

ON THE REACTION IN A MIXTURE  
OF  
HYDROUS FERROUS AMMONIUM SULFATE  
AND SODIUM CHLORIDE

by

Homer Thomas Newlon, A.B.

*Approved*  
*D. G. Brown*

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## 1 - Introduction

In connection with work in this laboratory it had been observed that a reaction takes place between hydrous ferrous ammonium sulfate and sodium chloride when they are intimately mixed and kept in tightly closed bottles, with the loss of ferrous iron.

### 11 - Purpose

The purpose of this investigation was to study the reaction. This was done by determining the percentage of ferrous iron in the mixture after definite intervals of time. Also the percentage of chlorine in the mixture under the same conditions.

### 111 - Methods of Analysis

The methods of analysis used were:

(1) Iron - titration with a standard potassium permanganate solution.

(2) Chlorine - to precipitate the chlorine present with an excess of standard silver nitrate solution and then titrate the excess of silver nitrate solution used with a standard ammonium thiocyanate solution, using a saturated solution of ferric alum as an indicator.

#### IV Testing of Materials for the Mixtures

A gram of Baker's Analyzed Hydrous Ferrous-Ammonium Sulfate was tested for the presence of ferric iron with a solution of potassium ferro-cyanide. Test negative. A similar portion was tested with a solution of ammonium thiocyanate. Test negative. A third portion was tested for chlorides with silver nitrate solution. Test negative.

A gram of Baker's Analyzed Sodium Chloride was tested for the presence of ferric iron as above. Both tests were negative. Two other similar portions were tested for ferrous iron with solutions of potassium permanganate and potassium ferri-cyanide respectively. The tests were negative.

## V - Preparation of the Mixtures

Baker's Analyzed Hydrous Ferrous Ammonium Sulfate, in small crystals, was ground in a mortar so that it would all pass a forty mesh screen.

Baker's Analyzed Sodium Chloride, coarsely crystallized, was ground to the same extent as the hydrous ferrous ammonium sulfate.

Five portions of the hydrous ferrous ammonium sulfate were then weighed out, consisting of ninety, eighty, seventy, sixty, and fifty grams respectively.

Five portions of the sodium chloride were weighed out, consisting of ten, twenty, thirty, forty, and fifty grams respectively. The weighing in both cases was accurate out to one milligram.

The two substances were then mixed in the following proportions:

	1	2	3	4	5	
Ferrous ammonium sulfate	90	80	70	60	50	grams
Sodium chloride	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>	"
Total	100	100	100	100	100	"

They were intimately mixed by placing the material upon a rubber sheet, alternate corners of which were grasped and the mass rolled over and over, care being taken not to spill any of the substance off the sheet. This was continued for five minutes. Then about one fourth of the mixture was placed in a mortar and ground for five minutes. This finely ground material was then poured upon a piece of black glazed paper. The remainder was ground in each of three portions for the same length of time. In the last fourth care was taken to brush off all particles clinging to the sheet into the mortar, and after grinding to brush out the mortar. The entire mixture was then transferred from the glazed paper back to the sheet and mixed as before, the mixing being continued for ten minutes. The mixture was then again returned to the mortar in four portions and ground for five minutes each. Then the total mass was once more mixed upon the sheet for five minutes. The intimate mixture thus secured was then placed in a wide mouth <sup>glass stoppered</sup> bottle ~~and corked~~. Each of the remaining mixtures was made and preserved in a similar way.

During the process of grinding the above mixtures the following phenomena were observed:

Mixtures 3,4, and 5, seemed to produce a greenish brown gas which looked somewhat like chlorine and also like the reddish fumes of nitric oxide. The depth of tint of the gas increased with increasing percentage of chloride in the mixture. These observations were made when the material stood in a pile upon the rubber sheet in contact with the air. When the pile was disturbed by lifting one corner of the sheet, the color would roll aside and the color of the particles beneath become plainer. Also by blowing upon the surface the colored gas could be dispelled. This was observed continually during the process of grinding. However, when the mixture was put into the bottle and corked, no color appeared in the empty space above the substance. For twenty four hours after mixing the phenomena could be repeated by pouring the material from the bottle again upon a piece of glazed paper.

