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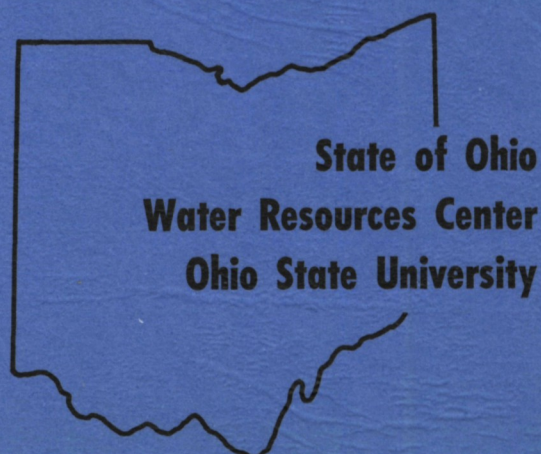
**PROJECT COMPLETION
REPORT NO. 444**

**Oxidation of Ammonia
in Water by
Ferrates (VI) and (IV)**

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**United States Department
of the Interior**

**CONTRACT NO.
A-031-OHIO**



OXIDATION OF AMMONIA IN WATER
BY FERRATES(VI) AND (IV)

by

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June 1976

This study was supported in part by the
Office of Water Research and Technology,
U.S. Department of the Interior under
Project A-031-OHIO

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SUMMARY OF MAJOR CONCLUSIONS

The following major conclusions appear to be supported by the results obtained during the course of this exploratory study:

1.) Two competing reactions, the oxidation of ammonia and the decomposition of potassium ferrate(VI) proceed simultaneously. The net oxidation rate of ammonia and the fraction of ammonia oxidized depends on the relative rates of these two reactions.

2.) The most important factor affecting the stability of ferrate(VI) (K_2FeO_4) in water solution is the pH, and as expected, pH has a pronounced effect on the oxidation of ammonia with ferrate(VI) in water solution. At least one of the fraction of NH_3 oxidized was observed in the vicinity of pH 10.5.

3.) Our preliminary work also showed that the pH not only affects the fraction of NH_3 oxidized but also affects the composition and relative quantities of the oxidation products. Generally, at pH values in the neutral and into the alkaline region the oxidation end products are elemental nitrogen, nitrate and nitrite, but with increasing pH the amount of nitrate and nitrite decrease.

4.) The fraction of ammonia oxidized by potassium ferrate(VI) also depends on the mole ratios of K_2FeO_4 to NH_3 . However, the increase diminishes with increasing mole ratio of K_2FeO_4 to NH_3 .

5.) The fraction of NH_3 oxidized was independent of temperature, in the range of 10°C to 40°C, but the rate of oxidation was considerably higher at higher temperature. It appears as though the change in the decomposition rate of the ferrate(VI) is offset by the change in the rate of the reaction

with ammonia.

6.) The maximum efficiency of K_2FeO_4 for NH_3 oxidation is at K_2FeO_4 concentration of approximately 0.7 m-moles/l and decreases with decreasing concentration of NH_3 .

7.) At K_2FeO_4 concentration of approximately 0.7 m-moles/l the m-moles/l NH_3 oxidized per one m-mole/l K_2FeO_4 "utilized for NH_3 oxidation" approaches one. This indicates that at K_2FeO_4 concentration of approximately 0.7 m-moles/l the NH_3 is preferentially oxidized to elemental nitrogen.

8.) Best results were achieved by addition of K_2FeO_4 , allowing the ferrate(VI) react completely, readjusting the pH, adding again ferrate(VI), etc. This "stepwise" procedure did not show any limitations on the fraction of NH_3 oxidized, in the concentration range investigated, but the efficiency of the oxidation decreased with each subsequent addition of K_2FeO_4 .

9.) Considering the results of the preliminary work and keeping in mind the practical purpose of the process, several preliminary runs, similar to those done on pure NH_3 solution, were carried out on secondary effluent of a sewage treatment plant. The runs showed satisfactory results with no interferences apparent. In a two step procedure up to 25 percent ammonia was oxidized predominantly to elemental nitrogen, which may be considered satisfactory at this point. It may be speculated that the buffering properties of the effluent and the probable catalytic effect of some organic compounds present may be responsible for the satisfactory results of ammonia oxidation by potassium ferrate(VI) in secondary sewage treatment plant effluent.

COD reductions were observed to be somewhat in excess of 30 percent.

Up to 27 percent phosphate removal was also observed.

10.) Considering the relatively low efficiency of ammonia oxidation with ferrate(VI), even by the involved stepwise procedure, the practical application of the process at present appears not feasible. However, considering the possible improvement of the efficiency of the process, particularly by using suitable catalysts, and the other lucrative properties of the ferrates(VI) as oxidants the investigator is inclined to believe that a process may be developed for practical application in some particular instances.

INTRODUCTION

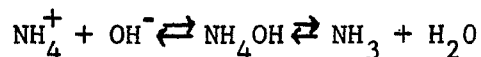
It is generally agreed that eutrophication of our lakes and streams is caused mainly by nutrients such as phosphorus and nitrogen. With regard to the control of algal growth, phosphorus may be the key element since nitrogen fixation, under favorable conditions, is generally sufficient to provide adequate nitrogen for growth. However, high concentrations of both nitrogen and phosphorus are generally necessary to start serious algal blooms which are usually less intense with lower concentrations (1).

Domestic wastewaters have been indicated as major sources of phosphorus and nitrogen compounds. Conventional treatment methods for municipal wastewaters are not designed to remove these nutrients effectively. Such methods usually result in a 30 to 50 percent removal of the incoming nitrogen (1). Therefore, the average total nitrogen content of secondary effluent from municipal wastewater treatment plants is about 15 mg/l (2). Generally, this amount is in the form of compounds of ammonia.

One of the problems associated with the nitrogen in treatment plant effluents is that ammonia can cause a dissolved oxygen depletion in the receiving waters. Also, ammonia is corrosive to copper fittings (2). In addition, for those operations involving treatment with chlorine, one mole of ammonia requires in excess of seven moles of chlorine for breakpoint oxidation. The breakpoint oxidation of ammonia in wastewater treatment is also objectionable because of the formation of chlorinated organic compounds, many of which are suspected carcinogens. Moreover, the presence of nitrates in the receiving waters is objectionable because of the possible health hazard of methemoglobinemia. As a result of these undesirable characteristics, there is an increasing need for ammonia removal from wastewater treatment plant effluents.

Recent methods tried for removing ammonia include ammonia stripping, ion exchange, and chemical destruction (2).

In most activated sludge treatment plants, the nitrogen remaining in the final effluent is mainly in the form of ammonium ion. When the pH is raised to approximately 11.0, the excess of hydroxyl ions converts the ammonium ion to ammonium hydroxide and dissolved ammonia.

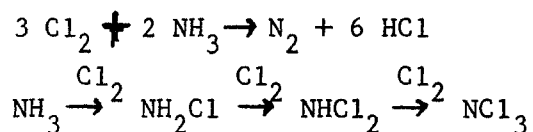


Bubbling air through the solution will then remove the ammonia. The drawback of this process is the high solubility of ammonia in water. In countercurrent contact at 20°C, the minimum air requirement to remove 90 percent of the ammonia from wastewater is about 220 cubic feet per gallon of water. This high air to water ratio requires the use of stripping towers with very low pressure drops. Another difficulty brought about by the high air requirement is poor cold weather performance - the wastewater is cooled by contact with air, and this further increases the solubility of the ammonia (2, 3).

The ammonium ion can be removed by contact with a cation exchange resin, but the reaction reaches an equilibrium when only part of the cations originally on the resin have been replaced. Also, with the cation exchange resins ordinarily available, selectivity for NH_4^+ over certain other cations is poor (2).

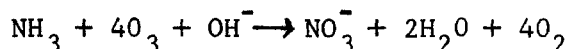
Although the nitrate ion can be removed by contact with an anion exchange resin, satisfactory materials that are selective for nitrates have not as yet been developed (2, 4, 5).

Chlorination reactions showing ammonia removal include the following:



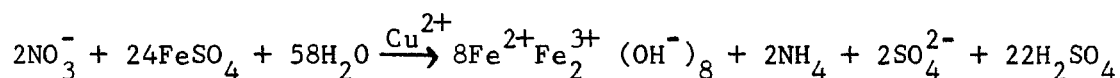
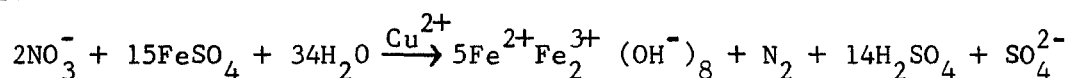
Chlorine requirements are high, as up to ten mg chlorine are required per one mg ammonia nitrogen.

Ozonization can also be used to remove ammonia from wastewaters:



This reaction is not efficient at low concentrations and it merely changes the form of the nitrogen present.

Nitrate can be reduced by ferrous iron (Fe^{2+}) by one of the following paths:



Obviously, a cheap source of ferrous sulfate is required, and there must be a convenient means for disposing of the sludge produced (2).

Electro-oxidation of ammonia to elemental nitrogen turned out to be less efficient than expected (6).

The method of ammonia removal studied by Mechalias et al. (7) involved bio-oxidation of ammonia to nitrate and the subsequent denitrification of the nitrate to nitrogen gas.

None of these methods is entirely satisfactory; thereby suggesting that more work is justified to improve existing methods and to develop new procedures for removing nitrogen and phosphorus compounds from wastewater.

Rose in 1843 (8, 9) found that potassium ferrate(VI) (K_2FeO_4) solutions were quickly decolorized by ammonia or ammonia salts. Wackenroder (10) found that ammonia and ammonium salts reduced potassium ferrate(VI). Moeser (11) reported that ammonia is oxidized at room temperatures to nitrogen by potassium ferrate(VI). Halferich and Lang (12) reported that in acid solutions ammonium ion is oxidized by potassium ferrate(VI) to nitrite and nitrate.

To our knowledge, no reports of ammonia oxidation by ferrates(VI) have appeared in the last twenty years.

Considering the similar properties of ferrates(VI) and permanganates and that ferrates(VI) are even more powerful oxidizing agents at room temperature, there is an indication that under specific conditions ammonia ions in sewage treatment effluents may be partially oxidized to elemental nitrogen; thus eliminating further pollution of the environment by nitrogen compounds. Also, considering that ferrates(VI) are capable of oxidizing organic compounds (13), of coagulating phosphates and of serving as bactericides, the possible application of ferrates(VI) and (IV) in wastewater treatment process appears very attractive. Moreover, none of the decomposition products of potassium ferrate(VI) (potassium hydroxide, ferric hydroxide and oxygen) are potential toxins; and if properly applied, no health hazard is expected.

The objectives of this research were to conduct an exploratory study on the oxidation of ammonia in water by ferrate(VI) and ferrate(IV) salts, and to evaluate the possible application of ferrates as potential oxidants of ammonia in wastewater treatment.

The exploratory study did include:

1. The preparation of a sufficient quantity of sodium ferrate(IV) and potassium ferrate(VI) to be used in the study, because the compounds are not available commercially.
2. The determination of the extent of ammonia oxidation by ferrates(VI) and (IV) and the relative amounts of the oxidation products formed at specified conditions.
3. The determination of the reaction rates of ammonia oxidation and ferrate decomposition at selected conditions.
4. The determination of the extent of ammonia oxidation by treating a sewage treatment plant secondary effluent with potassium ferrate(VI).

RELATED LITERATURE

Schreyer (14) was the first to prepare a pure, dry sample of potassium ferrate(VI). He did so by oxidizing ferric iron with potassium hypochlorite. The hypochlorite was prepared by chlorinating an 8 M solution of potassium hydroxide. He then proceeded to remove the unreacted ferric hydroxide by filtration, and precipitated the potassium ferrate by saturating the solution with potassium hydroxide.

Since that time many methods have been reported for ferrate preparation including the hypobromide method of Scholder (15), the electrochemical method of Poggendorf (16), and the method used in this work which was reported by Thompson, Ackerman and Schreyer (17).

Scholder (18) describes a procedure to prepare sodium ferrate(IV).

The first reports on ammonia oxidation by ferrates(VI) are found as early as 1843. Rose (8, 9) reports that ferrate(VI) solutions were quickly decolorized by ammonia or ammonium salts. Wackenroder (10) found that ammonia and ammonium salts reduce ferrate(VI). Moeser (11) reported that ammonia is oxidized at room temperatures to nitrogen by potassium ferrate(VI). Halferich and Lang (12) found that in acid solutions ammonium ion is oxidized by potassium ferrate(VI) to nitrite and nitrate. To our knowledge, no reports of ammonia oxidation by ferrates has appeared in the last 20 years. The publications surveyed included: Chemical Abstracts 1950-1971, Water Resources Research Catalog Volumes 1-6, and Selected Water Resources Abstracts 1968-1971.

Reports on the decomposition of potassium ferrate(VI) have been made by Haire (19), Gump (20), and Magee (21).

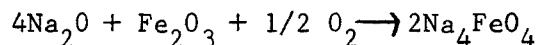
The references on analytical procedures will be given at the appropriate places in the report.

SECTION I

PREPARATION OF FERRATES

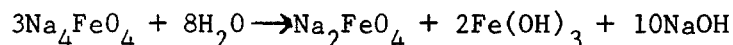
A. Preparation of Sodium Ferrate(IV)

Sodium ferrate(IV) was prepared by the method described by Scholder and Bunsen (18). Twenty-four parts of Fe_2O_3 and 40 parts of Na_2O (K & K Laboratories, Plainview, N.Y.) by weight were intimately mixed in a porcelain mortar in the absence of H_2O and CO_2 (in a powder box free of CO_2 and H_2O). The mixture was transferred to a refractory boat (sintered corundum) and placed in a tubular furnace at 150°C through which dry oxygen flowed. In the next 30 minutes the temperature was increased to 450°C and yielded sodium ferrate(IV) after one hour.



The procedure calls for nearly quantitative yields, but our preparation contained on the average only fifty percent sodium ferrate(IV). The discrepancy is attributed to the presence of small quantities of moisture in the materials and apparatus.

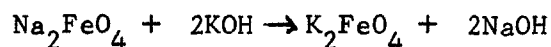
Sodium ferrate(IV) disproportionates in water or alkaline solutions according to the reaction:



Our observations showed that this disproportionation reaction proceeds nearly instantaneously to yield sodium ferrate(VI), and consequently, it was assumed that the oxidation of ammonia is principally accomplished by sodium ferrate(VI). It also appears that sodium ferrate(VI) has no advantage over potassium ferrate(VI) for the oxidation of ammonia, and further work with sodium ferrate(IV) and (VI) was discontinued.

B. Preparation of Potassium Ferrate(VI)

Two methods of preparing potassium ferrate(VI) were considered. The first, utilizing the ferrate(IV) disproportionating reaction and precipitation of potassium ferrate(VI) with saturated potassium hydroxide solution



did not appear favorable because of low yields. Therefore, potassium ferrate(VI) was prepared according to slightly modified procedure of Thompson, Ackerman and Schreyer (17):

A solution of 90 grams of sodium hydroxide in 225 ml of water was cooled and chlorinated with vigorous stirring while the temperature was kept below 10°C. Chlorination was continued until the weight of the solution had increased by 60 grams. Next, 210 grams of solid sodium hydroxide was added slowly with stirring while the temperature was allowed to rise as high as 25°C to aid in the dissolution of the sodium hydroxide. Foaming at this point usually indicated a considerable loss of product. The mixture was then cooled to below 10°C and the precipitated sodium chloride was removed by filtering through a fritted-glass filter of large surface area and coarse porosity. A milky solution was usually obtained and a clear solution indicated a loss of product.

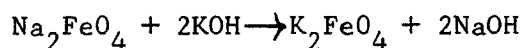
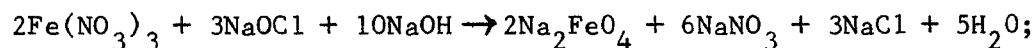
The alkaline hypochlorite solution was maintained at 25°C while 75 grams of pulverized iron(III) nitrate 9-hydrate was added in small portions over a period of 75 minutes. Sodium hydroxide was added to the solution until saturation was reached. During this operation the temperature was maintained at 25°C. At this point the solution was chilled to 15°C and centrifuged for 1 hour at 3200 rpm before filtering through a fritted-glass filter of coarse porosity.

The filtrate containing the sodium ferrate was transferred to a 600 ml beaker at 20°C, and 300 ml of saturated potassium hydroxide solution was added with stirring. Stirring was continued for 5 minutes and the solution cooled to 10°C before filtering through a fitted-glass filter of coarse porosity. The filtrate was discarded.

The precipitate was leached successively on the filter with four or five 30 ml portions of 3 M potassium hydroxide solution. All the washings were drawn through the filter into the same 150 ml volume of chilled, saturated potassium hydroxide solution. The residue remaining on the filter was discarded. The filtrate was transferred to a 1000 ml beaker, and some solid potassium ferrate(VI) remaining in the filter flask was washed out with a few ml of saturated potassium hydroxide solution. An additional 150 ml of chilled saturated potassium hydroxide solution was added. The final mixture was about 11 M in potassium hydroxide. This suspension was stirred for five minutes and then filtered through a fritted-glass filter of medium porosity.

The precipitate remaining on the filter was washed with 20 ml of benzene in order to remove the excess water. Three to five 20 ml portions of 95 percent methanol, which had been chilled to less than 10°C, were then drawn through the filter. The precipitate was then dried with 50 ml of anhydrous ethyl ether. During this drying operation, the filter funnel was sealed and air dried by a calcium chloride tube was admitted to the funnel to protect the potassium ferrate(VI) from the moisture in the atmosphere. Suction was continued for 20 minutes, and the final drying was accomplished in a vacuum desiccator.

By this procedure, samples ranging in purity from 60 to 70 percent potassium ferrate(VI) were obtained. The formation of the potassium ferrate(VI) is given by the theoretical equations:



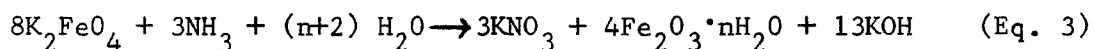
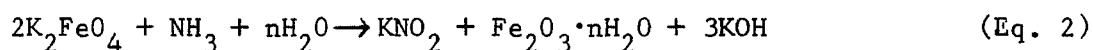
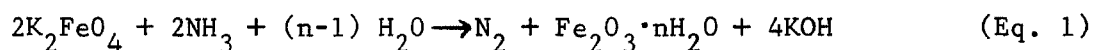
Since a higher purity product was desired, further purification was attempted. A sample of approximately 15 grams was dissolved in 75 ml of 6 M potassium hydroxide at 10°C. This solution was stirred for five minutes and cooled to 0°C. Approximately 94 ml of saturated potassium hydroxide was then added and the solution was cooled once again to 0°C while stirring. This suspension was then filtered through a fritted-glass filter of medium porosity and the precipitate treated with benzene, methanol, and ethyl ether as described above, before it was stored in a vacuum desiccator. The once purified product contained 85 to 87 percent potassium ferrate(VI).

