



Investigation on the rotatory power of ferritartaric acid and its application to the quantitative determination of the fluoride ion
by Hans H Denk

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
© Copyright by Hans H Denk (1951)

Abstract:

The wider scheme of this investigation was the determination of various influences on the optical rotation of active substances, and in addition, the possible analytical application of the change in rotatory power.

Specifically, mixtures of tartaric acid and ferric nitrate were used. The resulting complexes of varying composition are called ferritartaric acid or ferritartrates; their optical rotations were determined. Influences investigated were those of the concentration, the temperature, the pH, the change in the ratio $[C_4H_6O_6]: [Fe]$, salts not interacting with the fer-ritartrate complex, and salts interacting with the ferritartrate. The data were used to establish the formula for ferri-tartaric acid as $H_3[Fe(C_4H_4O_6)_3]$.

In the analytical part various mixtures were employed again to find the best conditions for the quantitative determination of the fluoride ion, based on the decrease of rotation exhibited by ferritartaric acid upon addition of, or in the presence of fluorides. Furthermore, by comparing its specific rotation in the absence of fluoride ions and that of ferritartaric acid in the presence of fluorides with that of tartaric acid alone, the stability of the complex was investigated over the pH range 0 to 11.5.

144
INVESTIGATION ON THE ROTATORY POWER OF
FERRITARTARIC ACID AND ITS APPLICATION
TO THE QUANTITATIVE DETERMINATION OF THE
FLUORIDE ION

by

HANS H. DENK

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

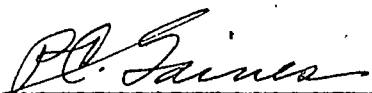
for the degree of

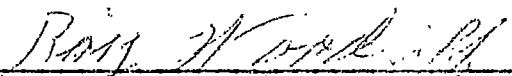
Master of Science in Chemistry

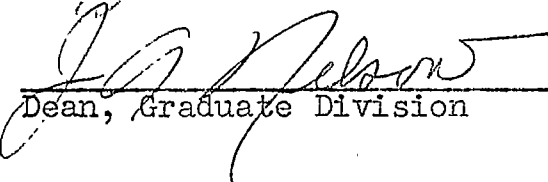
at

Montana State College

Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

Bozeman, Montana
June, 1951

N378
DA7i
cap. 3

1098*

TABLE OF CONTENTS

SECTION	PAGE
I. ABSTRACT.....	3
II. INTRODUCTION AND LITERATURE SURVEY.....	4
III. GENERAL PRINCIPLES.....	6
IV. FERRITARTARIC ACID AND ITS ROTATORY POWER.....	8
a) Chemicals and Apparatus used.....	8
b) Influence of various Ratios $C_4H_6O_6 : Fe$	9
c) Influence of Concentration.....	13
d) Influence of Temperature.....	15
e) Influence of the pH.....	17
f) Influence of other Salts.....	21
g) Composition and Stability of Complex.....	24
h) Analytical Behavior.....	27
V. DETERMINATION OF FLUORIDES.....	28
a) Influence of Fluoride on Tartaric Acid.....	28
b) Influence of Fluorides on Ferritartaric Acid.....	30
c) Outline of Procedure.....	33
VI. SUMMARY.....	34
VII. LITERATURE CITED.....	35
VIII. ACKNOWLEDGMENT.....	37

Handwritten notes on the left margin, including "Concentration" and "1098" written vertically.

I. ABSTRACT.

The wider scheme of this investigation was the determination of various influences on the optical rotation of active substances, and in addition, the possible analytical application of the change in rotatory power.

Specifically, mixtures of tartaric acid and ferric nitrate were used. The resulting complexes of varying composition are called ferritartaric acid or ferritartrates; their optical rotations were determined. Influences investigated were those of the concentration, the temperature, the pH, the change in the ratio $[C_4H_6O_6]:[Fe]$, salts not interacting with the ferritartrate complex, and salts interacting with the ferritartrate. The data were used to establish the formula for ferritartaric acid as $H_3[Fe(C_4H_4O_6)_3]$.

In the analytical part various mixtures were employed again to find the best conditions for the quantitative determination of the fluoride ion, based on the decrease of rotation exhibited by ferritartaric acid upon addition of, or in the presence of fluorides. Furthermore, by comparing its specific rotation in the absence of fluoride ions and that of ferritartaric acid in the presence of fluorides with that of tartaric acid alone, the stability of the complex was investigated over the pH range 0 to 11.5 .

II. INTRODUCTION AND LITERATURE SURVEY.

Ever since Biot (1,2,3,4,5) in 1837 discovered the influence of boric acid on the optical rotation of tartaric acid it has been known that various inactive substances bring about a positive or negative change in the rotatory power of optically active compounds. The reason for this is either complex formation, or chelate ring formation (9) or, in general, molecular addition in some other manner. A great many papers have been published on the subject, but all these observations were put to use only in a number of isolated cases for practical analytical purposes (15). As to ferritartrate complexes, first reference was made by Rosenheim and Vogelsang (24) and Paria (19) who gave the formula $H[FeC_4H_2O_6]$ and called this compound "Tartrato-ferrisäure". The nature and composition of the ferric salt-tartaric acid complexes is not exactly known, because most papers contain contradictory results or interpretations. Publications on this matter include those by Pickering (22,23), Jellinek and Gordon (13), Wark and Wark (29), Morton (17,18), Pariselle and Delsal (20), Franke (11), Treadwell and Wettstein (28), Delsal (8), Toropova (27), Bobtelsky and Jordan (6), Pavlinova (21), Sidgwick (25). The first two authors postulate a complex having two iron atoms to three tartrate radicals; Treadwell and Wettstein declare on the basis of electrometric titrations that two acid molecules are tied up with one atom

of iron, Pariselle and Delsal, as well as Franke found 1 Fe per molecule of tartaric acid. Bobtelsky and Jordan based their conclusions on polarographic, potentiometric, photometric, and conductometric results, giving the complex a composition of 3 Fe to 2 $C_4H_6O_6$. Pavlinova gives a still more complicated and higher molecular structure, while Sidgwick maintains that with dibasic organic acids ferric ion does not form polynuclear complexes, i. e. complexes with more than one atom of iron in them. One thing seems certain however, that there are several complexes, depending in their composition and stability mostly on the pH, not the relative amounts of ferric ion and tartrate in solution as Bobtelsky and Jordan would have it. The coordination number of the ferric ion seems to be six in these complexes. It is doubtful, if in a strongly acid medium one tartaric acid radical can supply more than two coordinative groups; in a basic solution coordination with the hydroxyl groups becomes more likely.

III. GENERAL PRINCIPLES.

Starting with the assumption that an active substance A forms an addition compound with an ion M, giving rise to a new substance MA which has a different optical rotation, we may subject this latter substance then to a second influence exerted by an inactive ion X, capable itself of complexformation involving M. The resulting decrease or increase of rotation, whatever the case may be, is a measure of the amount of X present. The principle is schematically pictured in Fig. 1:

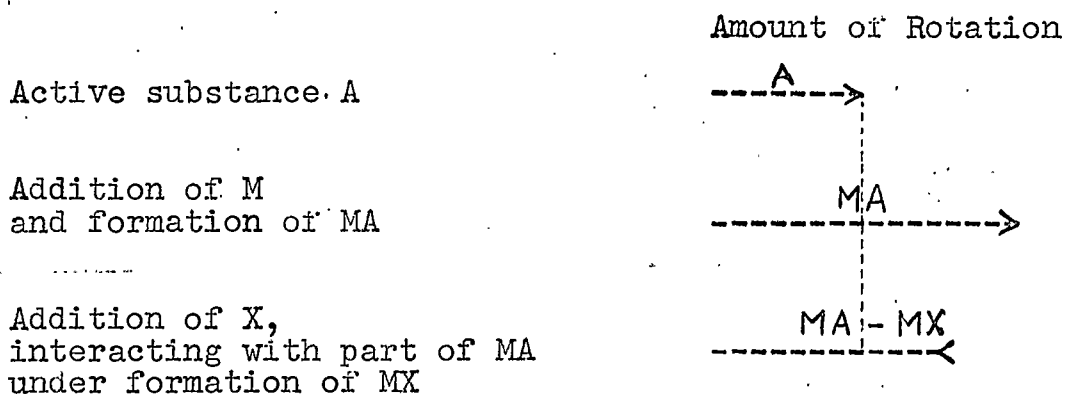


Figure 1
Principle of Method.

