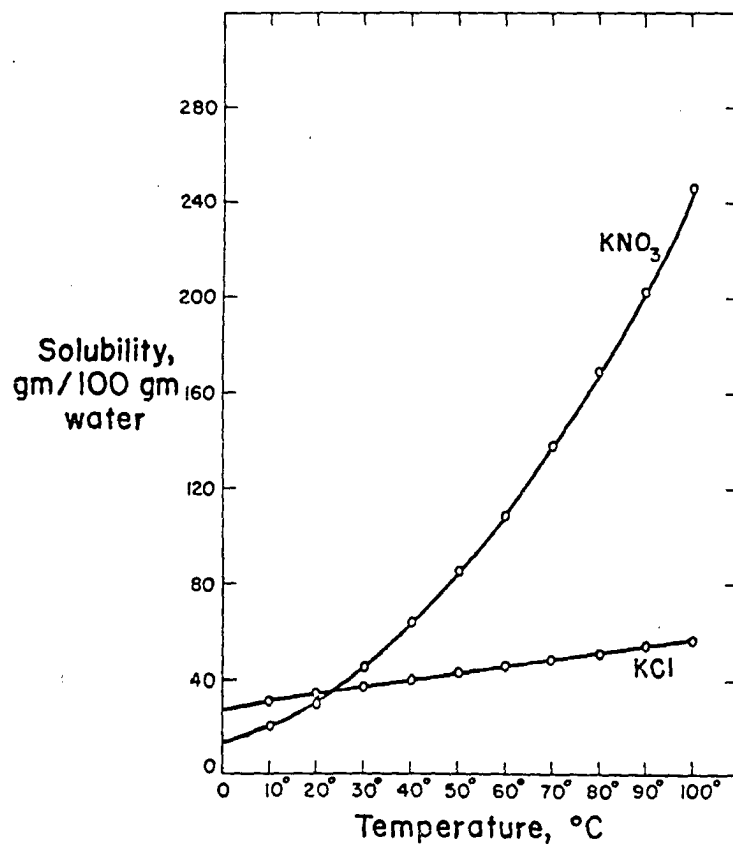
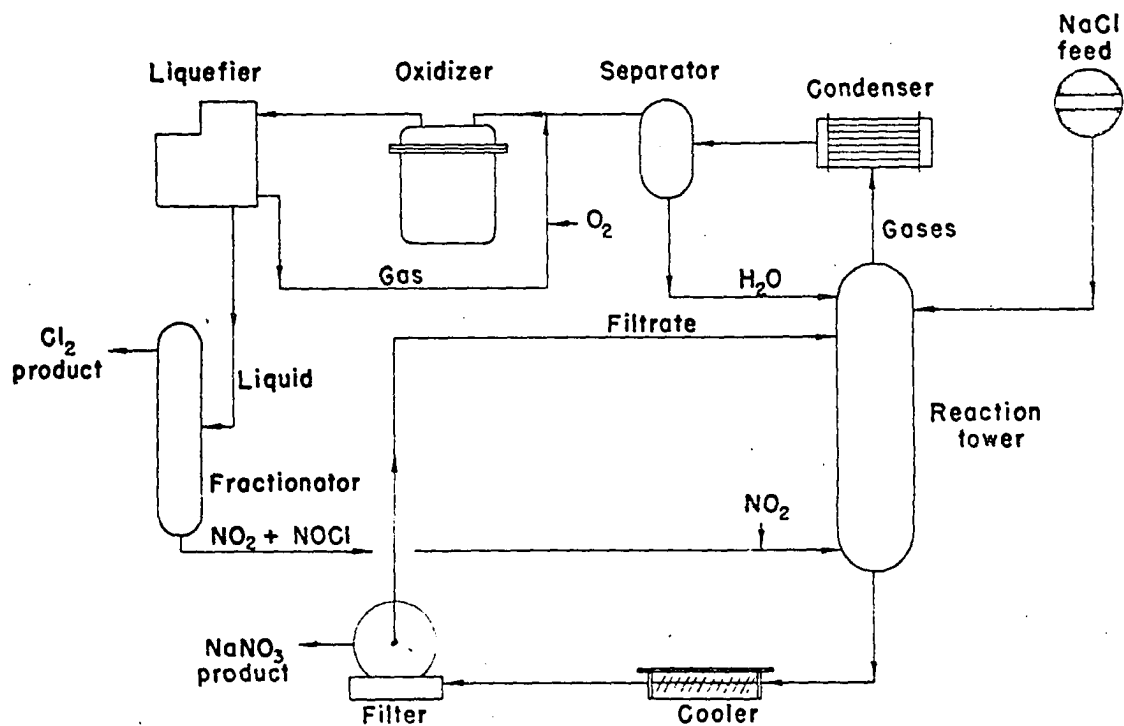
#### Solubility of KCl and KNO<sub>3</sub> in Water

Figure 2 shows the individual solubilities of KCl and KNO<sub>3</sub> in water (40). The KNO<sub>3</sub> solubility is much more temperature dependent

than the KCl solubility. These solubilities indicate the possibility of a fractional crystallization process in which  $\text{KNO}_3$  is crystallized, from a solution containing both KCl and  $\text{KNO}_3$ , by cooling the solution.

Figure 1. Solvay Process Company's sodium nitrate process (27)

Figure 2. Solubilities of  $\text{KNO}_3$  and  $\text{KCl}$  in water (40)





## GAS CHROMATOGRAPHY

## Introduction

Any reaction to produce  $\text{KNO}_3$  from  $\text{KCl}$  will probably form volatile compounds. A chromatographic analysis of these gases seemed to be the most desirable. Among these compounds there might be  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{NOCl}$ . Also air might be mixed with the gas from the reaction. Initially an attempt was made to separate all of these compounds. Later as the nature of the process was better defined and the gases actually present identified by wet methods of analysis many of these compounds were eliminated. In the final analysis it was only necessary to separate  $\text{NOCl}$ ,  $\text{Cl}_2$  and air. The development of a suitable chromatographic method for this separation is described below.

## Gas-Solid Chromatography

Silica gel

The column was prepared by filling a 1/4 in. o.d., 20 BWG 304 stainless steel tube 1.5 meters long with analytical grade silica gel. A particle size range of -20 + 35 mesh (U. S. Standard) was used. The column was then dried by heating at  $275^\circ$  for 2 hours.

Samples of  $\text{NOCl}$  and  $\text{NO}_2$  were injected into the column when it was at  $60$ ,  $80$  and  $100^\circ \text{C}$ . and the carrier gas flow rate was constant at 30 ml.  $\text{He}/\text{min}$ . No peaks were observed for either of these gases under

these conditions. However, at the same flow rate but a column temperature slightly higher than ambient, a  $\text{NO}_2$  sample showed a peak very close behind the air peak. At  $35^\circ \text{C}$ . peaks for both  $\text{NO}_2$  and  $\text{NOCl}$  were observed which were superimposed upon one another and overlapped the air peak. At  $40^\circ \text{C}$ . the air peak and the  $\text{NO}_2$ - $\text{NOCl}$  peak were farther apart but the  $\text{NO}_2$ - $\text{NOCl}$  peak had become quite low and flat. It was further observed at  $40^\circ \text{C}$ . that the  $\text{NO}_2$  or  $\text{NOCl}$  peaks became progressively lower and flatter when one sample after another was injected into the column. This was true even if the time between sample injections was increased to 20 min. and indicated that some gas from early injections may have been retained in the column, giving a poor analysis.

#### Glass beads

Minnesota Mining and Manufacturing Company's "Superbrite" glass beads (-200 + 325 mesh) were used to pack a column consisting of 10 ft. of 1/8 in. o.d., 20 BWG stainless steel tubing. Before being placed in the tubing the beads were washed in chromic acid and aqua regia and then dried.

Helium at 40 psig was used as the carrier gas. At gas flow rates of 11, 4.5 and 3.0 ml/min and  $-78^\circ \text{C}$ .,  $\text{NO}_2$  did not show a separate peak from air. Since the melting point of  $\text{NO}_2$  is  $-9.3^\circ \text{C}$ . it may have been retained in the column. At  $-25^\circ \text{C}$ . and 7.0 ml He/min flow rate neither  $\text{NO}_2$  nor  $\text{Cl}_2$  produced peaks which were distinct from the air peak. At room temperature and 6.0 ml He/min the introduction of a  $\text{NO}_2$  sample did

not produce a peak separate from the air peak.

#### Molecular sieves

A column was prepared from 7 ft. of 1/4 in. o.d., 20 BWG 304 stainless steel tubing and was packed with type 5A molecular sieves (-30 + 60 mesh). The column separated air at room temperature and a flow rate of 30 ml He/min. The O<sub>2</sub> came out at 6.5 min and the N<sub>2</sub> at 14 min. When Cl<sub>2</sub> was injected with air only the two original peaks showed up as was the case when linear temperature programming to 300° C. was employed.

At room temperature and a flow rate of 45 ml He/min the O<sub>2</sub> peak was at 4.6 min and the N<sub>2</sub> peak was at 11 min. When NOCl and NO<sub>2</sub> were individually injected into the column only a slight peak at 11 min was observed. This peak was probably due to air in the samples but in any case would not give a separation of these gases.

#### Alumina

An 8 meter by 1/4 in. o.d., 20 BWG copper tube was packed with F-20 Alcoa activated alumina (-20 + 100 mesh). At a flow rate of 30 ml He/min and room temperature air showed a peak in 6 min. A good NOCl peak appeared at 7 min but Cl<sub>2</sub> did not show a peak. Apparently Cl<sub>2</sub> was irreversibly absorbed.

When the flow rate was reduced to 20 ml He/min and the temperature increased to 50° C. the air peak appeared at 6.5 min and the

NOCl peak at 7.1 min. Again no peak was observed when Cl<sub>2</sub> was injected into the column.

### Gas Liquid Partition Chromatography

#### Aroclor 1232 on Halaport F

A 20 ft. by 1/4 in. o.d., 20 BWG stainless steel tube was packed with 1 part Aroclor 1232 on 20 parts Haloport F. At 27° C. and a flow rate of 195 ml He/min, air came out in a single peak at 1.2 min and NOCl, NO<sub>2</sub> and Cl<sub>2</sub> all came out in 1.4 min. At 22° C. and a flow rate of 115 ml He/min, air, NOCl, NO<sub>2</sub> and Cl<sub>2</sub> all came through the column in 1.1 min. The use of H<sub>2</sub> as the carrier gas did not improve the results.

#### 1, 2, 3 tris (2-cyanoethoxy) propane on Chromosorb P

A stainless steel tube 6 ft by 1/4 in. o.d., 20 BWG was packed with 40 gm of 1, 2, 3 tris (2-cyanoethoxy) propane on 100 gm of acid washed Chromosorb P. At room temperature and 85 ml He/min, NO<sub>2</sub>, Cl<sub>2</sub> and air all came through the column in 0.3 min. At 40 ° C. and 25 ml He/min, NO<sub>2</sub> and air still came out in a single peak at about 0.8 min, but chlorine appeared as a separate peak at about 1.1 min. The peak tailed badly, however, and in general was low and misshapen.

#### Dimethyl phthalate on Chromosorb W

Non-acid washed Chromosorb W was screened and the portion passing a 30 mesh screen and retained on a 60 mesh screen was used. This

material was coated with 50 gm of dimethyl phthate per 100 gm solid and was used to pack a 12 ft by 1/4 in. o.d., 20 BWG copper tube.

At room temperature and a flow rate of 30 ml He/min, air, Cl<sub>2</sub> and NOCl all came through the column in 1.3 min. At the same flow rate but at 75° C. these same gases gave a single peak at 1.2 min. Similar results were experienced at 50° C., 35° C. and room temperature with a flow rate of 92 ml He/min.

#### Triacetin on non-acid washed Chromosorb P

Non-acid washed Chromosorb P was coated with 25 gm triacetin per 100 gm Chromosorb and used to pack an 8 ft by 1/4 in. o.d., 20 BWG steel tube. This column was found to give separate peaks and was deemed satisfactory even though the NOCl peak led considerably. The best separation was observed at 75° C. and 100 ml He/min. The NOCl peak was better if the column was loaded with 5 ml NO<sub>2</sub> about 30 min before the analysis.

Figure 3 shows the peaks obtained when 400 ml of gas from the continuous reactor (containing air, Cl<sub>2</sub> and NOCl), was injected into the column. The air peak was attenuated to 1/4 of its relative size to insure that it did not go off scale.

Calibration plots were made showing volume of sample versus peak area. Figures 4, 5 and 6 show the calibrations used in the analyses made on the gases evolved during the continuous reactor runs.

Figure 3. Chromatographic analysis of reaction product gases using triacetin on non-acid washed Chromosorb P