The analyses of the potassium ferrate(VI) were made by the arsenite-bromate method and the arsenite-cerate method as given by Schreyer, Thompson and Ackerman (22).

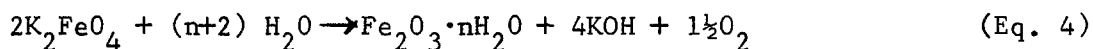
SECTION II

OXIDATION OF AQUEOUS AMMONIA BY POTASSIUM FERRATE(VI) AT SELECTED CONDITIONS

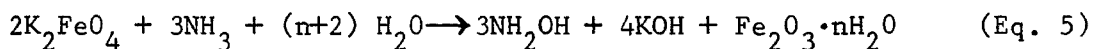
Moeser in 1897 (11) reported that ammonia is oxidized to nitrogen by potassium ferrate(VI) at room temperature. Halferich and Lang in 1950 (12) stated that in acid solutions ammonia ion is oxidized by potassium ferrate(VI) to nitrite and nitrate. On this basis it may be assumed that the oxidation of ammonia by potassium ferrate(VI) in water solution proceeds according to the following three theoretical overall reactions:



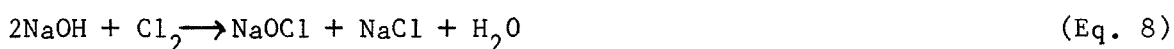
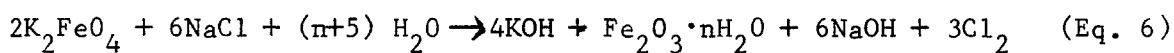
Since the first preparation of potassium ferrate(VI) it has been known that potassium ferrate(VI) decomposes in water solution according to the reaction:



In addition to the four above reactions, some other reactions are possible:



In the presence of chlorides:



In this study all work was done on ammonia solutions and ammonium sulfate solutions, and therefore the reactions shown in equations 6 to 11 could only be encountered in the few runs where chlorides were added for this purpose. Because of the exploratory nature of the work, the formation of hydroxylamine (Eq. 5), hydrazine and others was assumed to be negligible; and their detection and determination was not made.

For rigorous determination of the fraction of ammonia oxidized to elemental nitrogen (according to the reaction shown in Eq. 1), a direct determination of elemental nitrogen would be required. However, considering the exploratory nature of this study and the time required to perform the determinations, it was decided to estimate the fraction of ammonia oxidized to elemental nitrogen by differences; that is, to determine the ammonia nitrogen in the original solution before oxidation, then to determine the nitrite and nitrate nitrogen after oxidation and to assume that the difference represents the ammonia nitrogen oxidized to elemental nitrogen. It was recognized that considerable quantities of ammonia could be lost to the atmosphere when the oxidation was performed in open containers and when the pH of the solution was increased above 10.5 (at concentrations of ammonia of approximately 15 mg/l).

A. EXPERIMENTAL PROCEDURES

1. Preparation of Ammonia Solutions

An approximately 0.1 normal stock solution of NH_3 was prepared by diluting reagent grade, concentrated (30 percent) ammonia solution with demineralized double distilled water. It should be mentioned that throughout this work, the term water implies demineralized double distilled water. The exact concentration of the stock solution was determined by titration with 0.1 N hydrochloric acid using methyl red indicator. The dilute solutions used for the oxidation experiments were prepared by the dilution of the stock solution with water to the desired concentration. The dilute solutions were frequently checked with Nesslerization.

2. Oxidation of Ammonia with Potassium Ferrate(VI)

The oxidation of ammonia in water solutions was performed in beakers, sealed beakers and in a reactor shown on Figure 1. In the section entitled "Results and Discussion" the kind of equipment used will be stated at the appropriate places.

Eight hundred ml of the ammonia solution was measured into one liter beakers and adjusted to the desired initial conditions. A weighed quantity (± 0.0002 gm), of solid potassium ferrate(VI) corrected for purity was then added according to a specified mole ratio with the aqueous ammonia. After ferrate was added, the pH of the solution was measured, and then the solution was stirred (magnetic stirrer) continuously for 15 minutes. The pH and temperature were again recorded. The beaker was sealed and the reaction allowed to continue until decomposition of potassium ferrate(VI), as indicated by the disappearance of the specific red color of potassium ferrate(VI) was complete.

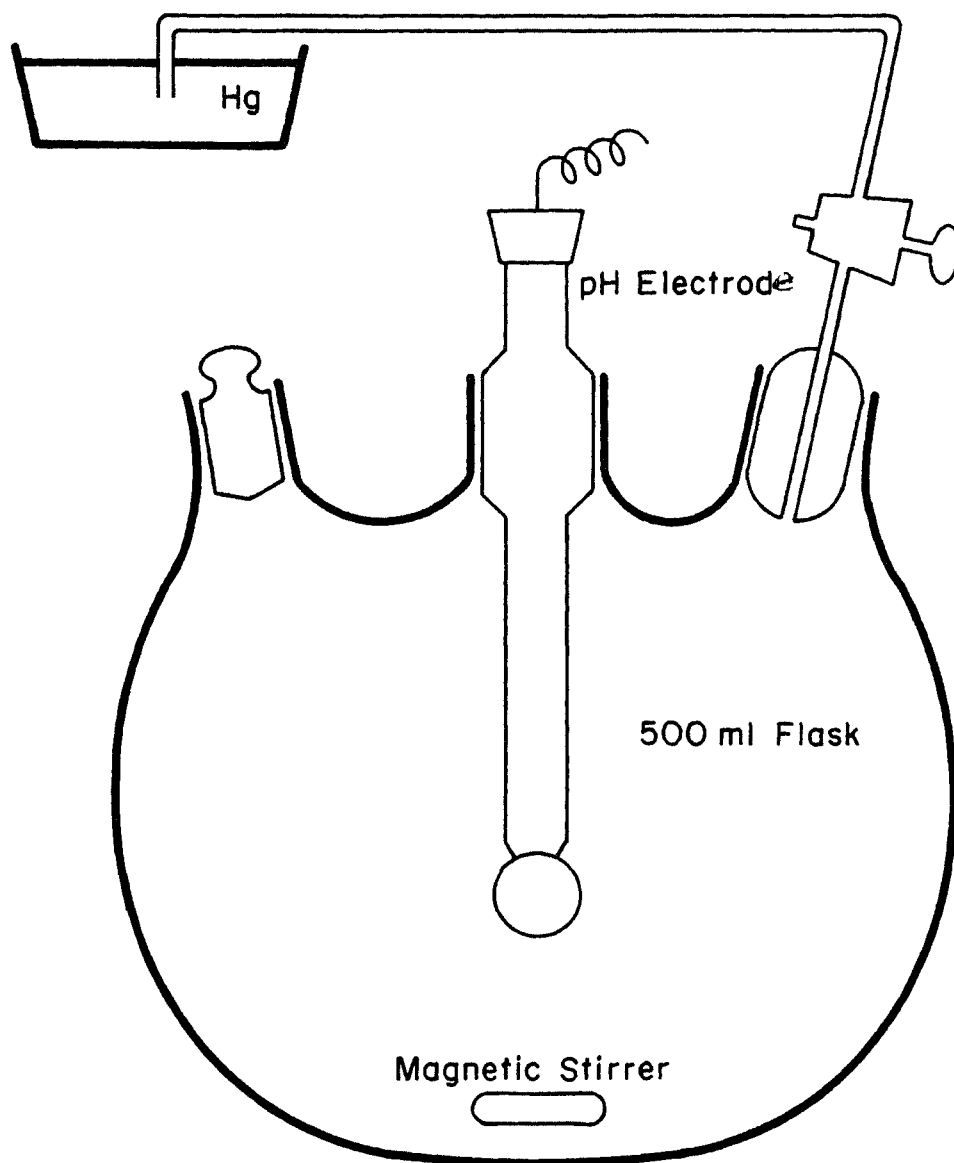


Figure 1. Reactor for determination of reaction products by oxidation of ammonia with potassium ferrate (VI).

Finally, the pH was recorded and then adjusted to slightly less than 7. The $F_2O_3 \cdot nH_2O$ that formed was allowed to settle before the samples for determination of ammonia, nitrate, and nitrite were taken.

Some ammonia losses to the ambient air during oxidation in open beakers was suspected, and similar experiments at the same conditions were conducted using potassium hydroxide instead of potassium ferrate(VI) to achieve the same final pH of the solution. The experiments showed that the losses of ammonia from the solutions of ammonia concentrations used in the study up to pH 11 could be neglected. It should be mentioned that in the experiments with potassium hydroxide instead of potassium ferrate(VI) one condition was omitted - the evolution of oxygen by potassium ferrate(VI) decomposition. The evolved oxygen will be in equilibrium with the ammonia solution and some ammonia may escape from the solution. The complete decomposition of 0.200 gm of K_2FeO_4 (a quantity frequently used in the experiments) yields approximately 18 ml oxygen at room temperature. The estimated losses of ammonia with the evolved oxygen, at the conditions of the experiments in this study, were too small to be considered significant when compared with the inherent errors of the analytical procedures.

Nevertheless, a series of runs were made in the reactor shown on Figure 1. The volume of the reactor was first calibrated with water. The reactor was filled with the ammonia solution so that all air was excluded from the flask. The solid stopper was inserted and the level of solution in the open neck of the flask was adjusted to that the insertion of the stopper-stopcock assembly would cause the solution to rise in the tubing up to a level below the stopcock. A weighted amount of solid K_2FeO_4 was added and the stopper-stopcock assembly inserted. The analytical procedure followed was similar to that for the oxidation performed in the open beakers.

3. Analytical Procedures

The ammonia determination was made by buffering 250 ml of the sample solution to a pH of 7.4 and distilling the solution. The ammonia was absorbed below the surface of a boric acid solution. Color was then developed by the addition of Nessler reagent, and the percent transmittance measured on a Beckman DU Spectrophotometer at a wavelength of 414 mμ. All samples were measured against a blank which was set at 100 percent transmittance. A calibration curve was prepared and checked frequently.

The nitrate nitrogen determination was made by the brucine method. This involved color development by addition of a brucine-sulfanilic acid reagent and concentrated sulfuric acid. All samples were measured for percent transmittance on a Beckman DU Spectrophotometer at a wavelength of 440 mμ. Again, a calibration curve was drawn and checked periodically.

The nitrite nitrogen was also determined colorimetrically. The color development was produced by addition of E.D.T.A. solution, sulfanilic acid, naphthylamine hydrochloride reagent and sodium acetate buffer solution. The percent transmittance was measured against a reagent blank on the Beckman DU at a wavelength of 520 mμ. Parallel checks were made frequently on the calibration curve to insure consistency.

One, five, and ten cm cells were used depending on the concentration of the component to be determined.

The detailed description of the analytical procedures are found in Standard Methods Edition 12 (Nitrate) and Edition 13 (Ammonia and Nitrite) (23, 24).

The pH was determined by Sargent Combination Electrodes on a Model DR pH meter.

B. RESULTS AND DISCUSSION

Extent of Ammonia Oxidation by Potassium Ferrate(VI)

1. Effect of pH

On Table 1 are shown the results of ammonia oxidation with potassium ferrate(VI) at ferrate to ammonia ratios of 1:1 and 2:1. Attempts were made to maintain the pH within acceptable limits. The initial pH of the solution was adjusted to the desired level with sulfuric acid or potassium hydroxide. Some of the experiments were conducted without any attempt made to keep the pH constant. In other experiments, the pH was maintained within reasonable close limits by the addition of buffers, and in some cases the final pH was controlled by the addition of dilute sulfuric acid solutions.

The sulfuric acid was added in predetermined quantities as quickly as possible and as soon as the potassium ferrate had dissolved. This procedure of sulfuric acid addition was chosen because the continuous addition of sulfuric acid to maintain the pH constant through the reaction caused the rapid decomposition of ferrate because of prolonged contact with local high acid concentrations. The phenomena will be discussed later in this report.

The results on Table 1 show that in the pH range 7.8-9.8 only six percent of the NH_3 was oxidized (No. 1); but in the pH range 9.5-10.5, on the average, 10-10.5 percent of the NH_3 was oxidized (No. 2,3). The results for test No. 4 appear high, but later experiments showed that the dissolution rate of potassium ferrate(VI) has an effect on the overall oxidation rate of ammonia. Tests No. 5-9 show the oxidation of ammonia at ferrate to ammonia rates of 2:1. In the pH range 8.0 to 8.5, the oxidation of ammonia is minimal and is explained by the very rapid decomposition of ferrate at the lower pH. The highest percent oxidation of ammonia (12.4 percent) was achieved in the pH range 8.6-9.0. Item No. 9 at ammonia nitrogen concentration of 40 ppm shows

TABLE 1

The Effect of pH on Oxidation of Ammonia With Potassium Ferrate(VI)

<u>No.</u>	<u>Test</u>	<u>NH₃-conc ppm N</u>	<u>K₂FeO₄:NH₃ mole ratio</u>	<u>pH</u>		<u>Percent NH₃ Oxidized</u>	<u>Remarks</u>
				<u>Initial</u>	<u>Final</u>		
1	12B	12.5	1:1	7.8	9.8	6.6	KH ₂ PO ₄ + K ₂ HPO ₄ Buffer
2	11B	12.5	1:1	9.5	10.6	10.5	No pH Control
3	25-26B	12.5	1:1	8.1	10.3	10.1	No pH Control
4	13B	12.5	1:1	9.1	10.5	19.8	H ₃ BO ₃ + NaOH Buffer
5	5B	12.5	2:1	8.1	8.0	0.5	H ₂ SO ₄ for pH Control
6	6B	12.5	2:1	8.5	8.5	0.5	H ₂ SO ₄ for pH Control
7	4B	12.5	2:1	7.9	8.8	5.3	H ₂ SO ₄ for pH Control
8	7B	12.5	2:1	8.6	9.0	12.4	H ₂ SO ₄ for pH Control + 100ppm NaCl
9	14B	40	2:1	9.4	12.0	7.5	No pH Control

a considerably lower percent ammonia oxidation. The lower percent oxidation is attributed to the high final pH but not to the higher ammonia concentration.

On Figure 2 a plot is shown of the percentage of ammonia oxidized by potassium ferrate(VI) as a function of the pH of the solution at a mole ratio of K_2FeO_4 to NH_3 of 1:1 and an ammonia nitrogen concentration of 40 ppm at 25°C. Each data point represents an average of several determinations. The plot shows that there is a maximum for ammonia oxidation at pH close to 10.4 in the pH range from 7 to 12.

2. Effects of Ferrate to Ammonia Mole Ratios

Table 2 records the results of ammonia oxidation with ferrate(VI) in the pH range of 9 to 11; concentrations of ammonia nitrogen of 12.5 and 40 ppm; ferrate to ammonia ratios from 0.5 to 7; and temperatures from 25 to 30°C. The results on Table 2 show that the percentage of ammonia oxidized increases with increasing mole ratios of K_2FeO_4 in the pH range from 9 to 10.5 (No. 10-14). It was also observed that the increase of NH_3 oxidation decreases with the increasing mole ratio of K_2FeO_4 to NH_3 . It was observed that the controlling factors are the pH and the rate of K_2FeO_4 decomposition in water solution. The rate of K_2FeO_4 decomposition in water solution increases with increasing concentration and decreasing pH. At pH less than 7 the decomposition of K_2FeO_4 in water is nearly instantaneous. This phenomena will be discussed in Section III on the kinetics of ammonia oxidation by potassium ferrate(VI). The results in Item 15 show a decrease of ammonia oxidation at a mole ratio of K_2FeO_4 to NH_3 of 7:1. This phenomena is attributed to the higher final pH of 11.1 which is above the optimal pH of 10.4. It should be mentioned that the tests designated by B were performed in sealed beakers, while the tests designated by S were conducted in a sealed reactor which will be described in Section III.

TABLE 2

Effect of K_2FeO_4 to NH_3 Mole Ratios on Ammonia Oxidation

<u>No.</u>	<u>Test</u>	<u>NH_3 conc ppm N</u>	<u>$K_2FeO_4:NH_3$ mole ratio</u>	<u>pH</u>		<u>Percent NH_3 Oxidized</u>	<u>Remarks</u>
				<u>Initial</u>	<u>Final</u>		
10	12a-12b S	40	0.5:1	9.8	10.1	6.5	$H_3BO_3 + NaOH$ Buffer
11	7-11	40	1:1	9.8	10.3	8.4	$H_3BO_3 \pm NaOH$ Buffer
12	13 S	40	1.5:1	9.8	10.6	10.2	$H_3BO_3 + NaOH$ Buffer
13	8 B	12.5	2:1	9.0	10.0	11.9	No pH Control
14	9 B	12.5	4:1	8.7	10.5	14.5	No pH Control
15	10 B	12.5	7:1	8.7	11.1	11.9	No pH Control

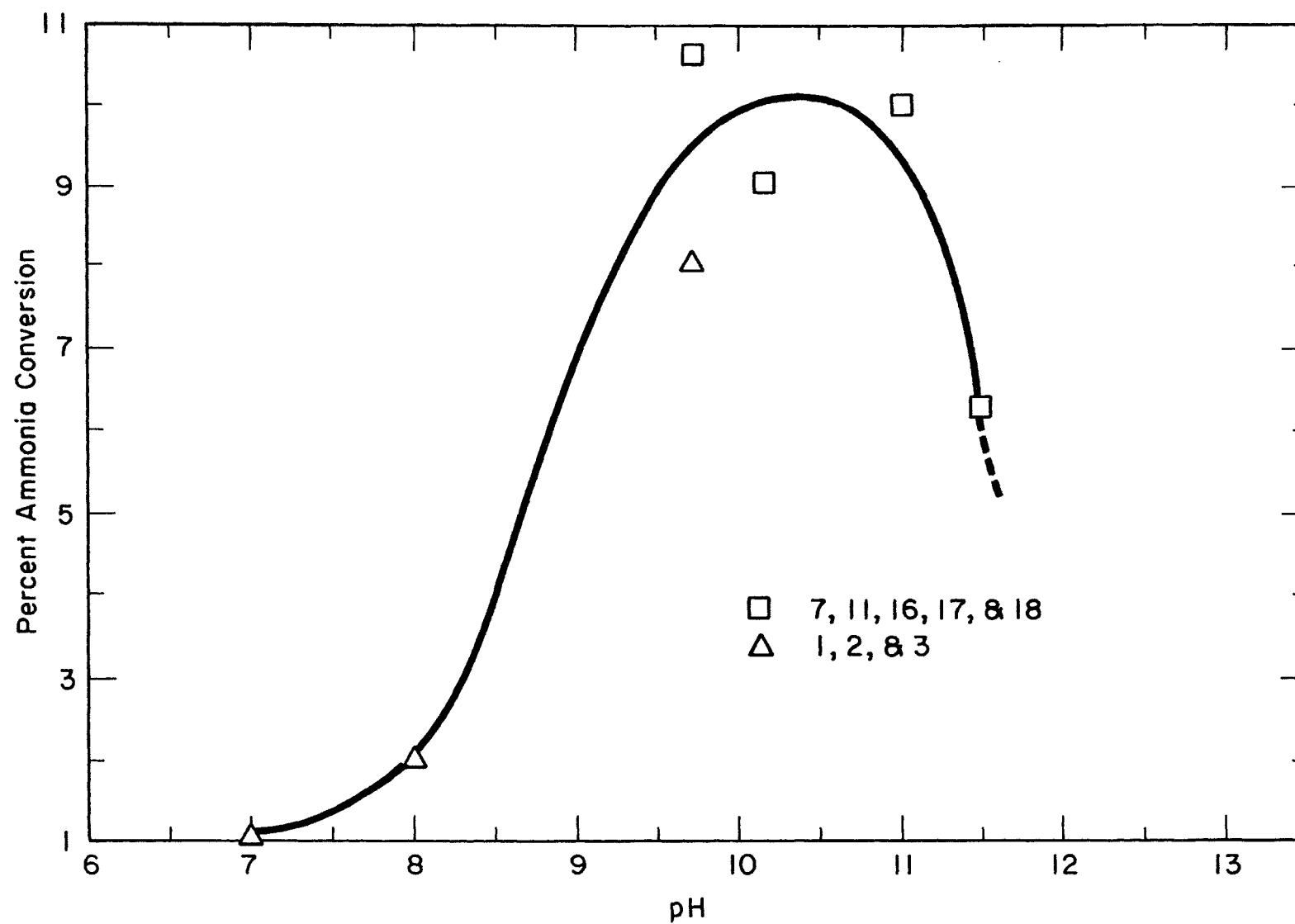


Figure 2. Percent of ammonia oxidized by potassium ferrate (VI) as a function of pH. Potassium ferrate (VI) to ammonia mole ratio 1:1.