The air space above the mixture in the bottles was tested for the presence of chlorine with starch-iodide paper. The test was negative. Also, a small portion of each of the mixtures 3,4, and 5, was tested for nitrates with concentrated sulfuric acid. The

test was negative. There was a distinct acid odor in the bottles after standing twenty four hours, it being strongest in number 5. Tests with litmus paper and silver nitrate solution on the end of a glass rod held down into the air space above the mixtures were negative.

All the above mixtures were the same tint when placed in the bottles. They were in a very fine powder and by reflected light were almost white, the color observed being slightly greenish-blue.

Upon examination after two weeks, number 4 had a decided yellowish tinge. The others seemed to be about the same color as when prepared. The corks in all the bottles were tight. Upon cautiously opening bottle number 1 the acid odor noticed before was very much more marked. This time the confined air gave an acid reaction with litmus paper. This was true of all the other mixtures. When a rod moistened with silver nitrate solution was held in each of the bottles, a white coating was formed upon the rod which dissolved in ammonium hydroxide solution and was precipitated by making the solution acid with dilute nitric acid. This proved that hydrogen chloride was one of the products of reaction.

The contents of the bottles were no longer freely moving. When the bottles were inverted the material remained in place. With slight tapping, however, the contents were again restored to free movement. Mixture number 4 was the most difficult to break of all the others but it went back to the individual particles readily.

#### V1 - Standardization of Solutions

##### Potassium permanganate solution

A stock solution of about one tenth normal potassium permanganate was standardized as follows:

Samples of the hydrous ferrous ammonium sulfate used in the preparation of the mixtures were weighed off into each of two <sup>Erlenmeyer</sup> dry flasks. A small quantity of sodium bicarbonate was added to each. One hundred cubic centimeters of distilled water were then added to each flask. A greenish precipitate formed at once. Ten cubic centimeters of dilute sulfuric acid (one part concentrated sulfuric acid to eight parts distilled water) were then

added to each flask. The green precipitate dissolved at once and the solution became colorless, ~~likexwaterx~~. The potassium permanganate solution was then run into the flasks from a burette until one drop produced a faint pink color which was permanent. The samples checked.

One cubic centimeter of the potassium permanganate solution was equivalent to .00555 grams of iron.

#### Hydrochloric acid

A stock solution of dilute hydrochloric acid was standardized as follows:

Two samples, each of about twenty five cubic centimeters, were precipitated with an excess of a ten percent solution of silver nitrate in the presence of nitric acid, the samples being diluted with one hundred cubic centimeters of water. The precipitated silver chloride was kept near the boiling point, with constant stirring until the precipitate was coagulated and the supernatant liquid clear, ~~likexwaterx~~. The precipitate was protected from the light as much as possible and

was but slightly tinged with purple when ready for filtration. The precipitate was collected in weighed Gooch crucibles, washed with hot water until free from silver nitrate solution, and heated to constant weight. The samples checked.

One cubic centimeter standard hydrochloric acid was equal to .003765 grams hydrogen chloride or .1033 normal.

#### Silver nitrate solution

The silver nitrate solution was made up so that it would be about two-tenths normal. Two samples of about twenty five cubic centimeters were precipitated with an excess of dilute hydrochloric acid, the samples being diluted ~~to~~ to one hundred cubic centimeters. The same procedure was observed from this point ~~on~~ as was used in the standardization of the hydrochloric acid. The Gooch crucibles were heated to constant weight and checked.

One cubic centimeter of the silver nitrate solution was equal to .03868 grams silver nitrate or .2277 normal.

Ammonium thiocyanate solution

The ammonium thiocyanate used was tested for chlorides. Test was negative.

Ferric alum used was tested for chlorides. The test was negative. One liter of a saturated solution of the ferric alum in water was prepared.

The ammonium thiocyanate was dissolved in water and standardized as follows:

About twenty five cubic centimeters of the standard silver nitrate solution were measured from a burette into a flask; one hundred cubic centimeters of water added and five cubic centimeters of the saturated ferric alum solution. The contents of the flask were then thoroughly mixed. Then ten cubic centimeters of dilute nitric acid (one part concentrated nitric acid to ten parts of water by volume) were added. The ammonium thiocyanate solution was then added cautiously until one drop produced a faint red tinge, due to the formation of the ferric sulphocyanate after all the silver had been precipitated as silver<sup>thio</sup>cyanate. These samples were run in triplicate and checked.

One cubic centimeter of the ammonium thiocyanate solution reacts with .6083 cubic centimeters of the standard silver nitrate solution or it is .1385 Normal.