After a considerable number of trials the ferric ion-tartaric acid complex was chosen as most suitable for the determination of fluorides which was the predetermined aim of this investigation. Generally speaking, the above principles could be extended also to precipitation reactions, however, MX would

need to be filtered off before the rotation of the solution is measured the second time. We see that the use of secondary influences on optically active addition compounds for analytical procedures should not be restricted to a few exceptional cases. In the course of this investigation it has been observed that certain polyvalent ions like iron, aluminum, zirconium (10), and titanium (30) have a rather general tendency to add onto active substances like tartaric acid, glucose, mannitol or, in general, organic hydroxyacids and sugars, as indicated by changes in optical rotation.

IV. FERRITARTARIC ACID AND ITS ROTATORY POWER.

a) Chemicals and Apparatus used.

The solutions were made up from Mallinckrodt d-Tartaric Acid, USP XIII; Mallinckrodt $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, no purity given; Baker & Adamson NaF, purity to ACS specifications. The amounts needed for 500 ml. of the desired strengths (4M, 1M, 0.85M, respectively) were weighed out to the nearest 0.1 gram.

The polarimeter used was a simple halfshadow model by Steindorff & Co. with a 360 degree scale. Its reading accuracy was 0.1° ; estimation was possible to 0.05° . The readings given are the average of three consecutive readings, taken with 2 dm-tubes having a volume of 30 cc. The temperature of the solutions was, if not otherwise stated, 24°C . in all cases.

As lightsource served a sodium vapor lamp, a SLA-5c model by G. W. Gates Co. All readings refer to the sodium D line, ($\lambda = 589 \times 10^{-7}$ cm). For the pH measurements a service model Beckmann pH meter was used. Calibration of the instrument was carried out before every measurement with a standard buffer solution.

The specific rotation is given according to
$$[\alpha] = \frac{\alpha \times 100}{l \times g}$$
 where α is the rotation observed, l the length in dm of the tube used, g the amount of substance in grams dissolved in 100 cc. of solvent.

b) Influence of various Ratios $[C_4H_6O_6] / [Fe]$.

Support for the formula $H_3[Fe(C_4H_4O_6)_3]$ is given by investigating at what ratio of $[C_4H_6O_6] : [Fe]$ the actual rotation, α , exhibits a maximum. Fig. 2 shows that this is near the point where R is equal to 3. The procedure used in plotting the graph is that described by Darmois (7) and Job (14) and called the "method of continuous variations". For this method one plots, as for any other two-component system, increasing amounts of substance A and B from the left and right side of the abscissa, respectively. The results obtained do not agree with the formula of Pariselle and Delsal (20) who employed the same method.

Table I
Influence of various Ratios $[C_4H_6O_6] : [Fe]$ on Rotation

4 M Tartaric Acid	1 M Ferric Nitrate	Ratio R	Rotation
4.0 cc.	16.0 cc.	1.0	9.0
6.0	14.0	1.71	10.5
8.0	12.0	2.66	11.0
8.6	11.4	3.02	11.2
10.0	10.0	4.0	11.1
12.0	8.0	6.0	10.7
14.0	6.0	9.33	10.3

The volume was made up to 30 cc. in each case. The rotation of 30 cc. 4 M tartaric acid was 10.7 .

In Fig. 3 we have again different ratios of tartaric acid/ferric ion, but this time the amount of tartaric acid is the same in all mixtures; this provides a chance of finding the degree to which the complex is formed or dissociated, since we can

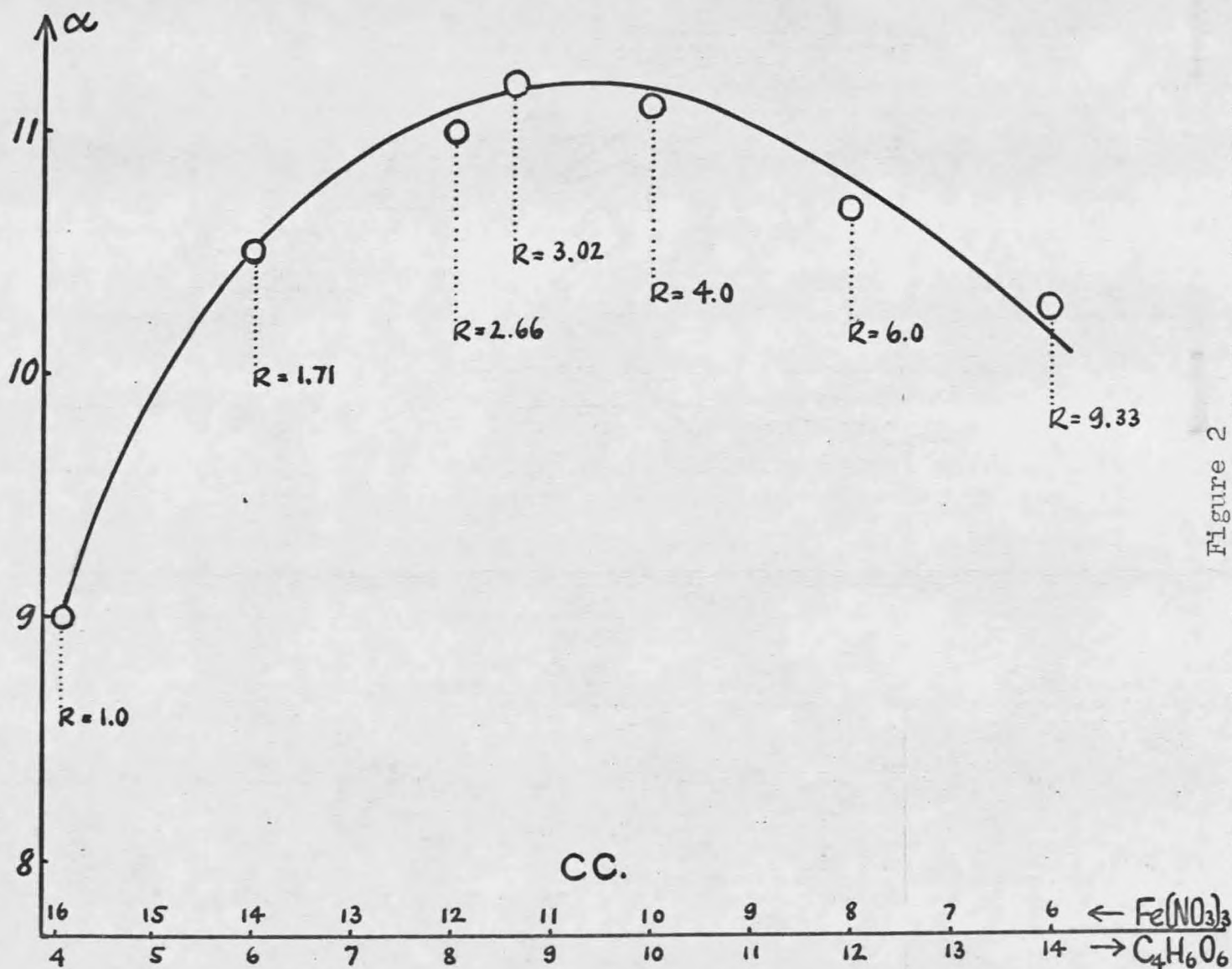
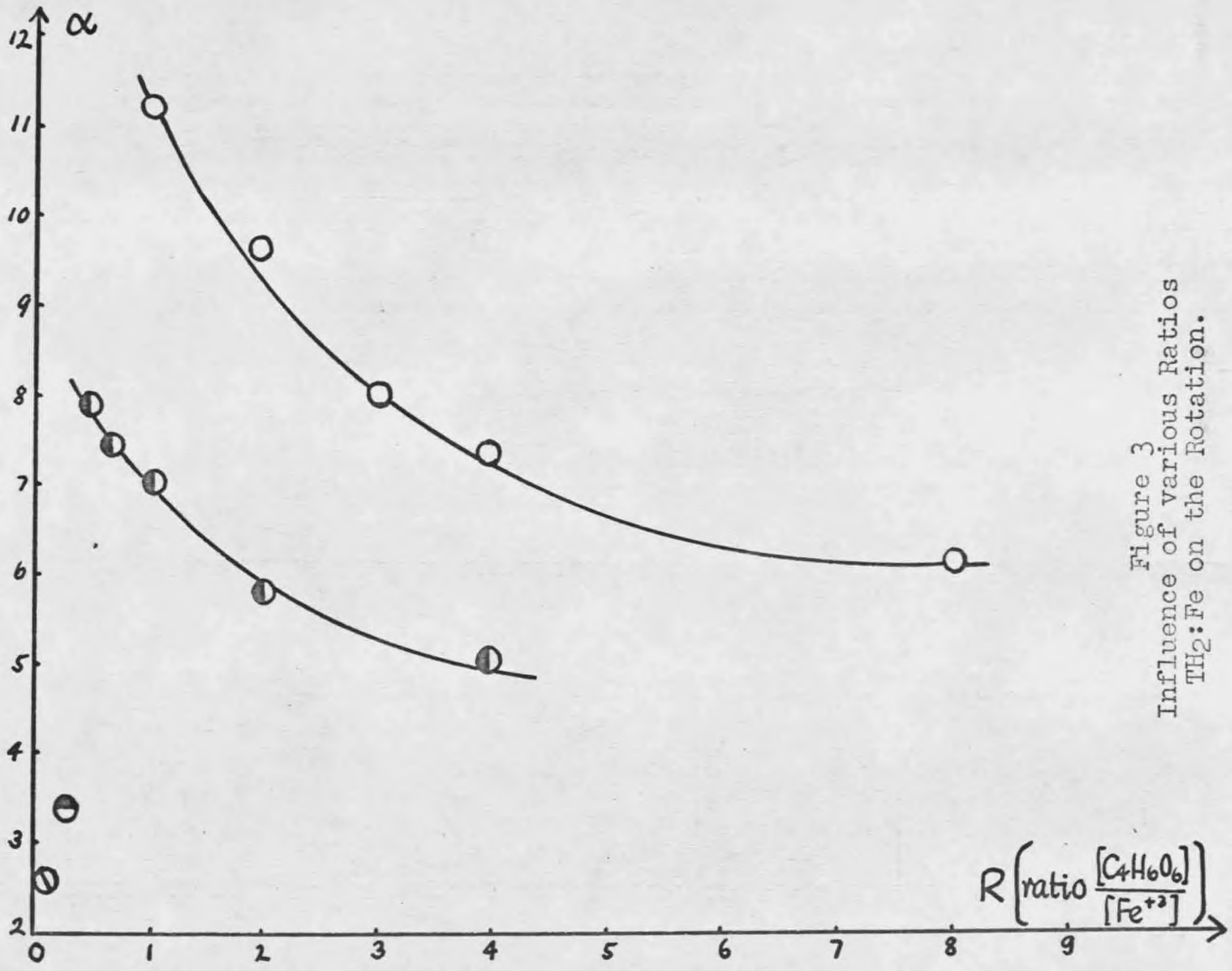


