THE PRECIPITATION OF IRON
AS A BASIC ACETATE

Thesis

by

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INTRODUCTION.

The object of this investigation was to determine the nature of the factors which influence the precipitation of iron as a basic acetate and the extent to which these could be varied with the view that such knowledge would help in perfecting the present basic acetate separations and in working out new ones. Some of these factors are the volume of the solution, and the amount of iron, the concentrations of acetic acid and acetate ion, and the presence of other substances. As an example of the latter, the effect of cerium in hindering the precipitation of iron invites question as to whether this effect is colloidal in nature or is due to mass-action changes and complex-ion formation.

A review of the literature shows that most of the work done on the precipitation of iron by this method is largely empirical in question, and gives descriptions of analytical procedures without extended study of the underlying principles. A list of the more important works consulted is given below.

EXPERIMENTAL PART.

The first phase of this question investigated was the determination of the maximum concentration of hydrogen ion at which it was possible to secure complete precipitation of the iron. From the results of Mittasch [1], who took 300 mg. of iron in a volume of about 400 cc. with varying amounts of ammonium acetate and acetic acid and determined the weight of the precipitate, the greatest hydrogen ion concentration which gave complete precipitation was calculated to be from 4 to 7 x 10^{-5} molal. From the results of Funk [2], who made a similar series, the value 5 to 9 x 10^{-5} was calculated. These results are rather doubtful because of the uncertainty of the initial hydrogen ion concentration and the composition of the precipitate. Accordingly, in order to more accurately determine this value, a series of experiments was made in which only a small amount of iron was taken and the initial concentrations of acetic acid and acetate were known. For the purposes of these and other experiments the following solutions were used.

Stock solution of ferric nitrate	64.54 mg. / cc.
Test solution of Fe^{+++}	10.0 mg. / cc.
Acetic acid solution	6.00 Normal
Sodium hydroxide	6.00 "
Sodium acetate solution	3.00 "
Standard HCl solution	0.6018 "
Standard base	0.4507 "

The $Fe(NO_3)_3$ stock solution was prepared from Baker's C.P. Ferric Nitrate. It was standardized by precipitating the iron with ammonium hydroxide, igniting, and weighing. The solution containing 10 mg. Fe^{+++} per cc. was prepared from this by diluting to the calculated volume. The sodium acetate solution was prepared from the 6.00 N HAc and NaOH by mixing equal volumes of the two solutions.

The method of making the experiment was to take 10 mg. of iron, add measured quantities of acetic acid and sodium acetate, make up to 100 cc., heat to boiling and continue gentle boiling for a definite length of time. The precipitations were made in 300 cc. Erlenmeyer flasks in the opening of which was placed a flanged test-tube containing cold water which prevented undue evaporation during the boiling. The solution was then filtered while still hot and the amount of precipitate estimated. When precipitation was nearly complete the iron in the filtrate was estimated colorimetrically with KSCN. The results of these experiments are given in Table 1. The concentrations of the acetic acid and acetate are corrected for the amount of iron precipitated. The composition of the precipitate is unknown but statements in the literature and experiments will later indicate that it is approximately one mole of acetate to two mols of iron (see Composition of Precipitate below). Therefore when 10 mg. of iron was precipitated it was assumed that 0.0005 equivalents of acetic acid were set free and the same amount of sodium acetate used up. The ratio HAc / NaAc was based on these corrected concentrations.

TABLE OF EXPERIMENTS.

Volume of solution 100 cc. Normalities and ratio HAC / NaAc calculated

Iron taken 10 mg. after precipitation has taken place.

No. Exp.	6N HAc cc.	3N NaAc cc.	Time of boiling minutes	Normality HAc	Normality NaAc	Ratio HAc / NaAc	Precipitate mg. Fe	Filtrate	Remarks
1	5.0	1.0	1 - 2	0.300	0.030	10.0	trace	colored	
2	5.0	2.0	1 - 2	.300	.060	5.0	small	colored	
3	5.0	5.0	1 - 2	.305	.145	2.1	10	no color	
4	5.0	3.0	1 - 2	.305	.085	3.6	10	no color	
5	5.0	2.5	1 - 2	.302	.073	4.1	3	colored	
6	5.0	2.5	1 - 2	.302	.073	4.1	3	colored	
7	5.0	2.7	1 - 2	.305	.076	4.0	10	no color	
8	5.0	2.6	1	.301	.077	3.9	1	colored	
9	5.0	2.7	1	.301	.080	3.8	2	colored	
10	5.0	3.0	0	.301	.089	3.4	1	colored	