Three other samples of about twenty five cubic centimeters were run as above, substituting dilute sulfuric acid for the nitric acid. These samples checked and the normality found was the same as with the nitric acid.

The adaptability of the method to the investigation in hand was tried as follows:

A quantity of hydrous ferrous ammonium sulfate was placed in three flasks. To each was added a portion of sodium bicarbonate, one hundred cubic centimeters of distilled water, and ten cubic centimeters of dilute sulfuric acid. The standard potassium permanganate solution was then added until the contents of the flasks were a light pink. Sufficient hydrous ferrous ammonium sulfate was then added to each flask to discharge the color of the permanganate solution. Then to each flask were added five cubic centimeters of the ferric alum solution and an additional five cubic centimeters of dilute sulfuric acid. Then a known volume of the standard

hydrochloric acid was run into each of the flasks. A known volume of the standard silver nitrate solution in excess was then added to each flask. The excess of the silver nitrate solution was titrated with the ammonium thiocyanate solution. Titration was discontinued when the first tinge of red was visible. The three samples checked well. The value found for the hydrochloric acid was .10333 Normal which compares favorably with a normality of .1033 by precipitation with silver nitrate solution. It was evident that this method could be used satisfactorily for the determination of chlorine in the mixtures after the ferrous iron content had already been determined.

## VII - Tests for Ferric Iron

Tests for ferric iron in the mixtures were made on three sets of material which had been standing for different periods of time. The solutions used for testing for the ferric ion were ammonium thiocyanate and potassium ferro-cyanide.

The set of mixtures which had been standing five weeks was tested first. Portions of the material were placed in test tubes; water added; solution was complete. The solutions were then tested with potassium ferro-cyanide solution. There was no blue color produced. With the ammonium thiocyanate solution there was no red produced. There was produced, however, with the latter solution a faint reddish yellow color which deepened a little as the percent of sodium chloride in the mixture increased. Therefore, ferric iron is absent.

Another set of mixtures which had been standing forty seven weeks was next tested. The reaction had evidently been different in this set of mixtures.

Portions of the mixtures were placed in test tubes and water added. They did not go completely into solution but left more or less cloudiness. With potassium ferro-cyanide solution there was a very faint blue color produced. The tint again increased in those mixtures containing the highest percent of chlorine. With the ammonium thiocyanate solution all the solutions gave the characteristic red of the ferric thiocyanate. The depth of color increased as with the potassium ferro-cyanide solution. The depth of color produced, however, was only sufficient to indicate the merest trace of ferric iron in solution. When dilute hydrochloric or sulfuric acid was added to the above solutions, the characteristic reaction for the ferric ion was produced at once.

A third mixture which seemed to have completely decomposed was next tested. It had been standing several years. The bottle was filled with a reddish-brown earthy material. Water was added to portions of it in test tubes. There was a large insoluble reddish-brown residue. The tests for

ferric iron with the ammonium thiocyanate and the potassium ferro-cyanide solutions were negative.

Therefore, it may be concluded that all the ferric iron present is either insoluble in water or else it has formed a compound in which a complex ion is present and in which no trace of ferric iron can be found. The fact that the mixtures which had been standing five weeks are completely soluble in water, yet in which some disappearance of the ferrous iron has taken place, would tend to indicate the presence of a complex ion. This complex ion is then decomposed producing a reddish-brown substance which may be a ferric hydroxide. This seems to be the end product of the reaction.

## VIII - Experiments on the Mixtures.

### Percent of ferrous iron

Five weeks after the mixtures had been prepared the analysis was begun.

The material in the bottles was about the same in color as at the end of two weeks. The only noticeable difference was they were more caked and required stronger tapping to shake loose.

Samples of about one and a quarter grams were weighed out to start with. The preliminary titrations with mixture number 1, did not give check results. The variation was too great to be due to over running the end point with the permanganate solution. Before weighing out another set of samples the contents of the bottle were poured upon glazed paper and thoroughly mixed. The mixture was then returned to the bottle, two additional samples weighed out and titrated. The samples checked well. In the subsequent work, the materials were poured from the bottles and thoroughly

mixed before sampling. No difficulty was experienced in getting concordant results. The titrations were conducted as nearly as possible as in the standardization of the permanganate solution. They were made every two weeks up to and including the nineteenth week. No data were secured from the nineteenth to the forty-seventh weeks.