Figure 2
Influence of various Ratios TH₂:Fe on the Rotation

measure the limiting values of rotation: the minimum by using 5 cc. of $C_4H_6O_6$ without any addition of iron, the maximum by extrapolating the curve of measured values until it meets the y-axis. Table II gives in addition some measurements for solutions of lower concentrations, since the transmittance of the solution containing 5 cc. of $C_4H_6O_6$ becomes greatly impaired for $R < 1$.

Table II
Influence of various Ratios $[C_4H_6O_6] : [Fe]$ on Rotation.

4 M $C_4H_6O_6$	1 M $Fe(NO_3)_3$	Rotation	Ratio R
5 cc.	0 cc.	2.5	
	2	5.4	10
	2.5	6.1	8
	4	7.4	5
	5	8.0	4
	10	9.7	2
	20	11.2	1
	very great amount	(≈ 13.0)	$\rightarrow 0$
2 cc.	2	4.1	4
	4	5.6	2
	8	7.0	1
	12	7.5	0.67
	16	7.9	0.5
0.5	16	4.4	0.125
0.2	16	2.6	0.05



c) Influence of Concentration.

The decrease of rotation observed with a decrease of concentration of ferritartaric acid is not linear; in other words dilute solutions show an increase of the specific rotation compared with solutions of higher concentrations. This fact is in general agreement with the behavior of pure tartaric acid solutions. Table III shows the specific and actual rotation of ferritartaric acid at various concentrations. Fig. 4 shows only one particular initial concentration, since the behavior of solutions of different strength can easily be predicted from it: All three curves must meet at infinite dilution.

Table III
Influence of Concentration.

4M $C_4H_6O_6$	1M $Fe(NO_3)_3$	H_2O	Actual Rotation	Specific Rotation	Total Volume
5 cc.	10 cc.	15 cc.	9.8	46.0	30 cc.
		45	6.3	63.0	60
		75	4.9	73.5	90
		105	4.1	88.0	120
		165	3.0	90.2	180
		225	2.6	104.0	240

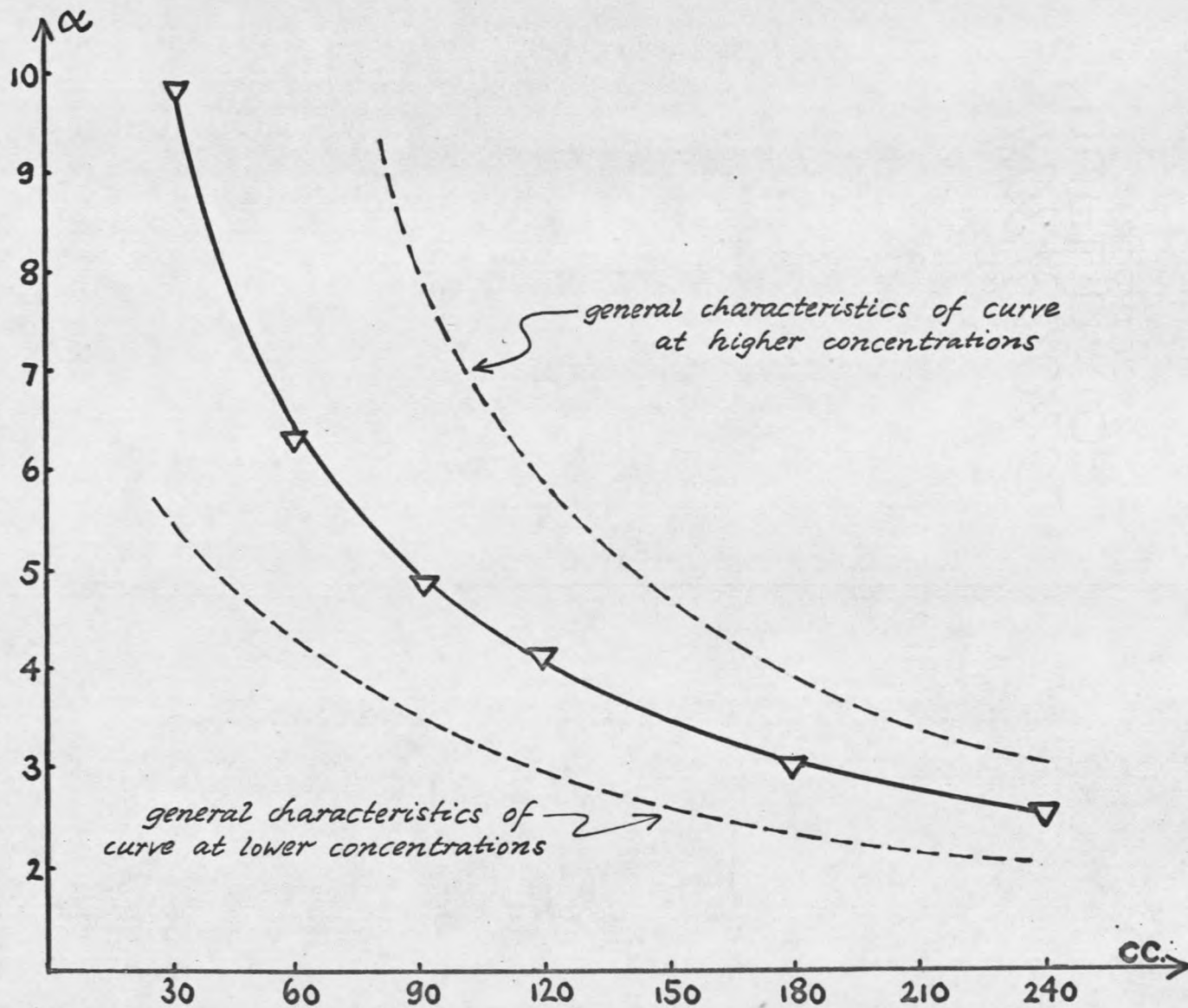


Figure 4
Change of Rotation
with Concentration

d) Influence of Temperature.

