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THE INVESTIGATION OF THE USE
OF N_2O_4 AS A CATALYST
OXYGEN-CARRIER FOR THE OXIDATION
OF FERROUS SULFATE IN WASTE
PICKLE LIQUORS

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1948



Autumn

THE INVESTIGATION OF THE USE OF N_2O_4 AS A CATALYST
OXYGEN-CARRIER FOR THE OXIDATION OF
FERROUS SULFATE IN WASTE PICKLE LIQUORS

by

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A THESIS

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INTRODUCTION

Since the advent of the modern practice in our steel industry, both the producers and fabricators of that industry have had to contend with a still unanswered problem. That problem is the disposal of the waste pickle liquors, the exhausted sulfuric acid solution used for the removal of the oxide scale formed on steel during any of the heat treating processes.

This pickle liquor contains varying amounts of free sulfuric acid, and of iron in the form of ferrous sulfate. This material is at the present time neutralized with lime and discarded. Although there has been a great deal of labor and time expended on the problem of salvaging this waste, so far no other process has proved to be economically feasible.

Within the past few years another factor has come into the picture which makes it imperative that a solution be found to this problem. National and local government authorities, spurred on by the efforts of conservation and natural wildlife organizations, have passed many laws to prohibit the dumping of this waste into the streams and waterways of our nation.

Because of this last event, the economic picture has changed to the extent that any process for the disposition of these wastes, in order to be economically sound, must produce saleable products only to the extent of paying for the process itself.

As an approach to the solution of this problem, Dr. C. C. DeWitt and various of his co-workers at Michigan State College have been working on a process to convert the acid wastes into saleable iron-oxide paint pigments. The overall process consists of the following steps:

1. Oxidation, by a continuous process, of the ferrous sulfates into ferric sulfate.
2. Conversion and precipitation of the oxide pigments from the resulting ferric sulfate.

It is with the first step that the work represented by this thesis is concerned.

The oxidation of ferrous sulfate to ferric sulfate can be accomplished with nitric acid, but here again the process becomes economically unsound. To overcome this objection it was proposed to accomplish the oxidation in a countercurrent, pressure, column using N_2O_4 as the oxidizing agent. The N_2O_4 would act by releasing two atoms of oxygen to the ferrous sulfate, but then under the temperature and pressure conditions within the column would combine with the free oxygen present and thus regenerate itself. The mixture of N_2O_4 , O_2 , and N_2 introduced into the column would be produced as needed from the catalytic oxidation of ammonia, and from the atmospheric air.

The present problem then evolved to the study of the oxidation process with regeneration of the catalyst oxygen-carrier using the range of gaseous mixtures obtainable from the ammonia oxidation process.

HISTORICAL

Hoak⁽³⁾ of Mellon Institute in a recent article in Industrial and Engineering Chemistry gives a very good overall picture of the work which has been done on the disposition of waste pickle liquors.

Some of the potential products upon which work has been done are: (a) copperas or other hydrates of ferrous sulfate, (b) recovery of sulfuric acid, (c) iron oxide as a first step for production of iron powder to be used in powder metallurgy, (d) ammonium sulfate, (e) iron oxide for paint pigments, (f) a constructional material, Ferron, made from the sludge when pickle liquor is neutralized with lime, (g) many miscellaneous inorganic compounds such as sodium natrojarosite, $\text{Na}_2\text{Fe}_3(\text{OH})_{12} \cdot (\text{SO}_4)_2$, ferric phosphate. None of these processes has been operated commercially as yet.

All of the processes developed have commercial possibilities but so far all have come up to the stone walls of too high cost and too little demand. Any of the various processes proposed are, because of the economics involved, limited to only large scale operations. This means that the smaller producers will always have to neutralize their liquor if other means of disposal are impractical. Extensive work has been done in order to provide the greatest possible economy for this type of treatment.

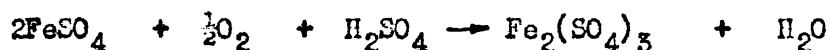
The present approach to the problem is not altogether new. Back in 1894, McCulloch (English patent 17112) described a process for the oxidation of ferrous sulfate to ferric sulfate with air

using nitric oxide as the oxygen carrier. In 1906, Manchot and Zechentmayer ⁽⁸⁾ published data on the equilibrium between nitric oxide and ferrous salts. Thomas and Williams, ⁽¹⁰⁾ and Friend ⁽²⁾ also published data on work done along this same line in 1921.

They showed, among other things, that the reaction rate was not slowed by the presence of the ferric products, the rate was somewhat proportional to the concentration of the nitric oxide catalyst, and that higher temperatures increased the reaction rate.

THEORETICAL

In order to explore the process from a theoretical standpoint, a study of the ΔF , ΔH , and equilibrium constant (K_a) was made. In its most simplified form the reaction studied is as follows:



The reactions involving the N_2O_4 are not considered since it is regenerated and therefore acts only as a catalyst.