The resulting percentage of ferrous iron found in mixture number 1, after thorough mixing was higher than the percentage of ferrous iron obtained by using the mixture as it came from the bottle without mixing. This would indicate that the portion near the top which is most exposed to the air is more completely changed over to the ferric condition and therefore contains less ferrous iron. This would also indicate that the air - either oxygen or moisture, or both - play an ~~important~~ part in the reaction.

At the end of forty-seven weeks a very marked change had occurred in the appearance of the mixtures. They had become a reddish green in color. A closer examination revealed the presence of reddish particles

scattered thru the substance. The material in the bottles was tough and resistant, and had to be pried from the bottles. When cut with a knife, it cut like so much stiff wax. After getting the material from the bottles it had to be ground up in a mortar before it could be satisfactorily mixed. When the particles were once broken apart no further difficulty was experienced in keeping the material quite friable so that it was readily mixed after the first time. Samples of these mixtures were very difficult to get into solution. Upon shaking the flasks containing the samples there would be a quantity of flaky looking material distributed thru the liquid, so that the whole of it appeared quite cloudy. These particles would quickly settle to the bottom and the liquid became clear.

The ferrous iron content had so far disappeared that it was necessary to use samples of four to five grams in order to have sufficient ferrous iron present to make an accurate determination. When sodium bicarbonate and water were added to the flasks, effervescence took place. The amount of the effervescence increased as the

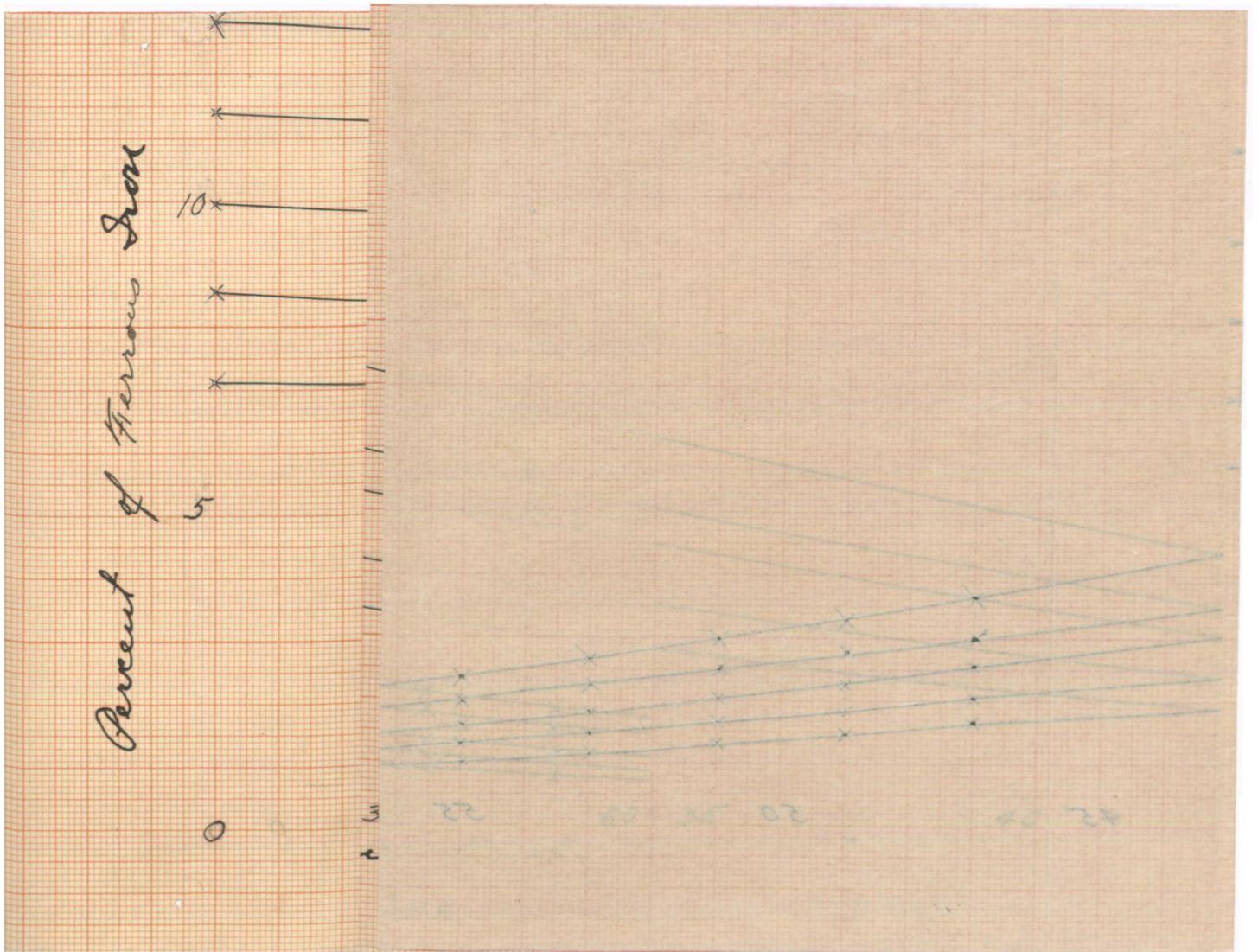
percentage of sodium chloride in the mixtures increased. Moreover, these mixtures did not form any precipitate with the sodium bicarbonate as did the mixtures when first prepared. Upon the addition of the dilute sulfuric acid to the samples the presence of the orange red substance mixed with the original material is more noticeable. Mixtures 1 and 2 effervesced but did not show the presence of any of this red substance. Mixtures 3, 4, and 5 contained the red substance in increasing quantities, number 5 having the largest quantity. When the flasks are agitated the red substance dissolved along with the remainder of the contents of the flasks. The solutions finally obtained were alike as far as could be observed. These solutions had a distinctly green color, showing the presence of ferrous iron in solution. The mixtures which had not stood so long in solution were colorless like water.