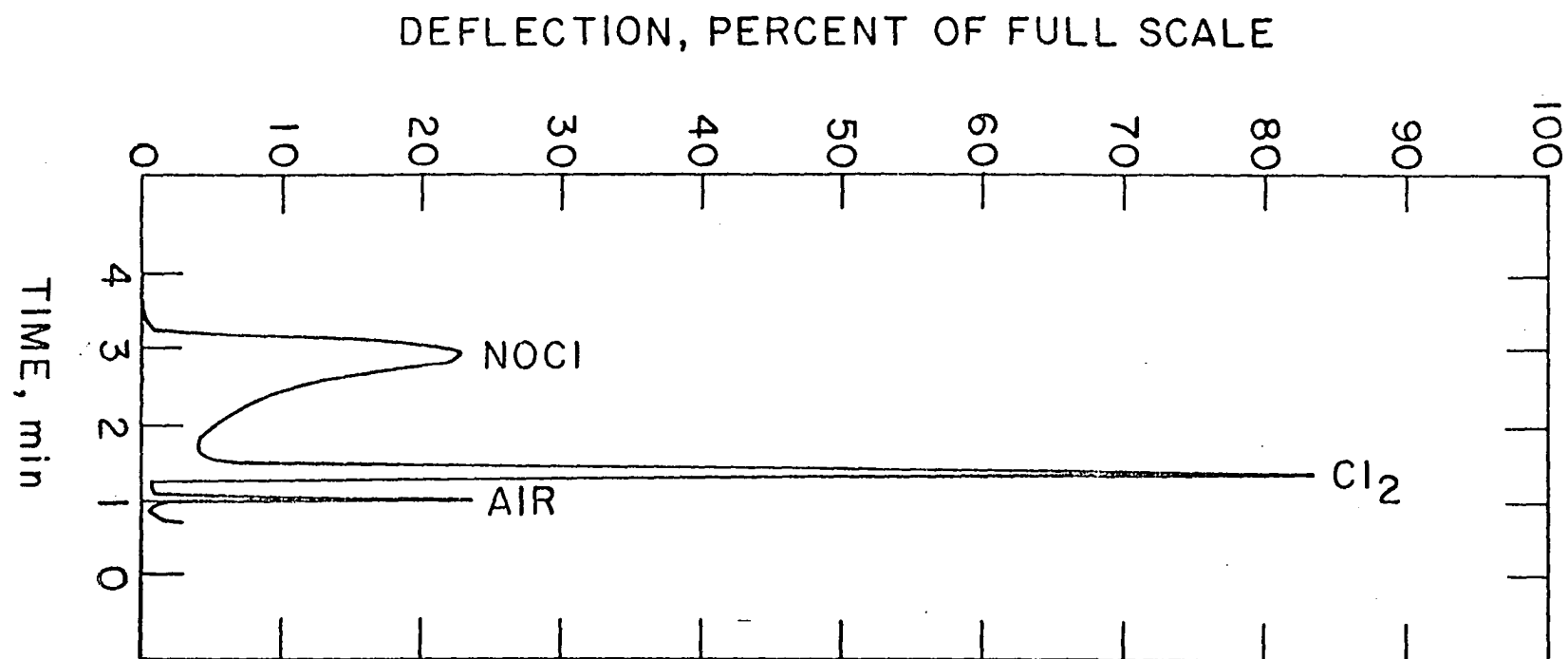


Figure 4. Peak area versus volume of air

Figure 5. Peak area versus volume of NOCl



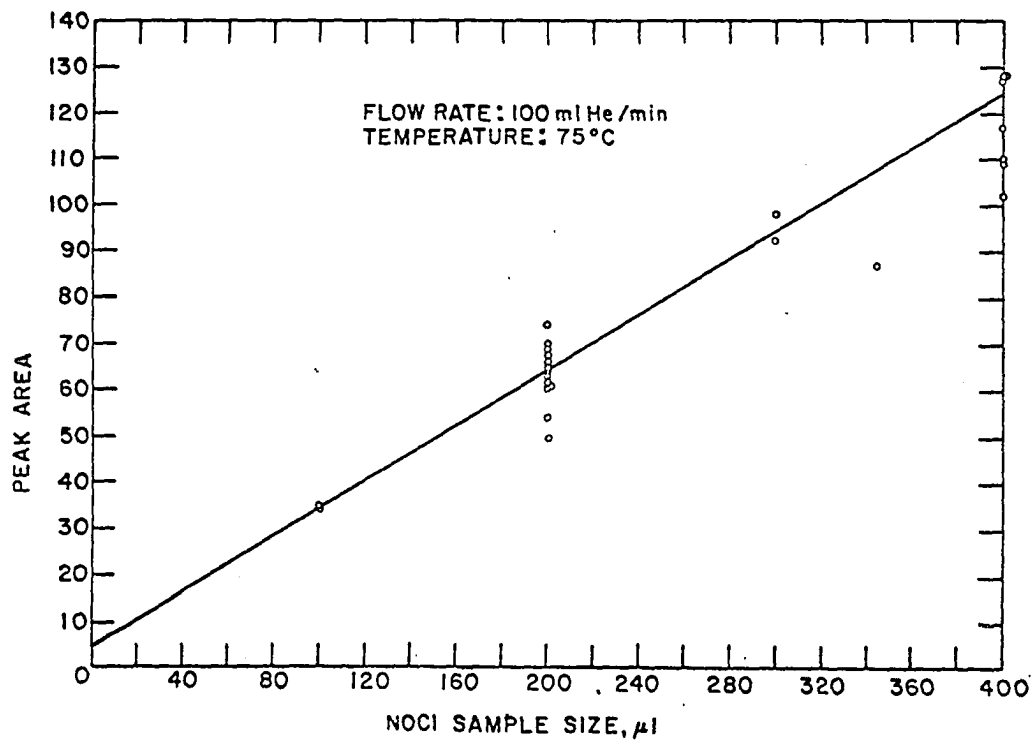
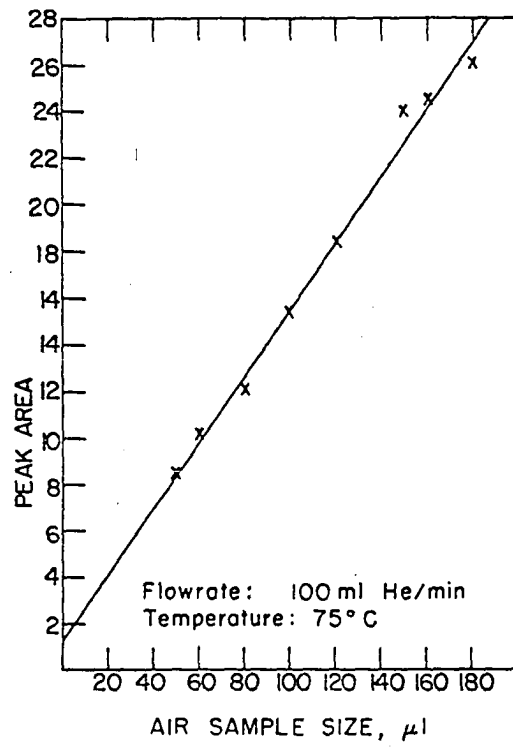
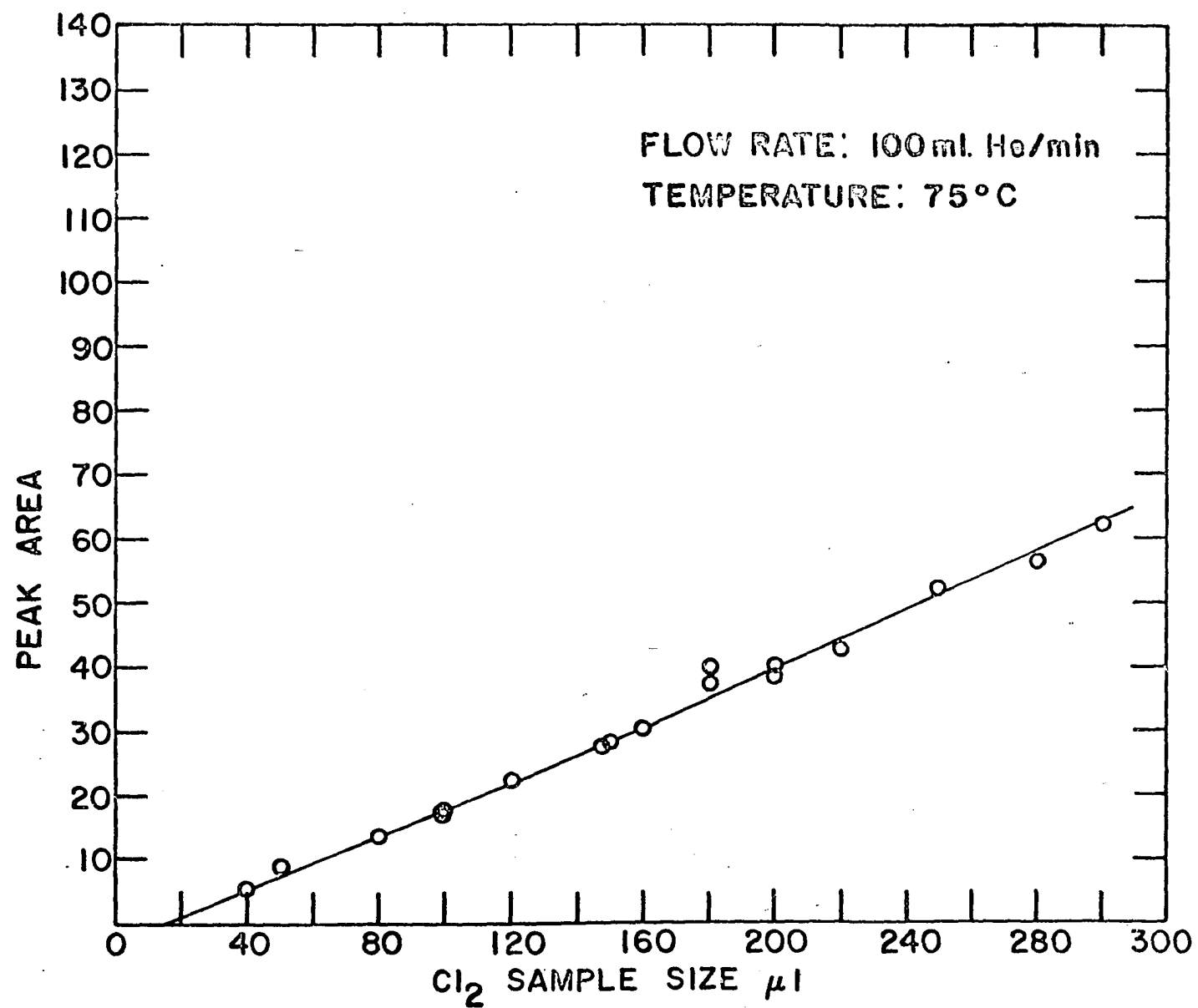


Figure 6. Peak area versus Cl<sub>2</sub> volume



## BATCH STUDIES

## Equipment and Procedures

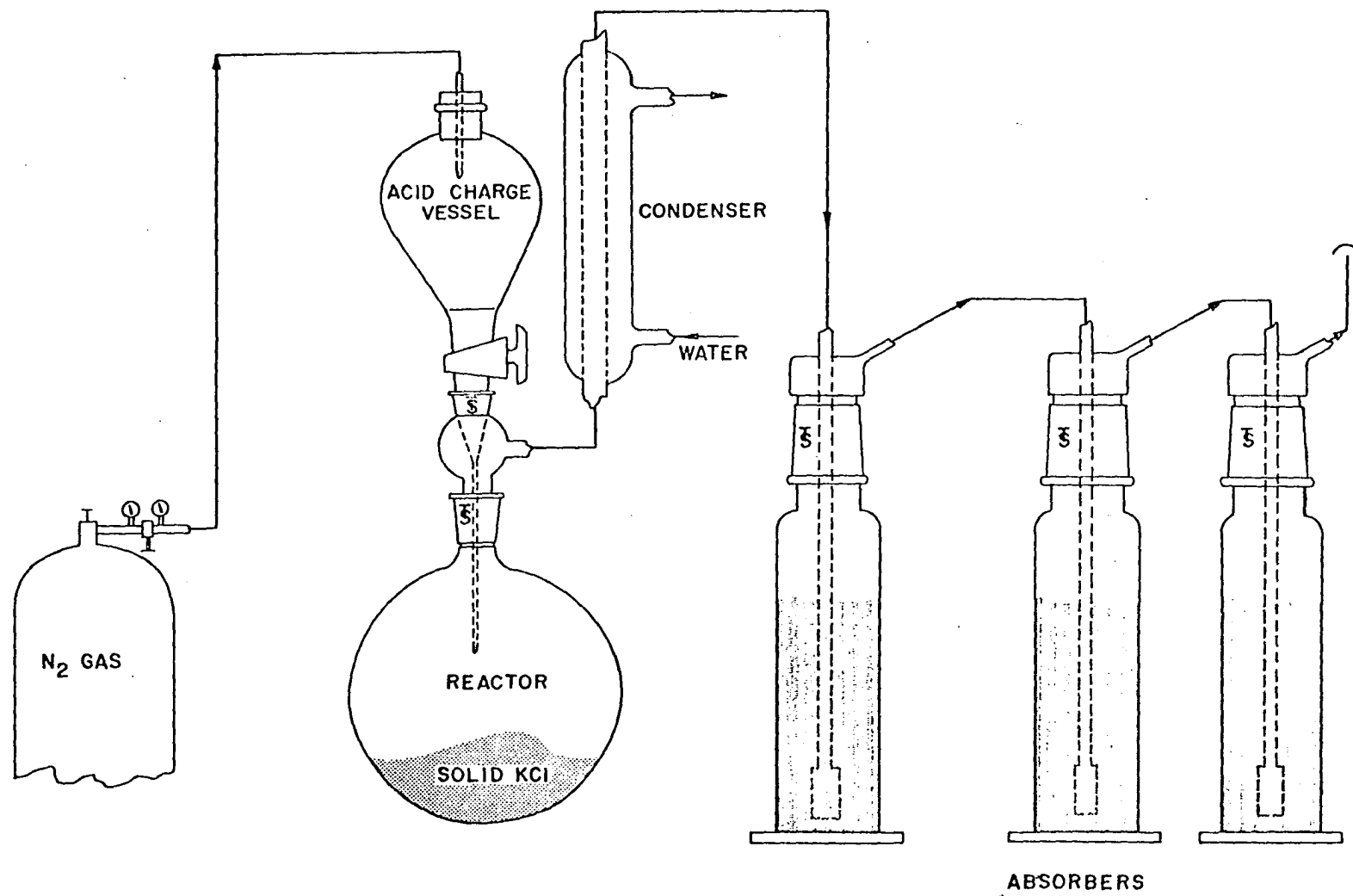
Figure 7 is a schematic drawing of the equipment. A 500 ml round bottom flask was used as the reactor and was fitted with a condenser and a vessel for adding the acid. The condenser in turn was connected to a series of absorbers fitted with fritted glass bubblers. Solid KCl was placed in the reactor and the reaction and absorption system was swept out with nitrogen gas. Then the acid was added to the reactor from the vessel and the reactor was kept in a constant temperature bath or heated with a flame. Normally the first two absorbers were charged with 96.7% sulfuric acid and the last one with a 10% solution of potassium iodide.

In the first two absorbers NOCl was expected to react to form  $\text{NOHSO}_4$  and HCl while the  $\text{Cl}_2$  was expected to react in the third absorber to form KCl and free iodine. Following the reaction the system was again swept out with nitrogen gas in order to pass any residual NOCl and  $\text{Cl}_2$  gas into the absorbers.

In some of the runs the first absorber was used as an oxidizer to oxidize the NOCl to  $\text{Cl}_2$  and nitrogen oxides. Nitric acid or manganese dioxide in hot nitric acid was used as the oxidizing agent.

Following the reaction the residue in the reactor was analyzed for  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions. The HCl which should have been formed in the first absorber by the reaction of NOCl with  $\text{H}_2\text{SO}_4$  was not found there.

Figure 7. Batch reaction equipment



Therefore, the  $\text{H}_2\text{SO}_4$  in the second absorber was replaced with water for one of the runs. The  $\text{HCl}$  was then absorbed in the water.

### Analytical Procedures

The chloride was determined by the gravimetric method for silver chloride. This was done by adding a solution of 0.25M silver nitrate to a solution of the material to be analyzed. Subsequently the precipitate of silver chloride was filtered, dried and weighed.

The nitrogen analysis was made by the method of Nelson (33). This method is described in Appendix A.

The method of Wolf and Schier (49), described in Appendix B, was used to analyze the products of the reactions between the gases and the various materials in the absorbers. The  $\text{KI}$  solution was analyzed for free iodine, using sodium thiosulfate.

### Results and Discussion

The data which were taken in the batch studies can be divided into two groups. One segment of the information consists of the data which were taken when there was an attempt in the first absorber to oxidize the nitrosyl chloride to free chlorine and other nitrogen products. The other part consists of those data that were taken when no attempt was made to alter the gases.

Runs I, III, VI, VII and VIII involved no attempt to oxidize the

nitrosyl chloride. Table 2 gives the material balances for these runs. During Run I the reactor was maintained in a constant temperature bath at 55° C; during the remainder of these runs at 72 to 74° C. The gases were bubbled through two sulfuric acid absorbers and then into a solution of 10% potassium iodide in water.

Table 2. Material balances for initial runs

Run temp, °C Item, moles	I 55		III 73	
	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
Used	0.0390	0.296	0.390	0.315
Residue	0.306	0.2152	0.360	0.2118
H <sub>2</sub> SO <sub>4</sub> absorber	0.0122	0.0128*	0.0333	0.0327*
Total N	(0.0122)		(0.0333)	
NO	(0.0128)		(0.0327)	
KI absorber		0.0160		0.0646
Total	0.3182	0.2440	0.3933	0.3091
Percent accounted for	81.85	82.50	100.8	98.2

\*Credit due to NOHSO<sub>4</sub> analysis, not actual Cl<sup>-</sup> analysis.



Table 2. (Continued)

Run temp, °C Item, moles	VI 73		VII 73		VIII 73	
	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
Used	0.388	0.296	0.388	0.302	0.388	0.300
Residue	0.360	0.187	(0.3555)	(0.2023)	(0.3381)	(0.1773)
Solid			0.1765	0.0668	0.2054	0.0511
Solution			0.1770	0.1355	0.1327	0.1262
H <sub>2</sub> SO <sub>4</sub> absorber	0.0338	0.0306*	0.0308	0.0302*	0.0370	
Total N	(0.0338)		(0.0308)		(0.0370)	
NO	(0.0306)		(0.0302)		(0.0382)	
KI absorber		0.0576		0.0536		0.0672
H <sub>2</sub> O absorber						0.0356
Total	0.3838	0.2752	0.3843	0.2861	0.3751	0.2801
Percent accounted for	99.00	93.00	99.15	94.80	96.70	93.50

The analyses were carried out as described above. From the results of Runs VII and VIII it can be seen that the solid residue was 20-25% KCl. This would naturally be an unacceptable level of chloride. Also from these material balances one can see that very little HCl or HNO<sub>3</sub> was evaporated from the reactor and that the expected reaction,



did occur. Runs were made with 4 moles of HNO<sub>3</sub> for every 3 moles of KCl.

Following the above experiments several were made in which the flask was heated with a flame and the solution was evaporated to dryness. It was hoped that by this method a product which was 100%  $\text{KNO}_3$  could be produced. Table 3 shows the compositions of the products of these runs.

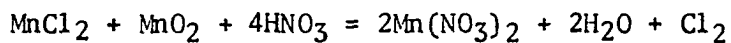
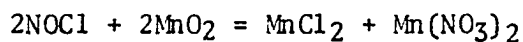
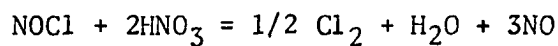
Table 3. Composition of material remaining in the flask after evaporating nearly to dryness

Run	$\text{NO}_3^-$ , moles	$\text{Cl}^-$ , moles	$\text{Cl}^-$ , mole %
IX	0.2822	0.106	3.6
XI	0.2705	0.0615	18.5
XII	0.300	0.056	15.7
XIII	0.292	0.0367	11.2
XIV	0.285	0.0284	9.1
XV	0.3122	0.029.	8.5
XVII	1.159	0.136	10.5

The data in Table 3 show that the residues of mixtures containing 4 moles of 60%  $\text{HNO}_3$  for each 3 moles of  $\text{KCl}$  contained excessive amounts of chloride ion. While the amount was not constant, it was in all cases too high to be acceptable.

Runs IX and XVII were also used to study the effectiveness of oxidizing  $\text{NOCl}$  with  $\text{HNO}_3$  or  $\text{MnO}_2$  in  $\text{HNO}_3$ . The reactions which were expected to occur when hot 70%  $\text{HNO}_3$  or  $\text{MnO}_2$  in 70%  $\text{HNO}_3$  was placed

in the first absorber are



From Table 4 it can be seen that these reactions did occur to a significant extent.

Table 4. Effectiveness of oxidizing NOCl with  $\text{HNO}_3$  or  $\text{MnO}_2$  in  $\text{HNO}_3$

Run	Oxidizing treatment	Portion of chloride evaporated from reactor which was found as free chlorine, percent
IX	none	65.2
XI	none	77.0
XII	$\text{MnO}_2$ in $\text{HNO}$	96.5
XIII	$\text{MnO}_2$ in $\text{HNO}_3$	91.5
XIV	$\text{HNO}_3$	92.6
XV	$\text{HNO}_3$	108.0
XVII	none	70.04

## SOLUBILITY STUDIES

## Technique

Laboratory

Aqueous  $\text{HNO}_3$  solutions containing both  $\text{KCl}$  and  $\text{KNO}_3$  and extending in concentration over the range of interest were added individually to an excess of both solid salts. These mixtures were then placed in a constant temperature bath. At equilibrium three phases were present which consisted of a solid phase for each of the two salts and an aqueous solution. After the system reached equilibrium part of the aqueous phase was decanted, weighed, placed in a volumetric flask and made up to volume in preparation for analysis. Solubility was studied at 0, 16, 30, 45 and 60° C.

Also aqueous solutions containing 0.304 gm of  $\text{HNO}_3$ /gm water were added to excess amounts of  $\text{KNO}_3$  and controlled amounts of  $\text{KCl}$ . These mixtures were allowed to come to equilibrium in a constant temperature bath at 30° C. At equilibrium two phases were present, solid  $\text{KNO}_3$  and an aqueous solution. Part of the solution was decanted, weighed and made up to volume with distilled water in a volumetric flask in preparation for analysis.

Analytical

Potassium was determined by a flame photometer using a propane flame and lithium as an internal standard. Chloride was found by the

silver chloride method. Nitrate was found by the standard Kjeldahl method. The acid content was found by titration with NaOH.

## Results and Discussion

### Mutual solubility of KCl and KNO<sub>3</sub>

Several figures were plotted to show the mutual solubilities of KCl and KNO<sub>3</sub> in aqueous solutions of nitric acid and various acid-water ratios and temperatures.

Figure 8 shows the solubilities at 0°C of KNO<sub>3</sub> and KCl in aqueous nitric acid solutions in contact with both KCl and KNO<sub>3</sub> solid phases. The curve reaches a minimum at about 0.31 gm HNO<sub>3</sub>/gm H<sub>2</sub>O. The value at this point is -0.312 gm KNO<sub>3</sub>/gm solvent or gm KNO<sub>3</sub>/gm (H<sub>2</sub>O + HNO<sub>3</sub>). Where the solubility is negative KCl has gone into solution and KNO<sub>3</sub> has salted out with the K<sup>+</sup> coming from the KCl in solution and the NO<sub>3</sub><sup>-</sup> coming from the nitric acid.