Ferritartaric acid as well as tartaric acid (15) shows an increase of rotation with an increase in temperature. The reason for this is most often explained, at least where charged complexes are involved, with the increase of dissociation brought about with increased temperature. Assuming the conclusions of this paper are valid, the complex to be considered here is $H_3 [Fe(C_4H_4O_6)_3]$. It is apparent that the change in rotation for a certain increase in temperature should be the greater, the higher the concentration of the solution. This is borne out by the experimental data given in Table IV and Figure 5.

Table IV
Dependence of Rotation on Temperature.

4 M $C_4H_6O_6$	1 M $Fe(NO_3)_3$	t°C.	Rotation
2 cc.	12 cc.	25	7.5
		15	7.3
		4	7.0
5 cc.	10 cc.	23	9.8
		21	9.6
		16	9.2
		5	8.4

The concentrations of ferritartaric acid in these two solutions are as 2.33 and 6.66 to each other. The slopes of the two curves given in Fig. 5 are:

$$\frac{\Delta \alpha}{\Delta t} = 0.025 \text{ and } 0.077 \quad \left[\frac{\text{degrees of rotation}}{\text{degree C.}} \right]$$

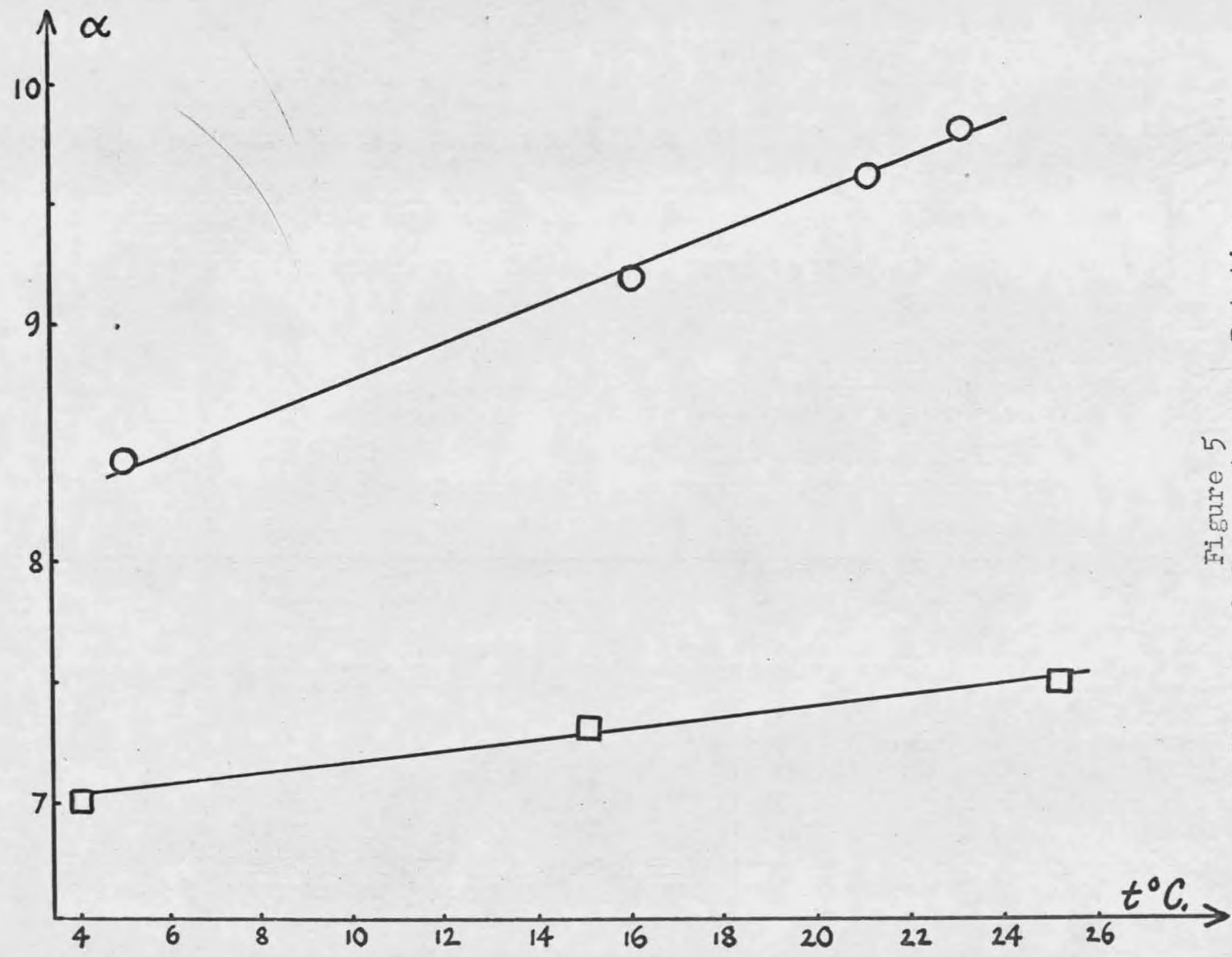


Figure 5
Influence of Temperature on Rotation

e) Influence of the pH.

On neutralizing ferritartaric acid (curve I) and plotting the specific rotation against the pH, we find two points of inflection, one at about pH 3.9 and the other one at a pH of about 8.5. This curve is compared with those obtained by neutralizing ferritartaric acid in the presence of a certain amount of fluoride (curve II) and by neutralizing tartaric acid alone (curve III). Franke (11) has made a colorimetric study of the ferritartaric acid during neutralization. He concluded the increase of color intensity from yellow to redbrown was an indication of the growing stability of the complex. He also obtained a bright yellow, crystalline precipitate, containing according to his analysis some iron. This result could not be reproduced in this investigation; the precipitate obtained, which was yellow at first, turned out to be only the rather insoluble bitartrate, $\text{NaHC}_4\text{H}_4\text{O}_6$. In the light of this knowledge it appears doubtful, if the stability of the ferritartrate complex really does increase during neutralization. The observed increase in the specific rotation could therefore be the result of the partial neutralization of tartaric acid, especially when one inspects the coincidence of the first point of inflection in curve I and II with a similar point in curve III, Fig. 6. According to Morton (17,18), the ferritartrate solution is indeed liable to precipitate $\text{Fe}(\text{OH})_3$ on long standing at a pH

of about 6.5 . With increasing pH, beginning at a pH of about 8, the existence of a new complex of much greater stability than the one existing in an acid medium is definitely indicated. Stability constants for it have been given from time to time (13, 27,29), but no agreement has been reached as to composition. Tables V, VI, VII give the numerical information pertaining to Fig. 6.

pH of solutions used: 4 M $C_4H_6O_6$ 0.36
 1 M $Fe(NO_3)_3$ 0.47

Table V
 Actual and Specific Rotation of
 Ferritartaric Acid during Neutralization

Tartaric Acid	Ferric Nitrate	Total Volume	pH	α observ.	$[\alpha]$
15 cc.	5 cc.	30 cc.	0.32	11.1	18.5
		40	1.40	10.1	22.4
		50	2.28	10.0	27.8
		60	2.81	9.9	33.0
		70	3.32	9.2	35.7
		80	3.58	8.4	37.4
		90	4.14	9.4	46.0
		100	5.76	8.9	49.5
		101.5	6.98	9.3	52.1
		102.5	8.10	9.8	55.6
		103	9.21	13.4	76.6
		105	11.0	13.5	78.5
		110	11.19	13.0	79.2

Table VI
Actual and Specific Rotation of Ferritartaric
Acid during Neutralization in the Presence of Na F .