The table containing the percentages of ferrous iron in the mixtures after various intervals of time follows.

Percent of ferrous iron:

Week	1	2	3	4	5
0	12.83	11.40	9.98	8.55	7.13
5	12.50	11.04	9.62	8.21	7.01
7	12.24	10.82	9.36	8.00	6.82
9	12.00	10.45	9.14	7.76	6.60
11	11.66	10.15	8.85	7.50	6.37
13	11.33	9.82	8.55	7.22	6.12
15	10.92	9.46	8.22	6.92	5.86
17	10.53	9.07	7.85	6.61	5.60
19	10.09	8.67	7.52	6.29	5.30
.....					
47	3.65	3.00	2.52	2.05	1.67
49	3.29	2.79	2.26	1.85	1.45
51	2.96	2.50	2.02	1.65	1.32
53	2.67	2.23	1.80	1.47	1.17
55	2.38	1.99	1.60	1.30	1.03
57	2.10	1.67	1.39	1.14	.91
59	1.87	1.55	1.23	.99	.79
61					

See supplemental file for unfolded graph.



There was very slight effervescence produced. With dilute sulfuric a red, muddy looking solution was formed with a large quantity of undissolved substance upon the bottom of the flasks. When titrated with the standard potassium permanganate solution 1.76 percent of ferrous iron was found. This is but slightly more ferrous iron than is contained in mixture number 1 after sixty-one weeks.

### Percent of chlorine

After the ferrous iron had been determined, a few crystals of hydrous ferrous ammonium sulfate were then added to the flasks to discharge the color of the permanganate solution. An excess of the standard silver nitrate solution was then added to each flask, also five cubic centimeters of the ferric alum solution and ten cubic centimeters of dilute sulfuric acid. The excess of the silver nitrate solution was titrated with the standard ammonium thiocyanate solution. Then the percentage of chlorine was calculated. No difficulty was experienced in titrating in the presence of all the other substances present. How well the results agree can be seen by reference to the table. The percent loss of the chlorine is very much less than that of the ferrous iron so that for a time the loss is almost undetectable.

In the last series of titrations for the chlorine no ferric alum solution was added to the flasks. There was sufficient ferric salt already present to serve as an indicator. There were no discrepancies in the results.

The addition of a ferric salt solution as an indicator in titrations of this nature could be omitted.

The table showing the percent of chlorine at the same intervals of time as the ferrous iron follows.