3. Effect of Initial Concentration of Ammonia

Table 3 includes the results of ammonia oxidation by potassium ferrate(VI) at higher ammonia concentrations; K_2FeO_4 to NH_3 mole ratios of 2:1 and 5:1; and in the pH range of 9.4 to 13.6. The results show that the percentage of ammonia oxidized increases with increasing ammonia concentration. The lower oxidation attained at higher mole ratios (5:1) is attributed to higher final pH and higher concentrations of K_2FeO_4 which in turn accelerates the decomposition rate of K_2FeO_4 in water.

4. Effect of Temperature

Table 4 shows the results of ammonia oxidation by ferrate at different temperatures.

The results indicate that the oxidation of ammonia by ferrate(VI) is independent of temperature in the range from 10° to 40°C. It seems as though the change in decomposition of the ferrate(VI) was offset by the oxidation with ammonia. The Items 23 through 25 will be discussed further in Section III.

5. Oxidation of Ammonia by Stepwise Addition of Potassium Ferrate(VI)

From the work accomplished thus far, it appears that the concentration of potassium ferrate(VI) could also be a factor in ammonia oxidation.

TABLE 3

Effect of Initial Concentration of Ammonia on Ammonia Oxidation by Ferrate(VI)

<u>No.</u>	<u>Test</u>	<u>NH₃-conc</u>	<u>K₂FeO₄:NH₃</u>	<u>pH</u>		<u>Percent NH₃</u>	<u>Remarks</u>
		<u>ppm N</u>	<u>mole ratio</u>	<u>Initial</u>	<u>Final</u>	<u>Oxidized</u>	
16	16B	32.7	2:1	9.4	12.0	11.9	No pH Control
17	15B	65.5	2:1	9.6	12.3	12.9	No pH Control
18	14B	131	2:1	9.6	12.6	17.3	No pH Control
19	19B	32.7	5:1	10.6	13.2	5.1	No pH Control
20	18B	65.5	5:1	10.9	13.3	8.8	No pH Control

TABLE 4

Effect of Temperature on Ammonia Oxidation by Ferrate(VI)

<u>No.</u>	<u>Test</u>	<u>NH₃-conc ppm N</u>	<u>K₂FeO₄:NH₃ mole ratio</u>	<u>pH</u>		<u>Temp °C</u>	<u>Percent NH₃ Oxidized</u>	<u>Remarks</u>
				<u>Initial</u>	<u>Final</u>			
22	11bB	12.5	1:1	9.5	10.6	25.0	10.5	K ₂ HPO ₄ + KH ₂ PO ₃ Buffer
23	7-11S	40	1:1	9.8	10.3	9.9	10.3	H ₃ BO ₃ + NaOH Buffer
24	14S	40	1:1	10.2	10.6	25.0	9.8	H ₃ BO ₃ + NaOH Buffer
25	15S	40	1:1	9.8	10.2	39.7	8.9	H ₃ BO ₃ + NaOH Buffer

It was not feasible to keep the concentration of K_2FeO_4 constant by the continuous addition of solid K_2FeO_4 because of the operational difficulties that were encountered. To simulate constant K_2FeO_4 concentration, the K_2FeO_4 was added incrementally until a desired final ratio of K_2FeO_4 to NH_3 was reached. After adjusting the initial pH of the ammonia solution to the desired level, an increment of K_2FeO_4 was added to a definite mole ratio of ammonia. The solution was stirred to quickly dissolve the solid K_2FeO_4 , and the reaction allowed to proceed for a predetermined time. The pH was again adjusted, additional K_2FeO_4 was added, and the procedure continued until the final desired mole ratio of ferrate to ammonia was attained. The results obtained from this adapted procedure, are shown on Table 5. Run No. 26 was made in sealed beakers with an initial NH_3 -concentration of 131 ppm. After each addition of K_2FeO_4 (ratio 1:1) the reaction was allowed to proceed for 24 hours. Before the next addition of K_2FeO_4 the clear supernatant was decanted to another beaker. The weight of K_2FeO_4 was adjusted for the decreased volume of the decanted supernatant. The separation of the solution from the ferric hydroxide was done to eliminate the catalytic effect of ferric hydroxide on the decomposition rate of K_2FeO_4 as pointed out by Magee (21). It became apparent during the course of the work that the precipitated ferric hydroxide does not affect the decomposition rate of K_2FeO_4 , but that the dissolved ferric iron $Fe(OH)_4^{-1}$ does. Run No. 26 shows a decrease of ammonia oxidized for each subsequent addition of K_2FeO_4 (ratio 1:1). Approximately 11.8 percent of the ammonia was oxidized at a cumulative K_2FeO_4 to NH_3 ratio of 3:1, compared with Runs. No. 13 and 14 where an estimated 13.4 percent of NH_3 was oxidized and practically no gain was observed. Run No. 27 was made in the sealed reactor (Section III) without separation of the precipitated ferric hydroxide. Nearly 16.2 percent of ammonia was oxidized by four additions of K_2FeO_4 which resulted in a

TABLE 5

Oxidation of Ammonia by Ferrate(VI) by Incremental Addition of K_2FeO_4

No.	Test	Initial NH ₃ -conc ppm/N	Number of K ₂ FeO ₄ Increments Added	K ₂ FeO ₄ :NH ₃ Mole Ratio		pH		Percent NH ₃ Oxidized		
				Added	Cumulative	Initial	Final	Per Addition	Total	
26	20B	131	1	1:1	1:1	7.0	10.6	6.0	6.0	
			2	1:1	2:1	7.0	9.8	3.8	9.8	
			3	1:1	3:1	7.0	9.8	2.0	11.8	
27	20S	40	1	0.5:1	0.5:1	9.7	10.5	3.4	3.4	
			2	0.5:1	1:1	9.8	11.3	4.0	7.4	
			3	0.5:1	1.5:1	9.6	11.4	3.9	11.3	
			4	0.5:1	2:1	9.5	10.8	4.9	16.2	
28	21S	40	1	0.5:1	0.5:1	9.6	10.4	3.6	3.6	
			2	0.5:1	1:1	9.5	10.6	3.9	7.5	
			3	0.5:1	1.5:1	9.6	10.8	5.5	13.0	
29	1E	40	6	0.5:1	3:1	9.1 to 10.1	10.3 to 11.2	Not Determined		21.3
30	2E	40	6	0.5:1	3:1	8.8 to 10.4	9.8 to 11.8	Not Determined		24.2
31	3E	40	6	0.5:1	3:1	9.5 to 11.5	10.3 to 11.5	Not Determined		22.2
32	4E	40	6	0.5:1	3:1	8.8 to 10.4	10.2 to 11.8	Not Determined		20.8
33	5E j	40	6	0.5:1	3:1	8.5 to 10.0	10.5 to 11.8	Not Determined		17.7

cumulative $K_2FeO_4:NH_3$ ratio of 2:1. Compared with Run No. 13 of 11.9 percent oxidized a considerable improvement was attained. Run No. 28 was performed with an initial ammonia solution of 4 liters in a sealed beaker and intermediate ferric hydroxide removal. Thirteen percent of ammonia was oxidized which is close to Run No. 27, at cumulative K_2FeO_4 to NH_3 ratio of 1.5:1, indicating negligible gain with intermediate ferric hydroxide removal.

Runs No. 29 through 33 were performed in the reactor (Figure 1) described at the beginning of this section and samples for analysis were taken after the last portion of K_2FeO_4 was added. Runs No. 29, 30, and 32 were conducted by allowing the reaction to proceed for 24 hours before the next portion of K_2FeO_4 was added but Runs. No. 31 and 33 were conducted by adding the K_2FeO_4 at intervals of one hour. The stepwise addition of K_2FeO_4 shows a considerable increase in ammonia oxidation but also shows a decrease of ammonia oxidized per portion of K_2FeO_4 added which may be attributed to the ferric iron introduced into the solution already by addition of the first batch of K_2FeO_4 . On the average the results indicate that probably there is an optimal concentration of K_2FeO_4 at which the most efficient oxidation of ammonia is attained.

6. Reaction Products

The results obtained on the determination of the reaction products should be considered critically, particularly with respect to the fraction of oxidized ammonia that is converted to elemental nitrogen. As mentioned earlier in this section, the fraction of oxidized ammonia that was converted to elemental nitrogen was estimated by differences, i.e., it was assumed that ammonia is oxidized by potassium ferrate(VI) to N_2 , NO_2^- , and NO_3^- only, and that the amount of N_2 produced may be estimated by subtracting the determined quantities of nitrate and nitrite nitrogen from the determined total quantity of ammonia nitrogen that is oxidized.

The inherent errors of each separate determination accumulate when the determined quantities are added together, and the total error appears in the quantities determined by differences. Relatively low initial concentrations of ammonia were used in this study to approach the realistic concentrations encountered in a sewage treatment plant effluents. The analytical procedures generally used for the determination of the compounds present in water at low concentrations do not pretend on the highest accuracy either. The decision to determine the elemental nitrogen by differences was made for the following reasons: 1) the time and the work to be spent on this exploratory study was limited, and 2) during the course of the work it was recognized that the fraction of ammonia oxidized at the selected conditions was smaller than expected, and therefore more work had to be spent on the exploration for optimal conditions of ammonia oxidation and particularly on the kinetics of the process.

Table 6 shows the relative quantities of oxidation products of ammonia with potassium ferrate(VI) at specified conditions.

Run No. 34 was made in the sealed beakers without pH control. Run No. 35 was a continuation of Run No. 34. Twenty four hours after Run No. 34 was terminated, the pH was adjusted to 8.6; samples for analysis were withdrawn; and another batch of K_2FeO_4 was added. The two runs show that when the first addition of ferrate was made, over 50 percent of the oxidized ammonia was converted to elemental nitrogen; but on the second addition, NO_3^- and NO_2^- were preferentially formed. Similar phenomenon were observed during the course of this work, and the dissolved ferric iron was suspected as the cause of the apparent catalytic effect. The restrictive time did not allow the investigation of this phenomena to be pursued further.

TABLE 6

Relative Quantities of Oxidation Products Formed by Oxidation
of Ammonia with Potassium Ferrate(VI)

No.	Test	Initial NH ₃ -conc ppm/N	K ₂ FeO ₄ :NH ₃ Mole Ratio	pH		Percent NH ₃ Oxidized	Reaction Products Relative %		
				Initial	Final		N NO ₃ ⁻	N NO ₂ ⁻	N N ₂
34	23B	12.5	1:1	8.1	10.3	8.9	43	0	57
35	24B	11.4	1:1	8.6	10.9	15.2	81	2	17
36	25B	12.5	1:1	8.1	10.3	12.4	25	18	57
37	26B	12.5	1:1	8.1	10.3	8.9	17	0	83
38	27B	12.5	1:1	8.0	9-10	7.6	30	9	61
39	28B	12.5	1:1	7.0	9-10	5.1	91	2	7
40	1E	40	0.5-3.0:1	9.1-10.1	10.3-11.2	21.3	98	2	nil
41	2E	40	0.5-3.0:1	8.8-10.4	9.8-11.8	24.2	99	1	nil
42	3E	40	0.5-3.0:1	9.5-11.5	10.3-11.5	22.2	77	23	nil
43	4E	40	0.5-3.0:1	8.8-10.4	10.2-11.8	20.8	99	1	nil
44	5E	40	0.5-3.0:1	8.5-10.0	10.5-11.8	17.7	61	39	nil
45	B1	43	2:1	8.1	12.0	15.3	53	18	29
46	B2	43	2:1	8.0	11.5	16.8	48	14	38
47	B4	43	3:1	7.7	12.0	19.6	60	15	25
48	B3	43	2:1	4.5	11.5	3.2	90	10	0

Test Runs No. 36 and 37 were performed similarly to Run No. 34 in order to check the reproducibility of results. Even higher percentages, (on the average over 70 percent) of the oxidized ammonia were converted to elemental nitrogen. Runs No. 38 and 39 were run similarly to Run No. 34 except that sodium bicarbonate was added to suppress the excessive pH increase. The results show that the overall oxidation of ammonia did not increase (Run No. 38) and that the amount of ammonia oxidized to elemental nitrogen was similar to Runs No. 36 and 37. Run No. 39 was started at a lower pH, and the results show a considerably lower overall oxidation of ammonia and a higher fraction of the oxidized ammonia converted to nitrate. This is in agreement with Halferich's and Lang's (12) statement that at lower pH ammonia is oxidized by ferrate(VI) to nitrate and nitrite.

Runs No. 40 through 44 were performed in the reactor shown on Figure 1 and are the same runs shown on Table 5 under numbers 29 through 33, but the relative amounts of oxidation products are shown on Table 6. The determination of nitrate nitrogen was done by the cadmium reduction method (24). The very small fraction of oxidized ammonia converted to elemental nitrogen was attributed to the contamination of the samples by atmospheric nitric oxides because of a prolonged contact of samples with the ambient air. In Runs No. 42 and 44 the addition of ferrate was done after only one hour elapsed for the reaction to proceed before the next batch of ferrate was added. The results show that a considerably larger fraction of the total oxidized ammonia was converted to nitrite when compared with Runs No. 40, 41, and 43 when ferrate was added at 24 hour intervals. This indicates that the oxidation reaction mechanism of ammonia with ferrate(VI) is not a simple one.

Experiments listed under Runs No. 45 through 48 were done for the dual purpose of determining the extent of ammonia oxidation and the relative amounts of reaction products in the presence of phosphate and of determining the percentage of phosphate precipitated from the solution. The experiments were performed in the reactor shown on Figure 1. Runs No. 45 and 46 were run at similar conditions to check the reproducibility of the results. The runs show an average oxidation of ammonia of 16 percent.

When compared with similar runs made without additions of phosphate, an increase in ammonia oxidation of approximately 3 percent is indicated. This may be attributed to the buffering properties of the phosphate and probably to the complexing of dissolved ferric iron by phosphate. Run No. 47 was made under similar conditions to Runs No. 45 and 46 except that the ferrate to ammonia ratio was 3:1 and higher concentrations of phosphate were used. The results, 19.6 percent ammonia oxidized, are approximately 6 percent higher than the results obtained at similar conditions in the absence of phosphate. Runs No. 45, 46 and 47 show that approximately 33 percent of the ammonia was oxidized to elemental nitrogen. Run No. 48 was done with a low initial pH of 4.5. The results show that only 3 percent of ammonia was oxidized to nitrate and nitrite and none was oxidized to elemental nitrogen. This again is in agreement with Halferich's and Lang's findings that at low pH the ammonia is oxidized preferentially to nitrate and nitrite. The low overall oxidation of ammonia is attributed to the low initial pH of the solution. At low pH a solution of potassium ferrate(VI) decomposes too rapidly to oxidize considerable quantities of ammonia. The process of ammonia oxidation, particularly to elemental nitrogen, is slow and is apparently due to the complicated reaction mechanisms and sensitivity to the imposed conditions.

7. Precipitation of Phosphate

Runs No. 45 through 48 were also done to determine the precipitation of phosphate by the ferric iron formed in the course of the oxidation of ammonia. Table 7 shows the results of these experiments.

TABLE 7

Phosphate Removal by Potassium Ferrate					
<u>No.</u>	<u>Test</u>	Initial PO ₄ -conc	Fe:PO ₄	<u>Final pH</u>	Percent PO ₄
		<u>ppm</u>	<u>mole ratio</u>		<u>Removed</u>
45	B1	104	2:1	12.0	26
46	B2	99	2:1	11.5	21
47	B3	102	3:1	12.0	27
48	B4	102	2:1	11.5	10

The results show that phosphate removal by ferrate(VI) is not efficient. The low phosphate removal efficiency may be attributed to the following:

1) The rate of ferric hydroxide formation during the decomposition of ferrate(VI) is faster than the rate of formation of ferric phosphate which is evident considering Run No. 48 when the decomposition of ferrate was fast (initial pH 4.5).

2) The final pH of the solution is above the range of minimum solubility of ferric phosphate.

SECTION III

EXPLORATORY STUDIES ON THE KINETICS OF AMMONIA OXIDATION BY POTASSIUM FERRATE(VI)

The literature search did not reveal any data on the kinetic rate of the oxidation of ammonia by ferrate(VI). Such data would be required to determine the optimum conditions to oxidize ammonia in wastewater. In fact, without such data it would be impossible to determine if this system could find practical application.

To limit the scope of this work the following assumptions and limitations were imposed on the laboratory work:

- 1) Only changes in pH, mole ratios of potassium Ferrate(VI) to ammonia, and temperatures were made during this study. No attempt was made to control or measure the ionic strength of the solutions.
- 2) Only the rates of change of ammonia and ferrate(VI) were studied.
- 3) The initial concentration of ammonium sulfate was kept close to 40 ppm ammonia nitrogen.
- 4) It was assumed that only the four equations (1), (2), (3), (4) of Section II took place.

Based upon the above criteria, an attempt was made to find the best operating conditions for the particular system.

A. EXPERIMENTAL PROCEDURES

The equipment for this study, shown as Figure 3, consisted of a 500 ml three neck flask for the reaction vessel, a variable speed stirrer with a ground glass adapter to fit the center neck of the flask, a combination pH electrode with a Teflon adapter to fit one of the side necks of the flask, a pH meter, a stirred jacketed water bath for the reaction vessel, a thermistor controlled heating/cooling unit, and a Beckman automatic titrating unit.