From the fact that all the reactants and products are present in dilute solutions, it is possible to figure the ΔF for the reaction directly from published data. From free energy of formation data given in the Handbook of Chemistry and Physics,⁽⁴⁾ the ΔF° at 25°C for the reaction was calculated.

$$\begin{aligned} 2\text{FeSO}_4 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4 &\longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \\ -[2(-196,740) + (-178,500)] &+ [(-535,740) + (-56,560)] \\ \Delta F^\circ &= -22,320 \text{ cal.} \end{aligned}$$

From this the equilibrium constant (K_a) at 25 deg. C. can be calculated.

$$\begin{aligned} \Delta F^\circ &= -RT \ln (K_a) \quad (11) \\ -22,320 &= -(1.987)(298) \ln (K_a) \\ \ln(K_a) &= 37.65 \\ (K_a) &= 4.46 \times 10^{37} \end{aligned}$$

The (K_a) is independent of pressure but varies with temperature according to the relation:

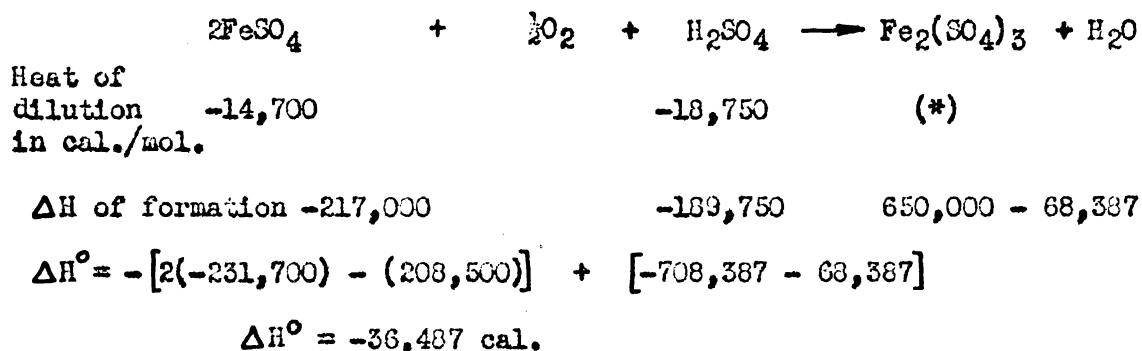
$$\frac{d [\ln(Ka)]}{d \left(\frac{1}{T}\right)} = - \frac{\Delta H^{\circ}}{R}$$

Integration gives:

$$\ln (Ka) = - \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T} \right) + C$$

In order to apply this relation to investigate the (Ka) at higher temperatures, it is first necessary to calculate the ΔH° for the reaction.

From Hougén and Watson⁽⁵⁾ and Latimer⁽⁷⁾ the ΔH of formation was taken and to it added the heat of dilution. It was also noted from graphs given in the same sources that the heat of dilution did not vary to a significant degree with increasing dilution after reaching a degree of dilution approximating that used in this work. Therefore, the data given in the tables, even though at very high or infinite dilution, approximates the conditions used in this work very closely. In the case of H_2SO_4 , an estimate was made in order to bring the results as close as possible.



From the values of (Ka) and ΔH° calculated above for T = 298°K

* ΔH given for dilute solution

the integration factor (C) is found

$$37.65 = \frac{36.487}{1.987} \left[\frac{1}{298} \right] + C$$

$$C = -23.60$$

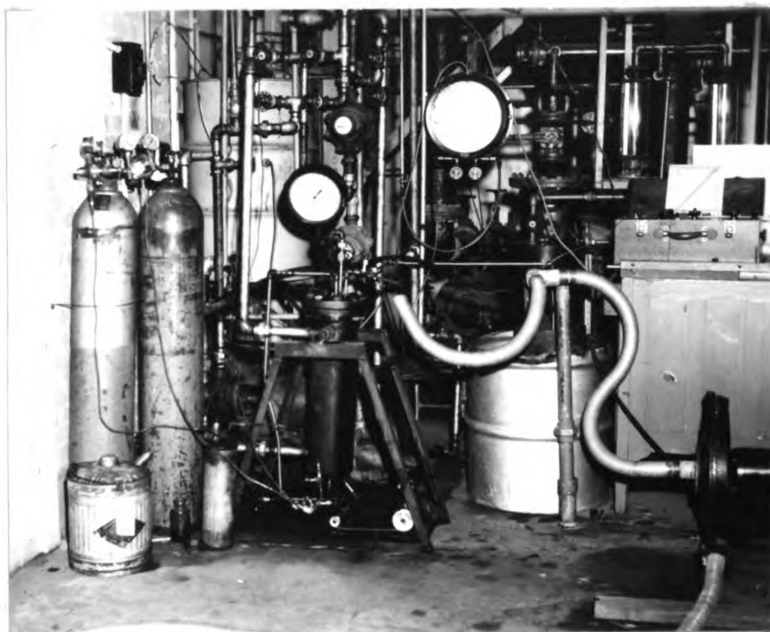
Assuming $H^\circ = H$ at 150°F , the (K_a) at 150°F is calculated:

$$\ln(K_a) = \frac{36.487}{1.987} \left[\frac{1}{338} \right] - 23.60$$

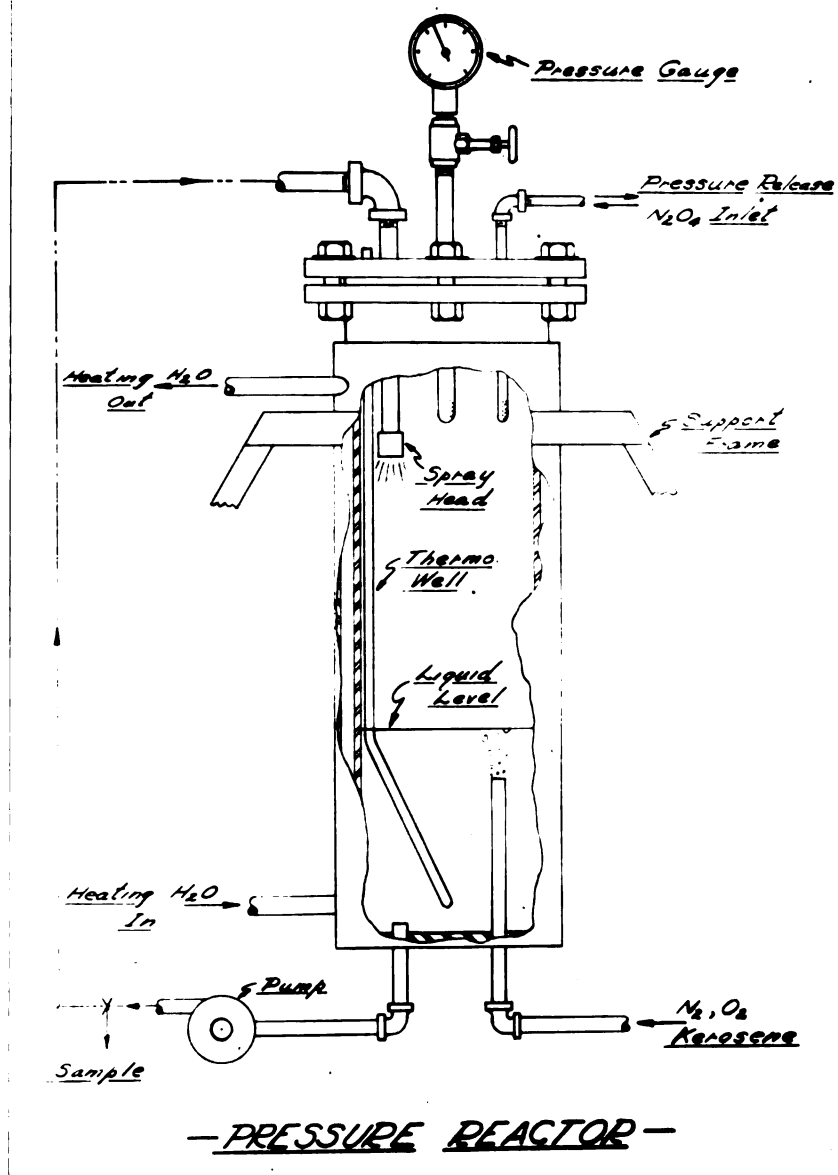
$$\ln(K_a) = 30.8$$

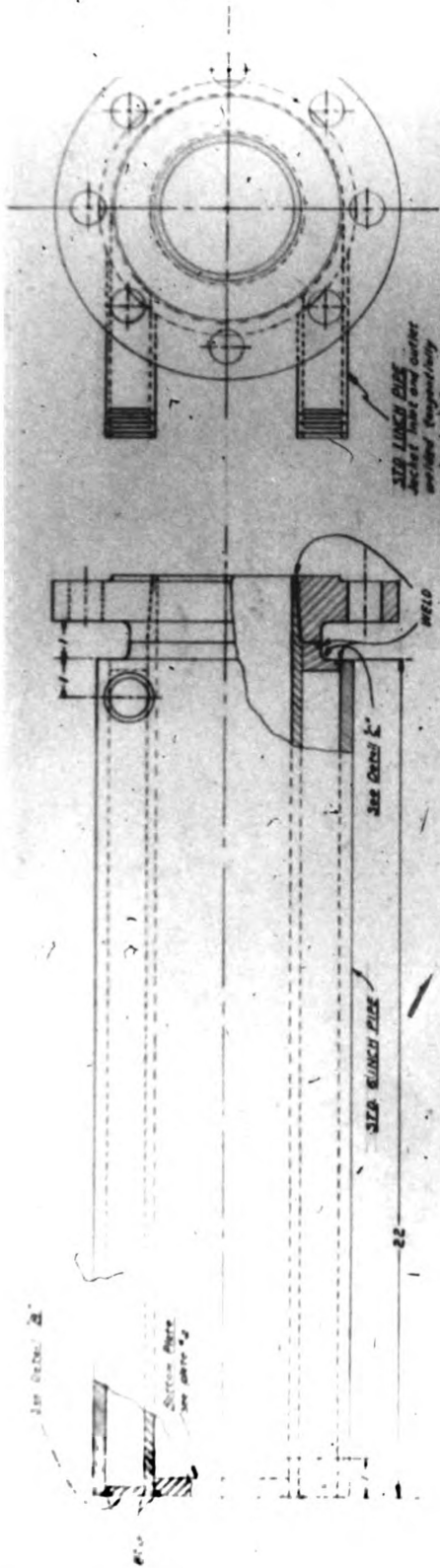
$$(K_a) \text{ at } 150^\circ\text{F} = 6.3 \times 10^{30}$$

As a final conclusion from these calculations, it can be seen that, under the experimental conditions, the equilibrium should not be a controlling factor. The large negative ΔF° and large (K_a) values indicate a very strong driving force for the reaction to go to completion. It is then to be a matter of resistance, or in other words, the reaction rates which will control. The reaction rates are in turn controlled by the conditions under which the reaction takes place and the effectiveness of the catalyst used. These then are the variables to be investigated.



PICTURE OF EQUIPMENT

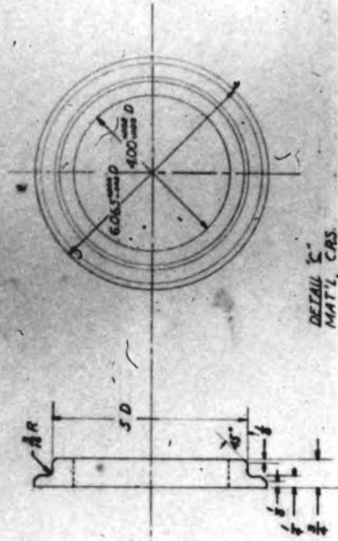




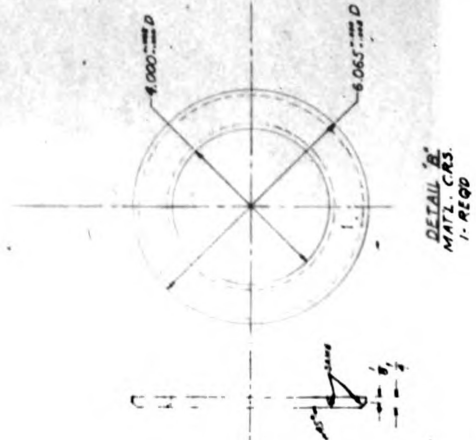
3/4" LUNCH PINE
Jacket tube and outlet
welded together
into jacket