Percent of chlorine:

Week	1	2	3	4	5
0	6.07	12.13	18.20	24.26	30.33
5	6.05	12.12	18.19	24.24	30.30
7	6.05	12.12	18.18	24.23	30.27
9	6.05	12.11	18.19	24.23	30.27
11	6.06	12.12	18.19	24.23	30.22
13	6.03	12.07	18.15	24.20	30.20
15	6.04	12.12	18.18	24.16	30.17
17	6.02	12.09	18.14	24.18	30.05
.....					
47	5.65	11.22	16.73	22.27	27.82
49	5.57	11.13	16.68	22.21	27.71
51	5.48	11.04	16.67	22.14	27.63
53	5.38	10.91	16.61	22.08	27.50
55	5.27	10.79	16.59	22.01	27.36
57	5.14	10.68	16.58	21.96	27.28
59	4.98	10.51	16.54	21.87	27.13

See supplemental file for unfolded graph.

50 52 30 32

Time in Weeks

220

Plate II

Discussion of curves on plate 11

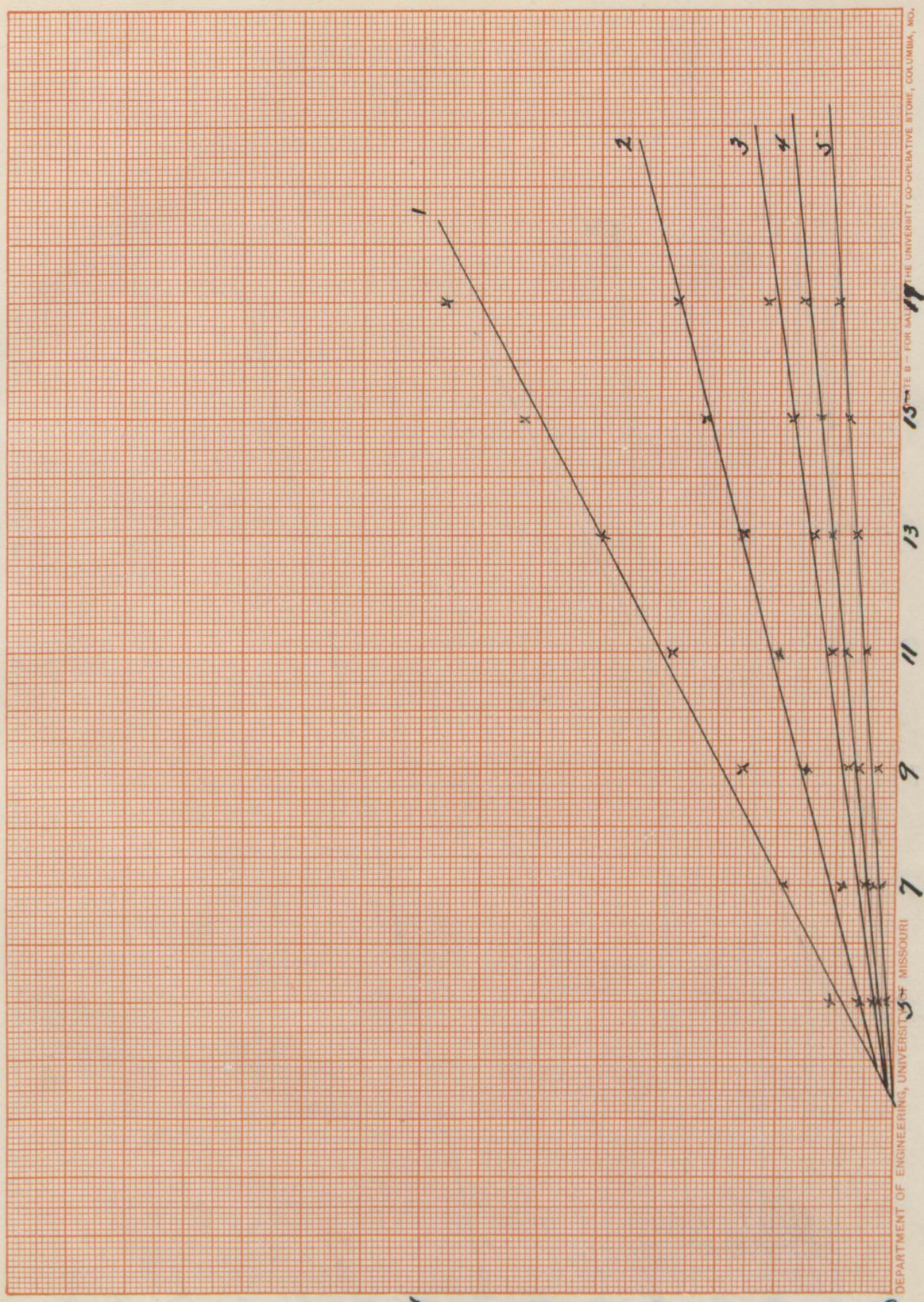
This group of curves appears in every way to be similar to the group of curves for the ferrous iron. The rate of change is very much slower than for the iron.