No. Exp.	6N HAc cc.	3N NaAc cc.	Time of boiling minutes	Normality HAc	Normality NaAc	Ratio HAc / NaAc	Precipitate mg. Fe	Filtrate	Remarks
11	5.0	3.0	1	0.305	0.085	3.6	10	light color	0.5 mg. Fe in fil
12	5.0	3.0	2	0.305	.085	3.6	10	no col. 0.04	
13	5.0	3.0	5	.305	.085	3.6	10	no col. .08	
14	5.0	2.5	2	.303	.072	4.2	5	l. col. 0.5	
15	5.0	2.5	5	.305	.070	4.4	10	no col. .02	
16	5.0	2.0	5	.304	.056	5.4	5 - 8	l. col. 0.6	
17	5.0	2.7	3	.305	.076	4.0	10	no col. .03	
18	5.0	2.5	3	.305	.070	4.4	10	no col. .1	
19	10.0	4.8	3	.602	.142	4.2	4	colored	
20	15.0	7.5	3	.900	.225	4.0	0		
21	2.5	1.1	3	.153	.030	5.1		colored	
22	2.5	1.5	3	.155	.040	3.9	10	no col. .04	
23	2.5	1.3	3	.154	.035	4.4		colored	
24	10.0	7.0	3	.603	.207	2.9	5 - 8	colored	

No. Exp.	6N HAc cc.	3N NaAc cc.	Time of boiling minutes	Normality HAc	Normality NaAc	Ratio HAc / NaAc	Precipitate mg. Fe	Filtrate	Remarks
25	10.0	10.0	3	0.604	0.296	2.0	9	l. col. 1 mg.	
26	12.5	12.5	3	.3	.07	4.	300	no col. .3	300 mg. Fe Volume 300 cc.
27	5.0	2.5	3	.305	.070	4.4	10	1st. part l. last no col.	5 g. NaCl added
28	5.0	2.6	3	.305	.073	4.2	10	no col. .03	5 g. NaCl added
29	7.5	3.7	3	.455	.106	4.30	10	1st part l. col.	last part of filtrate no col.
30	8.5	4.2	3	.515	.121	4.25	9 - 10	l. col. .5	
31	9.0	4.34	3	.545	.125	4.35	10	1st part l. col.	last part colorless
32	9.5	4.60	3	.571	.137	4.16	2	colored	
33	11.0	5.26	3	.660	.158	4.18	0.5	colored	
34	12.0	5.55	3	.720	.166	4.33	0.1	colored	
35	10.0	4.80	3	.602	.142	4.25	5	colored	
36	10.5	4.86	3	.630	.146	4.31	1	colored	
37	9.5	4.50	3	.572	.133	4.36	5	colored	
38	9.0	4.34	3	.545	.125	4.36	10	no col. .3	

No. Exp.	6N HAc cc.	5N NaAc cc.	Time of boiling minutes	Normality HAc	Normality NaAc	Ratio HAc / NaAc	Precipitate mg. Fe	Filtrate	Remarks
39	5.00	2.20	3	0.305	0.061	5.00	10	no col. .2	
40	7.5	3.20	3	.454	.092	4.94	8	colored	
41	8.5	3.60	3	.512	.106	4.84	5	"	
42	10.0	4.00	3	.602	.118	5.10	3 - 4	"	
43	12.0	4.84	3	.720	.145	4.97	.5 _ 1	"	
44	15.0	6.00	3	.900	.180	5.00	4	"	?
45	15.0	6.00	3	.900	.180	5.00	0.1	"	
46	10.0	5.94	3	.605	.173	3.50	10	l. col. .5	
47	15.0	8.67	3	.900	.260	3.46	0	colored	
48	12.0	6.90	3	.720	.207	3.48	1	"	
49	5.0	2.00	0	.301	.059	5.1	1 - 2	"	
50	5.0	2.00	5	.305	.055	5.5	10	l. col.	hard to filter
51	5.0	2.00	10	.305	.055	5.5	10	no col. .04	ppt. coagulated
52	5.0	2.00	3	.303	.057	5.3	5 - 7	colored	