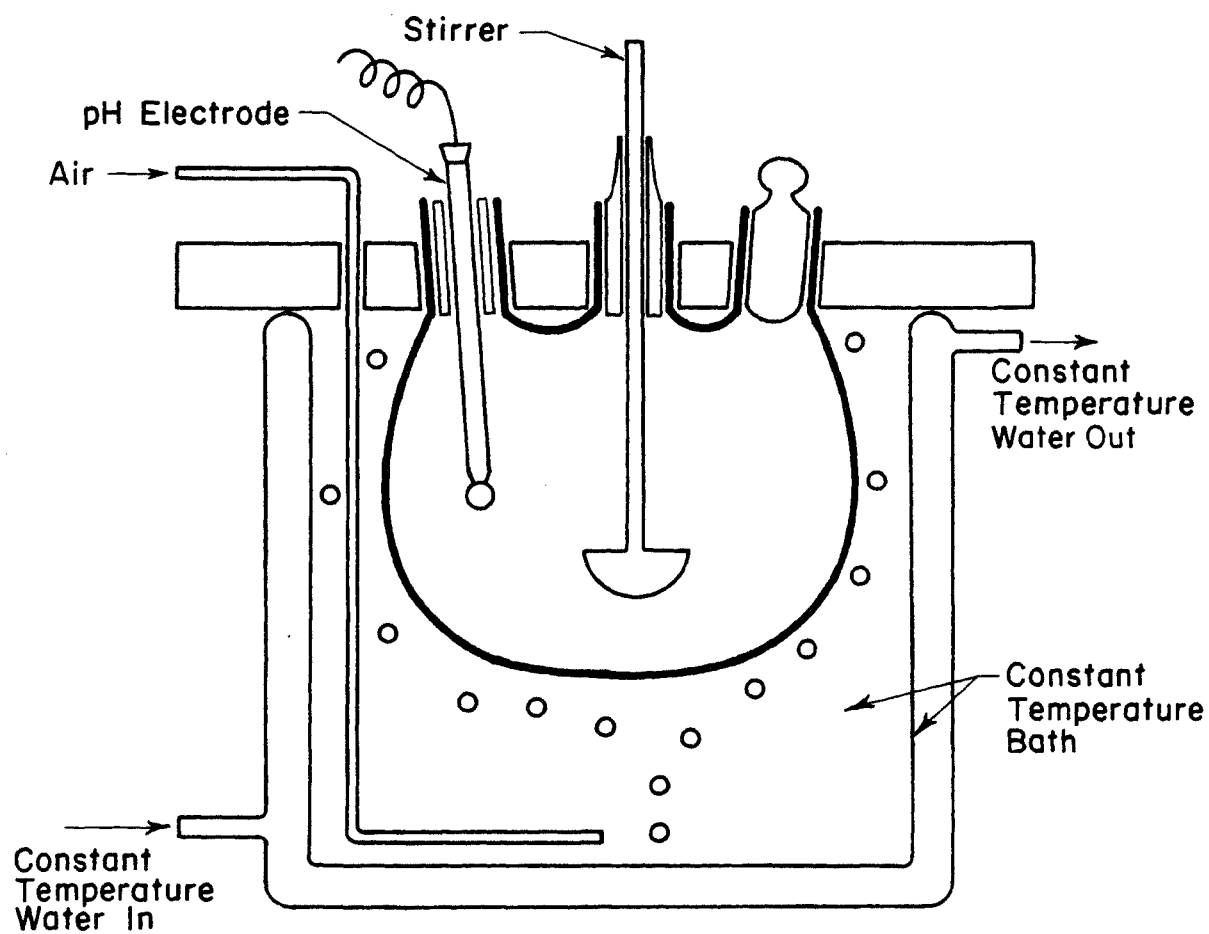


Figure 3. Reactor used for kinetic studies on ammonia oxidation by potassium ferrate (VI).

The solid ferrate(VI) was added through the third neck of the flask which was then kept stoppered at all times except when sampling.

The reaction mixture was constantly stirred and continually monitored for pH. The pH was suppressed by additions of either dilute sulfuric acid or boric acid-sodium hydroxide and phosphate buffers. The temperature was controlled by the constant temperature bath.

The reaction mixture consisted of ammonium sulfate solution from a 616 ppm standard solution and potassium ferrate(VI) from an 80.7 percent pure solid source.

Samples were taken at intervals and the following analyses were run.

Ammonia Determination.

A 25 ml sample was placed in 500 ml distillation flask, the pH was adjusted to a value greater than 8 as required, and enough water was added to make the total volume about 300 ml. The first 100 ml of the resulting solutions was distilled into a 250 ml volumetric flask containing 25 ml of a 20 gm/l solution of boric acid. The flask was then filled to the mark.

If the distillation was run slowly (over a 2 to 3 hour period), the sample was titrated with 0.0512 N HCl, using 6 drops of bromcresol green-methyl red (50 mg of each per 50 ml of 95% ethanol) mixed indicator. The color change was green to pink at the end point.

For faster distillation times, three 25 ml samples of the distillate were diluted to 50 ml each in volumetric flasks. To these flasks 4 ml of Nessler reagent was added. After standing for 20 minutes, the samples were measured for transmittance in a Beckman DU Spectrophotometer at 414 mμ wavelength. The concentration of ammonia was then read from a graph of standard ammonia values (23). The calibration curve was checked frequently with standard ammonia solutions.

Ferrate Determination.

To determine the amount of unreacted ferrate(VI) in the reaction mixture, 10.0 or 20.0 ml of sample were added to 5.00 or 10.0 ml of 0.02 N alkaline arsenite solution in a 500 ml Erlenmeyer flask. The resulting solution was acidified with 100 ml of 1:5 sulfuric acid and diluted with water to 200 ml. Two drops of osmate solution and one drop of ortho-phenanthroline ferrous complex indicator were added to the solution. The solution was then titrated with 0.01 N cerate solution (22). The concentration of ferrate(VI) was calculated as follows:

$$\text{mg/l(ppm) K}_2\text{FeO}_4 = \frac{(\text{ml AsO}_3^{3-} \times \text{N} - \text{ml Ce}^{4+} \times \text{N}) \times (\text{MWK}_2\text{FeO}_4) \times 1000}{3 \times \text{ml sample}}$$

Each batch of cerate solution was standardized before being used with 0.01 gms of primary standard arsenious oxide. To it 25 ml of water and 2 gms of solid NaOH were added. The resulting solution was diluted with 125 ml of water. Then 25 ml of 5 N sulfuric acid and two drops of 0.025 M orthophenanthroline indicator solution were added and the solution titrated with the cerate solution. The end point is pink to very light blue (25). The normality of the cerate solution is given by:

$$\text{N} = \frac{\text{gm As}_2\text{O}_3 \times 4000}{(\text{MW As}_2\text{O}_3) \times \text{ml Ce}^{+4}}$$

The arsenite solution had to be standardized before each run against the standard cerate solution. Using a 5.00 ml arsenite sample, the same procedure as was used for the ferrate(VI) determination was followed.

Buffer Solutions.

The boric acid-sodium hydroxide and other buffer solutions were prepared from standard tables in Lange's handbook (26).

B. RESULTS AND DISCUSSION

At the start of the kinetic studies it was thought that the ammonia could be determined directly from the reaction mixture by 1) stopping the reaction with sodium sulfite, 2) centrifuging the mixture to remove suspended iron hydroxide, and 3) running a Nesslerization reaction to determine the ammonia content. The first runs were analyzed in this manner. Only in the lower pH range where the iron hydroxide precipitated out readily could an order of magnitude of ammonia conversion be obtained. Also, it was observed that at an initial pH less than 7 there was essentially no conversion of ammonia. The ferrate(VI) decomposed almost instantaneously. This is in agreement with the results discussed in Section II.

Runs 6, 7, 9 and 12 were all tests to see if satisfactory results could be obtained from the distillation method for ammonia analysis, and to see if replication of results for a given set of conditions could be obtained. The results of the Runs 7, 11A, 11B and 11C are shown on Figures 4 and 5. A ferrate(VI) to ammonia ratio of 1:1 and a pH of about 10 at a temperature of 25°C were the conditions for these runs. It was discovered from Runs 6 and 9 that an initial ammonia sample prior to reaction with ferrate(VI) was needed because of the fluctuations in determining initial ammonia concentrations from the known standard's concentration and the volume of the standards added to the reaction vessel. The results show on the average close to 10 percent ammonia conversion at the imposed conditions and that the maximum conversion of ammonia and the nearly complete decomposition of potassium ferrate(VI) was reached in approximately 5 hours.

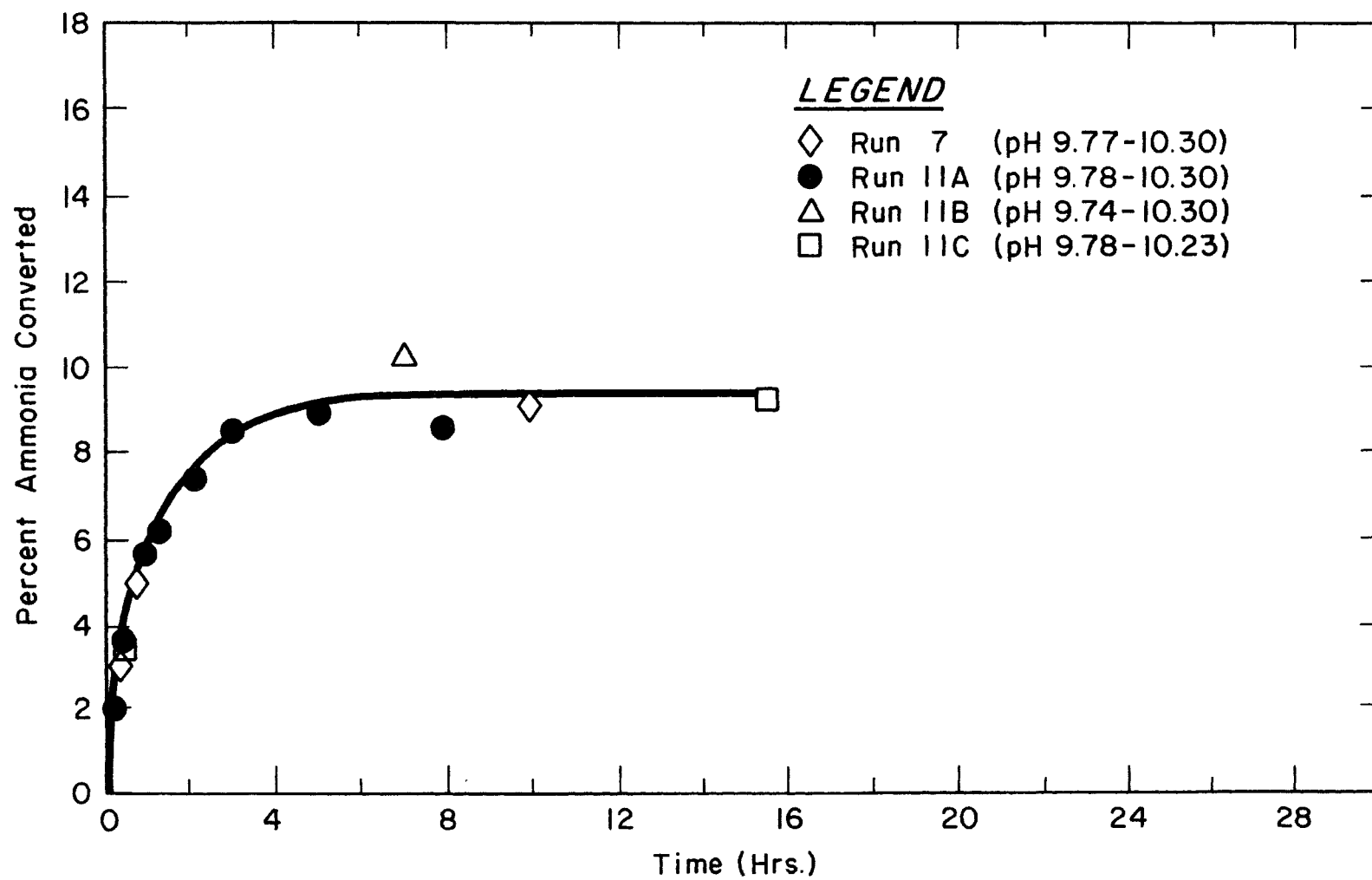


Figure 4. Ammonia conversion vs. time, potassium ferrate (VI) to ammonia mole ratio 1:1, temperature 25°C.

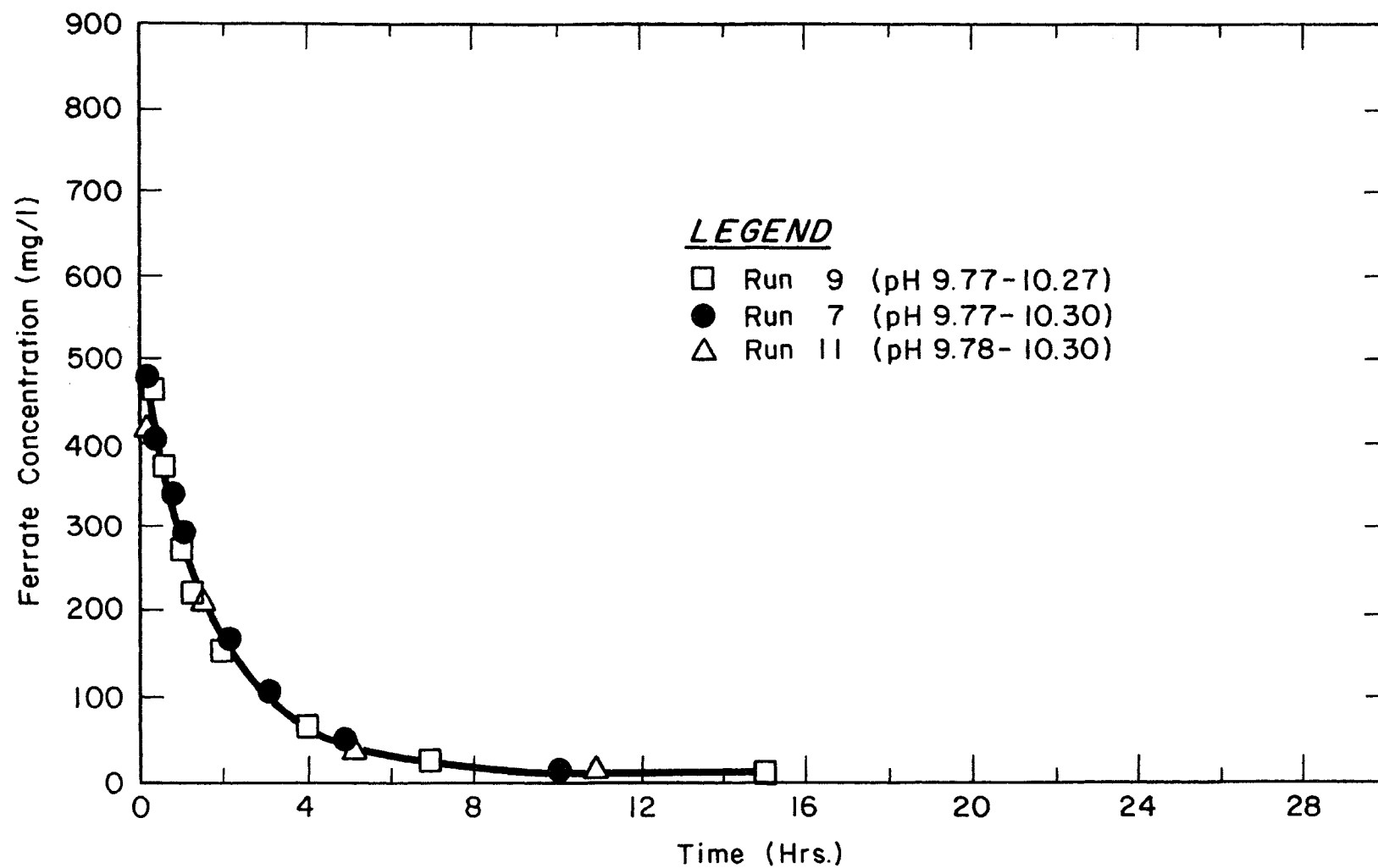


Figure 5. Potassium ferrate (VI) concentration vs. time. Potassium ferrate (VI) to ammonia mole ratio 1:1, temperature 25°C.

Runs 8 and 10, shown on Figure 6, were conducted without the addition of ammonia, but otherwise at exactly the same imposed conditions as Runs 6 and 7 which also are shown on Figure 6 for comparison. In addition, in Run 10, sodium sulfate was added to see if the sulfate ion had any effect on the rate of decomposition of the ferrate(VI). The comparison of the two pairs of curves show that the rate of ferrate(VI) disappearance is higher during the main period of reaction in the presence of ammonia and may be attributed to the oxidation of ammonia. The added sulfate (Run 10) may slightly hinder the decomposition rate of ferrate(VI), but it should be mentioned that nothing was done to maintain equal ionic strength in Runs 8 and 10.

Runs 11 and 12 were repeated using only one sample at the end of the run to see if ammonia losses were significant because of the increased volume of gases trapped over the reaction solution during the normal sampling of a run in progress. It was found that the final ammonia conversions were equivalent with or without intermediate sampling, and that ammonia losses were negligible for the adapted experimental procedures at the specified conditions.

Runs 7, 11, 12 and 13 (shown on Figures 7 and 8) compared the conversion of ammonia and the disappearance of potassium ferrate(VI) for various mole ratios of ferrate(VI) to ammonia. At ratios of 0.5:1, 1:1 and 1.5:1, 6.5 percent, 9.2 percent, and 10.8 percent of ammonia was converted respectively. These results and the results discussed in Section II show that the percentage of ammonia oxidized is not proportional to the ratio of ferrate(VI) to ammonia, but that the increase of ammonia oxidized decreases with an increased ferrate(VI) to ammonia mole ratio.