Ratios found by dividing percent of  
ferric iron by percent of chlorine:

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Week :	1	:	2	:	3	:	4	:	5
<hr/>									
5	.0545		.0297		.0197		.0140		.0039
7	.0975		.0478		.0286		.0227		.0102
9	.1372		.0784		.0397		.0326		.0175
11	.1931		.1031		.0566		.0433		.0251
13	.2487		.1309		.0716		.0549		.0334
15	.3162		.1601		.0913		.0674		.0420
17	.3821		.1927		.1119		.0802		.0509
19									
.....									
47	1.627		.7487		.4459		.2919		.1963
49	1.713		.7736		.4628		.3017		.2050
51	1.801		.8062		.4775		.3116		.2103
53	1.888		.8405		.4925		.3207		.2167
55	1.983		.8721		.5051		.3294		.2230
57	2.088		.9026		.5181		.3374		.2280
59	2.201		.9372		.5290		.3457		.2337
61									
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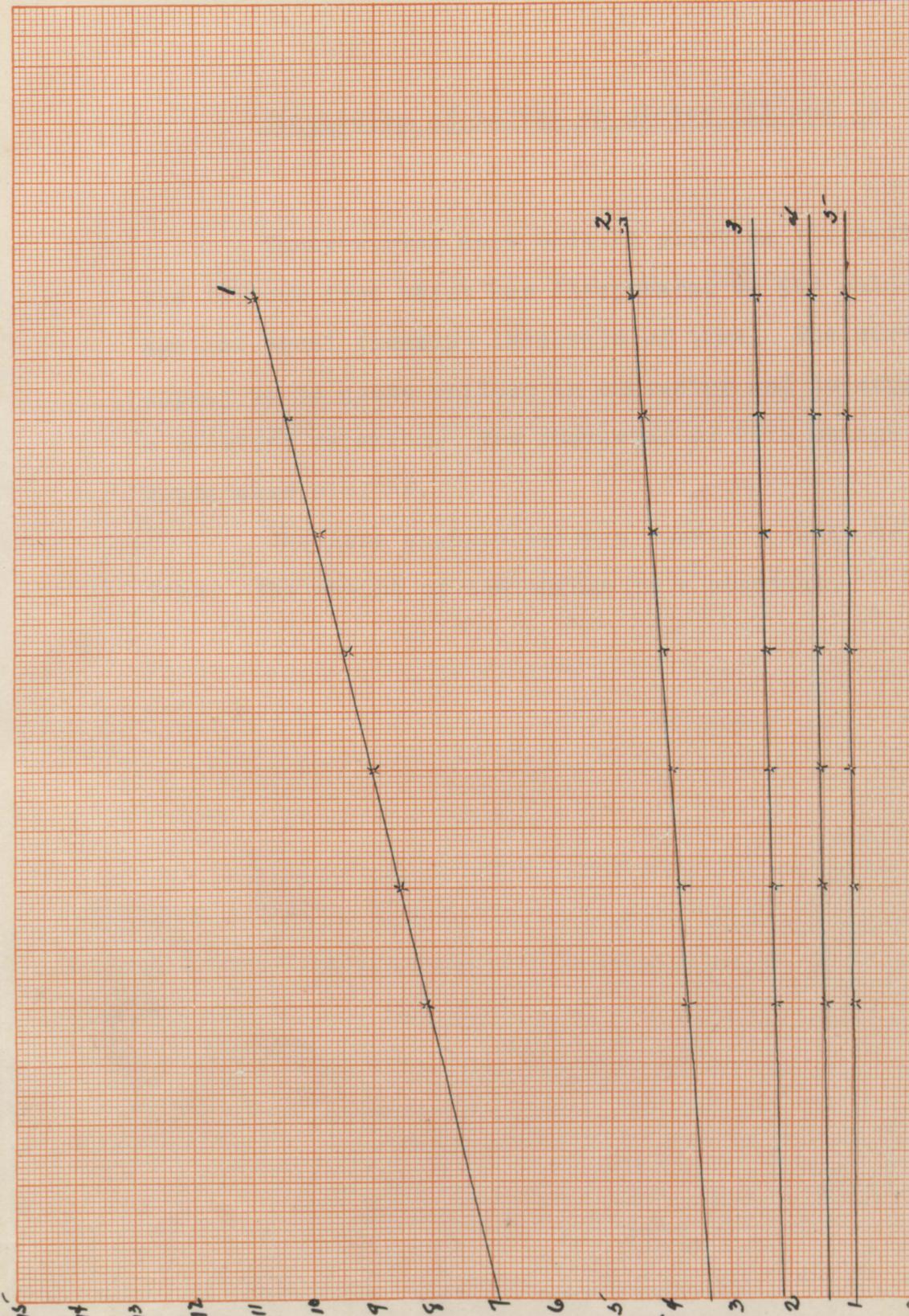
Ratio of Ferrous Iron<sup>lost</sup> to Chlorine  
 x 10.