4 M $C_4H_6O_6$	1 M $Fe(NO_3)_3$	0.85 NaF	Total Volume	pH	α obs.	$[\alpha]$
15 cc.	5 cc.	5 cc.	30 cc.	0.80	8.7	14.5
			45	1.63	7.6	19.0
			60	2.36	6.7	22.0
			80	2.90	6.5	28.8
			100	3.27	5.8	32.2
			120	3.60	5.2	34.6
			130	3.76	5.1	37.6
			140	3.92	5.0	38.7
			160	4.30	5.3	47.2
			174	5.64	5.1	49.5
			176.1	6.50	5.1	49.8
			177.1	7.05	5.3	52.0
			178.1	8.02	5.4	53.5
			179.1	8.90	6.9	68.7
			180.1	9.60	7.6	76.0

Table VII
Actual and Specific Rotation of
Tartaric Acid during Neutralization

4 M Tartaric Acid	Total Volume	pH	α observ.	$[\alpha]$
15 cc.	30 cc.	0.9	7.0	11.6
	50	2.3	6.4	17.7
	90	2.9	4.8	24.0
	130	3.4	4.0	28.8
	170	4.25	3.5	33.1
	180	6.7	3.5	35.0
	180.5	8.75	3.5	35.2
	181.5	11.2	3.5	35.4

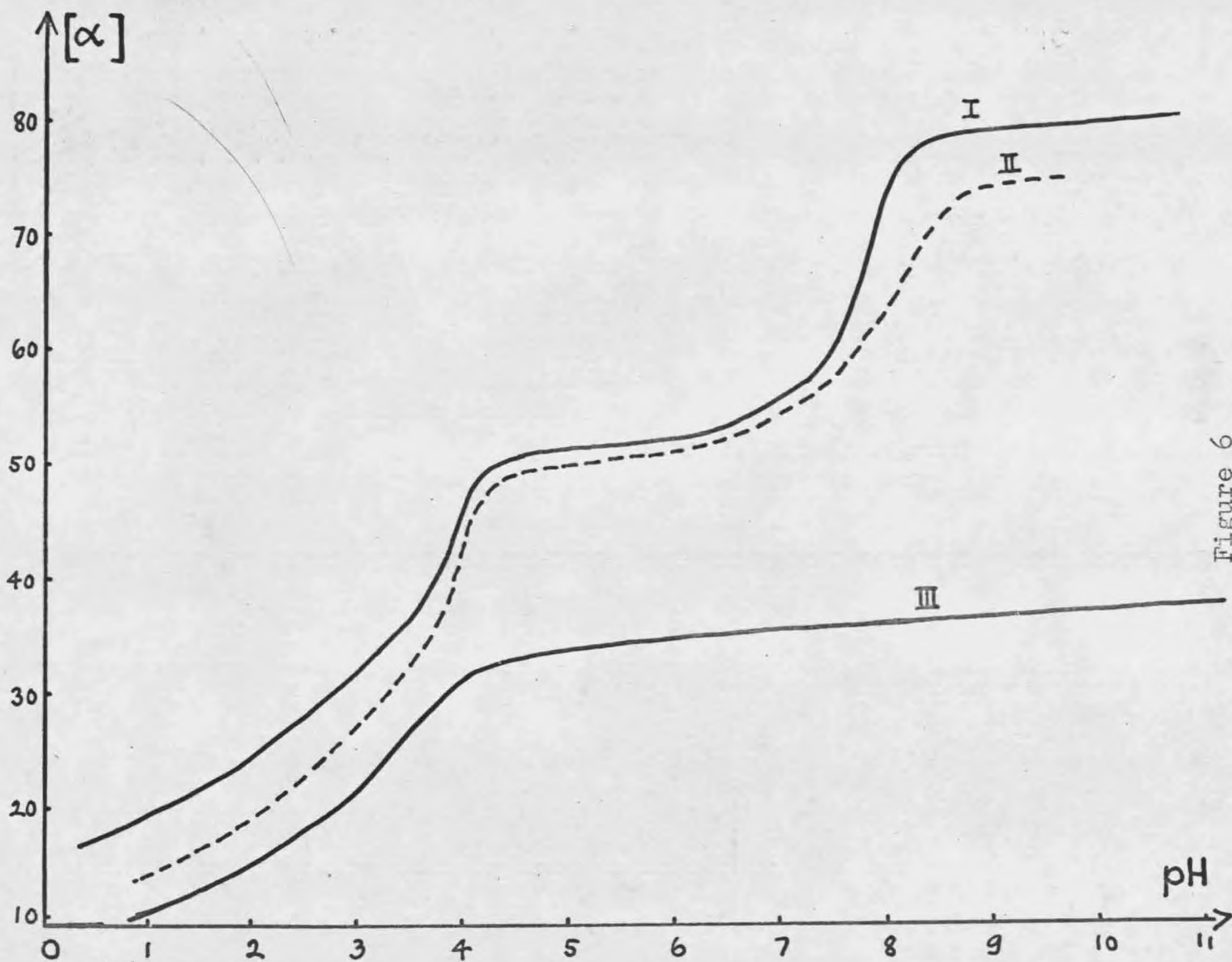
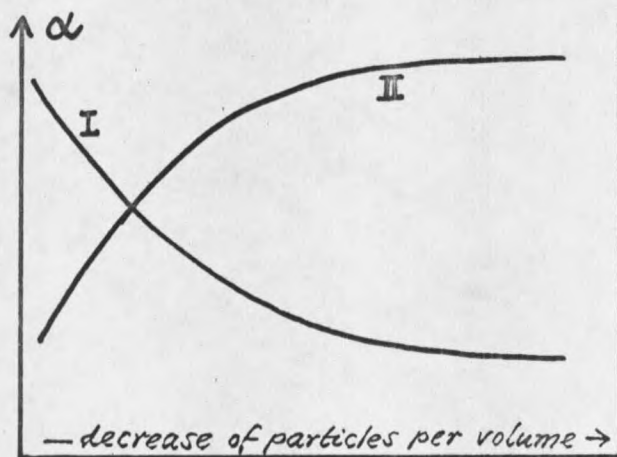


Figure 6
Change of Rotation with pH

f) Influence of other Salts.

The influence of other, optically inactive salts on tartaric acid has been given previous attention (12,16). In no instance has the study been extended to optically active addition compounds, such as ferritartaric acid where there was the added chance of having chemical interaction between the addition compound and the inactive salt. With this in mind, the influences of NaCl and NaF on ferritartaric acid were compared. The value of R was chosen rather high in order to tie up the ferric ion in the complex as much as possible. The curve obtained with sodium chloride suggests that this salt depresses the rotation by its mere presence, increasing the number of particles in solution, and the curve having therefore the same characteristics as the one in Fig. 4 (cf. diagram of Fig. 7).



Curve I:

Number of
Particles...const.

Volume.....increasing

Curve II:

Number of
Particles..increasing

Volume.....const.

Figure 7
Comparison of the Change in Rotation by
Changing the Concentration in two different Ways.

The values for Fig. 8 are compiled in Table VIII.

Table VIII
Comparison of the Influences of NaCl and NaF on the Rotation of Ferritartaric Acid.

4 M $C_4H_6O_6$	1 M $Fe(NO_3)_3$	1 M NaCl	Rotation
15 cc.	5 cc.	0 cc.	11.1
		2	11.0
		3	10.7
		5	10.4
		7	9.9
		0.85 M NaF	
		0 cc.	11.1
		3	9.7
		4	9.2
		5	8.7
		6	8.3
		7	7.8

The influence of NaF is different due to complex formation and is treated in the subsequent portion of this paper.