DETAIL A
HEATING JACKET ASSEMBLY

NOTE: ALL DIMENSIONS IN INCHES

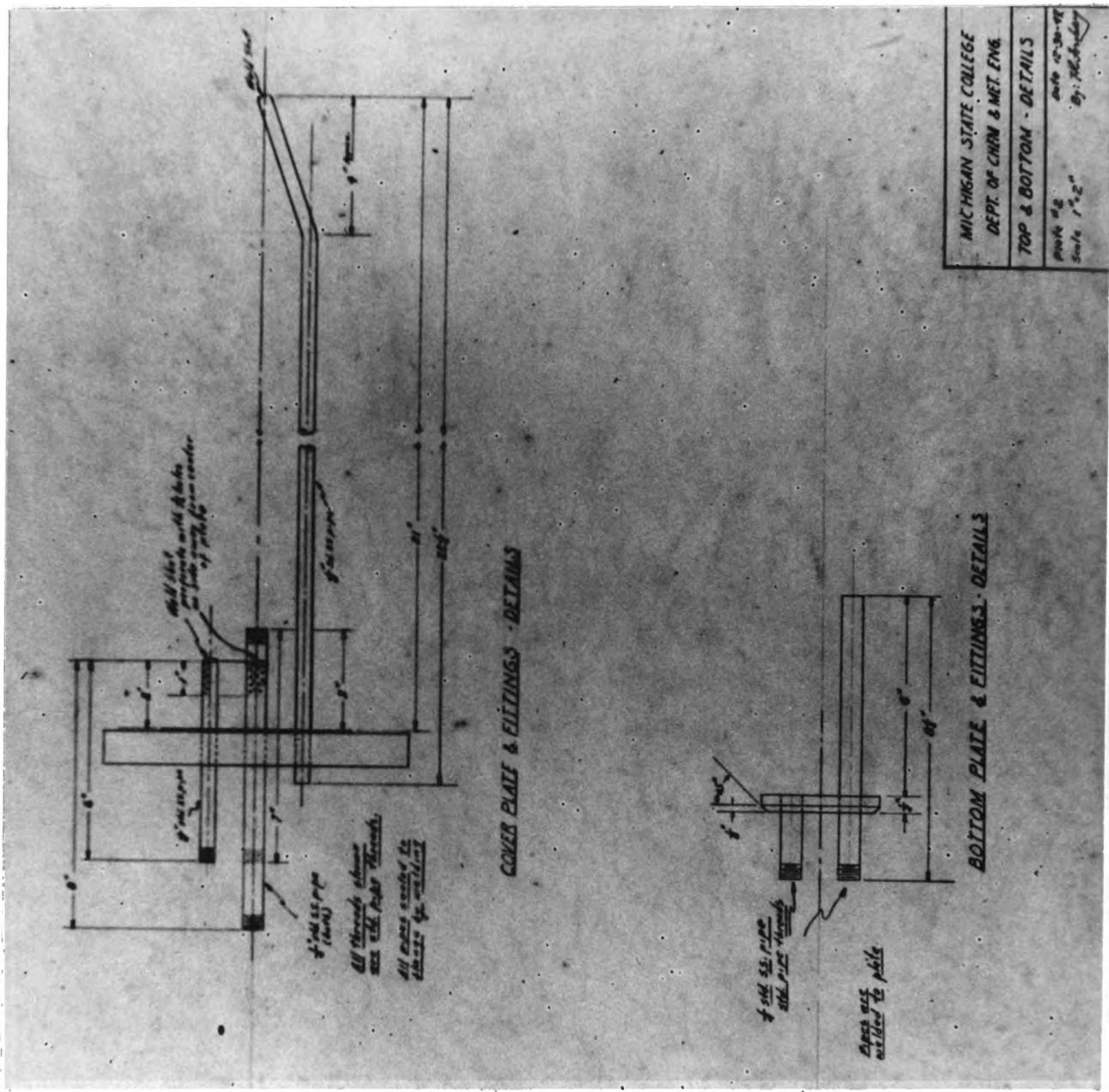


DETAIL C
MATH. CR3
1-REQD



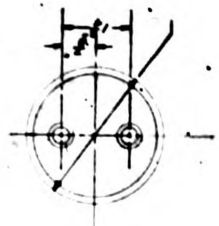
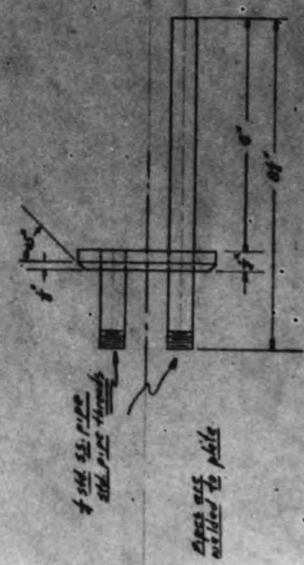
DETAIL B
MATH. CR3
1-REQD

MICHIGAN STATE COLLEGE	
DEPT. OF CHEM. MET. ENGR.	
JACKET DETAILS	
DATE	Dec 12 1954
SCALE	1/2"



MICHIGAN STATE COLLEGE
DEPT. OF CHEM. & MET. ENG.
TOP & BOTTOM - DETAILS
Scale 1"=2"
Date 12-30-18
By: H. H. H. H.