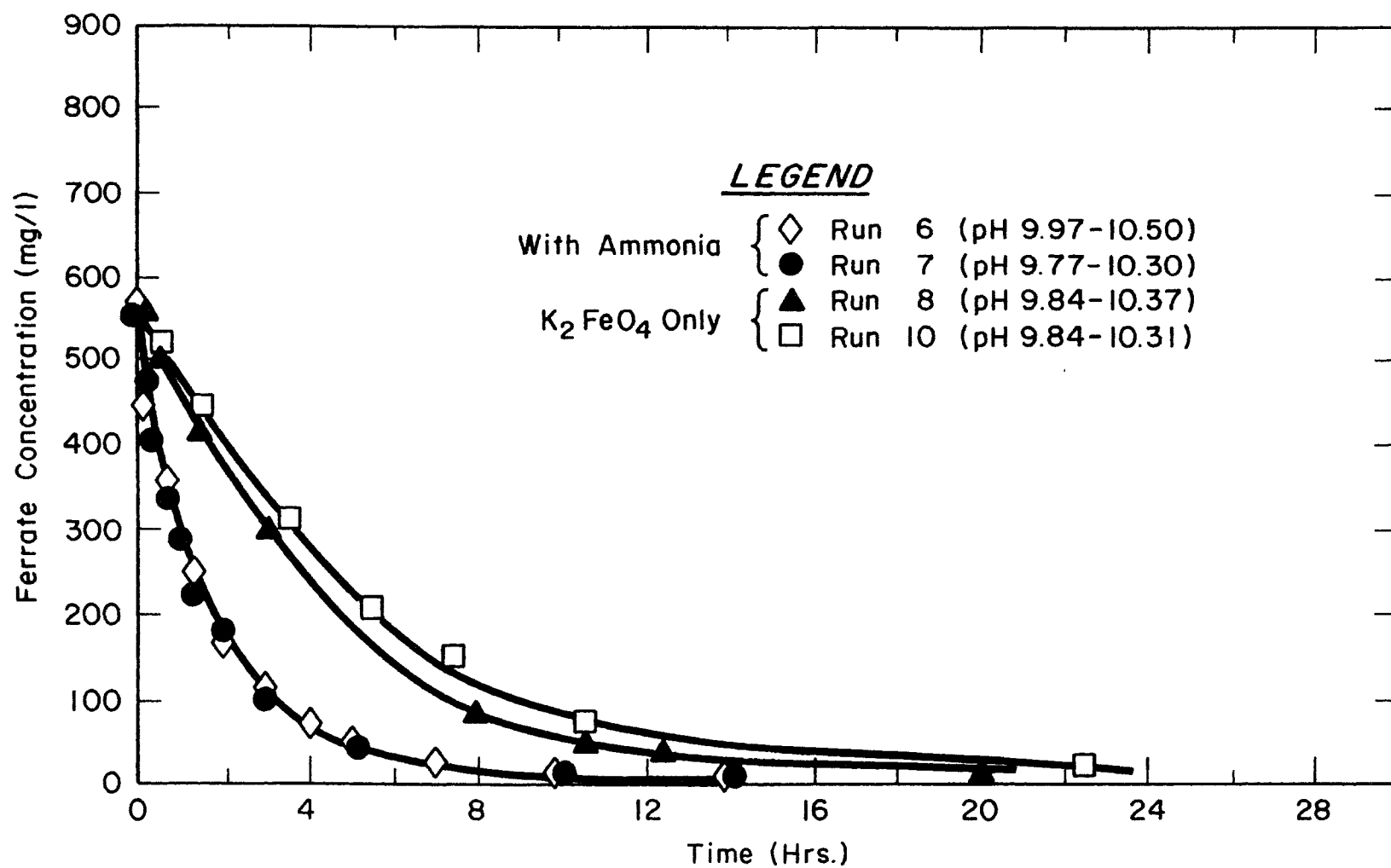


Figure 6. The decomposition of pure potassium ferrate (VI) solution vs. time and in presence of ammonia (mole ratio 1:1) and sulfate at 25°C.

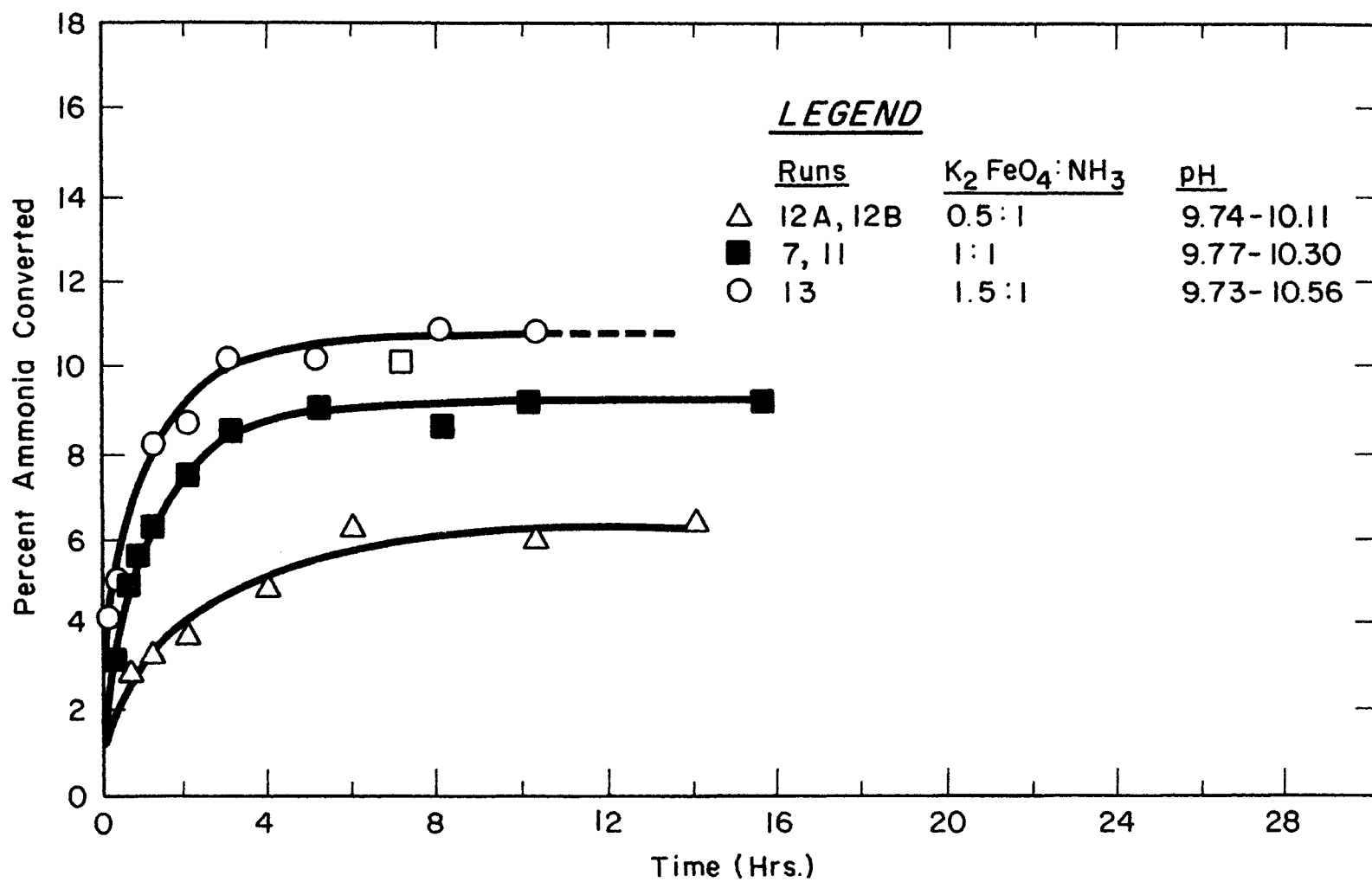


Figure 7. Ammonia conversion vs. time at different potassium ferrate (VI) to ammonia mole ratios and at 25°C.

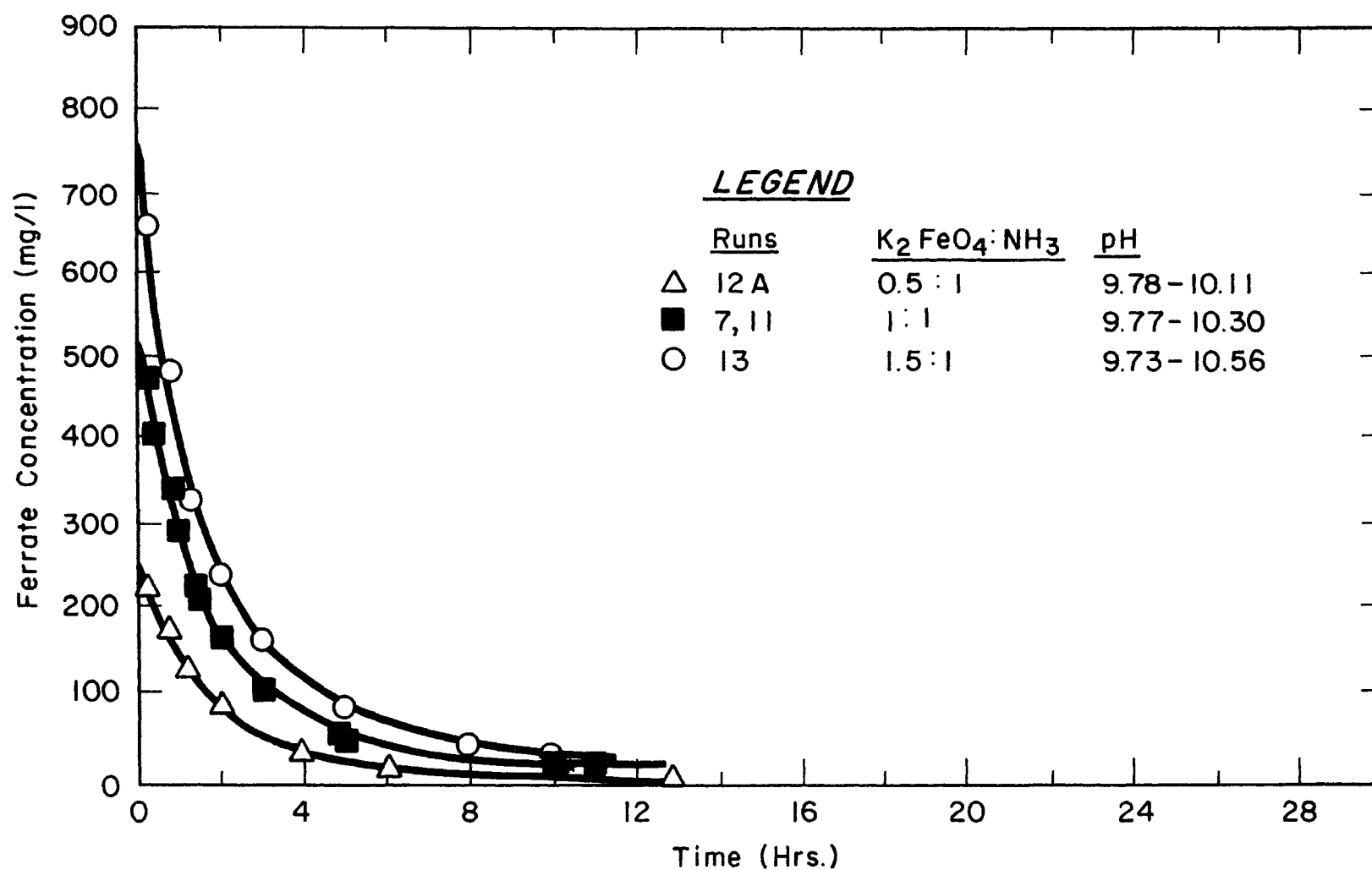


Figure 8. Potassium ferrate (VI) decomposition vs. time at different ferrate (VI) to ammonia mole ratios at 25°C.

Figures 9 and 10 compare the results of Runs 14 and 15 to those of Runs 7 and 11. Runs 14 and 15 were conducted at 9.9°C and 39.7°C respectively with a 1:1 ferrate(VI) to ammonia mole ratio and an average pH of 10. Runs 7 and 11 were operated at 25°C. The results indicate that the conversion of ammonia was independent of temperature within this temperature range. It seems as though the change in the decomposition rate of the ferrate(VI) is offset by the change in the rate of the reaction with ammonia. However, the time that the final conversion was reached was definitely dependent on the temperature of the reaction. The final conversion was reached much faster at 40°C than at 10°C.

Runs 7, 11, 16, 17 and 18 (Figures 11 and 12), were operated at 25°C with a 1:1 ferrate(VI) to ammonia ratio and different pH ranges to determine the pH range for maximum ammonia conversion. A plot of the conversion of ammonia as a function of pH shown on Figure 2 (Section II) along with the results of Runs 16, 17, and 18, and indicates that a pH of about 10.4 produced the best ammonia conversion. Comparing the results on Figures 11 and 12, it is shown that higher ammonia oxidation is attained at the slower ferrate decomposition rates.

For all these runs, buffer solutions were used to control the pH, and slow mixing was employed. Run 19 was made to see how automatic titration with 1 N sulfuric acid would affect the end results. In order to minimize local low pH when the acid was added, a stirrer speed of 150 rpm was used to insure rapid mixing and a more uniform concentration of reactants. The set point for control was a pH of 10.7. Run 19 produced an ammonia conversion of 4.9% while Run 16, which was operated in a similar pH range, produced an ammonia conversion of 10%. Apparently, despite the intensified mixing, the local pH in the vessel dropped below 7 and caused rapid ferrate(VI) decomposition.

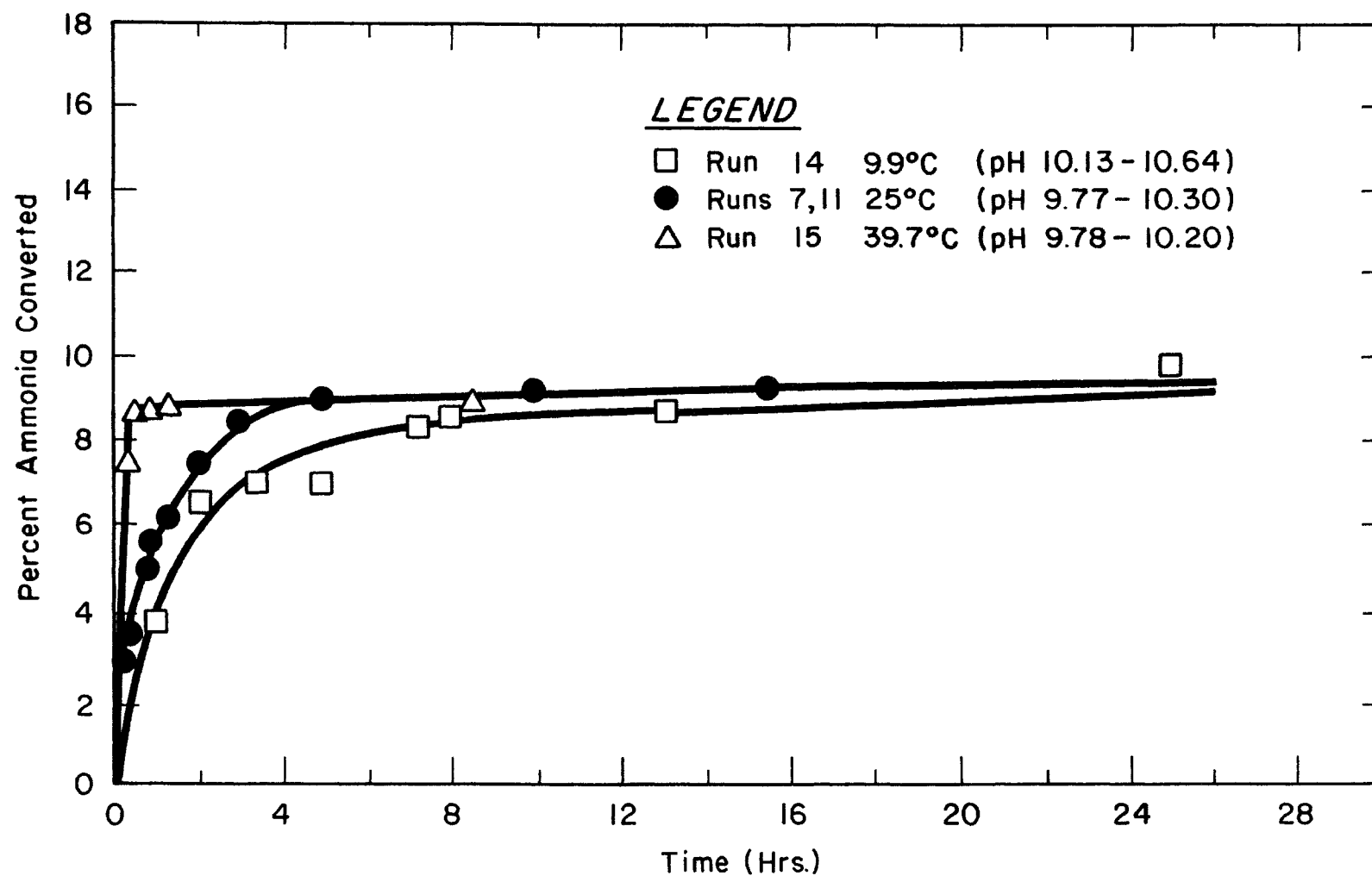


Figure 9. Ammonia conversion vs. time at different temperatures and ferrate (VI) to ammonia mole ratio 1:1.

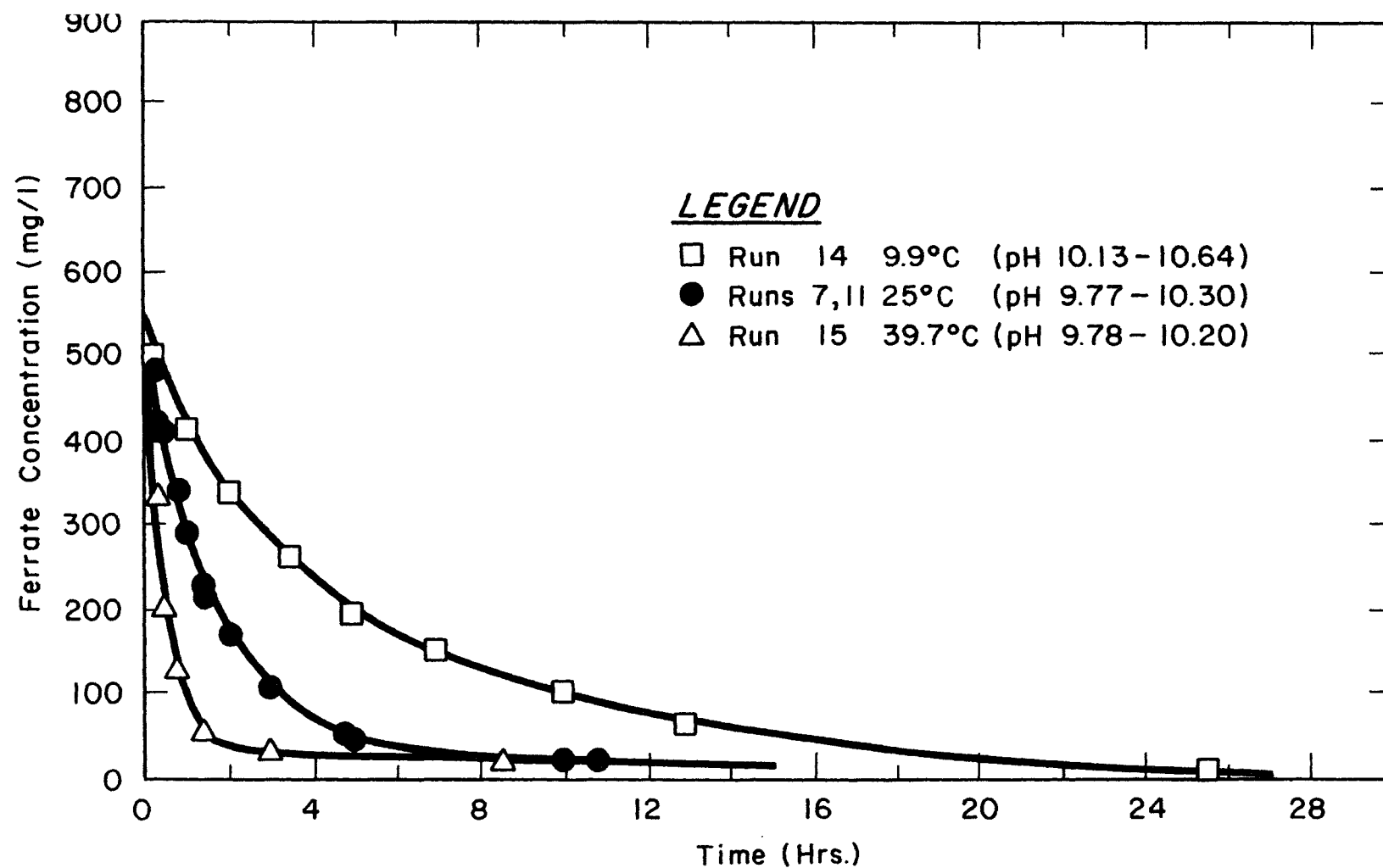


Figure 10. Potassium ferrate (VI) decomposition vs. time at different temperatures, ferrate (VI) to ammonia mole ratio 1:1.