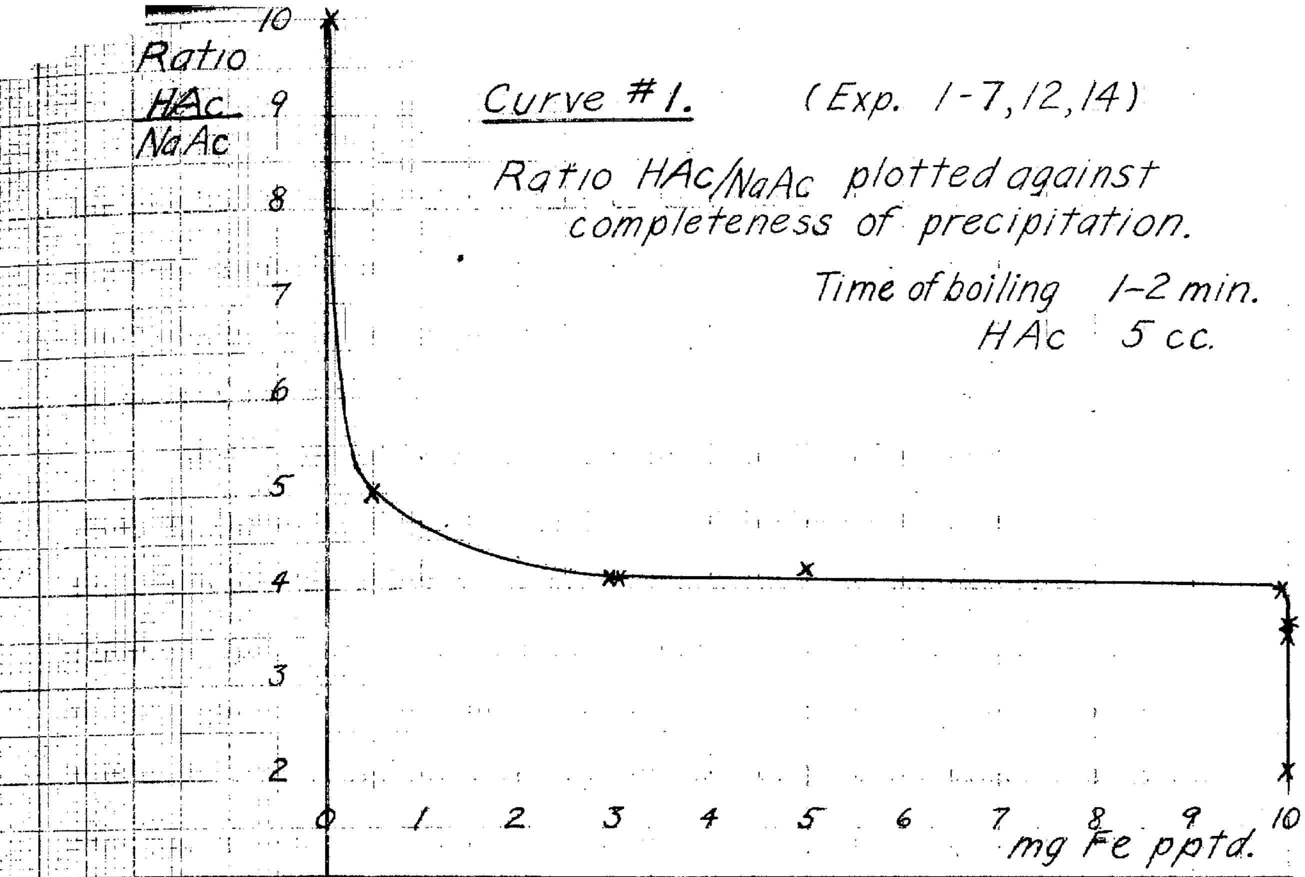
No. Exp.	6N HAc cc.	3N NaAc cc.	Time of boiling minutes	Normality HAc	Normality NaAc	Ratio HAc / NaAc	Precipitate mg. Fe	Filtrate	Remarks
53	3.3	5.30	0				200	l. color	200 mg. taken
54	3.3	5.30	3				200	no color	" " "
55	3.3	5.30	10				200	no color	" " "
56	0	5.0	1				200	no color	" " "
57	15.0	15.0	3	.901	.449	2.00	1.5 - 2	colored	
58	12.0	12.0	3	.721	.359	2.01	3	"	
59	20.0	20.0	3	1.200	.600	2.00	0	"	
60	1	6.0	1				200	no color	200 mg. taken

DISCUSSION OF RESULTS.

In Curve 1 are shown diagramatically the results of Exp. 1 - 7, and 12, 14, for which the time of boiling is one to two minutes and the amount of 6N HAc taken is 5.0 cc. The ratio HAc / NaAc is plotted against the mg. of iron precipitated. It is seen from the curve that precipitation is complete with a ratio of 4 or less. The sharpness of the break seems rather remarkable in view of the influence of the time of boiling on the completeness of the precipitation. Thus in Exp. 15 and 18 with three and five minutes heating the precipitation is complete even with a ratio of 4.4. The results discussed below also make this curve less significant from mass-action effects. However, such a break would be sharp if these effects were the deciding factor since the amount of iron is small.

LENGTH OF BOILING.