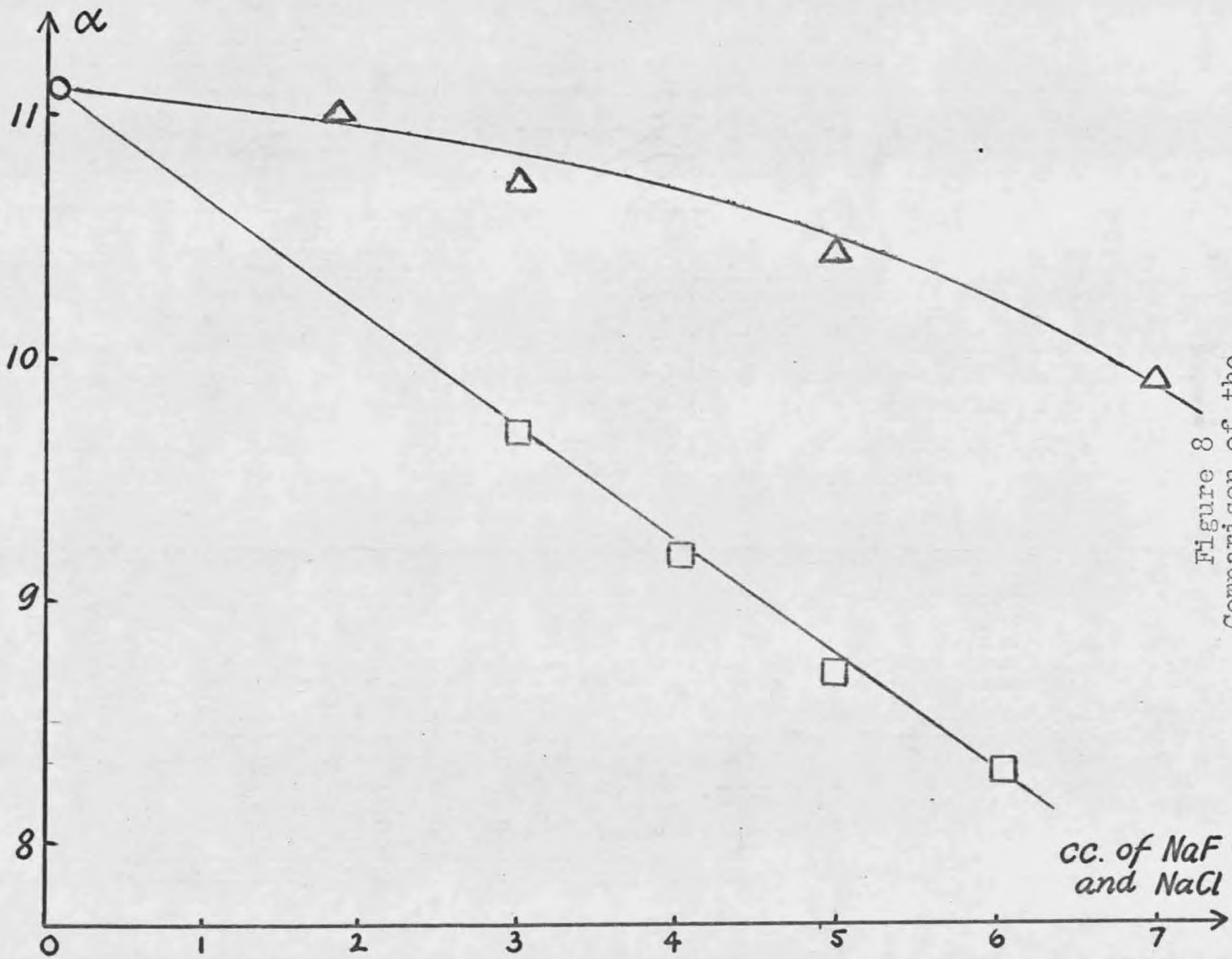


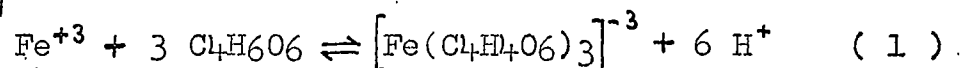
Figure 8
Comparison of the
Influences of NaF and NaCl

cc. of NaF —
and NaCl —

g) Composition and Stability of Complex.

As with any other complexes, the stability of the ferritartaric complexes is expressed by the complex stability constant:

$$\frac{[\text{Fe}^{+3}] [\text{TH}_2]^3}{[\text{FeT}_3^{-3}]} = k_1, \text{ assuming the underlying reaction to be}$$



The only numerical value of k_1 in the literature is given by Toropova (27) as 0.9×10^{-18} and calculated by polarographic studies. He postulates the complex as $[\text{Fe}(\text{C}_4\text{H}_4\text{O}_6)_3]^{-3}$ in the pH range of 3.4 to 7.0. Fig. 9 seems to indicate that the complex has indeed such a composition, but its stability does not seem to be that high as Fig. 3 shows, and since it allows the Fe^{+3} ion to be precipitated as Prussian Blue and as ferric hydroxide. On addition of fluoride we have to consider two competing complex reactions; reaction (1) as well as



The stability constant belonging to the second reaction is given by $\frac{[\text{Fe}^{+3}] [\text{F}^-]^6}{[\text{FeF}_6^{-3}]} = k_2$. This consideration also disproves a series of relative stabilities of Iron(III) complexes given by Thoms and Gantz (26), placing the tartrate above the fluoride. If this was the case, the fluoride would have no chance of taking the ferric ion out of the equilibrium with tartrate to the extent of its own demands; k_1 must therefore be greater than k_2 ; i. e. the ferric fluoride complex

more stable than the ferritartrate complex. Fig. 9 shows the sensitivity of various mixtures where the ratio $C_4H_6O_6/Fe$ is successively changed and designated as R 2, 2.5, 3, 4, 5, 10. The fluoride amounts introduced are in relative correspondence to the amounts of ferric ion in the different solutions. Table IX gives values for the initial rotation, as well as the final rotation after 2, 4, 5, 6.67, 8, and 10 cc. of 0.85 M fluoride solution have been added. The slopes of the curves increase until about $R=3$, and show from then on the same slope, indicating equal sensitivity. The reason for this fact is explained when we postulate that every ferric ion is tied up with three tartaric acid molecules, so that in cases where $R < 3$, only insufficient amounts of tartaric acid are present. Part of the ferric ion is therefore left over to combine with the fluoride without thereby affecting the optical rotation. This in turn explains the diminished slope of the curves for Rs smaller than 3.

Table IX
Sensitivity of H_3FeF_3 Solutions to NaF.

4 M $C_4H_6O_6$	1 M $Fe(NO_3)_3$	R	Initial Rotation	Final Rotation	NaF added
5 cc.	2 cc.	10	5.4	4.2	2 cc.
	4	5	7.4	5.2	4
	5	4	8.0	5.3	5
	6.67	3	8.6	5.5	6.67
	8	2.5	9.0	5.8	8
	10	2	9.7	6.1	10

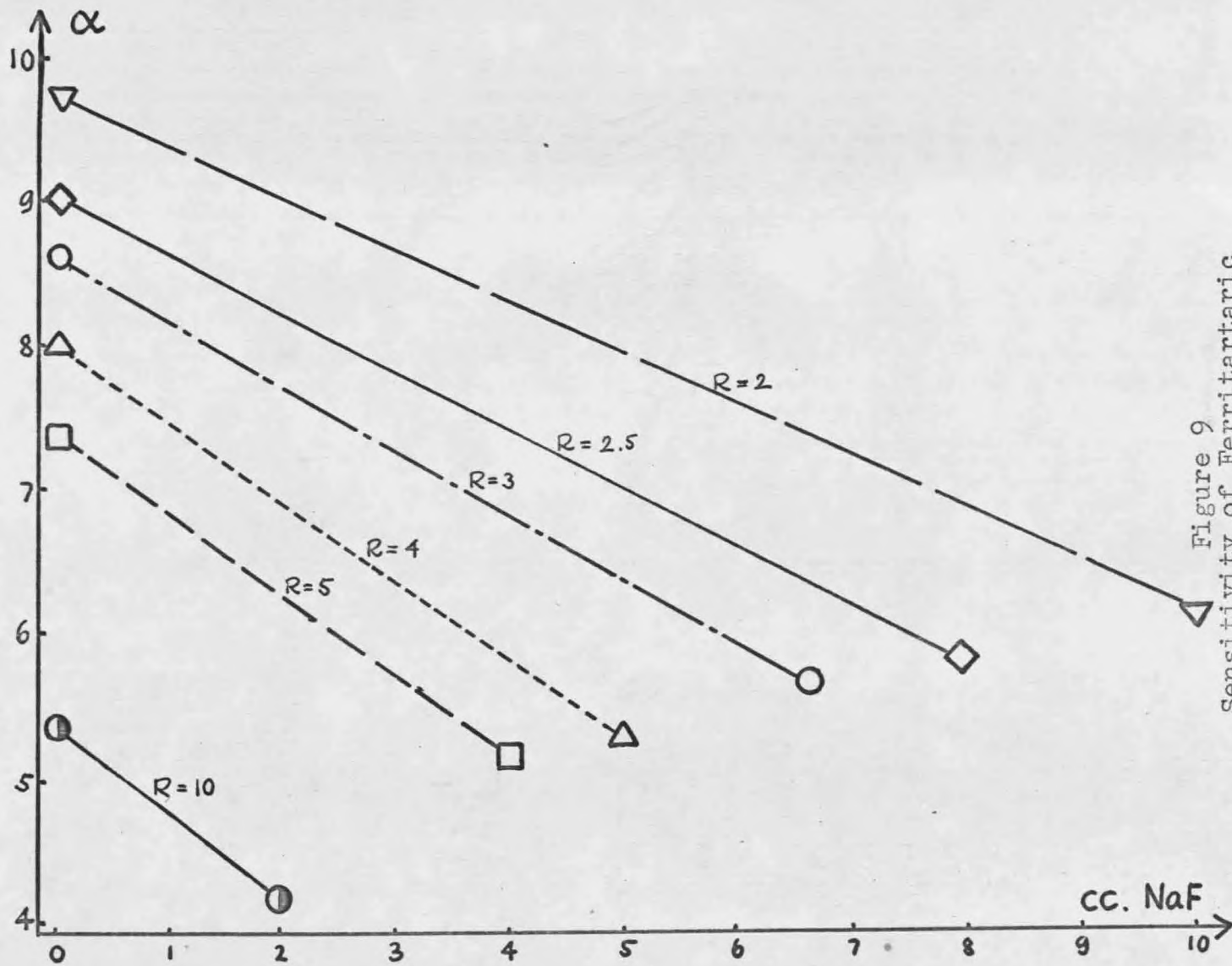


Figure 9
Sensitivity of Ferritartaric
Acid to Sodium Fluoride.

g) Analytical Behavior.