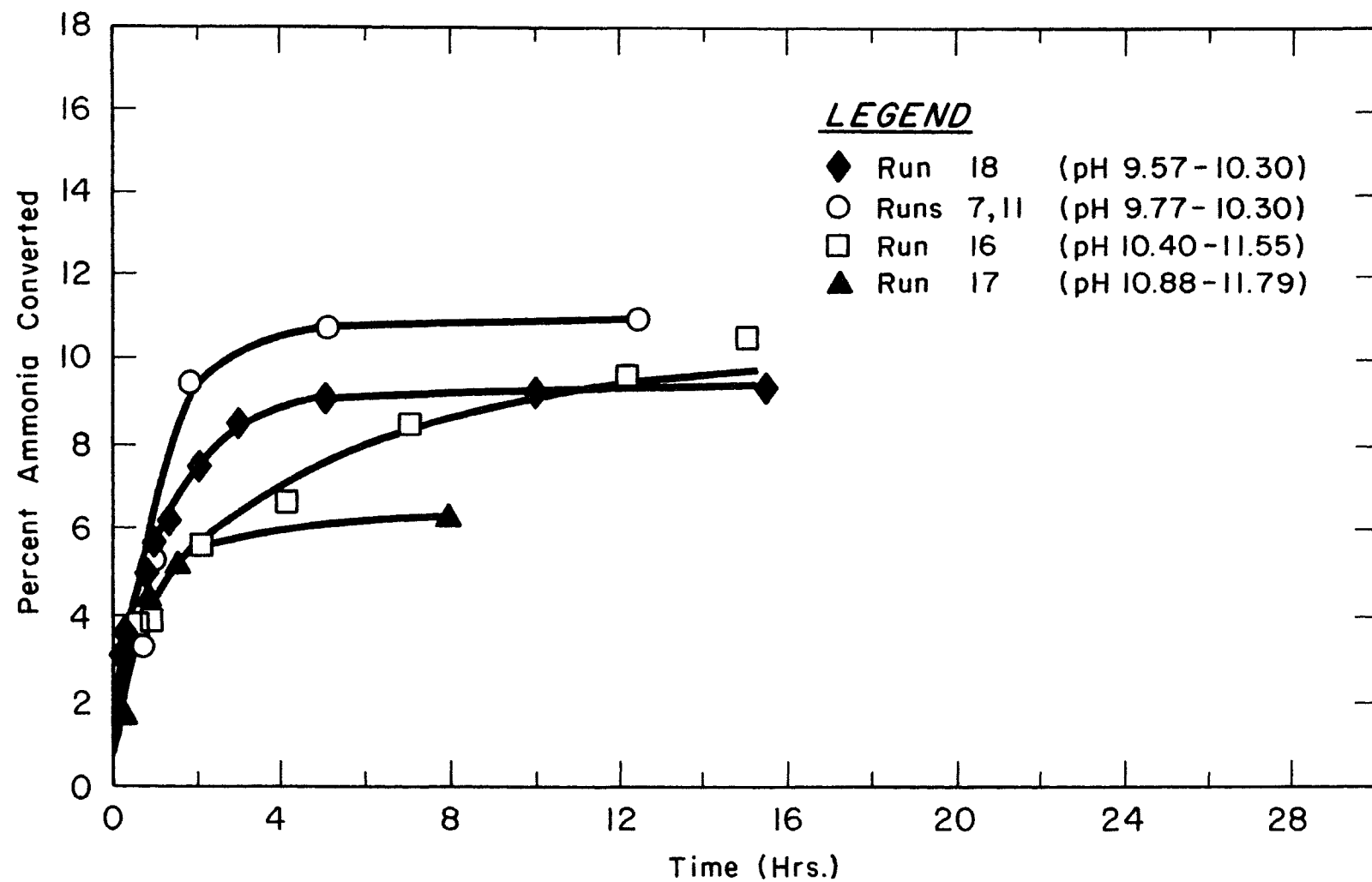


Figure 11. Ammonia conversion vs. time at different pH, ferrate (VI) to ammonia mole ratio 1:1, and at 25°C.

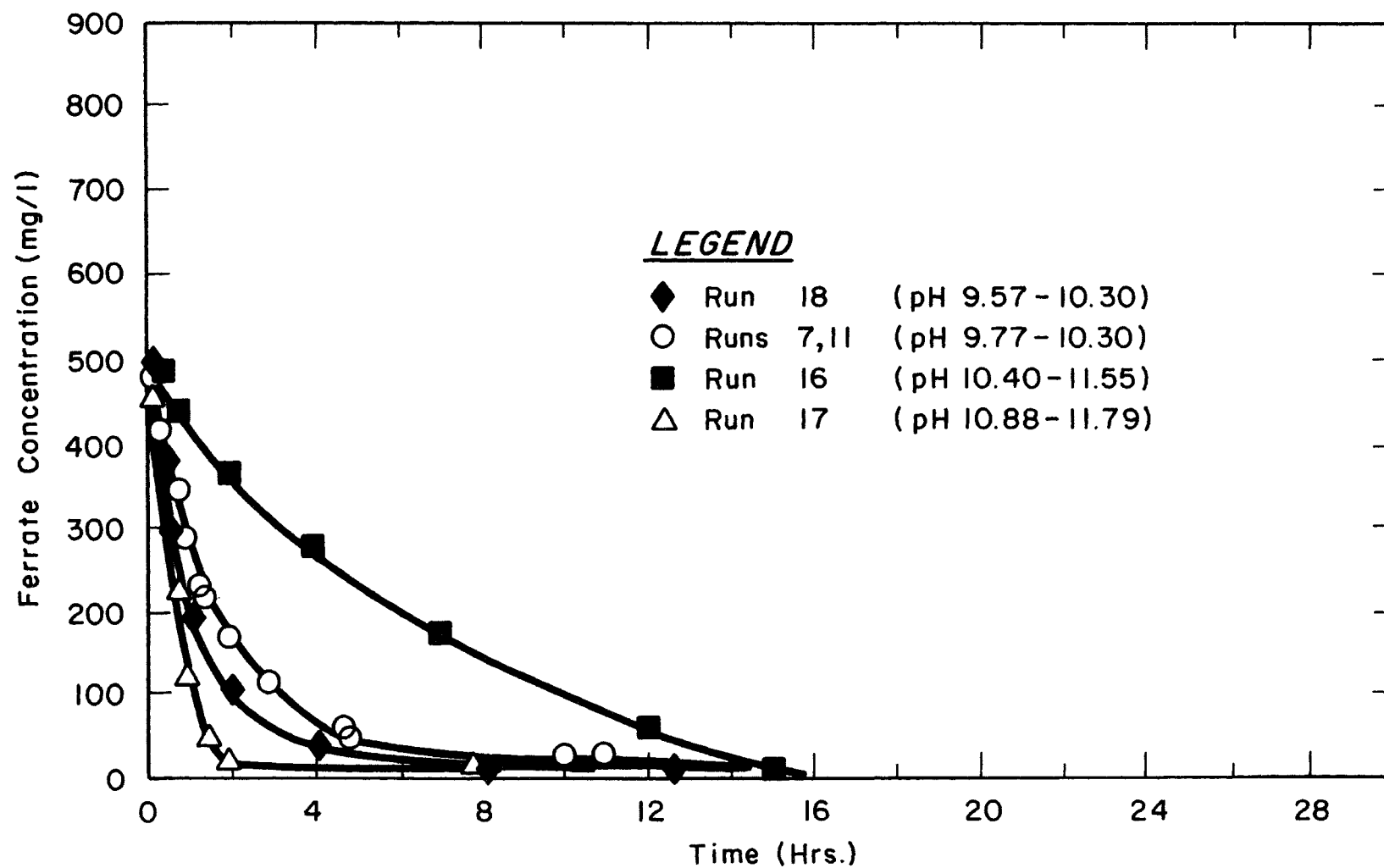


Figure 12. Potassium ferrate (VI) decomposition vs. time, at ferrate (VI) to ammonia mole ratio 1:1, and at 25°C.

The curves already shown on Figure 6, 7, and 8 have been redrawn on Figure 13, but the concentrations have been expressed in m-moles per liter. This figure also shows how the curves fit the experimental data. The initial ammonia concentration in all the runs was 2.63 m-moles/l. Mole ratios of potassium ferrate(VI) to ammonia were 0.5:1, 1:1, and 1.5:1, the pH was in the range from 9.8 to 10.5, and the temperature was 25°C. The decomposition curve of K_2FeO_4 in the absence of ammonia is also shown on the same plot. The curves and the experimental data from Figure 13 were used to evaluate the relationships and parameters in the following discussion.

Figure 14 shows a plot of K_2FeO_4 concentration as a function of time on a semi-logarithmic scale. After an initial accelerated decomposition period of approximately 0.75 hours, the decomposition rate of K_2FeO_4 (in the absence of ammonia) is described by the first order reaction rate equation with respect to K_2FeO_4 concentration.

$$\frac{d[K_2FeO_4]}{dt} = K[K_2FeO_4]$$

The reaction rate constant, K, for these data is $0.184hr^{-1}$ ($3.1 \times 10^{-3} min^{-1}$). This reaction rate constant is in good agreement with the constants obtained by Haire (19) and Magee (21). The initial accelerated decomposition rate of K_2FeO_4 is explained by considering that the K_2FeO_4 was added as a solid; and upon the dissolution of K_2FeO_4 , localized conditions develop which are significantly different from the imposed conditions on the resulting solution. The localized conditions then considerably increase the decomposition rate of potassium ferrate(VI).

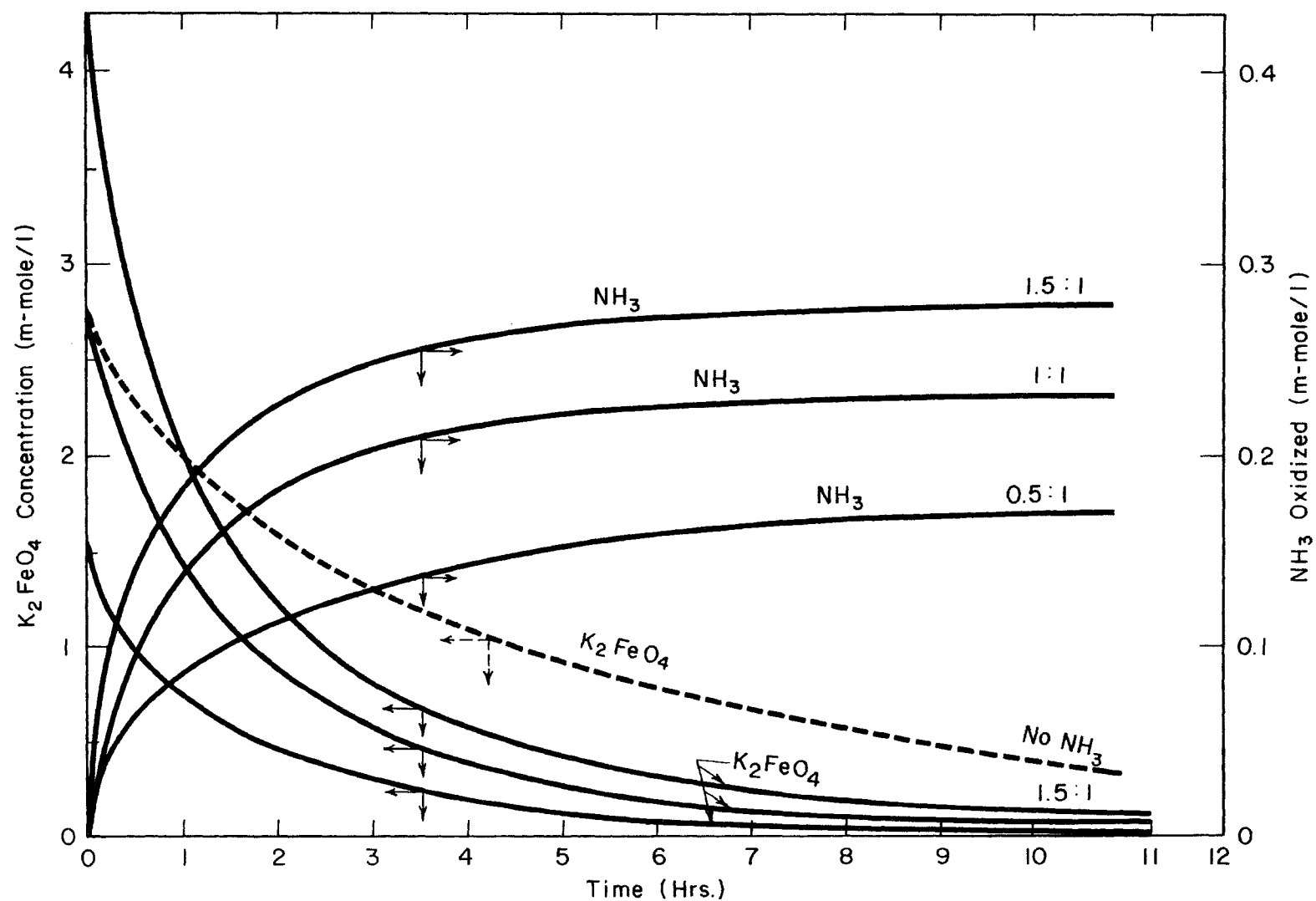


Figure 13. Ammonia oxidation and potassium ferrate (VI) decomposition vs. time at 25°C.

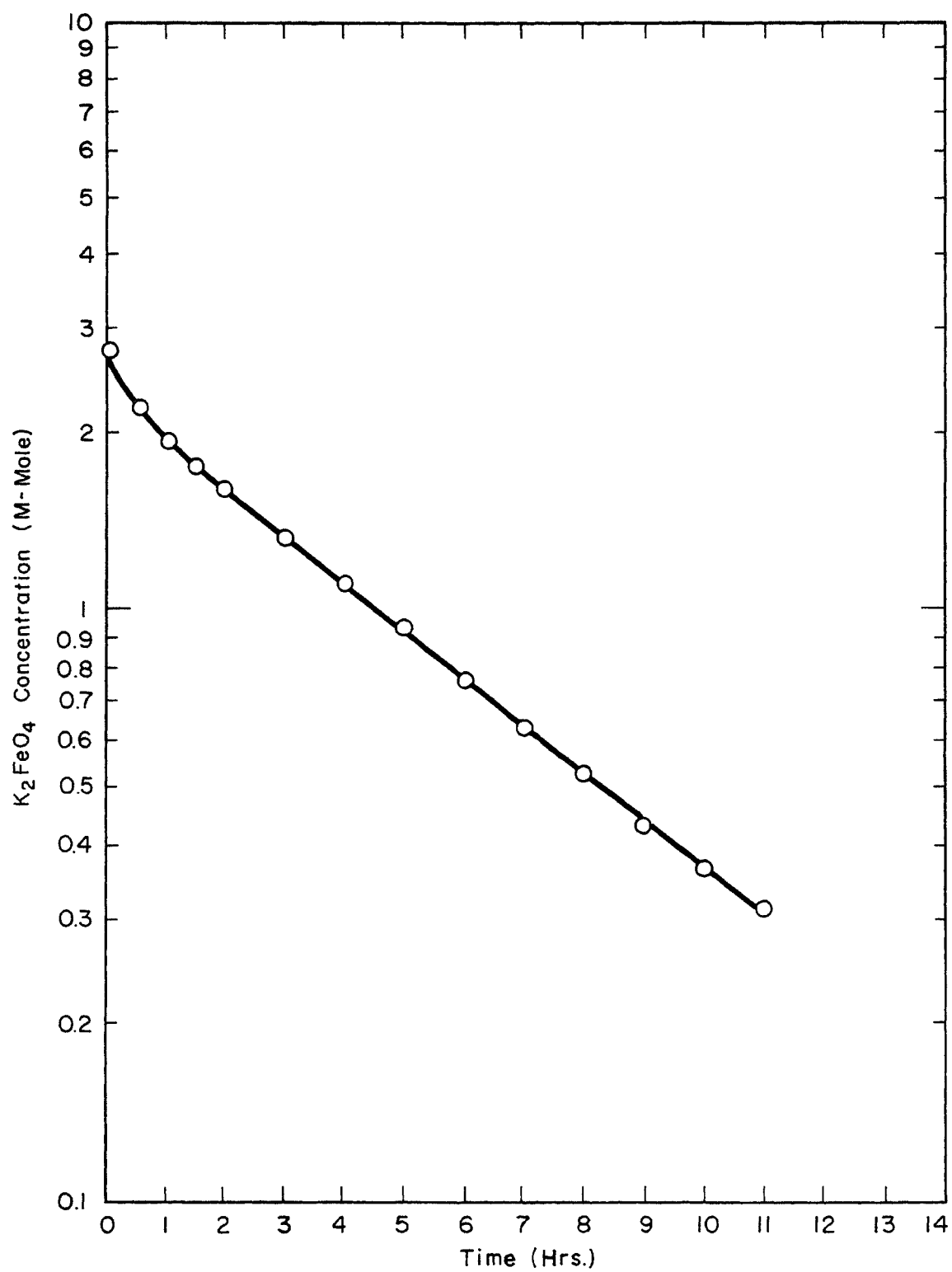


Figure 14. Decomposition of pure potassium ferrate (VI) solution (2.77 m-moles/ ℓ) vs. time in the pH range of 9.8 to 10.4 and at 25°C.