Figures 9, 10, 11 and 12 show the mutual solubility curves for KNO<sub>3</sub> and KCl solutions in contact with both KCl and KNO<sub>3</sub> at 16, 30, 45 and 60° C. The KNO<sub>3</sub> solubility curves for 0, 16, and 30° all have two relative minimums. The lower of the two minimums at 30° C occurs at about 0.30 gm HNO<sub>3</sub>/gm H<sub>2</sub>O. The solubility at this minimum is -0.195 gm KNO<sub>3</sub>/gm (H<sub>2</sub>O + HNO<sub>3</sub>). The KNO<sub>3</sub> solubility curves for 60 and 45° C have only one minimum each.

Figures 8, 9, 10, 11 and 12 also show the mutual solubility of KCl in solutions at 0, 16, 30, 45 and 60° C. These solutions are in

contact with solid KCl and  $\text{KNO}_3$ . Each KCl solubility curve shows a maximum and minimum. It can be observed that none of these curves extends into the negative region.

In general the solubility of both salts increases as the temperature increases, although this is not quite true for all of the curves. The KCl solubility does not respond very readily to temperature. Intuitively this would seem proper as in water the solubility of KCl does not increase with temperature nearly as much as does the solubility of  $\text{KNO}_3$ .

It was thought that the  $\text{KNO}_3$  curves should be similar at various temperatures. Therefore they were drawn as a series, i.e., the curves at 0, 16, 30° C were drawn in much the same manner even though the 16° C curve may have been drawn differently if no other data were taken. Also the KCl curves were drawn as a series. If only the data for 30° C were available this curve might have been drawn as a straight line.

At 0, 16 and 30° C the  $\text{KNO}_3$  solubility decreases rapidly from the value it has in water as the  $\text{HNO}_3/\text{H}_2\text{O}$  ratio is increased. This is due to a common ion effect. However, at about 0.3 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$  it reaches a low point and then increases rapidly. That the low points on the figures are the same as the actual low solubility point is doubtful for it would be fortuitous if the acid water ratio with the lowest  $\text{KNO}_3$  solubility had been chosen. However, there is little doubt that a rather abrupt minimum occurs. The KCl solubility does not

decrease very rapidly as  $\text{HNO}_3$  is added to the solution until a ratio of about 0.3 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$  is reached, or about the minimum  $\text{KNO}_3$  solubility point. Then as the  $\text{KNO}_3$  solubility increases rapidly the  $\text{KCl}$  solubility decreases rapidly. The  $\text{KCl}$  solubility experiences a minimum at the same place that  $\text{KNO}_3$  solubility experiences a relative maximum, 0.8 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$ . At 45 and 60° C much the same thing occurs at about 0.5 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$  but to a lesser extent. Apparently there is a fundamental change in the nitric acid-water system at a concentration of about 0.3 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$  at 0, 16, and 30° C with the same change occurring at a higher acid concentration at 45 and 60° C.

More data were taken at 30° C than at the other temperatures as this is a temperature which can be reasonably reached with cooling water and therefore is of more interest.

In order to separate  $\text{KNO}_3$  from  $\text{KCl}$  by a fractional crystallization process one needs a low  $\text{KNO}_3$  solubility and a high  $\text{KCl}$  solubility at a reasonable temperature such as the 30° C temperature previously proposed. Upon examining the 30° C solubility curves for the two salts one can see that at an acid to water ratio of about 0.30 the solubility of  $\text{KNO}_3$  is at its lowest value, -0.20 gm/gm ( $\text{H}_2\text{O} + \text{HNO}_3$ ) while the  $\text{KCl}$  solubility is high, about 0.30 gm/gm( $\text{H}_2\text{O} + \text{HNO}_3$ ). Therefore it would seem from solubility alone, ignoring other process requirements, best to crystallize  $\text{KNO}_3$  from a solution containing about 0.30 gm of acid per gm of water.

Solubility of  $\text{KNO}_3$  in solutions not saturated in KCl

It was desirable to know how much  $\text{KNO}_3$  might be crystallized upon cooling to  $30^\circ \text{C}$  any given solution containing 0.30 gm  $\text{HNO}_3$ / gm  $\text{H}_2\text{O}$  and various amounts of KCl and  $\text{KNO}_3$ . Therefore data were taken to determine the solubility curve shown in Figure 13. Point A is the mutual solubility point of KCl and  $\text{KNO}_3$  in a solution containing 0.304 gm  $\text{HNO}_3$ / gm  $\text{H}_2\text{O}$ . The solution is in contact with two solid phases, KCl and  $\text{KNO}_3$ . All other points on the curve represent solutions which are saturated with  $\text{KNO}_3$  but not with KCl. Above the curve is the unsaturated region and below it is the two phase region.

In the following section is a discussion of how much  $\text{KNO}_3$  could be crystallized by cooling reactor samples to  $30^\circ \text{C}$ . None of the typical samples taken would have become saturated in KCl by cooling to  $30^\circ \text{C}$ .



Figure 8. Mutual solubility of  $\text{KNO}_3$  and  $\text{KCl}$  at  $0^\circ \text{C}$

Figure 9. Mutual solubility of  $\text{KNO}_3$  and  $\text{KCl}$  at  $16^\circ \text{C}$

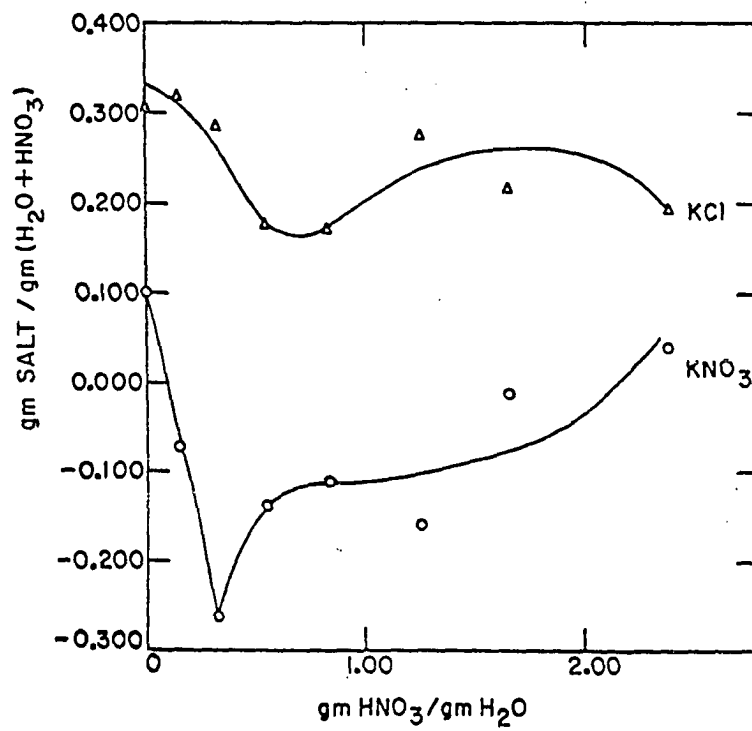
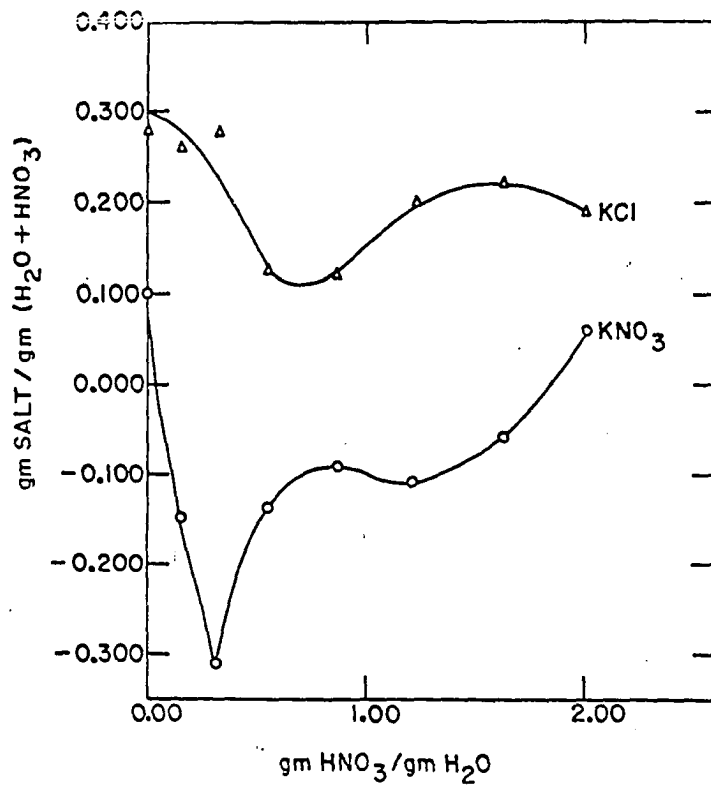


Figure 10. Mutual solubility of  $\text{KNO}_3$  and  $\text{KCl}$  at  $30^\circ \text{C}$

Figure 11. Mutual solubility of  $\text{KNO}_3$  and  $\text{KCl}$  at  $45^\circ \text{C}$

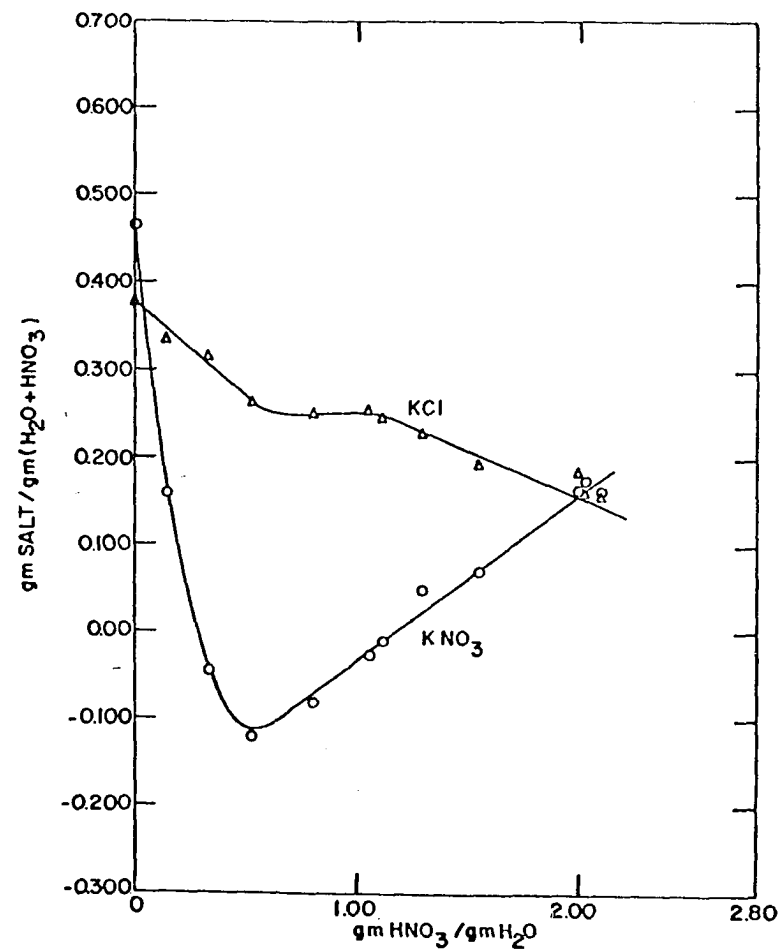
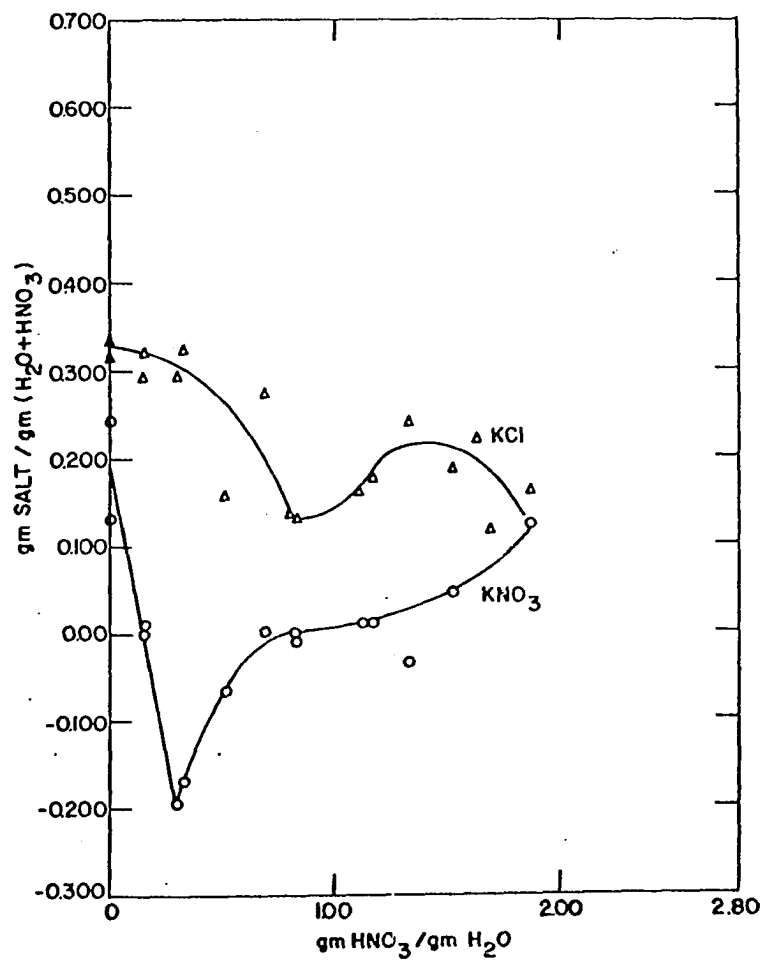
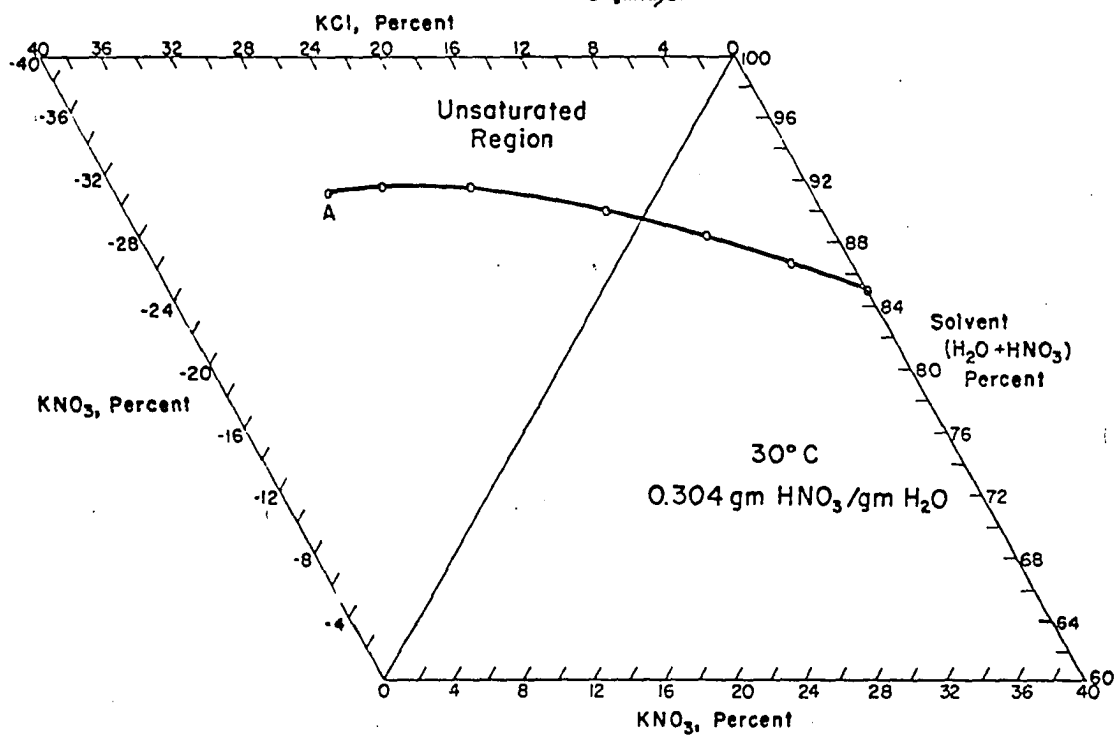
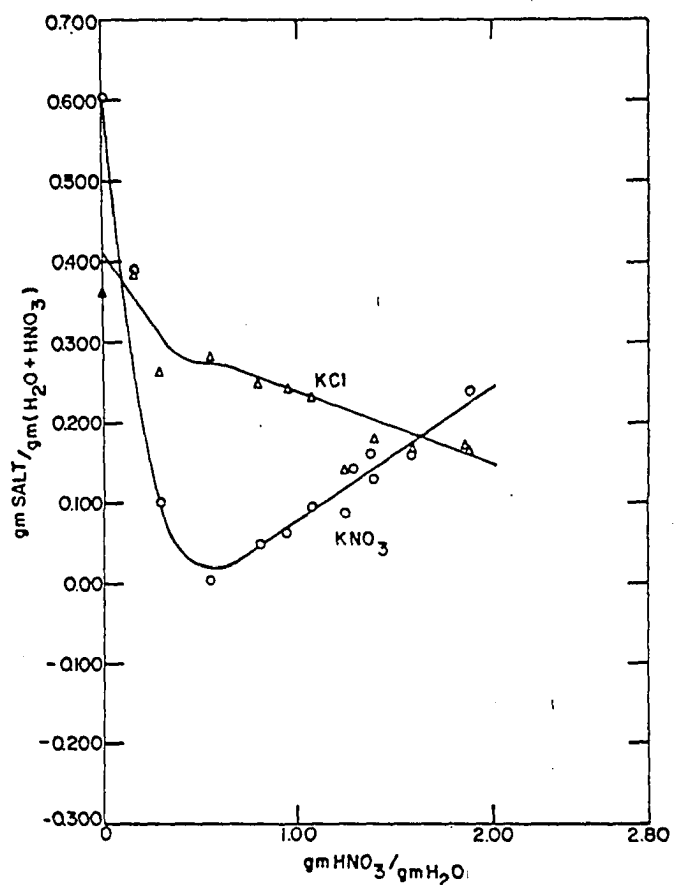


Figure 12. Mutual solubility of  $\text{KNO}_3$  and  $\text{KCl}$  at  $60^\circ \text{C}$

Figure 13. Solubility of  $\text{KNO}_3$  at  $30^\circ \text{C}$  in solutions of 0.304 gm  $\text{HNO}_3$ /gm  $\text{H}_2\text{O}$  containing various amounts of  $\text{KCl}$



## CONTINUOUS RUNS

## Runs without Supernatant Liquid Return

Equipment

Figure 14 is a schematic drawing of the equipment. The reactor was a three-necked, 1000 ml flask with a 600-watt heating mantle and a powerstat for temperature control. The reactor was fitted with equipment to withdraw the liquid, remove the gas formed, add solid KCl and nitric acid solution, and measure the temperature. Ejectors were used to maintain the vacuum.