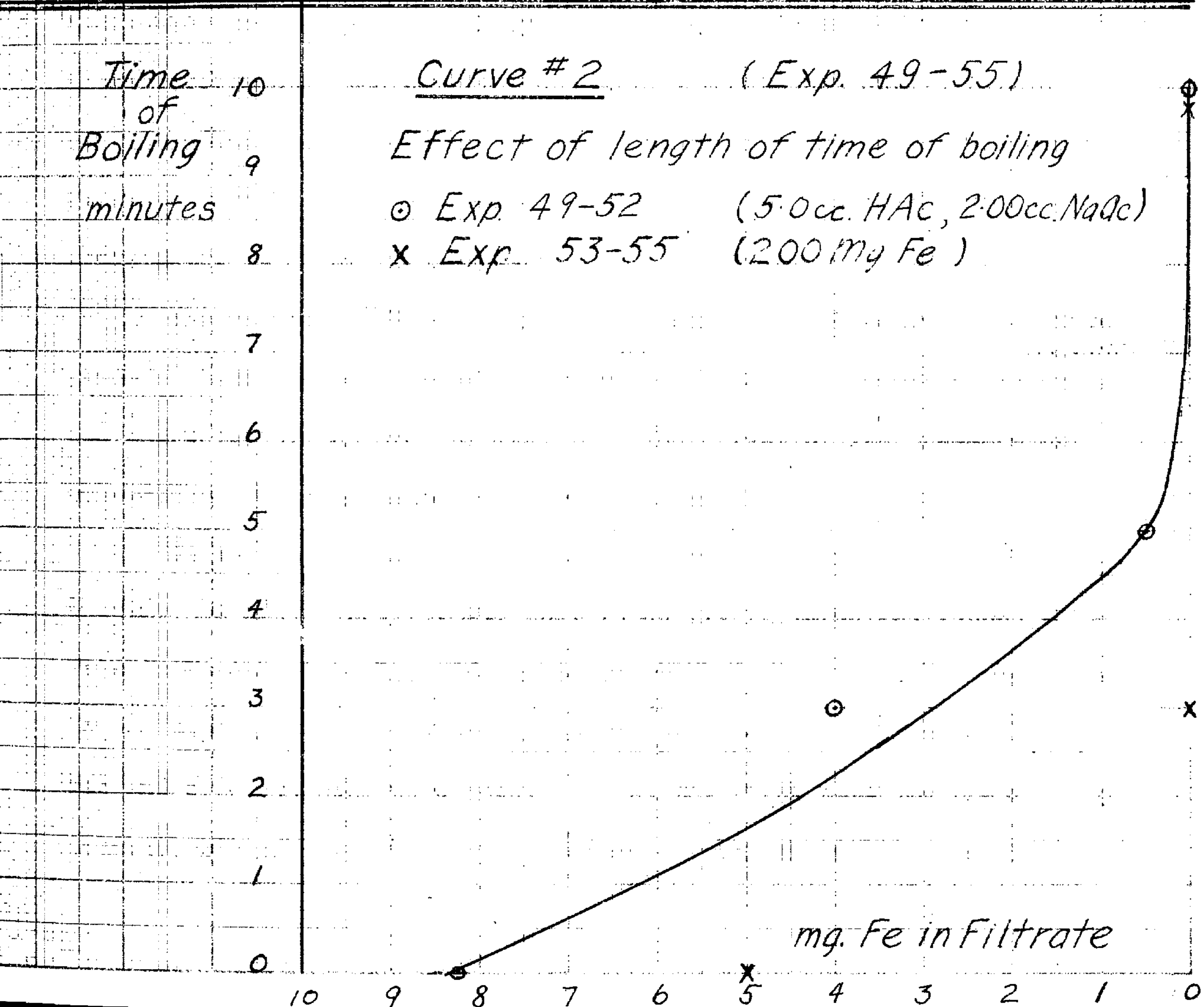
The length of boiling is an important factor in the precipitation of the iron. In the literature emphasis is placed on the necessity of only a short period of boiling in order to avoid slimy precipitates that are difficult to filter. Most directions call for a period of heating of from one to two minutes. In the experiments with only a small amount of iron present the length of boiling was found to have practically no effect on the character of the precipitate. Most of the precipitates obtained were somewhat difficult to filter but no better results were obtained even with very short boiling. In the first eighteen experiments 5 cc. 6N HAc were used, the NaAc (3 N) varied from 2.5 to 3.0 cc, and the time of boiling from one to five minutes.



Curve #1. (Exp. 1-7, 12, 14)

Ratio HAc/NaAc plotted against completeness of precipitation.

Time of boiling 1–2 min.
HAc 5 cc.



Curve #2 (Exp. 49-55)

Effect of length of time of boiling

⊙ Exp 49–52 (5·0 cc. HAc, 2·00 cc NaAc)
x Exp. 53–55 (2·00 mg Fe)

The results indicated that a time of three minutes was preferable for complete precipitation but that longer heating was unnecessary. Accordingly, boiling for three minutes was adopted for most of the subsequent work.

The effect of boiling on the completeness of precipitation is shown in Curve 2 (Exp. 40 - 55). Solutions containing 10 mg. of iron, 5.0 cc. HAc and 2.0 cc. NaAc were boiled for various times. There is almost no precipitation on heating just to boiling, but five minutes gives very fair precipitation, while ten minutes gives complete reaction. A similar tendency is shown with larger amounts of iron. Exp. 53, 54, and 55 with 200 mg. iron gave very slimy precipitates, but the longer boiling gave slightly more easily filtered solutions. In these experiments, the effects just mentioned are not due to boiling out the acetic acid from the solution, since in every case a test-tube filled with cold water was placed in the mouth of the flask and acted efficiently as a reflux condenser.