COVER PLATE & FITTINGS - DETAILS



EXPERIMENTAL AND PROCEDURE

The first step in this study was the design and construction of the necessary equipment. This equipment consisted of a cylindrical reactor (see accompanying drawings and picture) approximately $3\frac{1}{2}$ inches in diameter and 2 ft. long. The reactor was heated by controlled temperature water pumped through a jacket built around the reactor itself. Agitation and vapor-liquid contact was accomplished by pumping the reacting liquid from the bottom of the reactor through a spraying head into the gas-vapor space. The temperature was measured by a thermocouple inserted in a well which extended into the liquid in the reactor. Pressure was controlled manually by introducing an inert liquid, kerosene, from a blow case under nitrogen pressure. A laboratory standard pressure gauge indicated the pressure to an accuracy of better than one pound per square inch. The method of introducing the inert substance also made it possible to remove a sample of gas or liquid without varying the total pressure inside the reactor.

The reactor was constructed with all parts in contact with the reacting liquids and gases made of 18-8 stainless steel. Stainless steel needle valves were used throughout.

The three gases, N_2 , O_2 , and N_2O_4 were introduced from tank supplies, and their various proportions measured by their respective partial pressures. In order to increase the pressure of the N_2O_4 , which has a vapor pressure of one atmosphere at about (70°F), this cylinder was placed in a drum and heated with hot water.

To avert the danger of toxic atmosphere of N_2O_4 , which is fatal at a concentration of approximately 25 parts per million, a high-speed centrifugal blower was set up as an exhausting system, as can be seen in the accompanying picture.

The procedure for making the experimental runs as given below was followed with the exception of the run made at zero gauge pressure. The variations in this run, and any other minor variations on the other runs are noted along with the data.

In order to exclude the variation of composition which would be present in commercial pickle liquors, all tests were run using a synthetic solution made up as follows:

650 grams of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (Commercial grade)

75 grams of H_2SO_4 (conc.)

$2\frac{1}{2}$ liters of distilled water

After preparation, this solution was allowed to age overnight and then filtered and analyzed for ferrous and ferric iron. The permanganate method* of analysis was used.

The equipment was adjusted to the temperature desired. Next one liter of the pickle liquor was introduced and allowed to come to temperature. Placing the vessel under nitrogen pressure tested it for leakage.

Each of the three gases were introduced to the partial pressure required for the test and the recirculation pump turned on. Time was measured from the instant this pump was started. Little or no reaction

* See Appendix

went on before recirculation was started as evidenced by the fact that there was no pressure drop until that time.

As the reaction proceeded the total pressure fell proportionally as the oxygen supply was used. However, by introducing the inert kerosene, the total pressure of the test was held constant. Samples of the liquid were taken as a time function and analyzed for their ferrous iron content.

At the end of each run, which lasted usually from 30 minutes to one hour, a sample of the gas was drawn off into a modified Orsat equipment. Any acid gases were removed here by washing with KOH, and then the percent of remaining oxygen was found by absorption with potassium pyrogallate solution.

During the run, the pressure and temperature were recorded.

SUMMARY OF DATA

Run No.	Temperature OF	Pressure Psi. Gage	Approximate O ₂ Conc.	Total Time Min.	Final % Conversion	% O ₂ Remaining	Remarks
1-A	100	100	3 %	60	17.5 %	0.0 %	
1-B	100	100	13 %	50	43.7 %	0.0 %	
1-C	100	100	36 %	30	100.	6.8 %	
1-A	100	100	3 %	35	10.3 %	0.0 %	Rates
1-B	100	100	13 %	40	45.3 %	0.0 %	Rates
1-C	100	100	38 %	30	100.	8.0 %	Rates
2-A	100	135	3 %	45	13.	0.0 %	
2-B	100	135	13 %	45	63.6 %	0.0 %	
2-C	100	135	38 %	45	100.	15. %	
3-A	130	100	3 %	45	14.5 %	0.0 %	
3-B	130	100	13 %	45	43.5 %	0.0 %	
3-C	130	100	38 %	45	100.	3.5 %	
4-C	100	0.0	38 %	120	18.7 %	5.0 %	
5-C	100	50	38 %	60	85.0 %	0.0 %	Rates
8-C	100	25	38 %	60	50.7 %	0.0 %	Rates
9-C	100	100	38 %	45	71.7 %	19.8 %	Rates 1/2 N ₂ O ₄
Sp.1-B	100	100	13 %	45	5.1 %	11.2 %	Rates No N ₂ O ₄
Sp.1-C	100	100	38 %	50	7.4 %	32.1 %	Rates No N ₂ O ₄

Run Number 1-A

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. C Volume 1 liter Weight 1155 grams

Analysis: Ferrous 42.7 ml. KmnO_4 soln./5 ml. sample
 Ferric negligible

Oxygen partial pressure 3.2 psi. abs.

Nitrogen partial pressure 105.1 psi. abs.

N_2O_4 partial pressure 6.4 psi. abs.

Normality of KmnO_4 used 0.119

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KmnO_4 soln. per 5 ml. sample	% Conversion*	Remarks
10:25	100	99			Gas in
10:23	102	100			Pump on
10:39	"	103			
10:46	"	102.5			
10:56	"	102.5			
11:06	"	101.0			
11:21	"	100.5	25.1	17.5	End of Run

Oxygen in gas at end of Run: 0.0%

* Percent conversion found by: 100 times the ratio of the ml. KmnO_4 solution used to titrate 5 ml. sample of sample from run divided by the ml. of KmnO_4 solution used to titrate a 5 ml. sample of the original pickle liquor.