The liquid was withdrawn through a fritted glass tube and collected in a 250 ml graduated cylinder. A heating tape was used to heat the liquid draw line to prevent precipitation of  $\text{KNO}_3$ .

The gas passed through a condenser to remove the water and any acid in the vapor, and the condensate was collected in a second 250 ml graduated cylinder. The temperature in the reactor was sensed with a copper-constantan thermocouple and recorded with a millivolt meter strip chart recorder. An opening in the vapor line was connected to a mercury manometer for pressure measurement.

Procedure and difficulties

The following procedure was used in the first runs with this equipment: 1. The acid feed rate was arbitrarily fixed and from this, the KCl feed rate was determined as  $3/4$  as great mole per mole. 2. The

pressure was arbitrarily set using the ejectors. 3. The liquid was withdrawn at a rate such that the potassium inlet and exit rates were equal. Additional water was added to replace the water which was removed in the draw. 4. The powerstat and thereby the vaporization rate was set so that the water removed as vapor equaled the water added and produced by reaction. 5. The liquid and solid products from the liquid receiver were analyzed for  $H^+$ ,  $K^+$ ,  $NO_3^-$  and  $Cl^-$  ions.

Two semi-continuous runs were made with the 1000 ml reactor using 60% by weight  $HNO_3$  and dry  $KCl$  as feed stock. Several difficulties arose in feeding the  $KCl$ . Also the liquid draw line frequently became plugged due to the fact that  $KNO_3$  crystallized from the nearly saturated solution upon only slight cooling. These difficulties shut down these runs before any significant data could be taken.

Subsequent to these runs it was decided to use 30% by weight nitric acid in order to minimize the difficulty encountered in withdrawing the liquid from the reactor. After this change it was possible to operate the equipment although the feeding problem still remained. Runs C, D and E were carried out using 30% by weight  $HNO_3$  feed.

### Results and discussion

Figures 15, 16 and 17 give the concentrations in the reactor of  $NO_3^-$ ,  $Cl^-$ , and  $H^+$  in moles per liter for runs C, D and E. During these runs 30% by weight  $HNO_3$  was fed to the reactor. In each of these runs the reactor temperature varied from about 95 to 100° C. The pressure was maintained between 660 and 710 mm Hg. The reaction was started



Figure 14. Continuous tests apparatus as initially constructed

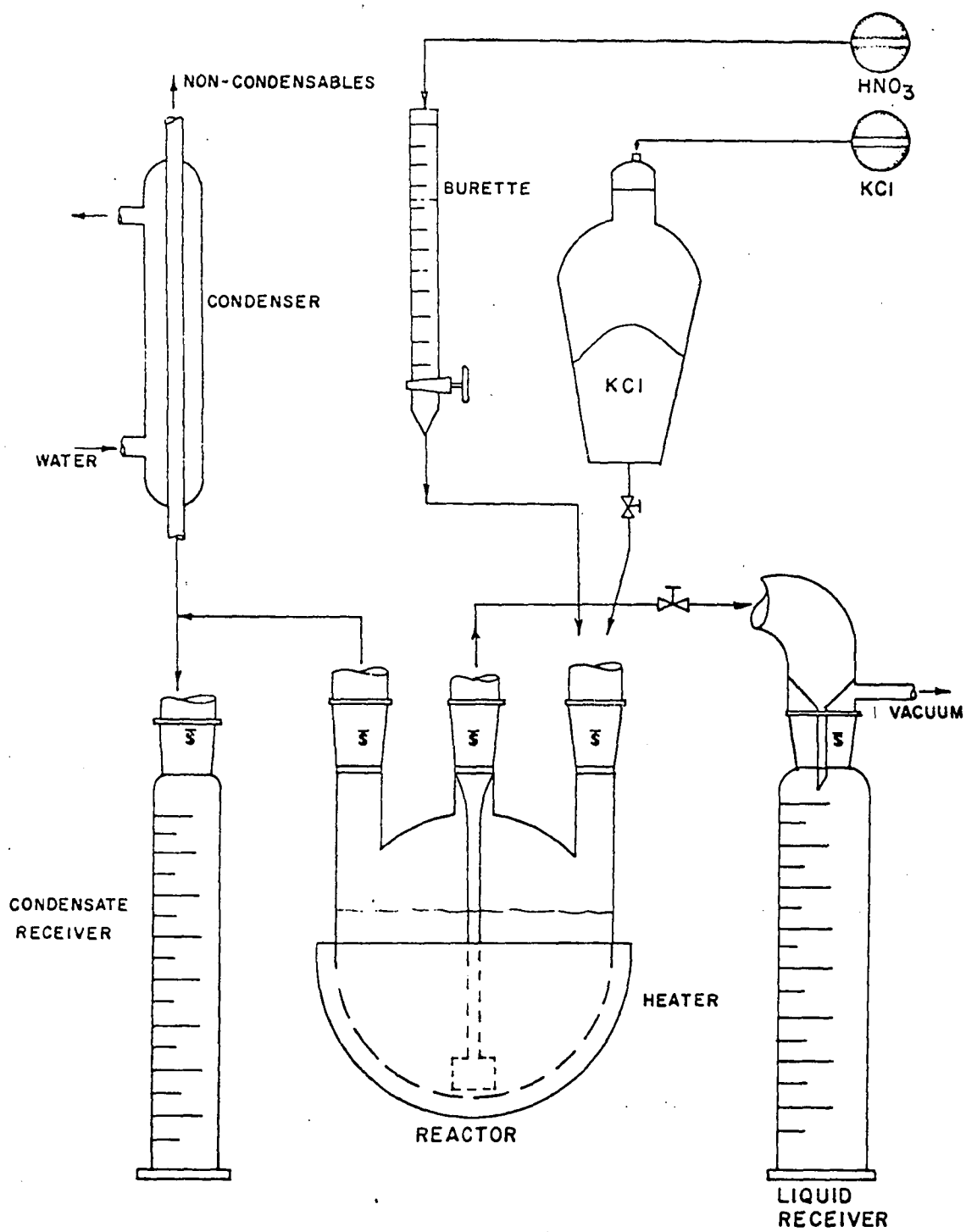
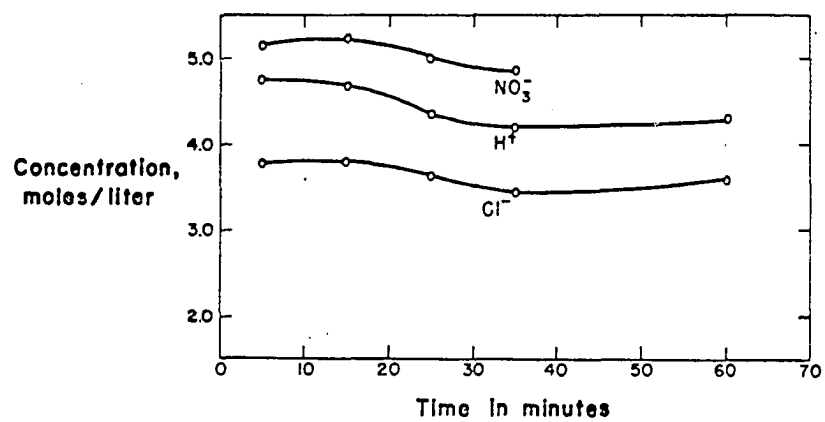
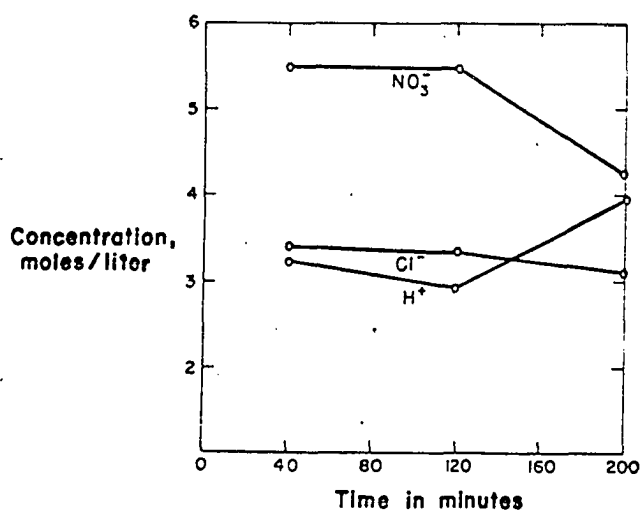
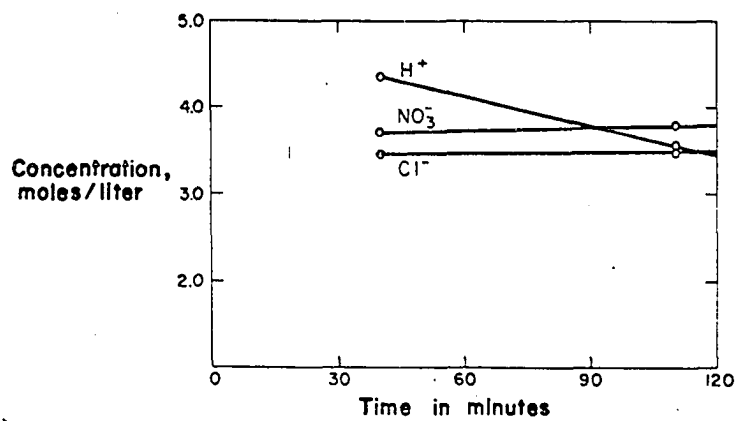


Figure 15. Draw composition for Run C with solid KCl and 30%  $\text{HNO}_3$  fed, reactor at  $100^\circ \text{C}$ .

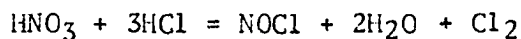
Figure 16. Draw composition for Run D with solid KCl and 30%  $\text{HNO}_3$  fed, reactor at  $100^\circ \text{C}$ .

Figure 17. Draw composition for Run E with solid KCl and 30%  $\text{HNO}_3$  fed, reactor at  $100^\circ \text{C}$ .



with reaction products equivalent to  $3/2$  moles of  $\text{KNO}_3$  formed in the vessel. Materials were added and withdrawn during each run at a rate of  $3/2$  moles of  $\text{KNO}_3$  formed per hour with an additional amount of water being added to compensate for the water withdrawn to the graduate cylinder. Considerable effort was expended to assure that these runs were the same. Nevertheless, one can see from the figures that the concentrations in the reactor were different for the different runs.

Further one can see that the ratio of  $\text{NO}_3^-$  to  $\text{Cl}^-$  did not increase much from the initial value of 4:3. This means that the reaction,



did not proceed as rapidly as desired at these concentrations. Also the figures show that there was considerable variation in the composition of the reactor solution between the three runs. This indicated that an approximation to a continuous process using the apparatus and procedure described was extremely difficult to attain and that a modified approach seemed advisable.

During these runs it was found that the material which crystallized from the liquid which was withdrawn from the reactor was pure  $\text{KNO}_3$ .

#### Runs with Crystallizer

##### Equipment and procedure

As a result of experience gained in the initial runs two changes were made in the equipment. The cylinder to which the reactor liquid

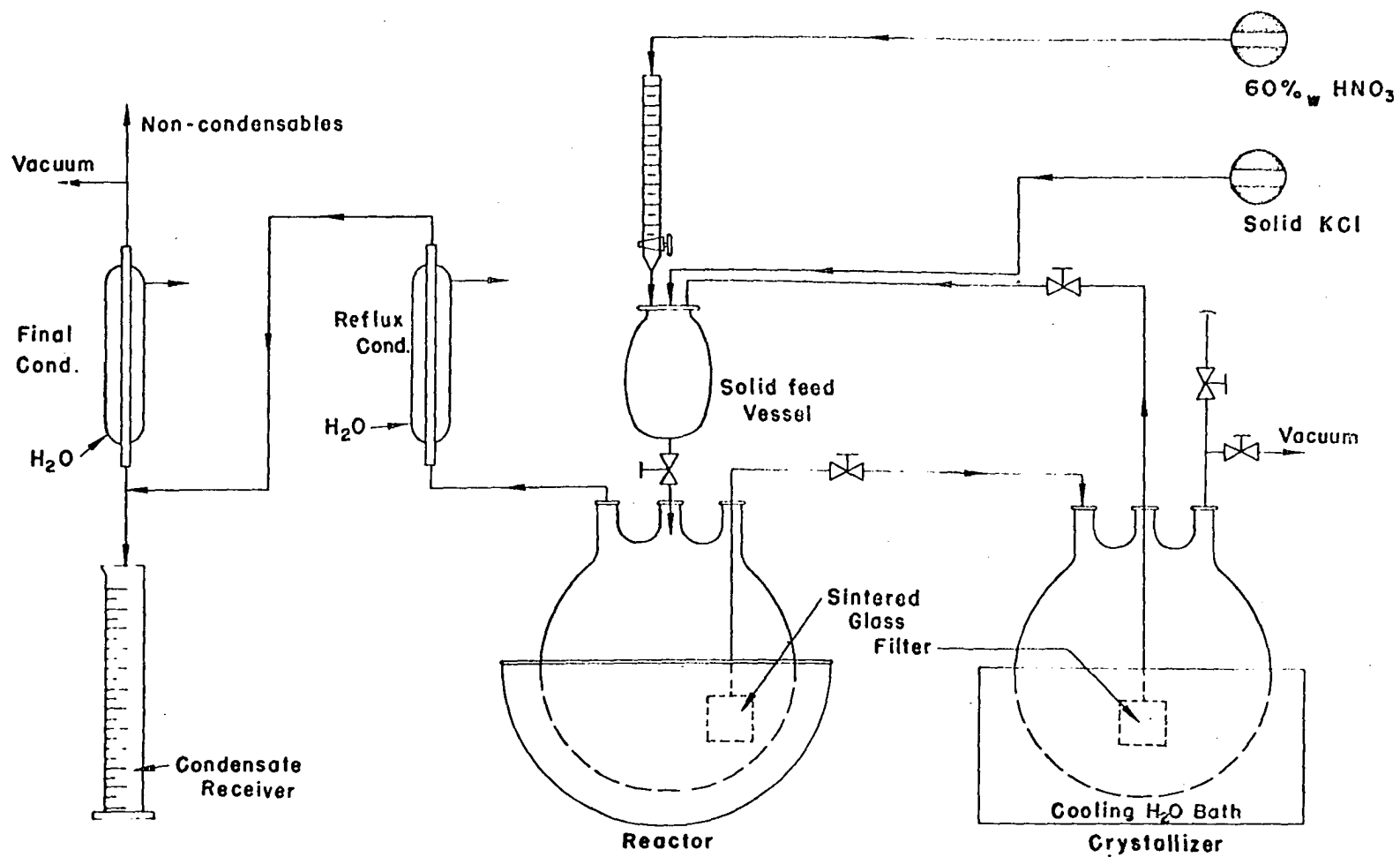
had previously been withdrawn was replaced with a three-necked 1000 ml flask cooled by a water bath. The flask contained a sintered glass filter from which a valved line was installed to the top of the solid feed vessel. A reflux condenser was added to the vapor line just above the reactor. The equipment so modified is shown in Figure 18.

Following these modifications the procedure was changed to the following:

1. An initial charge of 4 moles of acid per 3 moles of KCl was placed in the reaction flask.
2. The ejector was turned on and the pressure in the reactor was established at the desired value.
3. Water was allowed to flow slowly through the reflux condenser and at the normal rate through the final condenser.
4. The reactor heater was turned on.
5. Acid and KCl were added in the proper ratio. The acid was fed from a burette through the solid feed vessel. The KCl was charged to the feed vessel every 15 minutes and swept into the reactor by the acid feed and the returning supernatant liquid.
6. Liquid was withdrawn to the crystallizer from the reactor by opening the valve in the vacuum line to the crystallizer and at the same time opening the valve between the reactor and the crystallizer.
7. The liquid in the crystallizer was cooled to 30° C. to produce a crystal crop of  $\text{KNO}_3$ .
8. By reducing the vacuum in the crystallizer and opening the valve in the line to the solid feed vessel, the mother liquor was transferred to the solid feed vessel and on into the reactor.
9. Following the completion of the run the crystals were washed with an equal volume of water.

The rate of heat input to the reactor was used to control the rate

Figure 18. Apparatus used for continuous tests with crystallizer and reflux condenser added





of water removal as vapor from the reactor in such a manner as to avoid water build up or depletion in the reactor. The rate of solution transfer to the crystallizer was controlled so as to avoid a large build up of solids in the reactor.

### Results and discussion

Table 5 shows the results of Run 8. The acid was fed at the rate of 2 moles of  $\text{HNO}_3$  as 60% solution per hour and the solid KCl at a rate of 1.5 moles/hr. Initially the reactor was charged (1) with 60% solution containing 6.0 moles of  $\text{HNO}_3$  and (2) 4.5 moles of KCl. The run lasted 2 hrs and the average reactor pressure was 63 cm Hg absolute.

Table 5 shows the distribution of materials which were fed to the reactor. Only a small amount of  $\text{HNO}_3$  showed up in the condensate because only a small amount (100 ml) was collected. In order to keep water from building up in the reactor more condensate should have been collected.

The ratio,  $\text{Cl}^-/\text{H}^+$  was nearly the same in the supernatant liquid as it was in the crystals, i.e., 0.67. This indicates that the chloride reported as being in the crystals was actually in the supernatant liquid which was adhering to the crystals and not present as solid KCl. If it had been solid KCl the ratio of  $\text{Cl}^-$  to  $\text{H}^+$  would have been higher in the crystals than in the supernatant liquid.

The residue which shows up in the reactor is of little concern because in longer runs the amount of this material would be small when compared to the total processed.