The results of Exp. 27 and 28 indicate that the addition of five grams of NaCl has no noticeable effect either on the completeness of precipitation or on the character of the precipitate. The effect of the presence of ~~the presence of~~ other substances was not determined.

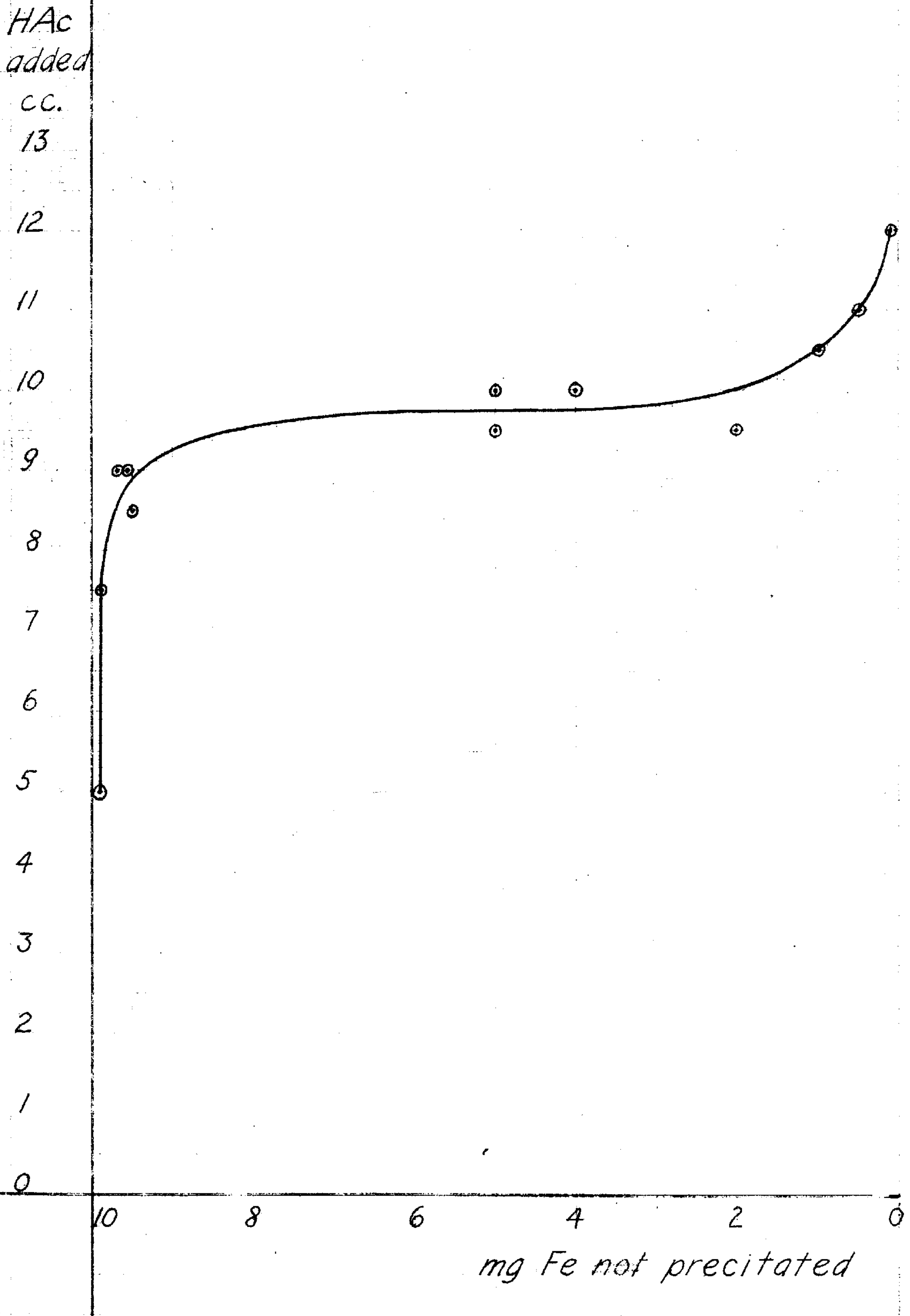
It is stated that the initial concentration of acid must be small in order to give a precipitate that is easily filtered and washed. This is borne out by Exp. 56 and 60 in which 200 mg. of iron were taken. In one experiment 5 cc. NaAc but no HAc was added, in the other 1 cc. HAc and 6.00 cc. NaAc were used. In the first case the precipitate obtained was very similar to that obtained with the use of ammonia and was easy to filter. The other, however, was somewhat more slimy and more difficult to handle.