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Time in weeks.

Plate III.



Ratio of Ferrous Iron to Chlorine  
 $\times 5^{-}$

Time in weeks.  
 Plate IV.

### Discussion of curves on plates 111 and 1V

These curves were made by plotting the ratio of the ferrous iron which has disappeared to the chlorine against equal (nearly) intervals of time. The curves appear to be quite uniform in character and to express a constant relation. The character of this change is in every case similar.

The mass changed bears a constant ratio to the time. The amount of the change is a constant.

## IX - Summary

The results of this investigation show that when hydrous ferrous ammonium sulfate and sodium chloride in intimate mixtures react:

1 Hydrogen chloride is one of the products of the reaction.

2 That the resulting salt formed from the oxidation of the ferrous iron is a complex one. That the iron present is in combination and does not give the reactions of the ferric ion. That the ultimate product formed is a water-insoluble ferric compound.

3 The amount of ferrous iron disappearing is a function of the time and this relationship may be expressed by a straight line.

4 After a period of time which seems to be a constant, regardless of the proportion of the components of the mixture, equilibrium is established between the ferrous iron and the ferric (?) iron.

5 That a similar constant relationship holds in the disappearance of chlorine from the mixtures as

hydrogen chloride.

6 That the change is directly proportional to the amount of ferrous iron disappearing.

7 When the ratio of the ferrous iron disappearing to the sodium chloride is the same, the change of the ferrous iron remaining is constant and is independent of the amount of the sodium chloride present.

#### References.

A diligent search was made of the literature for some reference that might be expected to have some bearing on this reaction but none was found.

### Acknowledgements

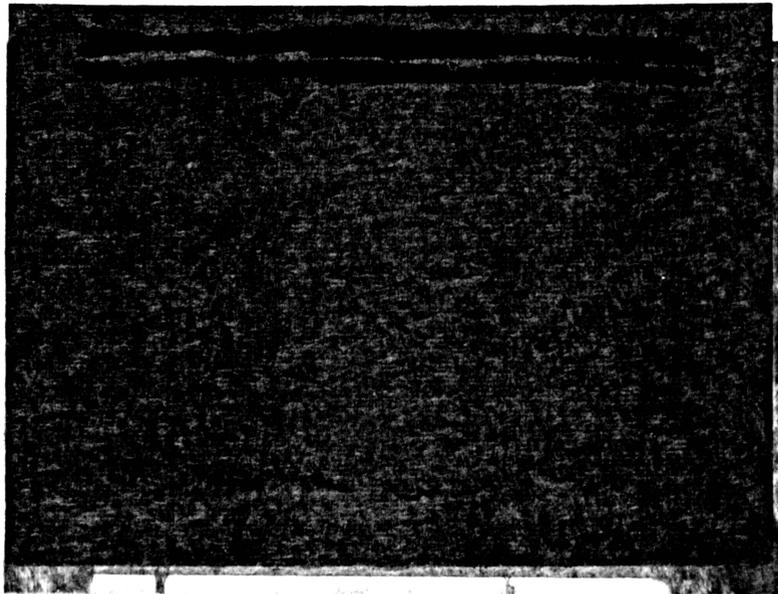
The work embodied in this paper was carried out under the direction of Dr.W.G.Brown, Professor of Technical Chemistry in the University of Missouri, at whose suggestion this investigation was undertaken. The author desires to thank him for much valuable advice, assistance, and encouragement.



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