Table 5. Material balance for continuous Run 8

Item	Cl <sup>-</sup>	Amount, moles			Ratio, moles/mole Cl <sup>-</sup> /H <sup>+</sup>
		NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>	
Condensate	0.0984	0.129	0.224	0.0036	
Supernatant from crystals	0.268	0.236	0.403	0.101	0.665
Crystals	0.776	4.43	1.14	4.06	0.681
Reactor residue	1.95	3.54	2.19	3.30	
Total accounted for	3.095	8.33	3.96	7.47	
Total added	7.50	10.0	10.0	7.50	
Percent recovered	41.3	83.3	39.6	99.6	

By examining Table 5 one can see the recovery of Cl<sup>-</sup>, and H<sup>+</sup> in the liquid and solid products was low, about 40%. The NO<sub>3</sub><sup>-</sup> was about 80% recovered in the liquid and solid products. The low recovery of these materials was due to the fact that they react to form NOCl and Cl<sub>2</sub> gas. The recovery of Cl<sup>-</sup> and H<sup>+</sup> was low for all runs. If the recovery of these materials were high it would indicate the reaction was not proceeding satisfactorily.

Table 6 shows the results of Run 9. The acid was fed at the rate of 2.0 moles of HNO<sub>3</sub> as 60% solution per hour and solid KCl at the rate of 1.5 moles/hr. Initially the reactor was charged with 6.0 moles HNO<sub>3</sub> as 60% solution and 4.5 moles of solid KCl. The run lasted

Table 6. Material balance for continuous Run 9

Item	Amount, moles				Ratio, moles/mole
	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup> /H <sup>+</sup>
Condensate	2.03	0.883	2.87	0.0501	
Wash of crystals	0.391	1.40	0.667	1.12	0.586
Supernate from crystals	0.167	0.205	0.287	0.0858	0.582
Crystals	0.006	5.131	-	5.19	
Reactor residue	0.334	2.50	1.93	0.901	
Total accounted for	2.93	10.1	5.76	7.35	
Total added	7.51	12.2	12.2	7.51	
Percent recovered	39.0	82.1	47.2	97.9	

1 hr and 10 min and the average reactor pressure was 52 cm Hg absolute.

Table 6 shows distribution of the materials which were fed to the reactor. The amount of condensate collected was larger than in Run 8. In this run 27.0% of the chloride, 10.6% of the nitrate and 22.4% of the acid appeared in the condensate. This illustrated the need for a counter current contacting device, such as a packed column between the reactor and the reflux condenser.

Again in Run 9 no KCl was crystallized. The ratio Cl<sup>-</sup>/H<sup>+</sup> was the same for the wash water as it was for the supernatant liquid,

indicating no solid KCl was dissolved by the wash water.

The water which was used to wash the crystals contained about 25% of the  $\text{KNO}_3$  which was crystallized. This showed that the wash water will have to be returned to the reactor and the need for a centrifuge or some similar device for separating the  $\text{KNO}_3$  crystals from the mother liquor and reducing the volume of wash water required.

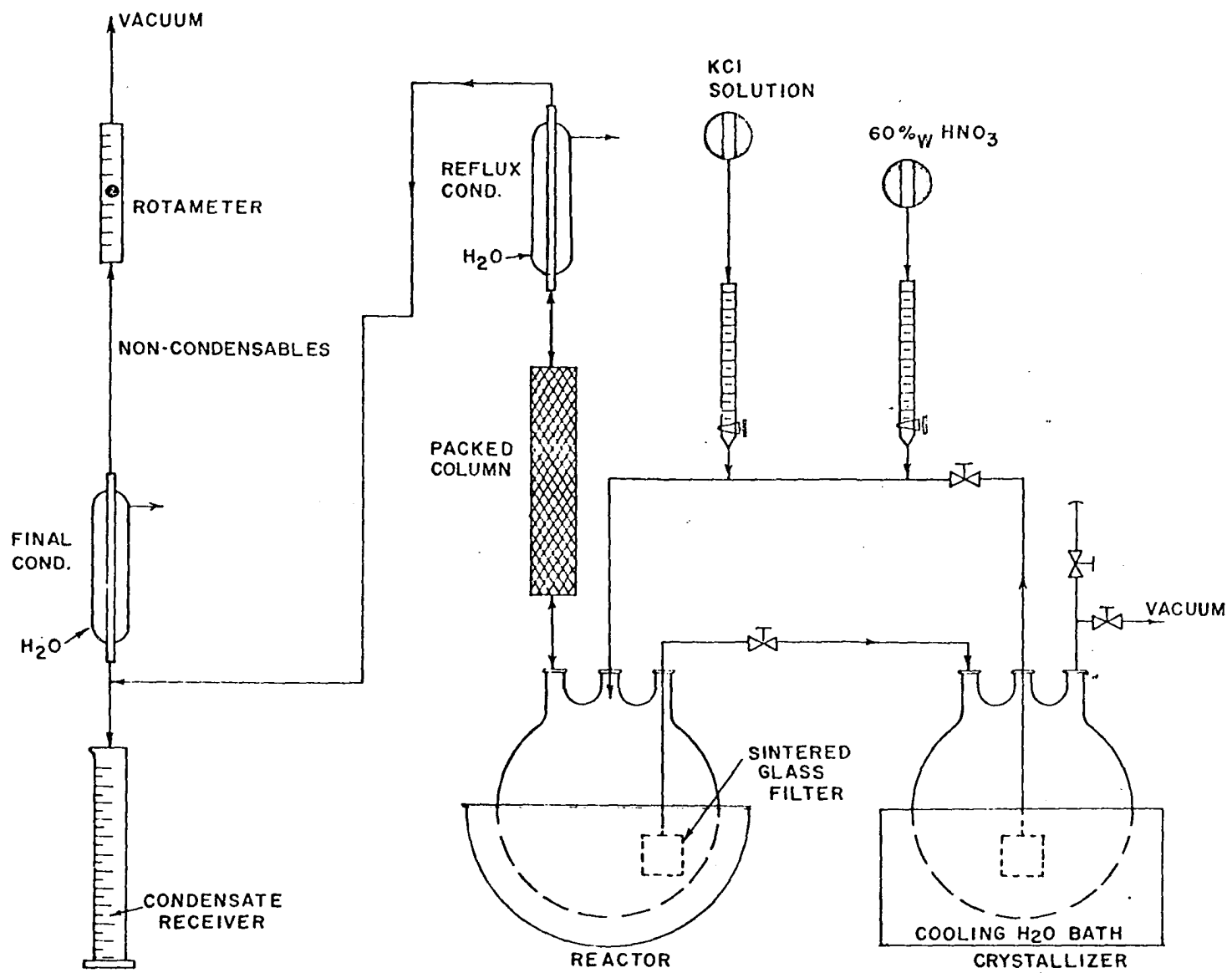
### Runs with Final Equipment Modifications

#### Equipment and procedures

One of the important final equipment modifications was the addition of a packed column, 2 1/2 in. o.d. by 18 in. long and packed with 1/2 in. Berl saddles, between the reactor and the reflux condenser. This column was added to the equipment to reduce the acid loss to the condensate from the final condenser. In a second change the solid feed vessel was replaced with a 100 ml burette. Finally, a rotameter was placed in the vacuum line to measure the flow of non-condensables. It was equipped with a Fischer and Porter precision bore flowrater tube FP-1/4-16-5/36 with a glass float, 1/4-C. D. The equipment with these modifications is shown in Figure 19.

The operating procedure was quite similar to that used previously. Some improvements were made possible by the equipment modifications. The condensate from the reflux condenser passed through the packed column, counter current to the gases evolved from the reactor. The column effluent then returned to the reactor. The KCl was added from

Figure 19. Continuous test apparatus with final modifications



the burette an aqueous solution with a concentration of 27.9 gm KCl/100 ml of solution. This allowed a steadier feed rate.

Measurement of the non-condensable gas flow rate in conjunction with the gas analysis allowed the reaction rate to be determined. Analysis of the various liquid products was carried out as described earlier. The gas was sampled periodically and analyzed as described in the section on gas chromatography.

### Results and discussion

Table 7 shows the results of Run 0-2, the duration of which was 3 hrs and 15 min. Four moles of  $\text{HNO}_3$  as a 60% solution and 3 moles of solid KCl were initially charged to the reactor. The reactor was fed 2.0 moles of acid and 1.5 moles of KCl per hour. Although the packed column had not yet been added and the rotameter was improperly installed this run is included in this section because KCl was fed as a solution. The run demonstrated the improvement resulting from the more uniform KCl feed rate.

During the run, four samples were taken from the reactor, the analyses for which are shown in Table 7. The samples were removed by attaching the existing draw line and a vacuum line to a sample bottle and opening the valve in the draw line. These samples represented typical material which might have been transferred to the crystallizer during the run.

In Run 0-2 about 20% of the chloride which was fed to the reactor as KCl was found in the condensate. The acid content ( $\text{HNO}_3$ , KCl, etc.)

Table 7. Material balance for Run 0-2

Item	Amount, moles			
	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>
Condensate	1.575	0.895	4.03	--
Supernate from crystals	0.894	0.558	1.10	0.340
Crystals	0.207	2.57	0.391	2.37
Reactor residue	0.313	3.69	0.398	3.61
Sample I	0.0676	0.272	0.0789	0.262
Sample II	0.0585	0.258	0.0772	0.236
Sample III	0.111	0.385	0.1450	0.364
Sample IV	0.0991	0.408	0.1488	0.366
Total accounted for	3.42	9.00	6.37	7.55
Total added	7.88	10.5	10.5	7.88
Percent recovered	43.4	95.0	60.6	95.9

was also high.

From the analyses the amounts of HNO<sub>3</sub>, KCl and KNO<sub>3</sub> in the reactor were determined. The ratio of gm HNO<sub>3</sub>/H<sub>2</sub>O gm was calculated for each sample withdrawn from the reactor. In each case the ratio was found to be between 0.3 and 0.4 and therefore near the value used in establishing Figure 13. Therefore, Figure 13 can be used as the solubility curve for these solutions at 30° C. A line from the KNO<sub>3</sub> vertex of the triangular plot, and the point given by the fraction KCl



and fraction  $\text{KNO}_3$  was drawn. The final composition of the solution upon cooling to  $30^\circ \text{C}$ . was given by the intersection of the line drawn through these two points with the solubility curve. Sample composition along with the amount of  $\text{KNO}_3$  which could be crystallized by cooling each solution to  $30^\circ \text{C}$ . and the  $\text{KCl}$  concentration of the resulting mother liquor are shown in Table 8. The results from two reactor samples withdrawn during Run 0-1 have been included.

As seen from Figure 13, the solubility of  $\text{KCl}$ , Point A, is 27.5% or 0.275 gm/gm of solution at  $30^\circ \text{C}$ . This is greater than any of the values which would be experienced upon cooling to  $30^\circ \text{C}$ . Therefore, no  $\text{KCl}$  would be crystallized from any of these solutions when they were cooled to  $30^\circ \text{C}$ .

From each of these solutions more  $\text{KNO}_3$  could be crystallized, upon cooling to  $30^\circ \text{C}$ ., than is reported as being in the solution. This is due to the fact that at  $30^\circ \text{C}$ . the mutual solubility of  $\text{KNO}_3$  solutions of these acid-water ratios and  $\text{KCl}$  contents is negative.

Tables 9, 10 and 11 show the results of Runs D-3, D-4 and D-5. These runs were carried out with the packed column in place and the results of Runs D-3 and D-4 indicate that the packed column did reduce the loss of  $\text{Cl}^-$  to the condensate. However, the respective values of 16.0% and 12.2% for loss of the  $\text{Cl}^-$  in the condensate are still too large. These losses indicate that a more effective contacting device or more reflux is needed. In Run D-4 an unexplainable low recovery of  $\text{K}^+$  ion was observed.

In Run D-5 19.1% of the  $\text{Cl}^-$  which was charged to the reactor was

Table 8. Potassium salts concentration in sample

Sample	Experimental			From plot	
	$\frac{\text{gm HNO}}{\text{gm H}_2\text{O}}$	$\frac{\text{gm KCl}}{\text{gm Sol'n}}$	$\frac{\text{gm KNO}_3}{\text{gm Sol'n}}$	gm KNO <sub>3</sub> cryt. on cooling to 30° C/ing to gm Sol'n 30° C.	Gm KCl/ gm Sol'n on cool- to 30° C.
I Run 0-2	0.362	0.116	0.451	0.527	0.245
II Run 0-2	0.399	0.110	0.459	0.522	0.230
III Run 0-2	0.319	0.117	0.350	0.409	0.198
IV Run 0-2	0.374	0.108	0.388	0.416	0.185
I Run 0-1	0.341	0.112	0.446	0.513	0.230
II Run 0-1	0.331	0.161	0.204	0.306	0.232

found in the condensate and only 40% was lost in the noncondensables. The run was carried out at 35 mm Hg and 192° F. as opposed to about 70 mm Hg and 220° F. for the other runs. This loss of Cl<sup>-</sup> to the condensate is rather high. The fact that total losses of Cl<sup>-</sup> and H<sup>+</sup> of only about 40% in each case, occurred indicated that the rate of generation of NOCl and Cl<sub>2</sub> was low.

For every mole of KNO<sub>3</sub> produced one mole of Cl<sup>-</sup> has to be removed from the system, otherwise the Cl<sup>-</sup> concentration will build up until KCl is crystallized with the KNO<sub>3</sub>. As the only provision for removing Cl<sup>-</sup> from the system is as Cl<sub>2</sub> and NOCl, the rate of generation of these gases indicates the rate of production of KNO<sub>3</sub>.

Table 9. Material balance for Run D-3

Item	Amount, moles			
	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>
Condensate	1.572	1.2746	2.8403	0.00
Wash from crystals	0.6042	0.8717	0.6638	0.8120
Supernate from crystals	2.065	0.8942	2.2886	0.7097
Crystals		6.950		6.950
Reactor residue	0.6365	1.155	0.8114	0.9412
Sample	0.1058	0.3886	0.1325	0.3596
Total accounted for	4.9835	11.534	6.7366	9.7725
Total added	9.850	13.00	13.00	9.850
Percent recovered	50.59	88.72	51.82	99.21

Table 10. Material balance for Run D-4

Item	Amount, moles			
	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>
Condensate	1.432	1.274	2.805	--
Wash from crystals	0.2916	0.6510	0.4018	0.5633
Supernate from crystals	2.477	1.650	3.361	0.8870
Crystals	--	3.833	--	3.833
Reactor residue	1.092	2.981	2.200	2.5166
Samples	1.010	2.492	1.353	2.161
Total accounted for	6.393	12.880	10.122	9.961
Total added	11.76	15.50	15.50	11.76
Percent recovered	54.36	83.09	65.30	84.70

Table 11. Material balance for Run D-5

Item	Amount, moles			
	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	K <sup>+</sup>
Condensate	1.592	0.8971	2.588	--
Wash from crystals	0.5421	0.6622	0.6546	1.198
Supernate from crystals	--	--	--	--
Crystals	--	4.941	--	4.941
Reactor residue	1.820	0.9095	2.202	0.6005
Sample	1.111	1.914	1.4644	1.657
Total accounted for	5.064	9.324	6.908	8.397
Total added	8.346	11.02	11.02	8.346
Percent recovered	60.68	84.64	62.71	100.6

A knowledge of the rate of the reaction was desired. The most direct method of measuring the reaction rate seemed to be to measure the rate at which gas was generated. It was for this purpose that the rotameter was added to the system. Because the system operated below atmospheric pressure it was expected that air would leak into the system. This was found to be true when samples of the gas were analyzed by gas chromatography. In order to find the product gas flow rate it was necessary to measure the total flow rate and multiply it by the percentage NOCl and Cl<sub>2</sub>.

Figure 20 relates rotameter reading and flow rate for a 50-50 mixture of Cl<sub>2</sub> and NOCl at 70° F. and 349 and 700 mm Hg absolute.

Figure 20. Rotameter reading for various flow rates of 50-50 mixtures of  $\text{Cl}_2$  and  $\text{NOCl}$  metered at 700 mm Hg abs.,  $70^\circ \text{F}$ . and at 349 mm Hg abs.  $70^\circ \text{F}$ . reported as cc/min of  $\text{NOCl}-\text{Cl}_2$  at  $75^\circ \text{F}$ ., 750 mm Hg abs.