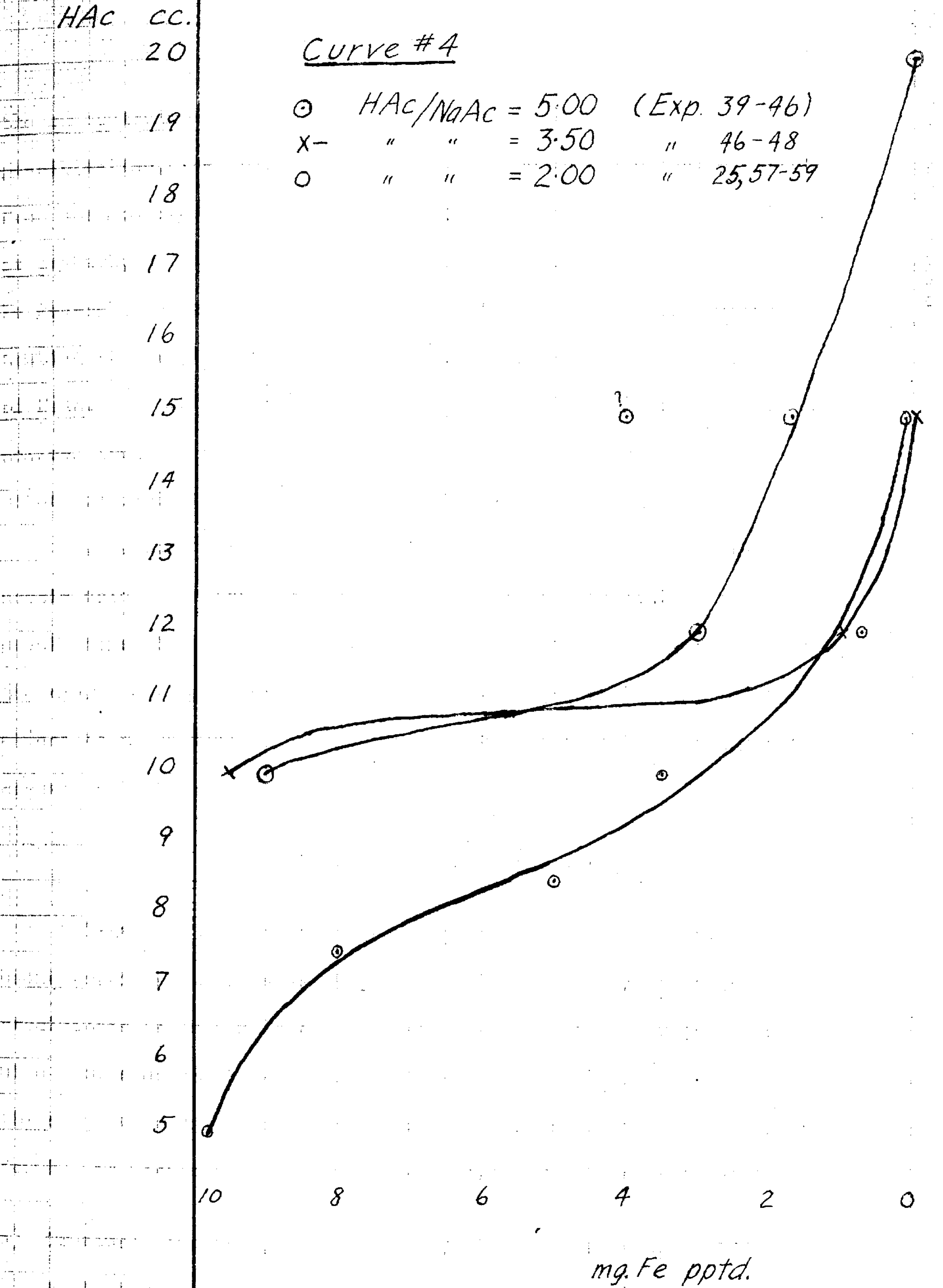
EFFECT OF CONCENTRATION OF ACETIC ACID.

The experiments to determine the effect of the total acetic acid present yielded results that appear rather surprising. The nature of the phenomena is illustrated in Curves 3 and 4. The manner of carrying out the experiments was the same as before except that in each series the ratio HAC / NaAc was kept constant, only the total concentrations of these reagents being varied. Thus for Exp. 18, 19, 29 - 38 the ratio HAc / NaAc was maintained at 4.35 but the HAc was varied from 5 to 12 cc. added initially. The amounts of acid and acetate used were calculated for a given ratio on the assumption that the precipitation would be complete. If the precipitation was not complete, the ratio would be less than calculated, but this only makes the results more certain. It is seen in Curve 3 that precipitation is complete when 7.5 cc. of acid are taken but with 11 cc. there is almost no precipitation. In Curve 4 are illustrated the same phenomena for ratios of 5.00, 3.50, and 2.00. The nature of the results is, however, best seen in Curve 3, in which the number of experiments is greater. Presumably, with the same ratio of acid to acetate, the hydrogen ion concentration is constant unless the activities of these two substances vary differently with concentration. For any usual mass-action expression for the formation of basic ferric acetate the concentration of the acetate ion is raised to a higher power than the acid. Accordingly, it would be expected that increasing