Run Number 1-B

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. D Volume 1 liter Weight 1155 gramsAnalysis: Ferrous 44.8 ml. KMnO_4 soln./5 ml. sample Ferric negligibleOxygen partial pressure 13.8 psi. abs.Nitrogen partial pressure 94.5 psi. abs. H_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge		Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion*	Remarks
	Pressure Psi.	Temperature °F.			
1:30	100	100.5			Pump on
1:40	101	101.5			Pres. holding
2:00	101	100.5			
2:20	101	101.5	23.2	43.2	End of Run

Oxygen in gas at end of run: 0.0%

* Pressure was held constant by addition of kerosene until this time. At this time the pressure started to hold constant without further addition of kerosene. This is an indication that a major portion of the reaction is complete.

Run Number 1-C

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor

Sample No. D Volume 1 liter Weight 1155 gramsAnalysis: Ferrous 44.8 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen partial pressure 40.4 psi. abs.Nitrogen partial pressure 67.9 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
4:15	100	99.5			Pump on
4:25	100	98.			Pres. holding
4:35	100	98.			
4:45	100	101.5	0.1	100%	End of Run

Oxygen in gas at end of run: 6.8%

Run Number 1-A

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. I Volume 1 liter Weight 1153 gramsAnalysis: Ferrous 42.2 ml. KMnO_4 soln./5 ml. sample
 Ferric negligibleOxygen partial pressure 3.2 psi. abs.Nitrogen partial pressure 105.1 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.1195

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
1:45	100	97.5			Pump on
1:46	100	97.5			Pres. holding
1:50	100	98.	38.6	8.4%	
2:00	100	98.	36.1	9.8	
2:20	100	98.5	37.8	10.3	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 1-B

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. I Volume 1 liter Weight 1156 gramsAnalysis: Ferrous 42.2 ml. KMnO_4 soln./5 ml. sample
 Ferric negligibleOxygen partial pressure 13.3 psi. abs.Nitrogen partial pressure 94.5 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.1195

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	%Conversion	Remarks
4:00	100	100			Pump on
4:05	100	100	26.3	37.7	Pres. holding
4:15	100	100	23.6	43.6	
4:26	100	104	23.1	45.2	
4:40	100	97	23.0	45.3	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 1-C

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor

Sample No. H Volume 1 liter Weight 1155 gramsAnalysis: Ferrous 42.6 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen partial pressure 40.4 psi. abs.Nitrogen partial pressure 67.9 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.119

Time	Gauge		Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
	Pressure Psi.					
11:00	100		99			Pump on
11:05	100		99.5	11.3	73.2%	
11:15	100		99.5	0.10	100 %	Pres. holding
11:30	100		99.5	0.05	100 %	

Oxygen in gas at end of run: 3.0%

Run Number 2-A

Conditions: Temperature 100°F. Pressure 135 psi. gauge

Reagents:

Pickle Liquor:

Sample No. E Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 44.7 ml. KMnO_4 soln./5 ml. sampleFerric negligibleOxygen partial pressure 4.3 psi. abs.Nitrogen partial pressure 136.7 psi. abs. N_2O_4 partial pressure 8.7 psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
2:15	133	101			Pump on
2:25	135	101			Pres. holding
2:35	135	101			
2:45	135	101			
2:55	135	101			
3:00	135	101	39.0	13%	End of Run

Oxygen in gas at end of run: 0.9%

Run Number 2-B

Conditions: Temperature 100°F. Pressure 135 psi. gauge

Reagents:

Pickles Liquor:

Sample No. E Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 44.7 ml. KMnO_4 soln./5 ml. sampleFerric negligibleOxygen partial pressure 13.6 psi. abs.Nitrogen partial pressure 122.4 psi. abs. N_2O_4 partial pressure 8.7 psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
3:45	130	101			Pump on
3:53	133	101			Pres. holding
4:05	133	101			
4:15	134	102.5			
4:30	134	103	15.1	63.6%	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 2-C

Conditions: Temperature 100°F. Pressure 135 psi. gauge

Reagents:

Pickle Liquor:

Sample No. F Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 45.1 ml. K₂MnO₄ soln./5 ml. sample
Ferric negligibleOxygen partial pressure54.6 psi. abs.Nitrogen partial pressure86.4 psi. abs.N₂O₄ partial pressure.....8.7 psi. abs.Normality of K₂MnO₄ used0.114

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. K ₂ MnO ₄ soln. per 5 ml. sample	% Conversion	Remarks
9:45	133	102			Pump on
9:55	134	98			Pres.
10:05	134	98			holding
10:15	134	93.5			
10:25	134	99			
10:30	134	99	0.1	100%	End of Run

Oxygen left in gas at end of run: 15%

Run Number 3A

Conditions: Temperature 130°F . Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. F Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 45.1 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen partial pressure..... 3.2 psi. abs.Nitrogen partial pressure.....105.1 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge Pressure Psi.	Temperature $^{\circ}\text{F}$.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
2:00	100	128.5			Pump on
2:10	101	132			
2:20	101	132			
2:30	101	130.5			
2:45	101.5	131.0	53.5	14.5%	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 3-B

Conditions: Temperature 130°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. II Volume 1 liter Weight 1152 gramsAnalysis: Ferrous 42.6 ml. KMnO_4 soln./5 ml. sample
 Ferric negligibleOxygen partial pressure13.8 psi. abs.Nitrogen partial pressure.....94.5 psi. abs. H_2O_4 partial pressure.....6.4 psi. abs.Normality of KMnO_4 used......119

Time	Gauge Pressure	Temperature °F	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
	Psi.				
10:00	100	132			Pump on Pres. holding
10:00	101	123			
10:20	103	124			
10:30	103	123			
10:40	104	126			
10:45	104	129	22.8	46.5%	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 3-C

Conditions: Temperature 130°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. J Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 42.5 ml. KMnO_4 soln./5 ml. sample
 Ferric negligibleOxygen partial pressure 40.4 psi. abs.Nitrogen partial pressure 67.9 psi. abs. N_2O_4 partial pressure 6.4 psi. abs.Normality of KMnO_4 used..... 0.1195