Figure 15 shows the rates of NH_3 oxidation, the rates of K_2FeO_4 decomposition, and the decomposition plus reduction vs. the concentration of K_2FeO_4 on log-log scale. The curves were obtained by graphical differentiation of the curves of Figure 13 except for the curve marked "calculated" the part of which was calculated from the first order reaction rate equation the graph of which is shown on Figure 14. It is observed that the reaction rates also depend on the initial concentration of potassium ferrate(VI). It should be mentioned that in this part of the exploratory study only 2.63 m-moles/l ammonia solutions were used at pH of 9.8 to 10.5. This pH range was chosen because the maximum rate of ammonia oxidation was observed in this pH range (see Figure 2). Because of the limited scope of this study, the dependence of ammonia oxidation rates on the initial concentration of ammonia was not determined. From Figure 15, it is noted that the oxidation rates of ammonia increase with increasing overall (decomposition and reduction) ferrate(VI) reaction rates, but that the ratio of ammonia oxidation rate to the ferrate(VI) overall reaction rate depends on the initial concentration of ferrate(VI) and consequently on the mole ratio of ferrate(VI) to ammonia. For example, at K_2FeO_4 concentrations of one m-mole/l the NH_3 oxidation rates at $\text{K}_2\text{FeO}_4:\text{NH}_3$ mole ratio of 0.5:1, 1:1, and 1.5:1 are 0.055, 0.036, and 0.020 m-moles/lxhr, respectively. Similarly, the ferrate(VI) reaction rates are 0.58, 0.42, and 0.37 m-moles/lxhr and the corresponding ratios are 0.095, 0.086, and 0.054 respectively. In other words, at a ferrate(VI) concentration of one m-mole/l, nearly twice as many m-moles of ammonia are instantaneously oxidized per m-mole of ferrate(VI) instantaneously reacting at 0.5:1 mole ratio of ferrate(VI) to ammonia than at mole ratios of 1.5:1. It is obvious that the efficiency of ammonia oxidation by potassium ferrate(VI) is strongly dependent on the ferrate(VI) to ammonia mole ratio and probably also on the ferrate(VI) concentration.

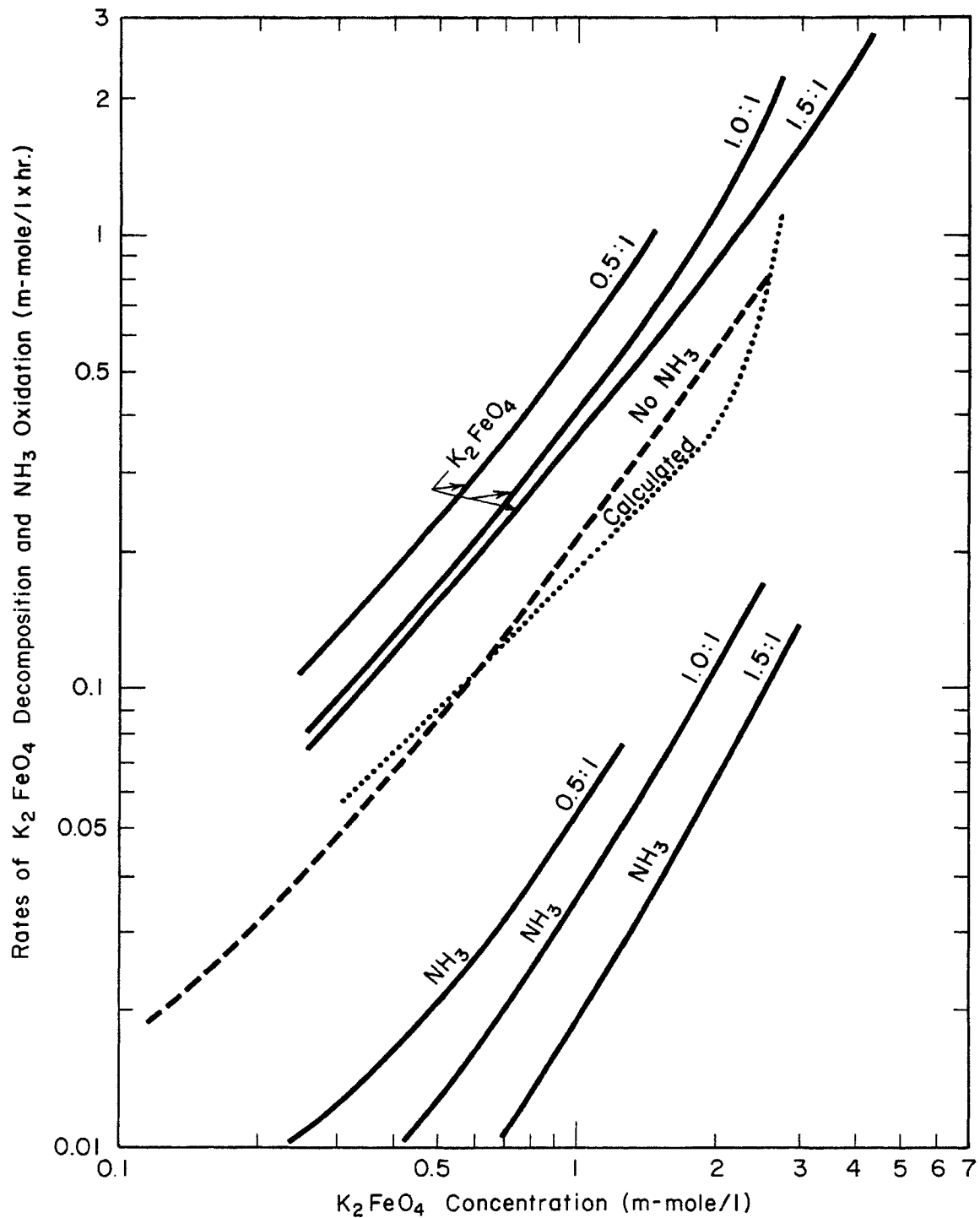


Figure 15. The rates of NH_3 oxidation, potassium ferrate (VI) decomposition and ferrate (VI) decomposition plus reduction vs. ferrate (VI) concentration at 25°C.

Figure 16 shows a plot of the m-moles NH_3 oxidized as a function of the m-moles K_2FeO_4 initially added and completely decomposed. The curve represents a continuous function in the K_2FeO_4 concentration range from 0 to 5 m-moles/l or $\text{K}_2\text{FeO}_4:\text{NH}_3$ mole ratios from 0:1 to 2:1. From the plot shown on Figure 16, one may calculate the m-moles NH_3 oxidized by one m-mole K_2FeO_4 at different mole ratios of K_2FeO_4 to NH_3 . Such a plot is shown on Figure 17. This plot indicates that at low K_2FeO_4 to NH_3 mole ratios, approximately 0.2 m-moles NH_3 are oxidized by each m-mole K_2FeO_4 . This value then gradually decreases and levels out at approximately 0.6 m-moles NH_3 oxidized per m-mole K_2FeO_4 at a K_2FeO_4 to NH_3 mole ratio of 2:1. It is obvious that the efficiency of ammonia oxidation by potassium ferrate(VI) decreases with increasing mole ratios of K_2FeO_4 to NH_3 . Figure 17 also shows the percentage of ammonia that is initially present that is oxidized by ferrate(VI) at different mole ratios of K_2FeO_4 to NH_3 .

During the kinetic studies of ammonia oxidation by potassium ferrate(VI), no determination of reaction products was attempted; and the efficiency of ammonia oxidation by ferrate(VI) still has to be defined. According to Eq(1) Section II, one mole K_2FeO_4 oxidizes one mole NH_3 to elemental nitrogen (N_2); but according to Eq(3) 8 moles K_2FeO_4 oxidize 3 Moles of NH_3 to nitrate (NO_3^-). In an actual process, ammonia is oxidized to N_2 , NO_2^- , and NO_3^- and therefore the efficiency (percent of K_2FeO_4 used for oxidation of NH_3) will be somewhere between these two limits. Most K_2FeO_4 is decomposed in water solution to oxygen (O_2), potassium hydroxide (KOH), and ferric hydroxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). Table 8 shows the efficiency of ammonia oxidation by ferrate(VI) as defined above. The figures on Table 8 show clearly that the efficiency of ammonia oxidation by ferrate(VI) decreases with increasing initial ferrate(VI) concentration. It appears that the efficiency of K_2FeO_4 utilization for NH_3 oxidation could have a maximum in some K_2FeO_4 concentration region. This may be visualized by

Table 8. Efficiency of Ammonia Oxidation by Potassium Ferrate(VI)*

$[K_2FeO_4]$ Initial m-moles/l	$[NH_3]$ Initial m-moles/l	$K_2FeO_4:NH_3$ Mole Ratio	$[NH_3]$ Oxidized m-moles/l	NH_3 m-moles/l Oxidized per 1 m-mole/l K_2FeO_4	Efficiency % When NH_3 is Oxidized to	
					N_2	NO_3^-
4.17	2.63	1.5:1	0.276	0.0662	6.6	17.7
2.77	2.63	1.0:1	0.229	0.0827	8.3	22.1
1.39	2.63	0.5:1	0.173	0.1245	14.5	33.2

* pH = 9.8 - 10.5

Temperature = 25°C

Efficiency: When 1 mole K_2FeO_4 oxidizes 1 mole of NH_3 to N_2 -- efficiency is 100%.
When 1 mole K_2FeO_4 oxidizes 0.375 moles NH_3 to NO_3^- -- efficiency is 100%.

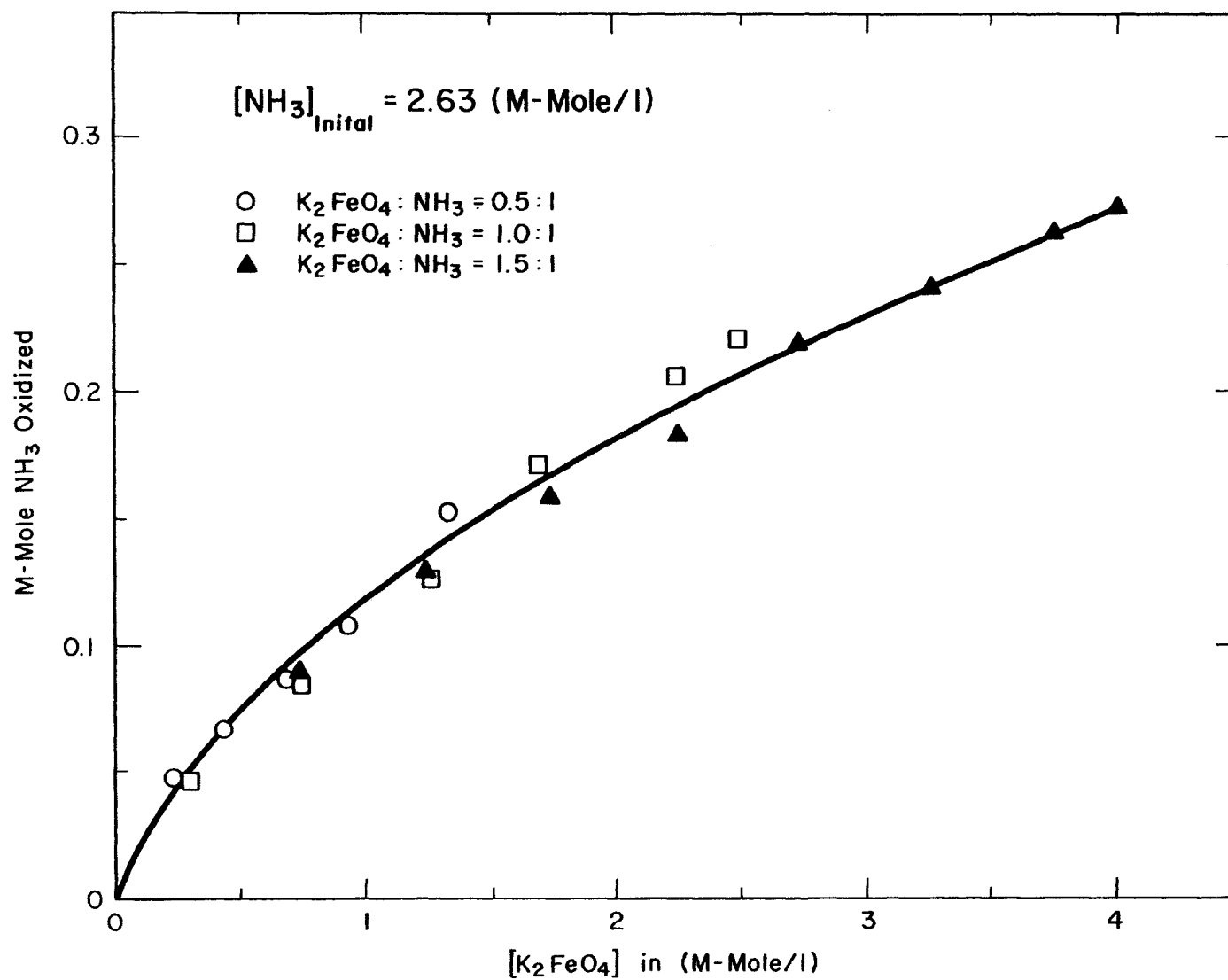


Figure 16. M-moles/l ammonia oxidized vs. m-moles/l potassium ferrate (VI) completely decomposed.

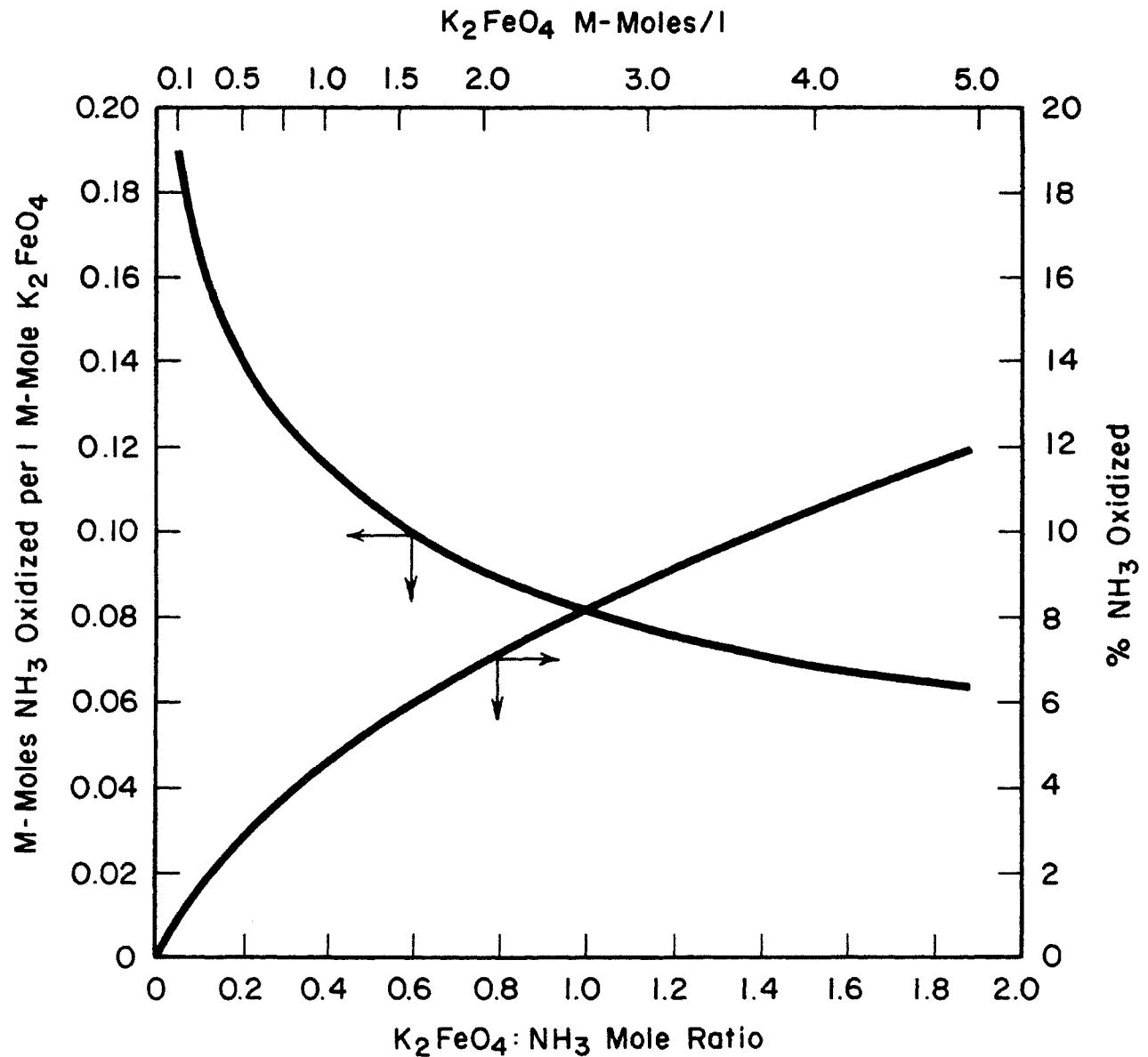


Figure 17. M-moles ammonia oxidized per one m-mole of potassium ferrate (VI) vs. potassium ferrate to ammonia mole ratio.

utilizing the concept of "the amount of potassium ferrate(VI) utilized for ammonia oxidation."