Curve # 3 (Exp. 18,19, 29-38)

Ratio $HAc/NaAc = 4 \cdot 35$




HAc cc.
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
Curve #4
⊙ HAc/NaAc = 5·00 (Exp. 39-46)
x– " " = 3·50 " 46-48
○ " " = 2·00 " 25, 57-59
?
10
8
6
4
2
0
mg. Fe pptd.

the concentration of both the HAc and NaAc would give more certain precipitation, that is, the lines would slope in the opposite direction from the observed. The crossing of the lines in Curves 3 and 4 is probably due to the inexact qualitative nature of the experiments. In general, however, the curves show that for any particular concentration of acid the precipitation is more complete for greater amounts of NaAc. In experiments with large quantities of acid it was noticed that the deep red color characteristic of the solution just before precipitation took place was absent.

J. Jewett[4] has reported this effect of large quantities of acetic acid. "He further ascertained that iron could not be precipitated in presence of a large amount of acetic acid by increasing the amount of sodium acetate." Possibly the explanation of the effect is to be found in the chemistry of colloidal iron produced from acetate solutions.

COMPOSITION OF THE PRECIPITATE.

Textbooks of quantitative analysis[a] give the composition of basic ferric acetate as $Fe(OH)_2Ac$. It is unlikely that the precipitate is as simple as this and possibly varies through rather wide limits under different conditions. Weinland[5] has studied the salts of ferric acetate complexes and has shown that solutions of $Fe(OH)_3$ in acetic acid contains the acetate of a hexa-acetatetriferric

[a] Treadwell and Hall, Quantitative Analysis, 5th. ed., p. 152.
A. A. Noyes, Qualitative Analysis, 8th. ed., p. 105.

~~acid contain the acetate of a hexa-acetatetriferric~~ base. The cation $Fe_3(C_2H_3O_2)_6^{+++}$ is the basis of the $FeCl_3$ reaction for acetic acid.

$$3\,FeCl_3 + 9\,NaAc + 2\,H_2O \rightarrow 9\,NaCl + Fe_3(C_2H_3O_2)_6(C_2H_3O_2)(OH)_2 + 2\,HAc$$

Wienland made two series of experiments on the composition of the ordinary basic acetate precipitate; (1) varying the volume of the solution, (2) varying the amount of sodium acetete. The results obtained lie close to the value of one mol of acetate to three mols of iron. With 300 - 1500 cc. volume he found Fe / Ac as 3 / 0.88, while with 100 cc. the proportion was 3 / 1.04. With 2 g. NaAc the proportion was 3/ 0.88, with 3 g. 3 / 1.14, and 9 g. 3 / 1.17. He assigns the composition of the dried precipitate as $Fe_3(C_2H_3O_2)(OH)_2O_3$. O.F. Tower [7] determined the composition of basic ferric formate and obtained also this formula.

It was desired to determine the composition of the precipitate under somewhat more varying conditions. By taking definite volumes of the standard iron solution it would only remain to determine the acetate in the precipitate. It was thought that distillation with phosphoric acid and titration of the distillate would accomplish this easily and accurately but it was found that the pronounced tendency of the mixture to bump made the method impractical. A combination of straight and steam distillation from a sulphuric acid solution was next tried and blank experiments showed that the method would be satisfactory.

However, only two preliminary determinations were made. Five cc. of Fe solution and 8 cc. NaAc were made up to 200 cc., heated to boiling, and boiled for three minutes. The precipitate was filtered with the aid of suction and washed with hot water until the washings no longer discolored a drop of NaOH in phenolphthalein solution. The filter and precipitate were transfered to a beaker and 50 cc. of standard KOH added, together with 100 cc. of water. This mixture was boiled for ten minutes, allowed to cool, and then titrated with HCl. After 20 cc. of acid had been added to the mixture, it was filtered and washed, and the titration completed. Volume acid, 32.30 cc. This gives Fe / Ac as 3 / 1.61.

In the second determination the amounts of material taken and the procedure were the same except that it was also attempted to determine the acid in the filtrate. The first 100 cc. of filtrate was titrated with standard base;(17.77 cc. base, 0.04 cc. acid). This gives ratio of 3 / 1.09. However, the loss of solution by evaporation during the filtration renders this result worthless. The precipitate was washed, boiled for a half hour with 25.00 cc KOH, diluted to 100 cc., filtered through a dry filter, and 50 cc. of the filtrate titrated with HCl solution. Standard Acid, 6.83 cc. Fe / Ac = 3 / 1.59.

The investigation was discontinued at this point.

SUMMARY AND CONCLUSIONS.