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
2:45	100	132			Pump on
2:55	100	124			
3:05	100	127			
3:15	100	129.5			
3:25	100	130			
3:30	100	129	0.05	100%	End of Run

Oxygen in gas at end of run: 3.5%

Run Number 4-C

Conditions: Temperature 100°F. Pressure Atmospheric

Reagents:

Pickle Liquor:

Sample No. J Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 42.5 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen 40.45*Nitrogen 53.2% H_2O_4 3.4%Normality of KMnO_4 used 0.1195

Time	Gauge		Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
	Pressure Psi.	Temperature °F.			
10:25					Gas in
10:40					P.L. in
10:45	0.0	95			Pump on
11:00	0.0	101.5			
11:10	0.0	99			
11:25	0.0	100			
11:30	0.0	99	35.5	16.5%	
12:35	0.0	98	34.6	18.7%	
1:00					End of Run

Oxygen in gas at end of run: 5.0%

* See next page

Special Note on Run 4-C

Since the total pressure in the reactor for this run was only one atmosphere, a different method was needed for measuring in the gases. This was done by filling the reactor with water and displacing definite proportions of the water with the respective gases.

Total volume of reactor = 3.5 liters

Volume of water displaced by each gas:

N_2O_4	6.4% of 3.5 l	= 224 ml.
O_2	40.4% of 3.5 l	= 1414 ml.
N_2	53.2% of 3.5 l	= 1862 ml.

After the gases were introduced, the liter of pickle liquor was introduced from a glass blow case under nitrogen pressure.

Run Number C-C

Conditions: Temperature 100°F. Pressure 50 psi. gauge

Reagents:

Pickle Liquor:

Sample No. K Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 42.0 ml. K₂MnO₄ soln./5 ml. sample
 Ferric not detectableOxygen partial pressure..... 26.2 psi. abs.Nitrogen partial pressure 34.5 psi. abs.H₂O₄ partial pressure 4.1 psi. abs.Normality of K₂MnO₄ used 0.1713

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. K ₂ MnO ₄ Soln. per 5 ml. sample	% Conversion	Remarks
3:45	50	97			Pump on
3:50	50	97.5	23.5	43.8%	
3:55	50	97.5	16.3	61.2%	
4:05	50	97	8.2	80.5%	
4:15	50	97	6.3	85.0%	
4:30	50	93	6.3	85.0%	
4:45	50	93			End of Run

Oxygen in gas at end of run: 0.0%

Run Number 8-C

Conditions: Temperature 100°F. Pressure 25 psi. gauge

Reagents:

Pickle Liquor:

Sample No. K Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 42.0 ml. KMnO_4 soln./5 ml. sampleFerric negligibleOxygen partial pressure..... 16.1 psi. abs.Nitrogen partial pressure 21.1 psi. abs. H_2O_4 partial pressure 2.5 psi. abs.Normality of KMnO_4 used..... 0.1018

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
1:30	25	94			Pump on
1:35	25	100	31.0	26.2	
1:45	25	99	24.5	41.7	
1:55	25	99	22.0	47.6	
2:10	25	100	21.0	50.2	
2:30	25	100	20.6	50.7	End of Run

Oxygen in gas at end of run: 0.0%

Run Number 9-C

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. L Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 41.7 ml. KMnO_4 soln./5 ml. sample Ferric undetectableOxygen partial pressure 41.8 psi. abs.Nitrogen partial pressure 69.6 psi. abs. N_2O_4 partial pressure 5.5 psi. abs.Normality of KMnO_4 used 0.1918

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
4:00	100	91.5			Pump on
4:05	101	96.5	25.5	38.8	
4:15	100	101.5	12.3	70.3	
4:25	100	101.5	11.9	71.5	
4:45	100	100.0	11.8	71.7	End of Run

Oxygen in gas at end of run: 19.8%

Run Number Special 1-B

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. G Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 44.7 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen partial pressure 13.8 psi. abs.Nitrogen partial pressure 100.9 psi. abs. N_2O_4 partial pressure No psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge Pressure Psi.	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
2:20	100	95			Pump on
2:30	100	100	43.1	3.3%	
2:45	100	99	42.5	5.0%	
2:55	100	100			End of Run
3:05	100	100	42.4	5.1%	

Oxygen in gas at end of Run: 11.2%

Run Number Special 1-C

Conditions: Temperature 100°F. Pressure 100 psi. gauge

Reagents:

Pickle Liquor:

Sample No. G Volume 1 liter Weight 1150 gramsAnalysis: Ferrous 44.7 ml. KMnO_4 soln./5 ml. sample
Ferric negligibleOxygen partial pressure 38 psi. abs.Nitrogen partial pressure 76.7 psi. abs. N_2O_4 partial pressure No psi. abs.Normality of KMnO_4 used 0.114

Time	Gauge	Temperature °F.	Sample Analysis ml. KMnO_4 soln. per 5 ml. sample	% Conversion	Remarks
	Pressure Psi.				
10:50	100	95			Pump on
10:55	100	101	42.2	5.7%	
11:10	100	100	41.6	7.2%	
11:20	100	100			
11:30	100	100	41.4	7.3%	
11:40	100	100	41.3	7.4%	End of Run

Oxygen in gas at end of run: 32.1%

DISCUSSION

As a starting place for the experimental work, the easily obtained conditions of 100 deg. F. and 100 psi. gauge were used. Six runs were made under these conditions, using various concentrations of nitrogen and oxygen. A constant concentration of N_2O_4 was used in these runs.

From Curtis⁽¹⁾ it was determined that from the oxidation of ammonia, concentration of NO_2 in the range around 12% could be obtained and an equivalent of 6.4% N_2O_4 was then used in most of the tests. Concentration of 3%, 13%, and 38% O_2 , with the remainder N_2 were investigated.