Figure 21. Rotameter reading at various flow rates for air metered at 700 mm Hg,  $70^\circ \text{F}$ . and at 349 mm Hg  $70^\circ \text{F}$ . reported as cc/min of air at  $75^\circ \text{F}$ ., 750 mm Hg

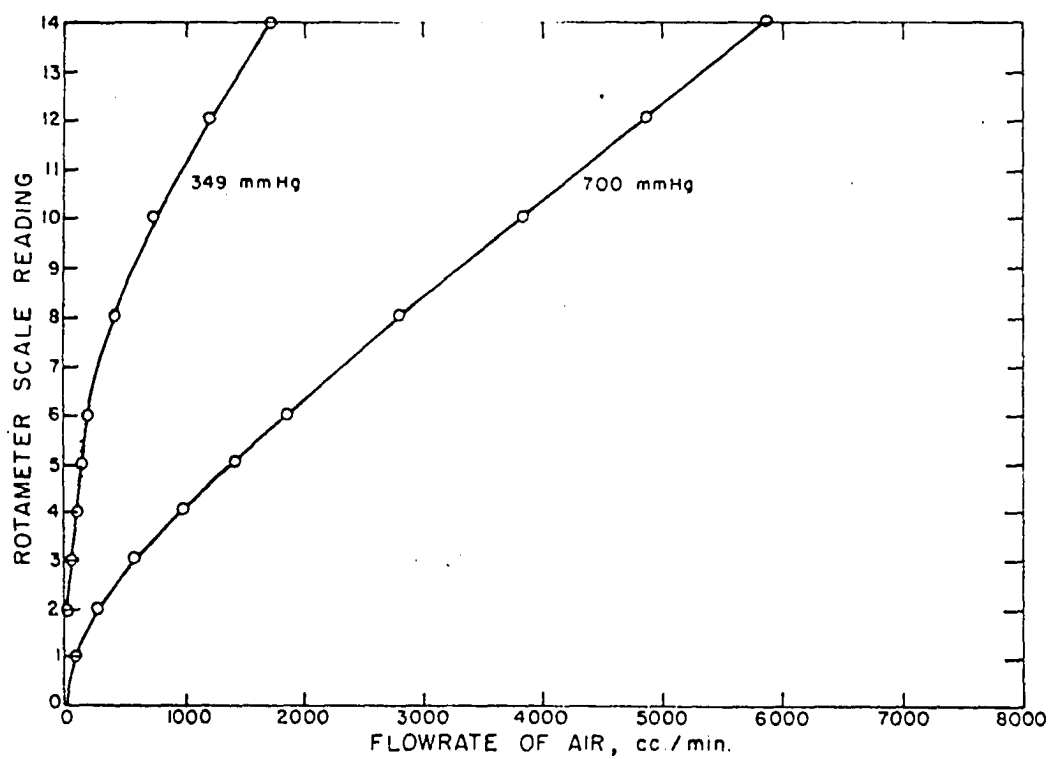
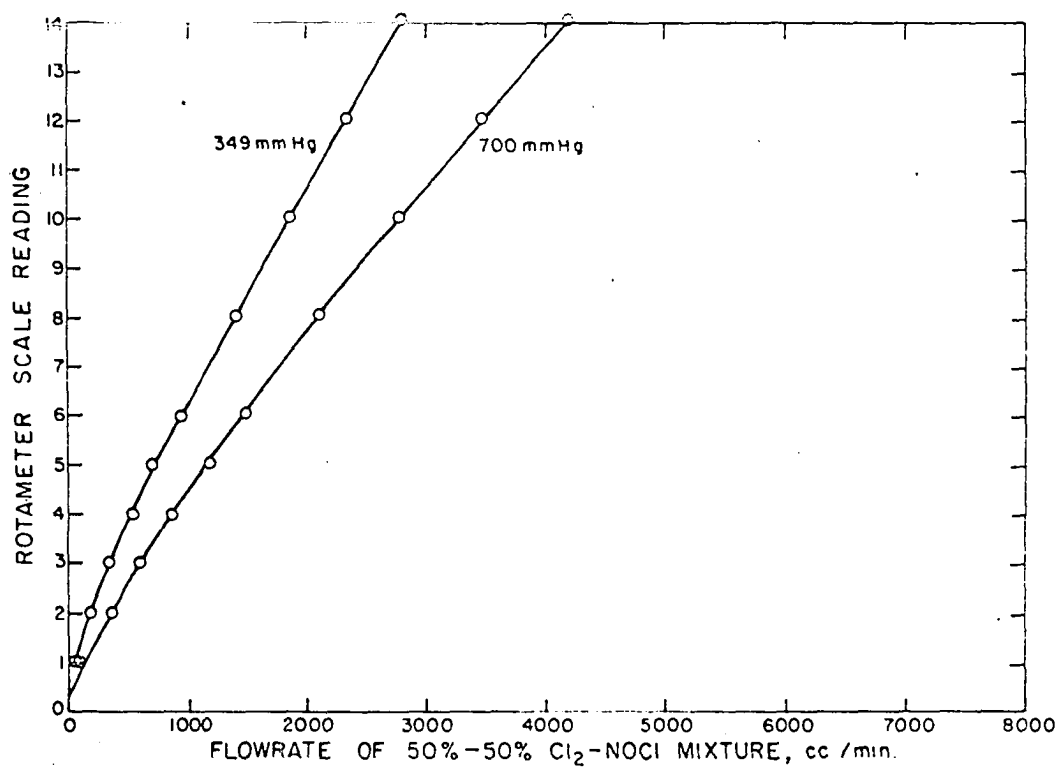
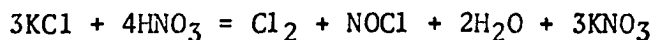


Figure 21 shows the same type of calibration curves for air. All of these curves were calculated from information given in Fischer & Porter catalog 10A910 (21), and are not based on experimental data. To use the curves the flow rates were estimated by reading the rotameter and then on the basis of gas composition interpolating between the two curves for a given pressure.

Run D-4 was made at a reactor pressure of 700 mm Hg pressure and temperature of 226° F., which was the boiling point of the solution at this pressure. Gas samples were taken and analyzed at the same time liquid samples were withdrawn. The latter were analyzed for  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{H}^+$  and  $\text{K}^+$  ions. From the gas analyses and the rotameter readings the rates were established.

A correlation between reaction rate and composition of the reactor solution was attempted. It was found that the rate did not correlate with any of the individual ion concentrations. Figure 22 shows the reaction rate plotted against the  $\text{H}^+$  ion concentration. The rate correlated no better with either  $\text{Cl}^-$  or  $\text{NO}_3^-$  concentration. The rate given here is the average flow rate of  $\text{Cl}_2$  and  $\text{NOCl}$  in moles per hour liter of liquids. This is a measure of the rate at which the following reaction occurred

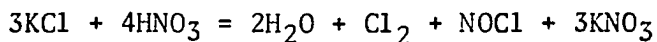


Following this initial attempt at finding a correlation between rate and composition an attempt was made to find a relationship of the type

$$R = K (\text{Cl}^-)^a (\text{H}^+)^b (\text{NO}_3^-)^c$$

by regression analysis, where;

(1) R = the rate of the reaction



in moles/(Hr) (liter of solution)

(2) K = the rate constant

(3) a, b and c are constants

The relationship was written in the form

$$\log R = \log K + a \log (\text{Cl}^-) + b \log (\text{H}^+) + c \log (\text{NO}_3^-)$$

Values of log K, a, b, and c for the data taken in Run D-4 were found by the method of least squares as shown in Ostle (35).

The relation found in this manner is

$$R = 1.70 \times 10^{10} (\text{Cl}^-)^{-4.7} (\text{H}^+)^{9.4} (\text{NO}_3^-)^{6.4}$$

The calculations are outlined in the appendix.

Figure 23 is a plot of the above equation. It can be seen that this experimental data do not fall very close to the line. Also the exponents are too large and the negative exponent for  $\text{Cl}^-$  concentration is questionable. Because of the negative exponent the relationship gives the nonsensical predication that if the  $\text{Cl}^-$  concentration were allowed to go to zero while the other concentrations remained above zero the reaction would proceed at an infinite rate. From the above it seemed logical to assume that the data did not fit a line of the type

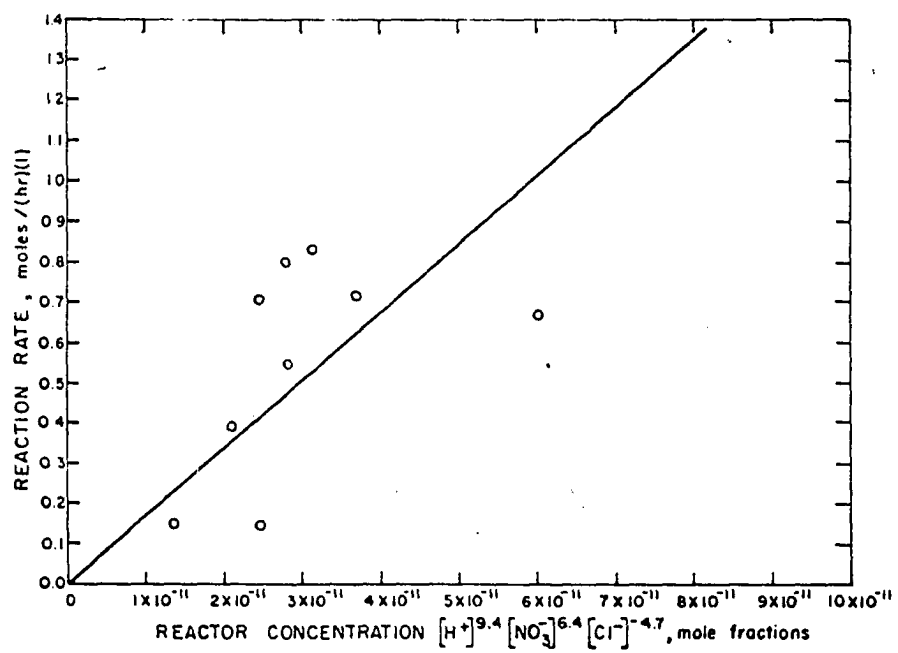
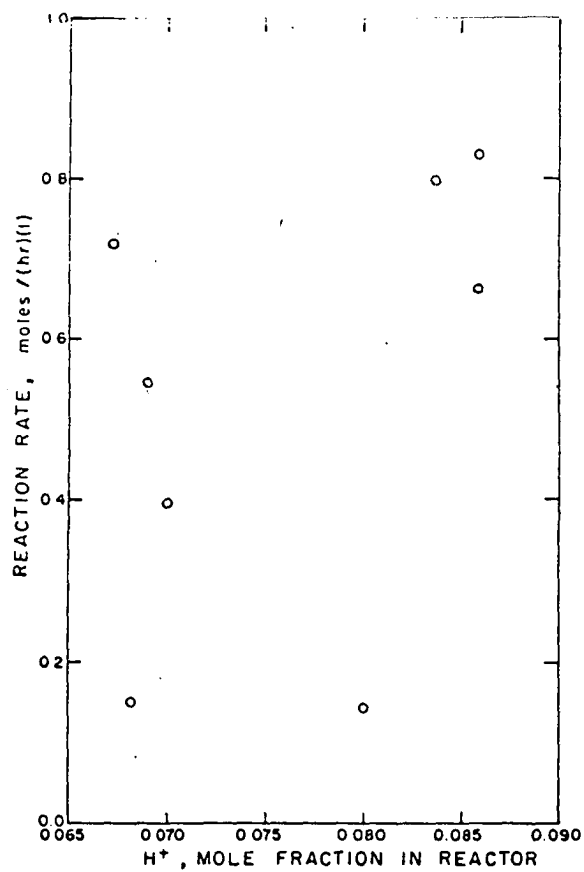
$$R = K (\text{Cl}^-)^a (\text{H}^+)^b (\text{NO}_3^-)^c$$

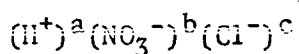
The rate was then plotted against the factor



Figure 22. Reaction rate plotted against  $(H^+)$  for Run D-4, 226° F.

Figure 23. Reaction rate as a function of the concentration factor  $(H^+)^{9.4}(NO_3)^{6.4}(Cl^-)^{4.7}$ , data and least squares line through the origin, data from Run D-4, at 226° F.





arbitrarily assuming whole integers for the exponents. While this is only a search method, it removes the restrictions that the line pass through (0,0) and that the line be straight. This allows for the possibility that the reaction may fall to zero before the concentrations reach zero.

Figure 24 shows the rate plotted against the factor  $(H^+)(Cl^-)$ , Figure 25 against the factor  $(H^+)^2(Cl^-)(NO_3^-)$ , and Figure 26 against the factor  $(H^+)^3(Cl^-)^2(NO_3^-)$ . Figure 26 seems to be the most satisfactory curve. A smooth curve can be drawn through most of the points. Through part of the points a straight line can be drawn. For this straight line portion of the curve the following relation can be written

$$R = 8.13 \times 10^7 (H^+)^3(NO_3^-)(Cl^-)^2 - 1.59 \times 10^{-7}$$

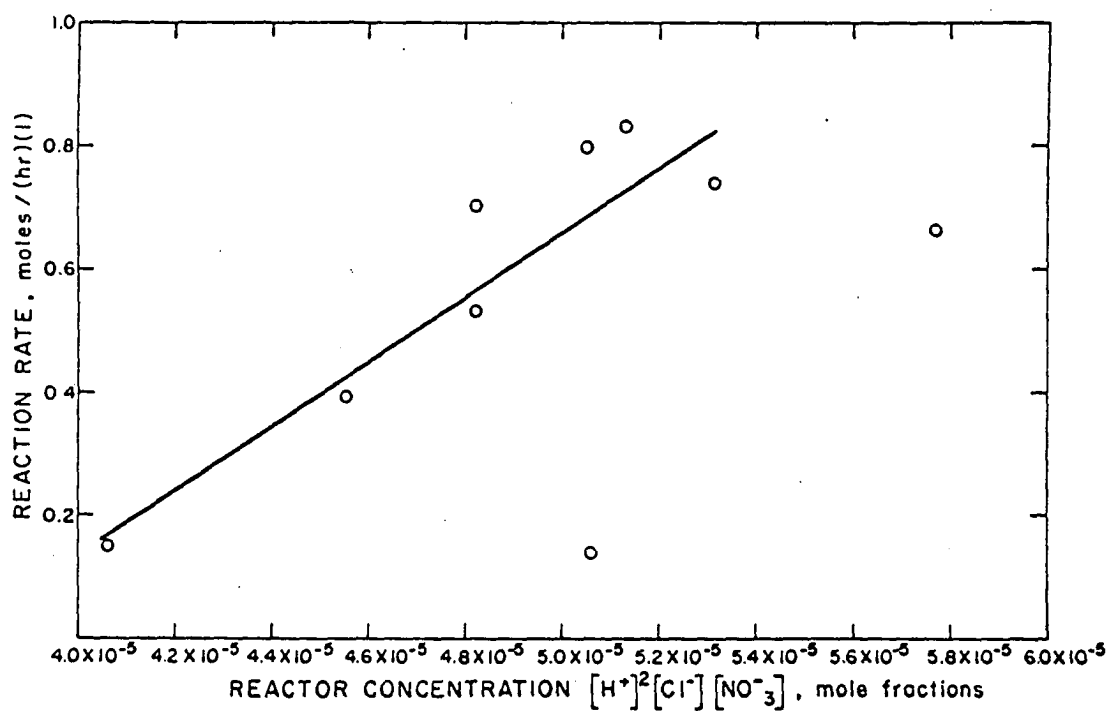
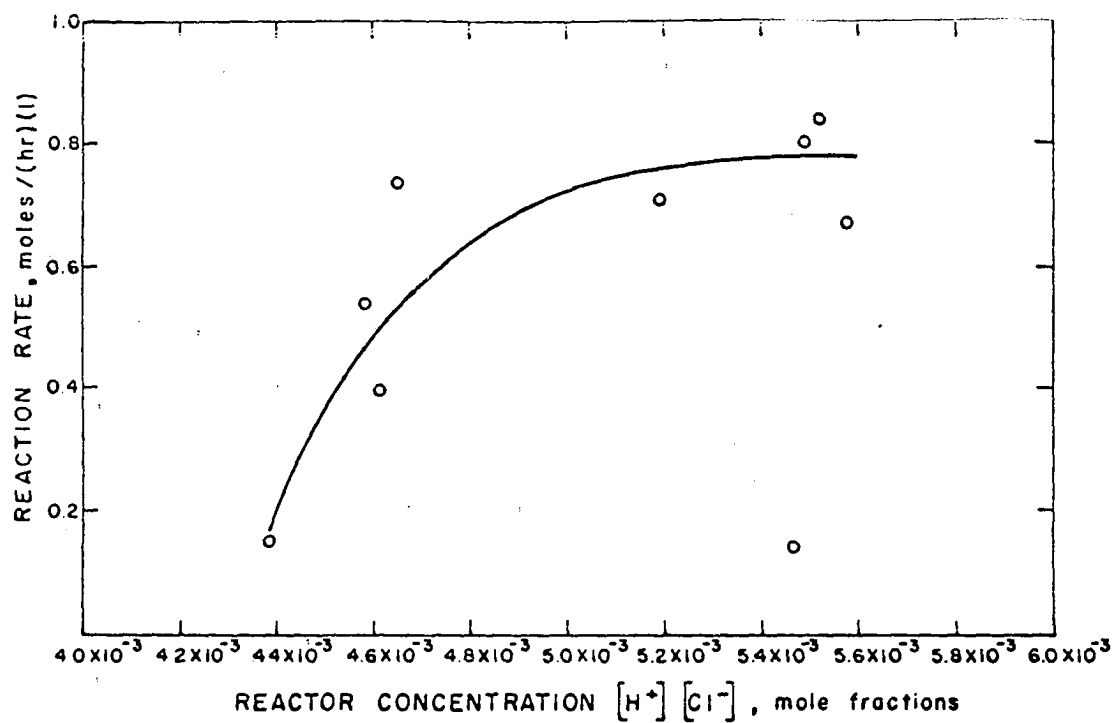
However this relationship cannot be used with confidence outside of the interval over which the plot is linear. Figure 26 shows the rate for Run D-5 plotted against the factor  $(H^+)^3(Cl^-)^2(H^+)$ : These data were taken at a pressure of 349 mm Hg absolute and 192° F.

The factor against which the reaction was plotted in Figure 26 seemed to involve many more elements than would enter into the rate controlling step of a reaction, six. However, it may be that two moles of HCl react with one mole of  $HNO_3$ . If this were true, a factor such as the one used would be necessary.

Comparison of Figure 26 with Figure 27 will show that the

Figure 24. Reaction rate for Run D-4 against the concentration factor  $(H^+)(Cl^-)$ , 226° F.

Figure 25. Reaction rate for Run D-4 plotted against the concentration factor  $(H^+)^2(Cl^-)(NO_3^-)$ , 226° F.



reaction rate falls off sharply as the temperature is decreased. This is true even though lower pressure accompanies the lower temperature. This lower pressure might cause the gas to be more readily removed from the reactor. Even so, the reaction was much slower at the lower temperature.

The possibility that the gas composition could be varied from the mole ratio of  $\text{Cl}_2$  to  $\text{NOCl}$  of unity did not seem too great. However, if it were possible to increase the ratio it would reduce the expense of processing the  $\text{NOCl}$ . This would make any process much more attractive. Studies were made at  $192^\circ \text{F}$ . and  $226^\circ \text{F}$ . to determine if changing the ratio of acid to chloride changed the gas composition and also to see if the reaction rate changed the gas composition. The results are shown in Figures 28 and 29. Only one point showed a significantly higher  $\text{Cl}_2/\text{NOCl}$  ratio. This point was at a very low gas flow rate. The samples at low reaction rates contained small amounts of  $\text{Cl}_2$  and  $\text{NOCl}$  relative to the amount of air present and therefore analysis was less reliable. Figures 28 and 29 show no correlation between acid chloride ratio and gas composition. Neither do they show a correlation between reaction rate and gas composition. By examining the data it can be seen that there is no significant change in gas composition when the temperature is changed from  $192^\circ \text{F}$ . to  $226^\circ \text{F}$ .

Figure 26. Reaction rate for Run D-4 plotted against the concentration factor  $(H^+)^3(NO_3^-)(Cl^-)^2$ , 226° F.

Figure 27. Reaction rate for Run D-5 plotted against the concentration factor  $(H^+)^3(NO_3^-)(Cl^-)^2$ , 192° F.