The ferritartrate complexes show the analytical reactions of the ferric ion either incompletely or not at all, depending again on existing conditions. In acid solution one can still precipitate the Fe^{+3} ion with ferrocyanide, but this is impossible in basic solution, indicating again the high stability of the complex formed there. Excess of base does not bring down the ferric hydroxide.

V. DETERMINATION OF FLUORIDES.

a) Influence of Fluoride on Tartaric Acid.

Having observed the unusual effect of NaF on ferritartaric acid, a countercheck as to the effect of the fluoride on tartaric acid seemed to be necessary. The data are recorded in Table X and Fig. 10; they show that an increase of rotation rather than a decrease results. This, of course, could be caused by a small change in the pH of the solution and probably has no basic significance.

Table X
Influence of NaF on $C_4H_6O_6$

<u>Tartaric Acid</u>	<u>Sodium Fluoride</u>	<u>Rotation</u>
10 cc.	0 cc.	4.1
10	5	4.4
10	10	4.9

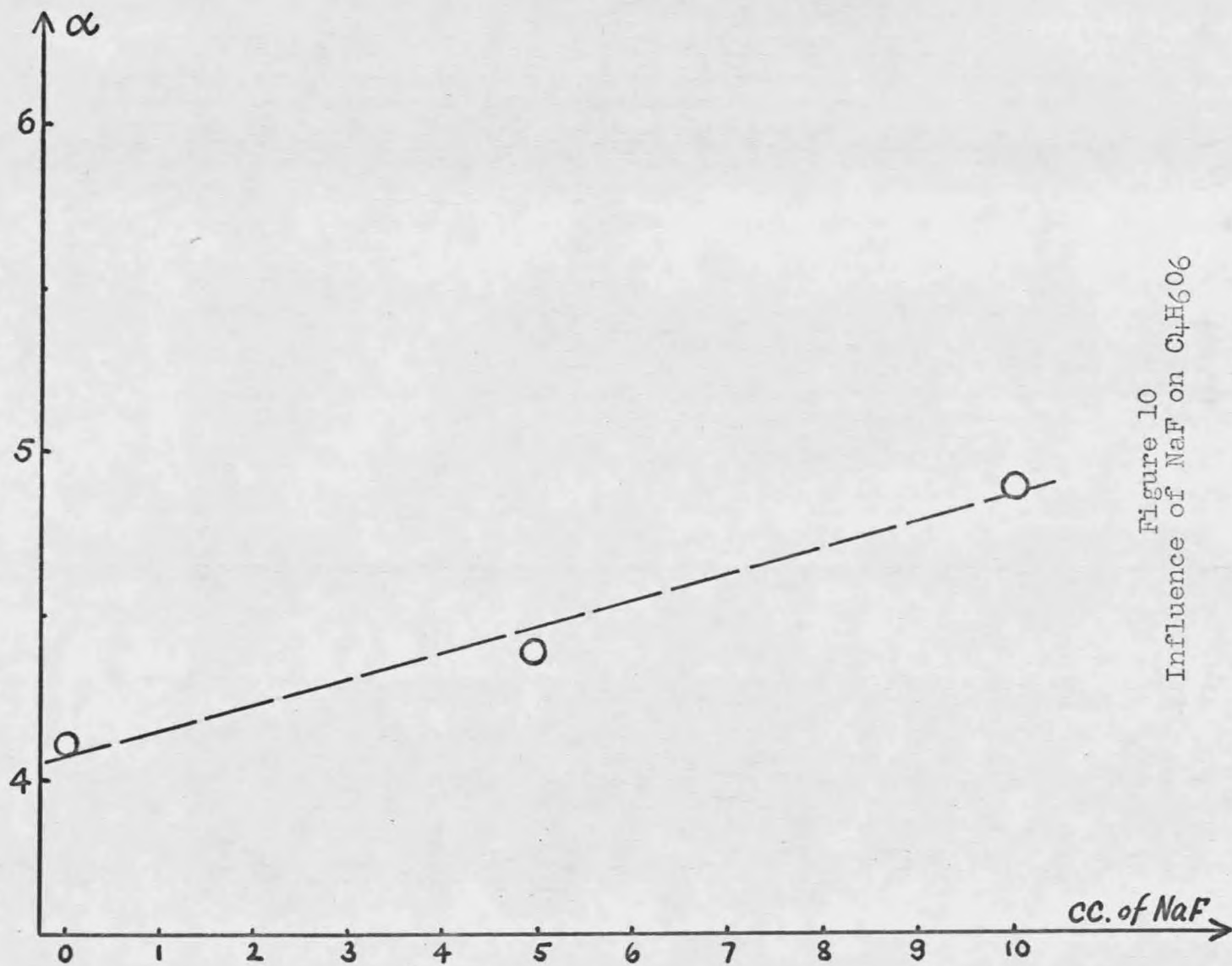


Figure 10
Influence of NaF on $C_4H_6O_6$

b) Influence of Fluorides on Ferritartaric Acid.

Considering the experimental data of Table XII, the inference of a few general conclusions is at once possible. Table XI and Fig. 11 explain the observations schematically with an example picked at random. Starting with a certain mixture (#1), we have four choices of either increasing or decreasing R (mixtures #2-#5) and keeping one component constant. For constant Rs we see why the sensitivity must decrease with increasing total concentration of ferritartaric acid by looking at mixtures #2 and #4, the excess of free Fe in mixture #2 being twice the amount of the one in #4. This holds true also for cases where R=3, as the complex renders a certain amount of Fe ions according to its dissociation equilibrium.

Table XI
General Sensitivity of Ferritartaric Acid

Mixture	$[C_4H_6O_6]$	$[Fe(NO_3)_3]$	R	$[H_3FeT_3]$	Excess $[Fe^{+3}]$
#1	2	2	1	0.67	1.33
#2	4	2	2	1.33	0.67
#3	2	4	0.5	0.67	3.33
#4	2	1	2	0.67	0.33
#5	1	2	0.5	0.33	1.67

The same argumentation applies to Fig. 11b, as a comparison of mixtures #1 and #3 easily shows. Here the concentration of tartaric acid is constant and R changes.