It was found from runs 1A, 1B, and 1C that in all cases the reaction went to completion, using up all of the oxygen present under the conditions of the lower oxygen concentrations, and giving complete conversion of FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$ in the case of the highest oxygen concentration. Two runs made at each of these conditions gave similar results. Checking of the time-rate function showed the reaction to go to completion for the amounts of material present in from 30 to 45 minutes.

Runs 2A, 2B, and 2C, made at 100°F., 135 psi. showed that an increase in pressure had no great effect. As the amount of free oxygen present was larger, however, due to the higher pressure, the percentage conversion of the ferrous to ferric was correspondingly greater.

Similar runs, 3A, 3B, and 3C, made at 130 deg. F., 100 psi. showed identical results with the other two sets.

Two other variables were investigated: very much lower pressures,

and lower concentrations of the catalyst.

Run 6C made at 100°F., 50 psi., using the highest concentration of O₂ showed no significant change from the other runs. Lowering of the pressure still further to 25 psi., run 8C, showed definite slowing of the reaction rate but nothing else. Run 4C made at atmospheric pressure gave a rate decrease to the point where the reaction was incomplete in 2½ hours as compared to the previous average time of 45 minutes.

Catalyst concentration was shown to be controlling in run 9C when it was dropped to one-half that used in the previous runs. Here incomplete reaction was found with excess oxygen present. It is believed that side reactions, such as the formation of nitrosyl-sulfuric acid may account for the disappearance of sufficient N₂O₄ to act as the oxygen carrier. Complete elimination of the N₂O₄ in runs Special 1B, 1C showed conclusively that, although some conversion took place, the action of the N₂O₄ was necessary for successful operation.

ACCURACY OF THE PROCEDURE

The methods of analysis used were standard methods as found in various books on quantitative analysis. The exact methods followed are given in the Appendix of this thesis. The synthetic pickle liquor was analyzed for both ferric and ferrous iron before it was used. However, the samples taken from each run were checked only for ferrous. All reductions were made with a Jones Reductor since there was no chloride ions present in the solution. The method of reducing with stannous chloride did not work on the sulfate solution.

CONCLUSIONS

On the basis of the experimental and theoretical work done, the author believes the following conclusions may be safely drawn:

1. In the oxidation of ferrous to ferric sulfate in waste pickle liquors the controlling factor is the rate of reaction.
2. Commercially feasible rates are obtainable at temperatures ranging from room temperature to 150 degrees F., at pressures from 25 psi. to 150 psi. gauge, using N_2O_4 as a catalyst, oxygen carrier.
3. Concentration of oxygen in the reaction mixture is not controlling as long as ^{than} more stoichiometric amounts are present.
4. Concentration of N_2O_4 is not controlling as long as sufficient N_2O_4 is present so that side reactions do not completely use it up.
5. Conditions of 100 degrees F., 100 psi. gauge pressure, 38% O_2 , 12% NO_2 , 50% N_2 are acceptable conditions for the reaction.
6. Operation at the O_2 concentration of natural air should be only a matter of introducing sufficient O_2 for the reaction, as it is independent of concentration.

SUGGESTIONS FOR FURTHER WORK

Much more work could be done on this process in order to give a more complete background for commercial plant design. Some of the factors the author suggests would be:

1. Investigation of rates at higher temperatures and pressures.
2. Theoretical investigation of the kinetics involved in the various reactions.
3. Corrosion studies on the reaction mixtures.
4. Determination of the absolute optimum conditions and concentrations with emphasis on excess of materials over the stoichiometric amounts.
5. Design and operation of the process as a continuous process instead of batchwise process.

APPENDIX

Analytical ProcedureFerrous Iron:

A 5 ml. sample of the sulfate solution of the iron salts was transferred to a 250 ml. erlenmeyer flask and diluted with about 50 ml. distilled water. 10-15 ml. of Zimmermann-Reinhardt solution was added and then it was titrated to a faint permanent (for at least 15 sec.) pink with 0.1 N KMnO_4 .

Ferrous + Ferric Iron:

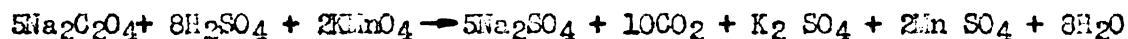
A 5 ml. sample of the sulfate solution was transferred to a 250 ml. erlenmeyer flask and diluted with 50 ml. distilled water. 2 to 3 ml. of concentrated H_2SO_4 was added. The solution was then run very slowly through a Jones Reductor upon which a blank had just been run. Following the solution, three or four 50 ml. portions of distilled water were put through the reductor and added to the original solution in a 750 ml. flask. The last few ml. of this wash water was collected separately and titrated. If a single drop of permanganate gave a permanent pink, washing was discontinued and the solution, after adding the Zimmermann-Reinhardt solution was titrated with the permanganate solution.

Makeup and Standardization of 0.1N KMnO_4 Solution

Eight grams of pure KMnO_4 were dissolved in $2\frac{1}{2}$ liters of distilled water. The solution was heated to just below boiling for at least two hours. The solution was then allowed to stand until cool

and filtered through glass wool.

Standardization was accomplished by weighing out 0.25-0.35 grams of dried, pure sodium oxalate, dissolving it in 50 ml. of distilled water and adding 25 ml. of 1:8 H_2SO_4 . This solution was heated just to boiling and titrated with the permanganate while hot. Normality of permanganate was calculated from the following reaction:



Preparation of Zimmermann-Reinhardt Solution

Dissolve 70 g. of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in 500 ml. H_2O . Add with stirring 125 ml. concentrated H_2SO_4 and 125 ml. 85% phosphoric acid. Dilute to approximately one liter.

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