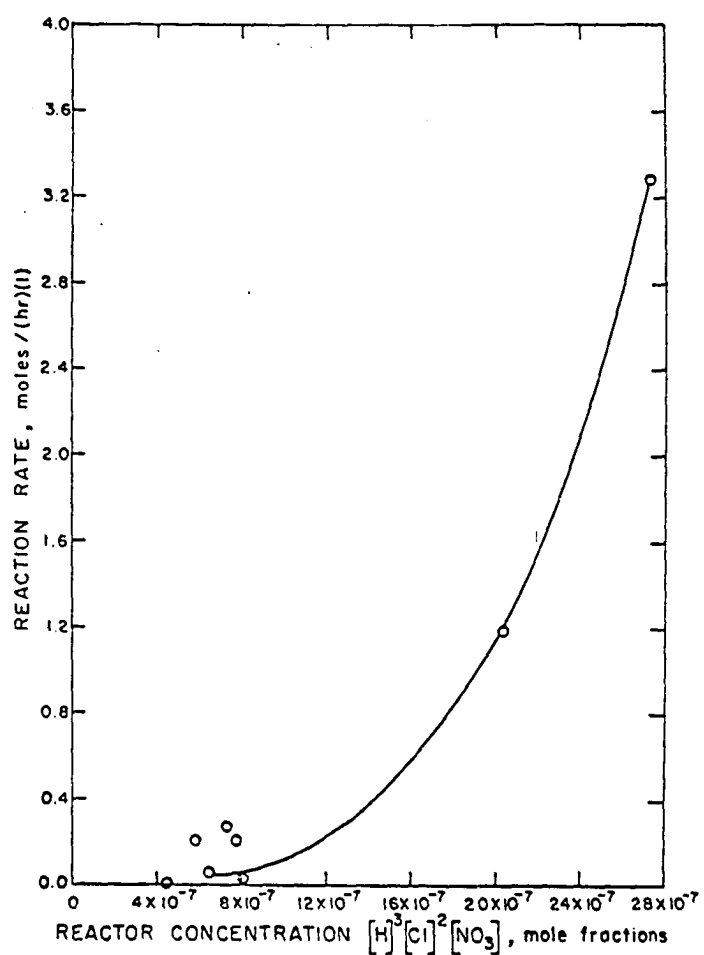
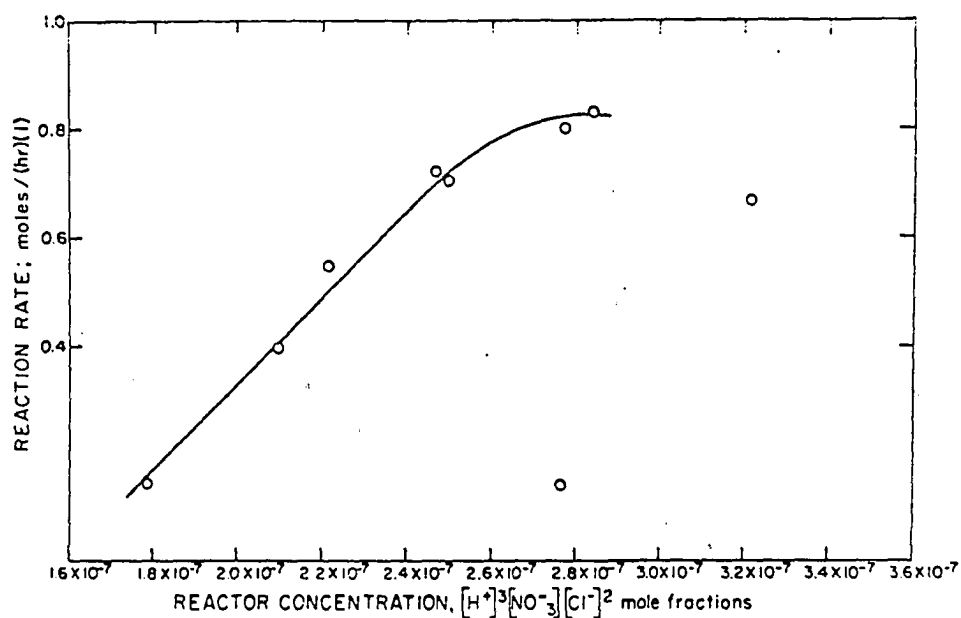
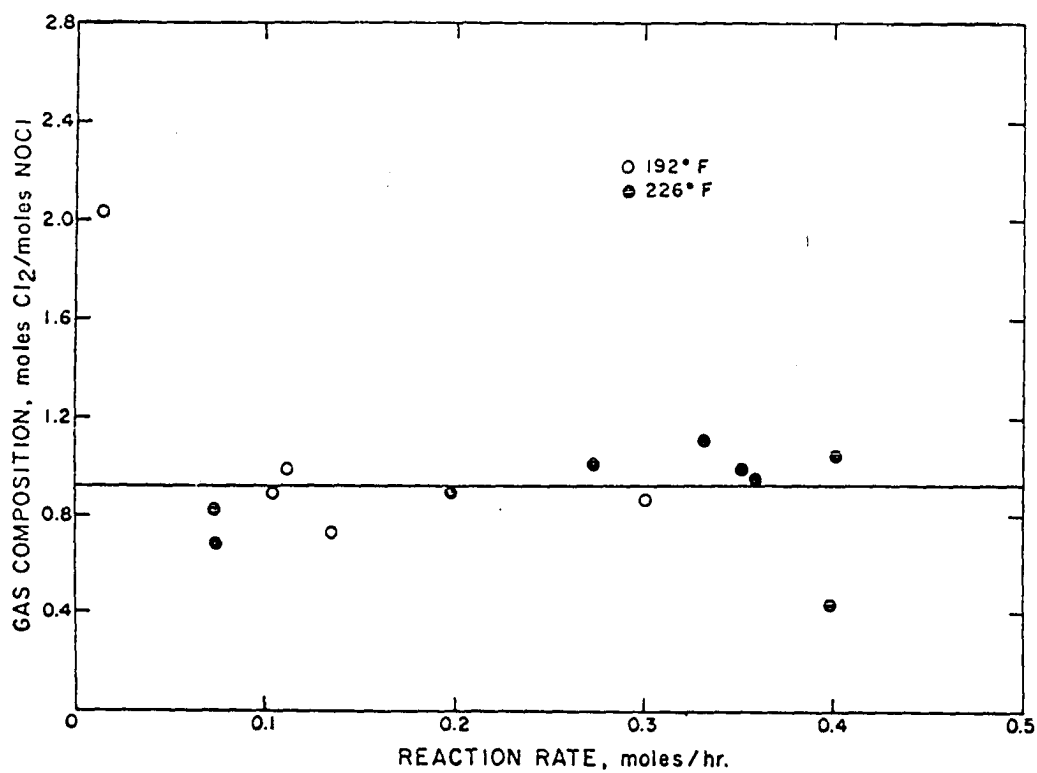
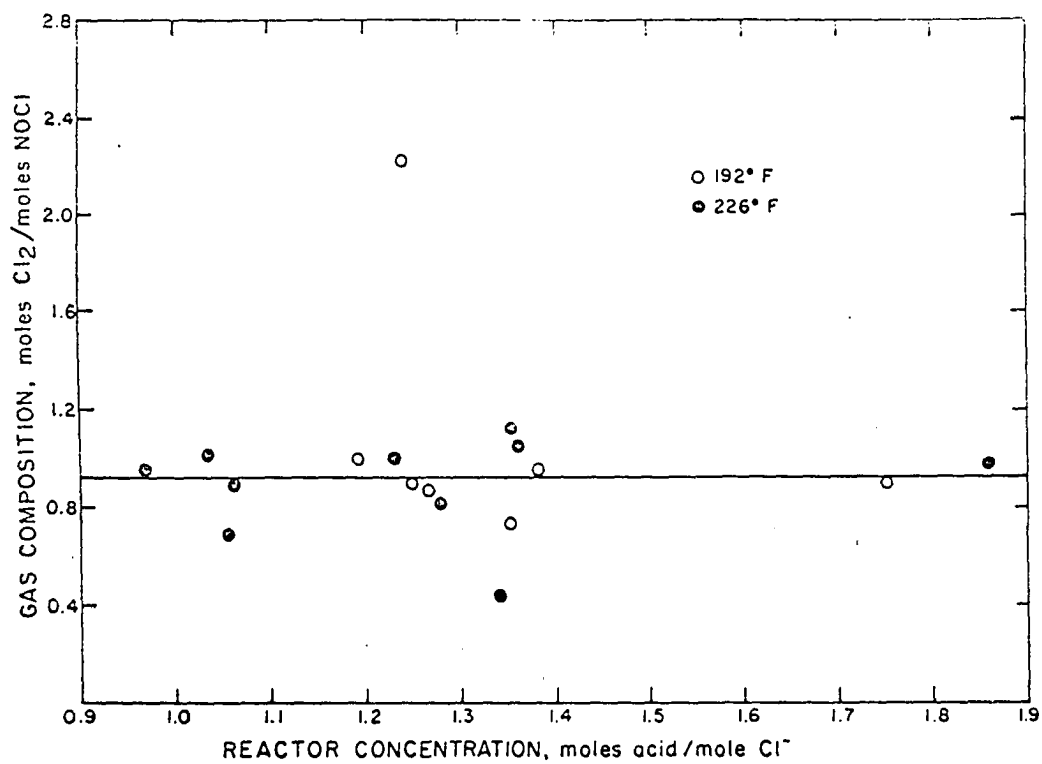




Figure 28. Gas composition plotted against acid: chloride ratio in the reactor at 192° F. and 226° F.

Figure 29. Gas composition plotted against reaction rate at 192° F., and 226° F.



## PROPOSED PROCESS

## Cost Analysis for Commercial Process

A preliminary cost analysis was made for the process. This cost analysis, for a plant at Houston, Texas, indicated that the cost of plant nutrients as  $\text{KNO}_3$  would be about twice as much as the same plant nutrients would cost if purchased as  $\text{KCl}$  and  $\text{NH}_4\text{NO}_3$ . However, this is not a detailed cost estimate and upon a thorough study of the process it might be found that the  $\text{KNO}_3$  would not be this expensive. Also, as was noted in the literature survey, certain crops are damaged by excessive chloride ion concentration, and a premium for potassium, which does not contain chloride, might be in order.

The capital investment per annual ton of plant capacity was estimated from an article which appeared in the May, 1951, Chemical Engineering magazine (47). This cost was considered to be similar to the cost of plants for the manufacture of other inorganic chemicals such as soda ash, calcium cyanamide and sodium bichromate. A cost of \$61.50 per annual ton of  $\text{KNO}_3$  was chosen. The cost was then changed from the 1950 value to today's cost, \$110.07/ton, using the Engineering News-Record (ENR) Construction Cost Indices of 510 for 1950 (17) and 920.1 for February, 1964 (18). The capacity of the plant would be 100 to 200 tons  $\text{KNO}_3$  per 24-hour day.

The raw material costs as well as the comparative costs for bagged  $\text{NH}_4\text{NO}_3$  and  $\text{KCl}$  were obtained from the May 16, 1964, Oil Paint

and Drug Reporter (16). The conversion was estimated to be 97%. The labor requirements were estimated from an article by C. H. Chilton which appeared in the February, 1951, Chemical Engineering (15). An article by S. P. Smith in the March, 1953, Chemical Engineering (42) was used to estimate the shipping costs. The working capital was estimated at 15% of the fixed capital costs or \$16.59/annual ton of  $\text{KNO}_3$  capacity.

The projected price for  $\text{KNO}_3$  is \$125.20/ton or \$125.20 per 277 lb of N and 933 lb of  $\text{K}_2\text{O}$ . These nutrients could be purchased as 827 lb of bagged  $\text{NH}_4\text{NO}_3$  (33.5% nitrogen) at \$70.00/ton for \$28.92 and 1,555 lb of bagged KCl (60% of  $\text{K}_2\text{O}$ ) at \$39.50/ton for \$29.00 for a total of \$58.02. The KCl price includes an \$8.00/ton freight differential which a southeast U. S. consumer might expect to pay for KCl from Carlsbad, New Mexico, as opposed to  $\text{KNO}_3$  from Houston, Texas.

A product which costs twice as much as competitive products should not be expected to replace the less expensive items except where these are mitigating circumstances. In the production of tobacco, such a condition exists. Nevertheless, it would seem that with such a price differential a tobacco grower who needed  $\text{K}_2\text{O}$  would apply as much in the chloride form as he could by law or as much as he could without changing his product so that he would receive a lower market price. Additional  $\text{K}_2\text{O}$  might be applied as  $\text{KNO}_3$ . Perhaps  $\text{KNO}_3$  will find its greatest consumption in mixed fertilizers which also contain the permissible amount of KCl.

Table 12. Production cost estimate for  $\text{KNO}_3$  at Houston, Texas

Item	Units/ton $\text{KNO}_3$	Cost/unit	Cost/ton $\text{KNO}_3$
DIRECT COSTS			
Raw materials			
KCl as $\text{K}_2\text{O}$	48.05	\$0.40 unit	\$19.22
Freight from Carlsbad, N. M.	0.825 tons KCl	10.00/tonKCl	8.25
$\text{HNO}_3$ , 100%	0.644 tons	78.00/ton	50.15
Freight, local	0.963 tons 60% $\text{HNO}_3$	6.00/ton	5.677
Labor			
Operators	2.0 hr/ton	2.50/hr	5.00
Supervisors	0.25hr/ton	3.25/hr	0.81
Services			
Power			0.70
Steam			0.65
Water			0.08
Maintenance			
(5% of fixed capital investment			5.50
Packaging	24 bags	0.15/bag	3.60
INDIRECT COSTS			
Depreciation (10% of fixed capital investment			11.01
Taxes and insurance (5% of operating labor)			0.25
Plant overhead (50% of operating labor)			2.50
TOTAL PRODUCTION COST			\$113.39

Table 13. Percent return on investment for  $\text{KNO}_3$  plant at Houston, Texas

Item		
<hr/>		
Selling price		
$\text{KNO}_3$ \$125.20/ton		\$125.20
$\text{Cl}_2$ \$3.25/100 lb    704 lb/ton $\text{KNO}_3$		22.90
Total sales		<u>\$148.10</u>
Production cost		<u>-113.39</u>
Gross profit		34.71
Administration, 7% of sales		<u>-10.36</u>
Net profit before income tax		24.35
Federal income tax (48% of net profit)		<u>-11.68</u>
New earnings		12.67
Percent return on investment		
$\frac{\text{New earnings}}{(\text{fixed capital} + \text{working capital})} = \frac{12.67}{110.07 + 16.59} = 10\%$		

### Corrosion Study

The corrosive nature of aqua regia is well known. Very similar conditions will occur in a reactor built to react  $\text{KCl}$  with  $\text{HNO}_3$  and corrosion difficulties may develop throughout a plant built to produce  $\text{KNO}_3$ . Kobe (27) states that many corrosion problems are inherent in Solvay Process Company's sodium nitrate process.

Previous to the construction of a pilot plant, a study of possible materials of construction is necessary. A corrosion study to find

materials of construction suitable for the various pieces of equipment is recommended.

### Pilot Plant

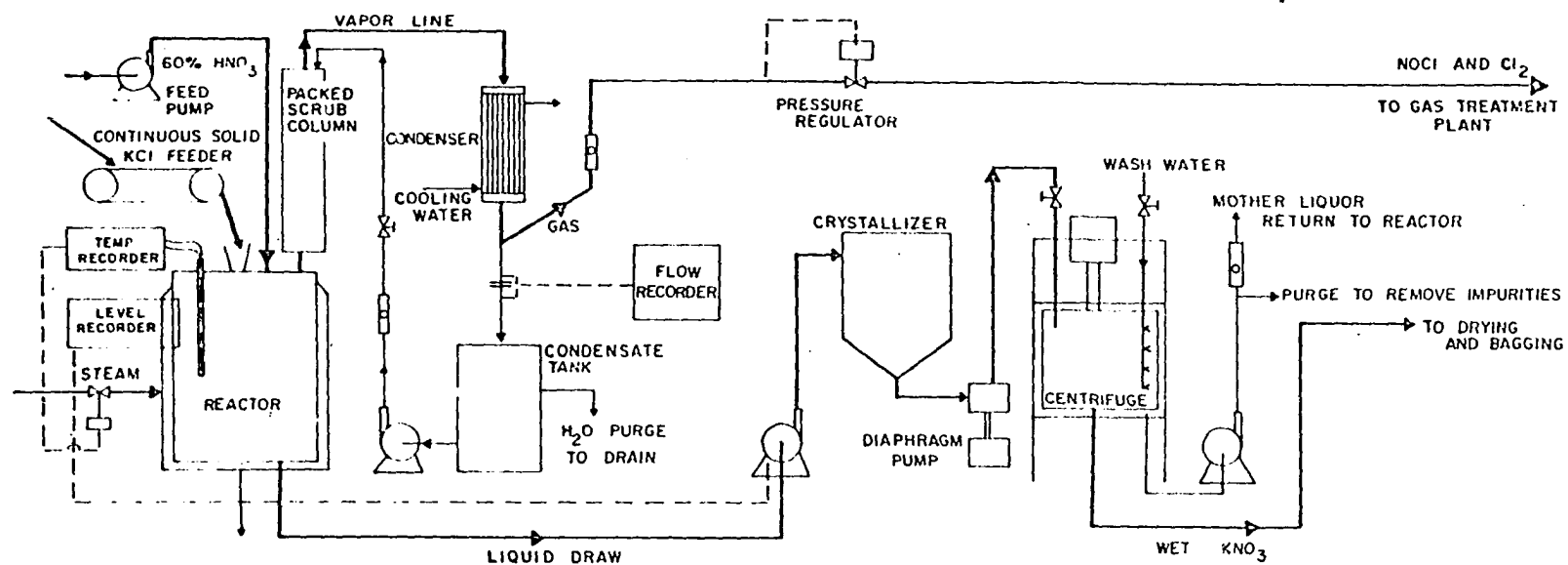
In the recommendations section is a suggestion that a pilot plant be constructed. This step would follow development of a method for treating the reactor off gas to recover  $\text{Cl}_2$  and the nitrogen oxides as  $\text{HNO}_3$ . A possible flow sheet for the pilot plant is shown as Figure 30. This pilot plant should be constructed so it could operate continuously at pressures both above and below atmospheric.

As is shown in the flow sheet, three control devices are needed. The steam flow rate to the reactor jacket should be controlled in order to maintain the temperature and thereby the concentration constant. The liquid draw from the reactor should be controlled in order to maintain the liquid level. The gas flow rate to the gas treatment plant should be controlled in such a manner as to maintain the reactor pressure constant.