The two curves on Figure 13 were drawn using data from two experiments conducted at the same imposed conditions except for the presence of ammonia. The first curve represents the K_2FeO_4 concentration decrease with time at K_2FeO_4 to NH_3 mole ratio of 1:1, and the other curve shows the K_2FeO_4 concentration decrease with time without the addition of ammonia. If it is assumed that the difference in concentration of K_2FeO_4 , as obtained by subtracting the concentration of K_2FeO_4 in the presence of ammonia from the concentration of K_2FeO_4 in absence of ammonia at the same elapsed time interval, is the quantity of K_2FeO_4 used for the oxidation of ammonia, a curve may be drawn of "potassium ferrate(VI) utilized for ammonia oxidation" as a function of the potassium ferrate(VI) concentration. It should be emphasized that this assumption is only valid when the decomposition of potassium ferrate(VI) by water is not affected by the presence of ammonia. There is evidence that the effect of ammonia on the decomposition rate of potassium ferrate(VI) by water is minimal, at least at the experimental conditions imposed in course of this study. The plot of the m-moles of ammonia oxidized per m-mole of potassium ferrate(VI) utilized for oxidation of ammonia as a function of the concentration of potassium ferrate(VI) is shown on Figure 18. The curve goes through a maximum at ferrate(VI) concentrations of approximately 0.6 m-moles/l. For convenience, the abscissa shows the concentration of ferrate(VI), the m-moles of ferrate(VI) decomposed and the elapsed time in hours. More expressly, the effect of ferrate(VI) concentration on the oxidation of ammonia is shown in a plot of an increment of ammonia oxidized per increment of ferrate(VI) utilized for ammonia oxidation as a function of the ferrate concentration. As expected, this curve also shows a sharp maximum at ferrate(VI) concentration of approxi-

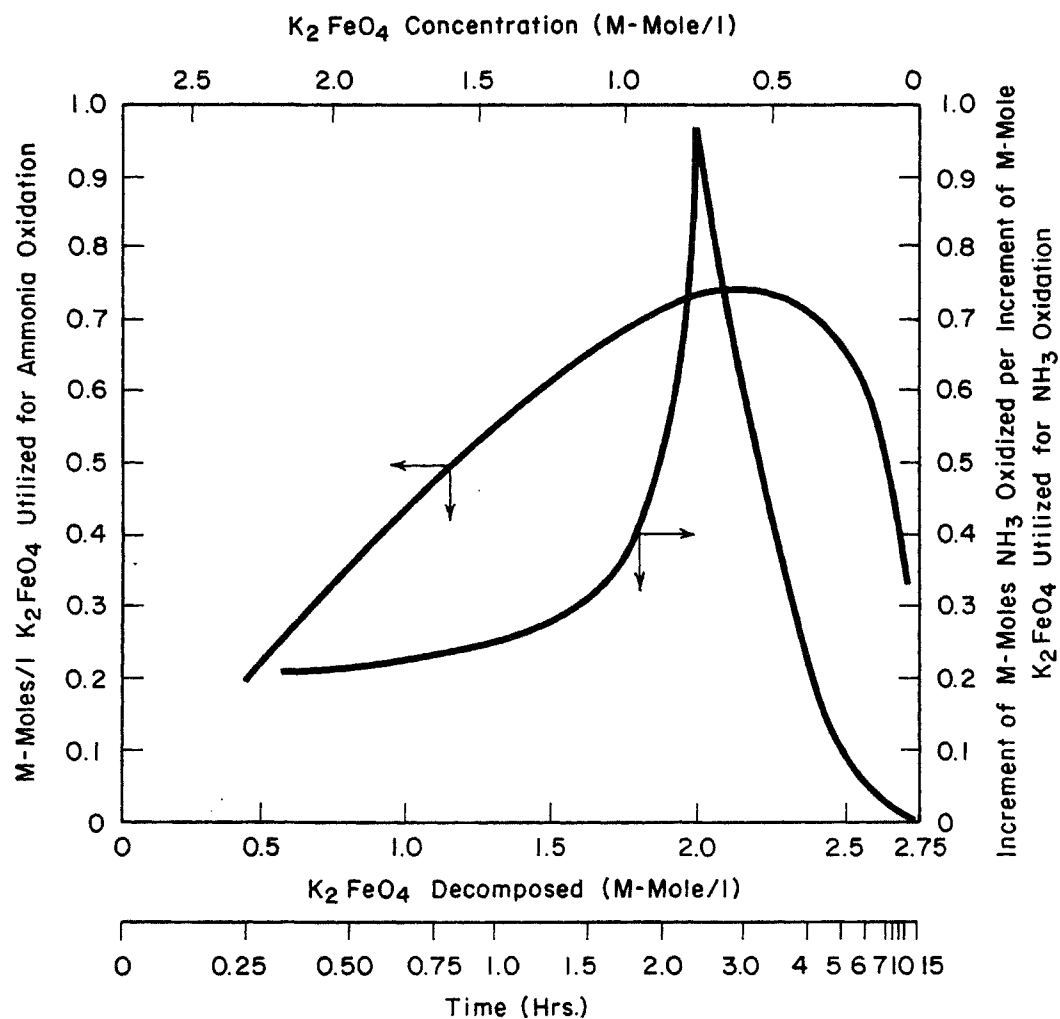


Figure 18. Potassium ferrate (VI) utilized for ammonia oxidation vs. potassium ferrate (VI) concentration.

mately 0.7 m-moles/l. It should be mentioned that the potassium ferrate(VI) decomposition in water was measured only at the particular conditions of this project, and that the optimal concentration of ferrate(VI) for maximum efficiency of ammonia oxidation that was evaluated only applies at the conditions imposed in these experiments. However, there is circumstantial evidence that the range of optimal concentrations of ferrate(VI) is narrow, and that the optimal concentration evaluated in these experiments may be valid for conditions deviating considerably from the conditions of these experiments. From the discussion on the relative amounts of reaction products formed by ammonia oxidation with potassium ferrate(VI) in Section II, it appears that the relationship last discussed, also show that at a ferrate(VI) concentrations of approximately 0.6 to 0.7 m-moles/l, the ammonia is principally oxidized to molecular nitrogen because the ratio of an increment of m-moles/l ammonia oxidized per an increment of m-moles/l potassium ferrate(VI) utilized for ammonia oxidation at potassium ferrate concentration of approximately 0.6 to 0.7 m-moles/l approaches one.

The results discussed in Section II were obtained before the kinetic studies were conducted. The lowest initial concentration of K_2FeO_4 used in these experiments was approximately 1.75 m-moles/l at K_2FeO_4 to NH_3 mole ratio of 0.5:1 and initial concentration of NH_3 of 40 ppm. The stepwise addition of K_2FeO_4 , as discussed in Section II, in steps of $K_2FeO_4:NH_3 = 0.5:1$ therefore corresponds an initial concentration of 1.75 m-moles/l of K_2FeO_4 . The results of the kinetic studies indicate that the maximum efficiency of ammonia oxidation by ferrate(VI) is in the range of ferrate(VI) concentration of 0.6-0.7 m-moles/l which is approximately three times lower than the concentration used in the runs by stepwise addition of K_2FeO_4 . Therefore, it could be expected that by stepwise addition of K_2FeO_4 in quantities such that the concentration of K_2FeO_4

does not exceed 0.7 to 0.6 m-moles/l, the efficiency of ammonia oxidation by ferrate(VI) could be significantly improved and the relative amount of ammonia oxidized to elemental nitrogen would be increased.

SECTION IV

OXIDATION OF AMMONIA BY POTASSIUM FERRATE(VI) IN A SEWAGE TREATMENT PLANT SECONDARY EFFLUENT

Several preliminary runs, similar to those done on pure ammonia solutions, were carried out on secondary effluents from the Columbus Sewage Treatment Plant in order to detect unexpected interferences early in the course of the exploratory studies. Some of the results of these experiments are shown on Table 9. The first line shows the quantity in mg of potassium ferrate(VI) of 88% purity added to one liter of effluent and demineralized double distilled water. The second line shows the amount in mg and m-moles of 100% pure K_2FeO_4 added to one liter of effluent and demineralized double distilled water. The K_2FeO_4 was added to high purity water in order to estimate the amount of nitrate nitrogen introduced in the effluent by K_2FeO_4 . The third line shows the concentration in mg/l and m-moles/l of ammonia nitrogen in the original effluent and after treatment with K_2FeO_4 . Similarly lines 4 and 5 show the concentration of nitrate nitrogen and COD. The reaction of K_2FeO_4 with ammonia and oxidizable substances (COD) present in the effluent were carried out in sealed one liter beakers and 800 ml of effluent. K_2FeO_4 was added as solid and quickly dissolved by stirring with a magnetic stirrer. The reaction was allowed to proceed for 48 hours and the clear supernatant solution was analyzed for N_{NH_3} , $N_{NO_3}^-$, and COD (chemical oxygen demand). Lines 7 and 8 show the pH on dissolution and K_2FeO_4 (approximately 5 minutes) and after 48 hours. Line 9 shows the quantity of $N_{NO_3}^-$ introduced by K_2FeO_4 in the corresponding batch and line 10 shows the $N_{NO_3}^-$ concentration as summ from the $N_{NO_3}^-$ introduced by K_2FeO_4 and N_{NO_3} originally present in the effluent. Line 11 shows the concentration increase of $N_{NO_3}^-$ (difference in concentration of line 4 and 10) which is attributed to ammonia nitrogen oxidized to nitrate. Line 12

TABLE 9.

Oxidation of Ammonia by Potassium Ferrate(VI) in
Sewage Treatment Plant Secondary Effluent

	Water		Original Effluent		Effluent after Treatment with Potassium Ferrate(VI)										Line No.
	mg/l	m-moles/l	mg/l	m-moles/l	mg/l	m-moles/l	mg/l	m-moles/l	mg/l	m-moles/l	mg/l	m-moles/l	mg/l	m-moles/l	
K ₂ FeO ₄ added 88% pure	517.1		0	0	260.8		516.0		1043		1571		2x1043		1
K ₂ FeO ₄ added 100% pure	455.0	2.297	0	0	229.5	1.159	454.1	2.293	917.9	4.635	1383	6.983	2x917.8	2x4.634	2
N _{NH₃}			15.5	1.106	15.0	1.071	14.6	1.042	13.8	0.985	13.6	0.971	11.6	0.828	3
N _{NO₃} ⁻	2.4	0.171	2.2	0.157	3.4	0.243	4.8	0.343	7.0	0.500	9.3	0.664	14.0	1.000	4
COD			28		18.8		22.1		18.5		19.6		17.9		5
pH Effluent			7.52		7.52		7.52		7.52		7.52		7.52		6
pH after 5 minutes on addition of K ₂ FeO ₄	10.7				9.2		9.8		10.4		10.9		10.4		7
pH after 48 hours on addition of K ₂ FeO ₄					9.2		10.1		11.9		12.7		12.6		8
N _{NO₃} ⁻ from K ₂ FeO ₄					1.2	0.086	2.4	0.171	4.8	0.343	7.2	0.514	9.6	0.685	9
N _{NO₃} ⁻ from K ₂ FeO ₄ + Eff.					3.4	0.243	4.6	0.328	7.0	0.500	9.4	0.671	11.8	0.842	10
N _{NO₃} ⁻ from NH ₃ oxidation					0.0	0.00	0.2	0.015	0.0	0.00	-0.1	-0.007	2.2	0.158	11
K ₂ FeO ₄ : NH ₃ mole ratio					1.05 : 1		2.07 : 1		4.19 : 1		6.31 : 1		2x4.19 : 1		12
COD reduced %					33		21		34		30		36		13
NH ₃ oxidized %					3.2		5.8		11.0		12.3		25.2		14

shows the mole ratio of K_2FeO_4 to NH_3 . It should be mentioned that a fraction of K_2FeO_4 added is also consumed for COD reduction and the percent of COD reduction are shown on line 13. On the last line - 14 are shown the percentages of ammonia removed.

The last column shows the results of ammonia oxidation by addition of potassium ferrate(VI) in two batches. After 48 hours on addition of the first portion of K_2FeO_4 (1.043 gr/l, the pH of the effluent increased from 7.52 to 10.4 on dissolution of K_2FeO_4 in 5 minutes and the pH increased to 11.9 after 48 hours), the solution was neutralized to pH of 6.9 and the supernatant clear solution was decanted to another beaker. Another portion of K_2FeO_4 (1.043 gr/l) was added, the pH of the solution increased from 6.9 to 10.4 on dissolution of K_2FeO_4 in 5 minutes and increased in 48 hours to 12.6. From the clear supernatant solution samples were taken for analysis. The determination of ammonia and nitrate was done according to the procedures described in Section III. The determination of COD was performed according to the Standard Methods (24).

The results of ammonia oxidation by ferrate(VI) in the effluent when compared with the results of ammonia oxidation in water solutions show lower percent of ammonia oxidized at lower K_2FeO_4 concentrations but approach the percent of ammonia oxidized in water solutions at higher K_2FeO_4 concentrations. The discrepancy may be attributed to the fact that a fraction of K_2FeO_4 is used for lowering the COD in the effluent. On addition of 2.293 m-moles of K_2FeO_4 to the effluent the mole ratio of K_2FeO_4 to NH_3 is 2.07:1 but subtracting the quantity of K_2FeO_4 (1.166 m-moles) to decrease the COD of 28.0 to ml, 1.127 m-moles of K_2FeO_4 are left for oxidation of 1.10 m-moles NH_3 or the ratio is close to 1:1. At these conditions 5.8% of ammonia is oxidized in the effluent which is considerably lower than 9.8% attained by ammonia oxidation in water solution. The COD was reduced by 21%. Similar calculations show that at a mole ratio close to 2:1, corrected for K_2FeO_4 required to eliminate COD,

11.0% of ammonia was oxidized in effluent which is close to 11.9% oxidized in NH_3 -water solution.

In one aspect, the relative distribution of oxidation products are considerably different in effluent than in ammonia water solutions. The fraction of ammonia oxidized to nitrate is relatively low when compared with the fraction of NH_3 oxidized to nitrate in ammonia water solutions. The cause of this phenomenon is not known and therefore more work is required to explain the phenomenon which is beyond the scope of this study. If one assumes that the intermediate reaction products include hydroxyl amine ($\text{NH}_2\cdot\text{OH}$) and nitrite (NO_2^-) it may be speculated that in presence of definite organic compounds the oxidation of NH_3 by K_2FeO_4 may be directed toward formation of elemental nitrogen.

The results also show a 30% or more decrease of COD by treating the effluent with potassium ferrate(VI).

CONCLUSIONS

The following major conclusions appear to be supported by the results obtained during the course of this study:

1.) Two competing reactions, the oxidation of ammonia and the decomposition of potassium ferrate(VI) proceed simultaneously. The net oxidation rate of ammonia and the fraction of ammonia oxidized depends on the relative rates of these two reactions.

2.) The most important factor affecting the stability of ferrate(VI) (K_2FeO_4) in water solution is the pH, and as expected, pH has a pronounced effect on the oxidation of ammonia with ferrate(VI) in water solutions. At least one maximum of the fraction of NH_3 oxidized was observed in the vicinity of pH 10.5, up to 11 percent of NH_3 was oxidized at the mole ratio of K_2FeO_4 to NH_3 of 1:1.

3.) Our preliminary work also showed that the pH not only affects the fraction of NH_3 oxidized but also affects the composition and relative quantities of the oxidation products. Generally, at pH values in the neutral and into the alkaline region the oxidation end products are elemental nitrogen, nitrate and nitrite, but with increasing pH the amount of nitrate and nitrite decrease. The fraction of NH_3 oxidized to elemental nitrogen was 30 to 80 percent of the oxidized ammonia depending on the imposed conditions.

4.) The fraction of ammonia oxidized by potassium ferrate(VI) also depends on the mole ratio of K_2FeO_4 to NH_3 , but the fraction of ammonia oxidized increases considerably slower with increasing mole ratio of K_2FeO_4 to NH_3 than required by the simple stoichiometric relationship. Preliminary work showed that up to approximately 15 percent of the NH_3 was oxidized by addition of K_2FeO_4 in quantities corresponding to mole ratio of K_2FeO_4 to NH_3 as 2:1.

5.) By the decomposition of K_2FeO_4 and NH_3 oxidation large quantities of KOH are formed which increase the pH. In considering the practical application of K_2FeO_4 , the use of buffers is not feasible because of high concentration required to keep the pH constant. Preliminary oxidations of NH_3 were performed without use of buffers and only the pH of the initial NH_3 solution was varied. The pH increased from 2 to 5 units during the experiment, depending on the conditions, and the concentration of K_2FeO_4 .

The kinetic studies were undertaken to evaluate the most favorable conditions for NH_3 oxidation with potassium ferrate(VI) in aqueous solutions, approximately 50 mg/l NH_3 . Buffer solutions were also used to minimize the large pH changes during the reaction. The results showed that:

1.) The fraction of NH_3 oxidized was independent of temperature, in the range of 10°C to 40°C, but the rate of oxidation was considerably higher at higher temperature.

2.) The fraction NH_3 oxidized increased with increasing mole ratio of K_2FeO_4 to NH_3 . However, the increase diminished with increasing mole ratio of K_2FeO_4 to NH_3 .

3.) At least one maximum of the fraction of NH_3 oxidized was observed in the vicinity of pH 10.5, up to 11 percent of NH_3 was oxidized at the mole ratio of K_2FeO_4 to NH_3 of 1:1. The oxidation rate of NH_3 was approximately one tenth of the reduction rate of K_2FeO_4 over the entire concentration range of K_2FeO_4 of the particular experiment or stated otherwise the overall efficiency of NH_3 oxidation with respect to K_2FeO_4 was only approximately 10 percent.

4.) Using the concept "the fraction of K_2FeO_4 utilized for NH_3 oxidation" we may define the efficiency of ammonia oxidation by potassium ferrate(VI) on the basis of the stoichiometry. The efficiency of 100 percent may be assigned for two extreme cases: when ammonia is oxidized to elemental nitrogen only and

when ammonia is oxidized completely to nitrate. The efficiency in percent, at the two extremes and at mole ratios of K_2FeO_4 to NH_3 of 1.5:1, 1:1, and 0.5:1, were found 6.6 - 17.7, 8.3 - 22.1 and 14.5 - 33.2 respectively. In an actual case when NH_3 is oxidized to N_2 , NO_2^- , and NO_3^- the efficiency will be somewhere in between the two extreme values.

5.) The maximum of the fraction of K_2FeO_4 utilized for NH_3 oxidation is in the vicinity of 0.7 m-moles/l K_2FeO_4 and the maximum of m-moles/l NH_3 oxidized per m-mole/l K_2FeO_4 utilized for NH_3 oxidation is also in the vicinity of 0.7 m-moles/l K_2FeO_4 , or stated otherwise the maximum efficiency of K_2FeO_4 for NH_3 oxidation is at K_2FeO_4 concentration of approximately 0.7 m-moles/l and decreases with decreasing concentration of NH_3 .

6.) At K_2FeO_4 concentration of approximately 0.7 m-moles/l the m-moles/l NH_3 oxidized per one m-mole/l K_2FeO_4 utilized for NH_3 oxidation approaches one. This indicates that at K_2FeO_4 concentration of approximately 0.7 m-moles/l the NH_3 is preferentially oxidized to elemental nitrogen.

7.) Continuous control of the pH with sulfuric acid during the oxidation process was impractical because of the localized low pH, even at high stirring speeds, resulting in extremely rapid ferrate(VI) decomposition.

8.) Best results were achieved by addition of K_2FeO_4 , allowing the ferrate(VI) decompose completely, adjusting the pH, adding again ferrate(VI), etc. This "stepwise" procedure did not show any limitations on the fraction of NH_3 oxidized, in the concentration ranges investigated, but the efficiency of the oxidation decreased with each subsequent addition of K_2FeO_4 .

Considering the results of the preliminary work and keeping in mind the practical purpose of the process, several preliminary runs, similar to those done on pure NH_3 solutions, were carried out on secondary effluent of Columbus Sewage Treatment Plant in order to detect unexpected interferences early in the course of the exploratory studies.

The runs showed satisfactory results with no interferences apparent. In two step procedure up to 25 percent ammonia was oxidized predominantly to elemental nitrogen, which may be considered satisfactory at this point. It may be speculated that the buffering properties of the effluent and the probable catalytic effect of some organic compounds present may be responsible for the satisfactory results of ammonia oxidation by potassium ferrate(VI) in secondary sewage treatment plant effluent.

COD reductions were observed to be somewhat in excess of 30 percent.

Some experiments were conducted on phosphate removal. The results showed a phosphate removal of 21 to 27%. The relatively low phosphate removal may be explained by the faster rate of ferric hydroxide formation as compared to phosphate formation and the pH which was not in the range of lowest ferric phosphate solubility.

Considering the low efficiency of ammonia oxidation with ferrate(VI), even by the involved stepwise procedure, the practical application of the process at present appears not feasible. However, considering the possible improvement of the efficiency of the process, particularly by using suitable catalysts, and the other lucrative properties of the ferrates(VI) as oxidants the investigators are inclined to believe that a process may be developed for practical application in some particular instances.

No time nor the funds were available for an extensive research of the basic and applied scientific problems to develop a process for practical application of the process. The remaining work has to be accomplished in the future.

ACKNOWLEDGEMENTS

I should like to express my sincere appreciation and gratitude to undergraduate student Barry Bayne and graduate student Mamdouh A. Elmaraghy for their help with much of the routine work on this project and to the graduate students whose thesis work is included in this report.

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