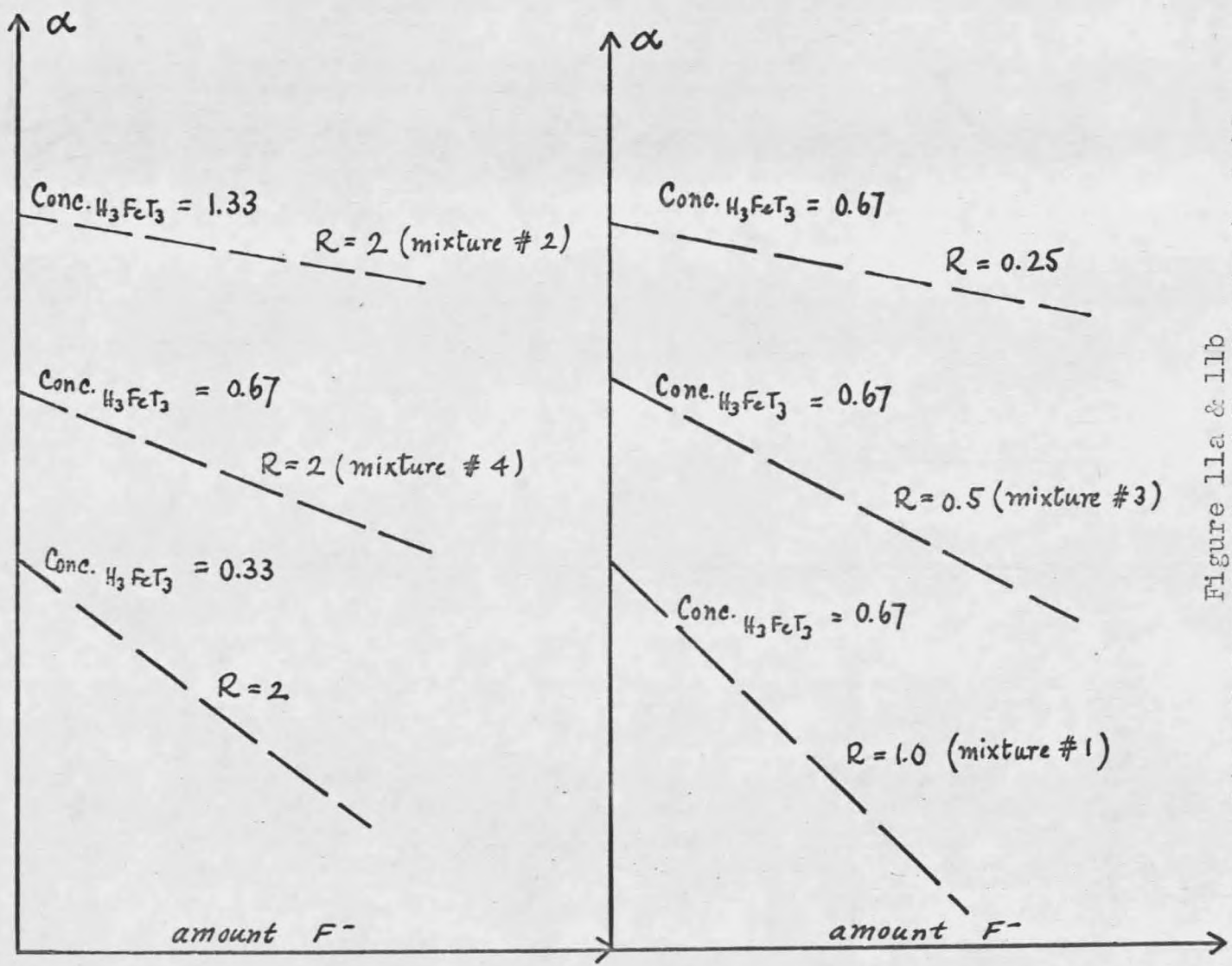


Figure 11a & 11b
General Sensitivity of Ferritartaric Acid

Table XII
Sensitivity of Ferritartaric
Acid Solutions toward NaF

C ₄ H ₆ O ₆	Fe(NO ₃) ₃	NaF	Ratio R	Rotation
14 cc.	6 cc.	0	9.33	10.2
		2		9.3
		5		8.5
12	8	0	6	10.7
		2		9.9
		5		9.2
10	10	0	4	11.1
		1		10.7
		3		9.7
		4		9.3
		5		8.8
		7		8.1
8.6	11.6	0	3.02	11.2
		2		10.2
		5		9.3
8	12	0	2.67	11.0
		1		10.7
		2		10.3
		3		9.9
		4		9.5
		5		9.2
4	16	0	1	9.0
		1		8.8
		3		8.5
		5		8.1
		7		7.9
2	16	0	0.5	7.9
		2		7.5
		4		7.2
		6		6.9
2	12	0	0.67	7.5
		2		7.1
		4		6.6
		6		6.2
2	8	0	1	7.0
		2		6.3
		4		5.6
		6		5.0

c) Outline of Procedure.

The numerous complicating factors we have to deal with in the measurement of the rotation of ferritartaric acid make it impossible to give any procedure which is applicable for all, or even the majority of cases.

The usefulness of this method is therefore restricted to routine analysis where the same conditions, (pH of solutions, amount of other salts present) more or less always exist. An example is the fluoride determination of waters, where the nature and the approximate amount of other salts present are known. The calibration of the solution of ferritartaric acid used is however necessary in every single instance. The accuracy of the method depends, in addition to that consideration, very much on the reading accuracy of the polarimeter and on the reliability of the volume measurements. The temperature, the length of tubes and strength of solutions require equal attention.

This analytical procedure should prove to be satisfactory, since speed and convenience are more than sufficient compensation, once all these initial precautions are dealt with.

VI. SUMMARY.

- 1) Mixtures of tartaric acid and ferric nitrate react to form ferritartaric acid. The other reaction product is nitric acid, as the pH of the solution after mixing is smaller than the pH of either component before.
- 2) The rotatory power of the ferritartaric acid was determined as such, and in regard to various influences.
- 3) Several observations led to the conclusion that the formula of ferritartaric acid corresponds to $H_3 [Fe(C_4H_4O_6)_3]$.
- 4) It was found that fluorides, due to their complex formation with ferric ion, decrease the rotation of ferritartaric acid in a way which is proportional to the amount of fluoride ion present. This fact was proposed as basis for a new analytical procedure for the determination of fluorides.
- 5) Using other optically active compounds and other complexing inorganic ions, this phenomenon can be extended generally and put to use in other quantitative analytical methods.

VII. LITERATURE CITED

- (1) Biot, J.B., Mem. Acad. France 16, 229 (1837)
- (2) -----, Ann. Chim. Phys. 11, 82 (1844)
- (3) -----, Ann. Chim. Phys. 29, 341 (1850)
- (4) -----, Ann. Chim. Phys. 29, 490 (1850)
- (5) -----, Ann. Chim. Phys. 59, 229 (1860)
- (6) Bobtelsky, M., and Jordan, J., J. Am. Chem. Soc. 69, 2286 (1947)
- (7) Darmois, E., J. chim. phys. 23, 665 (1926)
- (8) Delsal, J.L., J. chim. phys. 35, 350 (1938)
- (9) Diehl, H., Chem. Rev. 21, 39 (1937)
- (10) Falinski, M., Compt. rend. 201, 69 (1935)
- (11) Franke, W., Annalen 486, 242 (1931)
- (12) Hung-Chun Kung, and Fa-Si Li, J. Chin. Chem. Soc. 12, 113 (1945)
- (13) Jellinek, K., and Gordon, H., Zeitschr. phys. Chem. 112, 207 (1924)
- (14) Job, P., Ann. d. chim. 9, 113 (1928)
- (15) Landolt, H., The Optical Rotating Power, 751 pp.
The Chemical Publishing Co., Easton, Pa. (1902)
- (16) Ling-Yang, and Pin-Fong Hu, J. Chin. Chem. Soc. 10, 184 (1943)
- (17) Morton, C., Chem. Zentr. 102, II 3569 (1931)
- (18) -----, Chem. Zentr. 104, I 753 (1933)
- (19) Paria, B., Ber. 47, 1773 (1914)
- (20) Pariselle, H., and Delsal, J.L., Compt. rend. 198, 83 (1934)

- (21) Pavlinova, A.V., Zhur. Obshchei Khim.(USSR) 19, 238 (1949)
- (22) Pickering, S.U., J. Chem. Soc. 103, 1358 (1913)
- (23) ----- , J. Chem. Soc. 105, 464 (1914)
- (24) Rosenheim, and Vogelsang, Anorg. Chem. 48, 205 (1906)
- (25) Sidgwick, N.V., The Chemical Elements and their Compounds,
Vol. II, 1363 pp. Oxford University Press
(1950)
- (26) Thoms, D.D., and Gantz, E. St.Clair, Proc. Indiana Acad.
Sci. 56, 130 (1946)
- (27) Toropova, V.F., Zhur. Obshchei Khim.(USSR) 15, 603 (1945)
- (28) Treadwell, W.D., and Wettstein, E., Helv. Chim. Acta
18, 200 (1935)
- (29) Wark, E.E., and Wark, J.W., Zeitschr. phys. Chem.
157, 310 (1931)
- (30) Yeu Ki Heng, J. chim. phys. 33, 386 (1936)

VIII. ACKNOWLEDGMENT.

I wish to take the opportunity, and express my appreciation to Dr. Ray Woodriff and Dr. C. N. Caughlan, both of the Department of Chemistry, for many helpful suggestions and discussions.

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10013557 1

N378

D417i

cop.3

Denk, Hans H.

Investigation on the
rotatory power of ferritartaric
acid and its

NAME AND ADDRESS

WERRA ALDEN
902 DELON ST. 1/4

N378

D417i

cop.3