A number of basic acetate precipitations have been made taking 10 mg. of iron and determining the effect of varying the amounts of sodium acetate and acetic acid and the length of boiling on the character of the precipitate and the completeness of precipitation. The results have been illustrated by several diagrams. These experiments indicate that:

1. The length of boiling has only a slight effect on the character of the precipitate.
2. Increasing the length of boiling increases the completeness of the precipitation.
3. Increasing the amount of sodium acetate increases the completeness of precipitation.
4. The reaction cannot follow any simple mass-action expression.

Curves 3 and 4 illustrate a phenomena which has not yet been explained.

Two determinations give the composition of the precipitate as Fe / Ac = 3 / 1.60. The precipitate may therefore consist of approximately equal amounts of $Fe(OH)_3$ and $Fe(OH)_2Ac$.

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PART B. ANALYSIS OF THE IRON GROUP.

In connection with the work on the precipitation of iron as a basic acetate some experiments were made on a proposed modification of the analysis of the iron group. In the present method for the detection of manganese by potassium chlorate in concentrated nitric acid solution (Procedure 61. A. A. Noyes, Qualitative Analysis) small quantities of manganese are sometimes missed; possibly due to the reduction of the $KClO_3$ by the filter paper pulp present in the solution. Also, the separation of nickel and cobalt from iron with ammonia is unsatisfactory because of the large fractions carried down by much ferric hydroxide. It was thought that the following scheme would offset these difficulties to some extent, and in general be more simple.

ANALYSIS OF THE IRON GROUP.

<table>
<tr><td colspan="3">Precipitate: $Fe(OH)_3$, MnO_2, $Ni(OH)_2$, $Co(OH)_3$, (Zn, alkaline-earths).
Treat with HCl, add NaAc and heat.</td></tr>
<tr><td rowspan="2">Precipitate
$Fe(OH)_2Ac$.</td><td colspan="2">Solution: Mn^{++}, Ni^{++}, Co^{++}, (Zn, alkaline-earths).
Add Br_2 and heat.</td></tr>
<tr><td>Precipitate
MnO_2</td><td>Solution: Ni^{++}, Co^{++}, (Zn^{++}, alk.-earths).
Follow usual procedure.</td></tr>
</table>

If phosphate was present the procedure would be the same except that a separate small portion would be tested for iron and also iron added to the main portion with the sodium acetate unless a red precipitate had already formed.

The first point investigated was the conditions under which manganese would be precipitated by bromine in acetic acid, sodium acetate solutions. Calculation showed that with about 500 mg. Fe and using 15 cc. 3N NaAc, with volume 100 - 150 cc., the concentrations of HAc and NaAc after precipitation of the iron would correspond to 5 cc. 6N HAc and 7 cc. 3N NaAc in 100 cc. Experiments were made using these and other concentrations with various amounts of manganese and bromine and determining the effect of heating. The following procedure was found to give complete precipitation of the manganese. Add 1cc. liquid bromine to the solution, shake for about a minute, heat on the water bath for 5 minutes, boil until bromine fumes are no longer noticeable, and then boil five minutes longer. (Dark brown or black precipitate; presence of manganese.) Filter. If the precipitate is more than 100 mg. add 1.3 cc. 6N NaOH to the filtrate and 0.2 cc. bromine and boil for five minutes.

This is a very sensitive test for manganese and 0.1 mg. can be detected because of the dark color of the precipitate. Although most of the manganese is easily precipitated, the last few traces are difficult to get down, but the above procedure gives satisfactory results. The precipitate is quite compact and the hot solution is easy to filter. A couple of trial analyses were made with 500 mg. Fe and 1 mg. Mn and both gave a very distinct test for manganese by this method.

So far this method would seem to be very satisfactory, but the behaviour of cobalt and nickel with bromine renders the method worthless. Five hundred milligrams of cobalt was taken with 15 cc. NaAc and 1 cc. HAc and treated with bromine according to the above procedure. During the heating a black slimy precipitate formed,(about 400 mg.).

The filtrate was pink colored. It was neutralized with sodium hydroxide, 1 cc. HAc added and then 1 cc. bromine, and the mixture heated. A black precipitate formed, (150 mg.). The filtrate was colorless.

Five hundred milligrams of nickel with 15 cc. NaAc, 1 cc. HAc, and 1 cc. bromine in 100 cc. solution was heated for five minutes and then boiled to expel the bromine. About fifty milligrams of a dark colored precipitate formed. The filtrate was green.

While these results render this proposed method for the iron group useless, possibly conditions could be worked out for the separation of cobalt from nickel by means of bromine in acetate solutions which would serve better than the present tests with dimethylgloxime and potassium nitrite. With respect to the oxidation of cobalt, Lundell (J. Am. Chem. Soc. 45, 2600,(1923) shows that cobalt interferes with the bismuthate method for manganese because it is oxidized.