The amount of materials fed to the reactor should be controlled quite carefully as must the amount of wash water used. At steady state the amount of materials removed from the system as gas, condensate and in the solid  $\text{KNO}_3$  product should equal the feed. Thus no build up of any materials should occur.

Figure 30. Flow sheet for proposed pilot plant





## CONCLUSIONS

1. A batch process does not produce pure  $\text{KNO}_3$ . In batch processes the product contained  $\text{KCl}$  as well as  $\text{KNO}_3$ . This was true if the flask containing the acid and  $\text{KCl}$  was placed in a constant temperature bath or if the contents were heated to dryness.
2. The solubility data which were taken indicate that a continuous fractional crystallization process is possible. The solubility of  $\text{KCl}$  in aqueous nitric acid solutions at  $30^\circ \text{C}$ . is high whereas the solubility of  $\text{KNO}_3$  under similar conditions is quite low.
3. The continuous process gave encouraging results. A continuous fractional crystallization process resulted in a solid product which was pure  $\text{KNO}_3$ .
4. The reaction rate is a function of temperature. Increasing the reaction temperature from  $192^\circ \text{F}$ . to  $226^\circ \text{F}$ . increased the reaction rate quite significantly.
5. The reaction rate increases with concentration. Below a threshold concentration the rate is insignificant. However, at  $226^\circ \text{F}$ ., over a limited concentration range the rate increases as a linear function of the factor  $(\text{H}^+)^3(\text{Cl}^-)^2(\text{NO}_3^-)$ .
6. The gas composition ratio of  $\text{Cl}_2$  to  $\text{NOCl}$  was not a function of acid to chloride ratio over the range studied. Neither was the gas composition found to be a function of temperature or reaction rate.
7.  $\text{NOCl}$  can be converted to  $\text{NO}_2$  and  $\text{Cl}_2$  by reacting it with hot

concentrated  $\text{HNO}_3$ .

8.  $\text{NOCl}$  can be reacted with  $\text{MnO}_2$  in hot nitric acid to give  $\text{Cl}_2$  as the gas product.

## RECOMMENDATIONS

1. It is recommended that a corrosion study be made in order to determine what materials would be suitable for construction of the reactor, the crystallizer, the column, and the condensers and to determine what materials would be suitable for piping and other necessary construction.
2. It is recommended that a study be conducted to determine the best way to treat the affluent gas in order to separate the  $\text{Cl}_2$  and  $\text{NOCl}$  and convert the  $\text{NOCl}$  into commercially valuable forms.
3. It is recommended that following the completion of the projects mentioned above that a pilot plant be constructed.

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## ACKNOWLEDGEMENTS

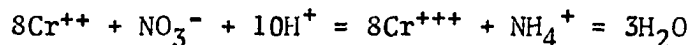
The author wishes to express his gratitude to Dr. George Burnet who suggested the problem and guided the investigation.

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# APPENDIX A. NELSON'S METHOD FOR DETERMINATION OF NITROGEN

Nelson has suggested a method for analysis of solutions for total nitrogen (33). This method which employs a chromous solution to reduce nitrate



in an acid solution is more suitable for some solutions of  $\text{NO}_3^-$  in  $\text{H}_2\text{SO}_4$  than Kjeldahl methods which reduce the nitrogen in a basic solution.

Nelson suggests the following procedure:

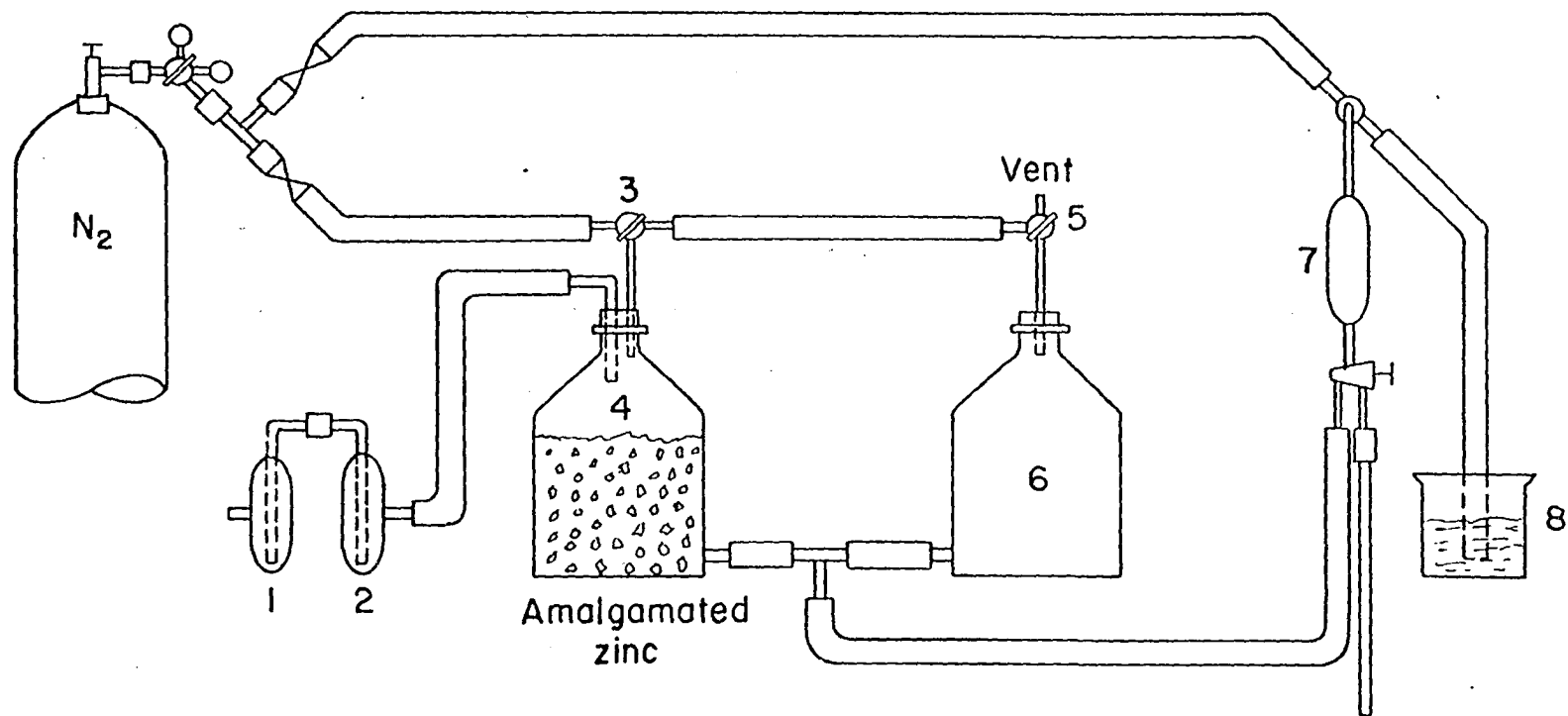
## Apparatus and Reagents

(a) Chromous solution reductor - See Figure 31. Consists of 2 L aspirator bottles, one a reductor and the other a solution reservoir; an automatic 50 ml pipet; and a source of nitrogen or other inert gas. The reductor contains 2 Kg amalgamated Zn and is closed with a 2-hole rubber stopper through which is inserted a 3-way stopcock and a vent tube connected to a water sealed trap. The solution reservoir is closed with a one-hole rubber stopper through which is inserted a 3-way stopcock. Connections between the bottle and pipet are made with Tygon tubing. Break off the original tip of the pipet to permit a fast delivery and replace with an 11" extension (the pipet should deliver 50 ml in 17 seconds or less).

(b) Amalgamated zinc. -- Place 2 Kg reagent grade mossy Zn in a 4 L beaker and add 1700 ml of 1+ 1 HCl containing 27.6 g  $\text{HgCl}_2$ . Let the Zn amalgamate for about 5 minutes while stirring with a heavy glass rod. Decant the acid and wash the Zn four times by decantation with distilled water. Transfer the zinc to the reductor (Figure 2).

(c) Chromous solution, 1N (2.7N with sulfuric acid). -- Dissolve 267 g  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 805 ml (by graduate) of water to which 70 ml concentrated  $\text{H}_2\text{SO}_4$  has been added and mix.

Figure 31. Apparatus for preparation of chromous solution. 1: 250 ml Haberman bulb, 50 ml of water. 2: 250 ml Haberman bulb trap. 3: 3-way stopcock with plug clamp. 4: reductor; 2 L aspirator bottle. 5: 3-way stopcock with plug clamp. 6: chromous solution storage; 2 L aspirator bottle. 7: 50 ml automatic pipet with 11 inch glass tube extension. 8: 250 ml beaker for overflow and seal against air. Connections are of Tygon tubing. Connections between the bottles should be long enough to permit shaking of the reductor by hand to promote a rapid reduction if desired (33)



Pour the solution into the reductor, (lower outlet tubing is clamped off) stopper, and close the 3-way stopcock to the reductor. The solution will reduce in about 3 hours, changing from a dark green color to the characteristic sky blue of the chromous ion. A small amount of hydrogen is evolved and vented through the Haberman bulb traps. Oxygen from air above the solution is of no consequence, as it will be consumed in the reduction.

Purge the solution reservoir and pipet with nitrogen. Transfer the reduced solution under about 3 lbs. of nitrogen pressure to the reservoir. During the transfer the reductor vent is clamped, the lower outlet tubing is unclamped, the automatic pipet is closed, and the storage bottle is vented to permit the solution to flow. After the transfer, clamp the reductor outlet, unclamp the reductor vent, and position both 3-way stopcocks to apply 3 lbs of nitrogen pressure to the reservoir for filling the pipet. Nitrogen pressure is unnecessary during idle periods of the apparatus. A small flow of nitrogen is maintained over the top of the automatic pipet during dispensing. If air should accidentally get into the reservoir bottle and oxidize the solution it can be transferred back to the reductor with nitrogen pressure. Additional chromous solution can be prepared in the reductor while that in the storage bottle is being used. If the amalgamated zinc becomes inactivated, treat it with 1 + 1 HCl for 5 minutes and then wash four times with distilled water.

(d) Aludum boiling stones. -- Norton 14X (A. H. Thomas Cat. Code UEVOR).

#### Determination

Nitrogen fertilizer solution samples--Pipet a 25 ml aliquot of appropriately diluted solution to contain 0.061 g or less of nitrate nitrogen ( $0.35 \text{ g NH}_4\text{NO}_3$ ) into a 650 ml Kjeldahl flask. Wash down any sample adhering to the sides of the flask with 2-3 ml distilled water. (solutions containing no free ammonia may be weighed directly into the flask and then diluted with 25 ml distilled water.)

Add 50 ml 1N chromous solution from the apparatus shown in Figure 2. The extension tip of the automatic pipet should be positioned about 1" above the surface of the sample solution during the addition so as to minimize exposure of the reagent to the atmosphere. Swirl to mix and let stand for about 1 minute or longer. Add 25 ml coned  $\text{H}_2\text{SO}_4$  and 2-3 g boiling stones, and swirl to oxidize any residual chromous ion.

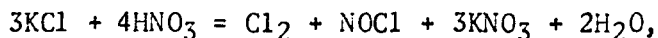
Place the flask in an inclined position of about  $15^\circ$  from horizontal on a heater (preheated if electrical; do not use asbestos ring or wire gauze with heater) and digest at full heat. Remove the flask from the heater when the chromic sulfate is precipitated as a rose-colored insoluble form which causes bumping of the solution. Do not turn off the heat and leave the flask to cool on the heater at this point, as the solution may bump severely enough to cause the flask to jump and break against the heater. Fuming will continue about 4-6 minutes, which will convert urea nitrogen completely to ammonium sulfate.

Cool the flask and add 200 ml distilled water. Cool to room temperature or below and add 2-3 g 20 mesh zinc and 100 ml 50% NaOH solution. Tilt the flask to layer the NaOH underneath the acid mixture. Connect the flask immediately to a condenser, mix thoroughly, and distill the ammonia (200 ml distillate is sufficient) into 40 ml 0.5N standard acid contained in a 500 ml Erlenmeyer flask. Add 6-9 drops methyl red indicator and titrate the excess acidity with 0.25N NaOH. Correct the titration for nitrogen contained in the reagents by making a blank determination.

When analyzing three samples of  $\text{NaNO}_3$  Nelson found a mean recovery of 99.90% with a standard deviation of 0.035% and a standard deviation of the mean of  $99.90 \pm 0.020$ .

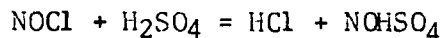
## APPENDIX B. WOLF AND SCHIER GAS ANALYSIS

In the reaction of KCl and HNO<sub>3</sub>,

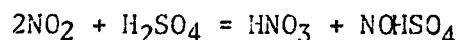


Cl<sub>2</sub> and NOCl are given off as gas. In the batch studies the method of Wolf and Schier (49), which was developed for the analysis of NOCl, NO<sub>2</sub> and Cl<sub>2</sub>, was used to analyze the gas evolved.

The gases are bubbled through two vessels which each contain 90% H<sub>2</sub>SO and then through a vessel containing 10% KI solution. The reaction of nitrosyl chloride is



The nitrogen dioxide reacts as follows:



The elemental chlorine is only slightly soluble in H<sub>2</sub>SO<sub>4</sub> and therefore it passes through the acid to react with the KI. The reaction products of the nitrogen containing gases are in the H<sub>2</sub>SO<sub>4</sub> solution. The NO<sub>2</sub> and NOCl are then determined by the method of Whitnack et al (48). The total nitrogen is determined by the method of Nelson as outlined above. Then the trivalent nitrogen (NOHSO<sub>4</sub>) is determined by titration with a solution of potassium permanganate using the following technique. An aliquot is added to an excess of potassium permanganate. Then an iron (II) sulfate solution is added until the permanganate that remains is used up and an excess of iron (II) sulfate is present. The excess iron (II) sulfate is then back titrated with permanganate. A

blank should be run. The  $\text{NO}_2$  absorbed is two times the difference between the total nitrogen and the trivalent nitrogen.

The chlorine absorbed in the third bottle is then determined by titrating with  $\text{Na}_2\text{S}_2\text{O}_3$  to determine the elemental  $\text{I}_2$ .



APPENDIX C. OUTLINE OF CALCULATION OF COEFFICIENTS  
FOR RATE CONCENTRATION RELATIONSHIP

The values of  $a$ ,  $b$ ,  $c$  and  $K$  were needed for the relationship

$$R = K(\text{Cl}^-)^a(\text{H}^+)^b(\text{NO}_3^-)^c$$

The relationship was then written in the form

$$\log R = \log K + a \log (\text{Cl}^-) + b \log (\text{H}^+) + c \log (\text{NO}_3^-).$$

The following substitutions were made

$$X_0 = 1$$

$$X_1 = \log (\text{Cl}^-)$$

$$X_2 = \log (\text{H}^+)$$

$$X_3 = \log (\text{NO}_3^-)$$

$$Y = \log R$$

$$b_0 = \log K$$

$$b_1 = a$$

$$b_2 = b$$

$$b_3 = c.$$

Then the relationship was written in the form

$$Y = b_0X_0 + b_1X_1 + b_2X_2 + b_3X_3$$

From Run D-4 nine data points were available. For each of the points the values of  $(\text{Cl}^-)$ ,  $(\text{H}^+)$ ,  $(\text{NO}_3^-)$ , and  $K$  were known. The logarithms of these values were taken giving the values of  $X_1$ ,  $X_2$ ,  $X_3$  and  $Y$  for each data point.

Table 14. Data from Run D-4

Sample	(Cl <sup>-</sup> ), mole fraction	(H <sup>+</sup> ), mole fraction	(NO <sub>3</sub> <sup>-</sup> ), mole fraction	Reaction rate moles/(l)(hr)
III	0.0692	0.0672	0.1700	0.718
IV	0.0666	0.0689	0.1526	0.545
V	0.0658	0.0700	0.1412	0.396
VI	0.0644	0.0681	0.1361	0.148
VII	0.0649	0.0800	0.1161	0.704
VIII	0.0653	0.0836	0.1110	0.141
IX	0.0640	0.0858	0.1072	0.797
X	0.0637	0.0868	0.1069	0.830
XI	0.0642	0.0868	0.1193	0.663

The logarithms of the values in Table 14 were found and Table 15 was constructed.

From Table 15 the values needed in the following relationships were found.

$$b_0 \sum X_0 X_0 + b_1 \sum X_0 X_1 + b_2 \sum X_0 X_2 + b_3 \sum X_0 X_3 = \sum X_0 Y$$

$$b_0 \sum X_1 X_0 + b_1 \sum X_1 X_1 + b_2 \sum X_1 X_2 + b_3 \sum X_1 X_3 = \sum X_1 Y$$

$$b_0 \sum X_2 X_0 + b_1 \sum X_2 X_1 + b_2 \sum X_2 X_2 + b_3 \sum X_2 X_3 = \sum X_2 Y$$

$$b_0 \sum X_3 X_0 + b_1 \sum X_3 X_1 + b_2 \sum X_3 X_2 + b_3 \sum X_3 X_3 = \sum X_3 Y$$

The solution of these 4 equations gave the following:

$$b_0 = 10.229301 = \log_{10} K$$

$$b_1 = -4.701415 = a$$

Table 15. Logarithms of data for Run D-4

Sample	X <sub>0</sub>	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Y
III	1	-1.15989	-1.17263	-0.76955	-0.14375
IV	1	-1.17653	-1.16178	-0.81645	-0.26328
V	1	-1.18177	-1.1549	-0.85017	-0.40209
VI	1	-1.19111	-1.16685	-0.86934	-0.82962
VII	1	-1.18776	-1.09691	-0.93517	-0.15255
VIII	1	-1.18509	-1.07779	-0.95468	-0.85140
IX	1	-1.19382	-1.06651	-0.96981	-0.09832
X	1	-1.19586	-1.06148	-0.97102	-0.08092
XI	1	-1.19246	-1.06148	-0.92336	-0.17836

$$b_2 = 9.36387 = b$$

$$b_3 = 6.374009 = c$$

Then the rate relationship was written as follows:

$$R = 1.70 \times 10^{10} (\text{Cl}^-)^{-4.7} (\text{H}^+)^{9.4} (\text{NO}_3^-)^{6.4}$$