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
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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 f'erritartaric acid or ferritartrates; their optical rotations were determined. Influences investigated were those of the concentration, the temperature, the pH, the change in the ratio [C4H6O6]: [Fe] , salts not interacting with the fer-ritartrate complex, and salts interacting with the ferritar-trate. The data were used to establish the formula for ferri-tartaric acid as H3[Fe(C4H4O6)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.

INVESTIGATION ON THE ROTATORY POWER OF
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TO THE QUANTITATIVE DETERMINATION OF THE
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HANS H. DENK

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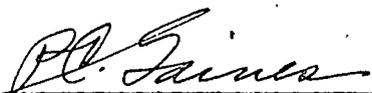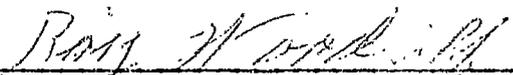partial fulfillment of the requirements
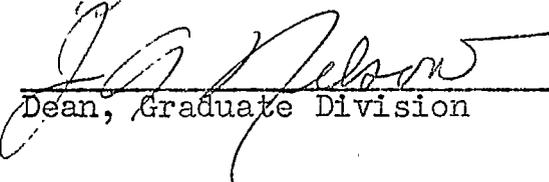
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Approved:

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Head, Major Department

_____
Chairman, Examining Committee

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Dean, Graduate Division

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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 sub-
stance MA which has a different optical rotation, we may sub-
ject this latter substance then to a second influence exerted
by an inactive ion X, capable itself of complexformation in-
volving 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:

Amount of Rotation

Active substance. A

Addition of M
and formation of MA

Addition of X,
interacting with part of MA
under formation of MX
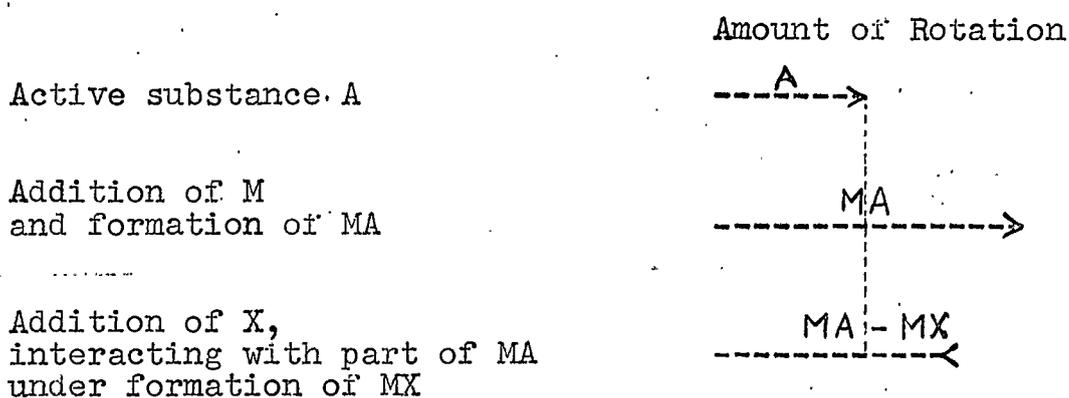
Figure 1
Principle of Method.

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 investi-
gation. Generally speaking, the above principles could be ex-
tended 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 in-

fluences on optically active addition compounds for analytical

procedures should not be restricted to a few exeptional 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 $Fe(NO_3)_3 \cdot 9 H_2O$, 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 $[\alpha] = \dfrac{\alpha \times 100}{\ell \times g}$ 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 TH_2:Fe on the Rotation
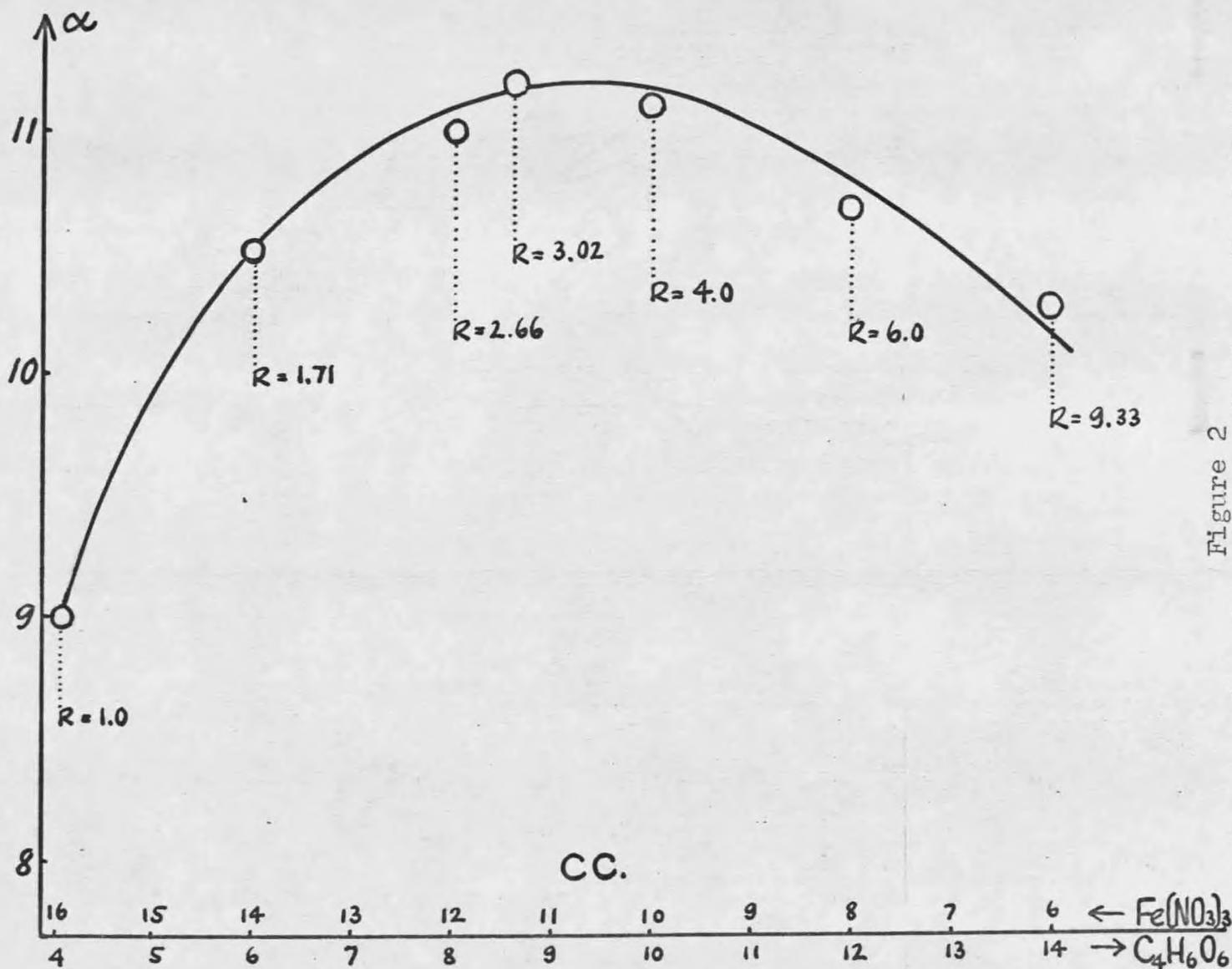
measure the limiting values of rotation: the minimum by using 5 cc. of $C_4H_6O_6$ without any addition of iron, the maximum by extrapolating the curve of measured values until it meets the y-axis. Table II gives in addition some measurements for solutions of lower concentrations, since the transmittance 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)	→ 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
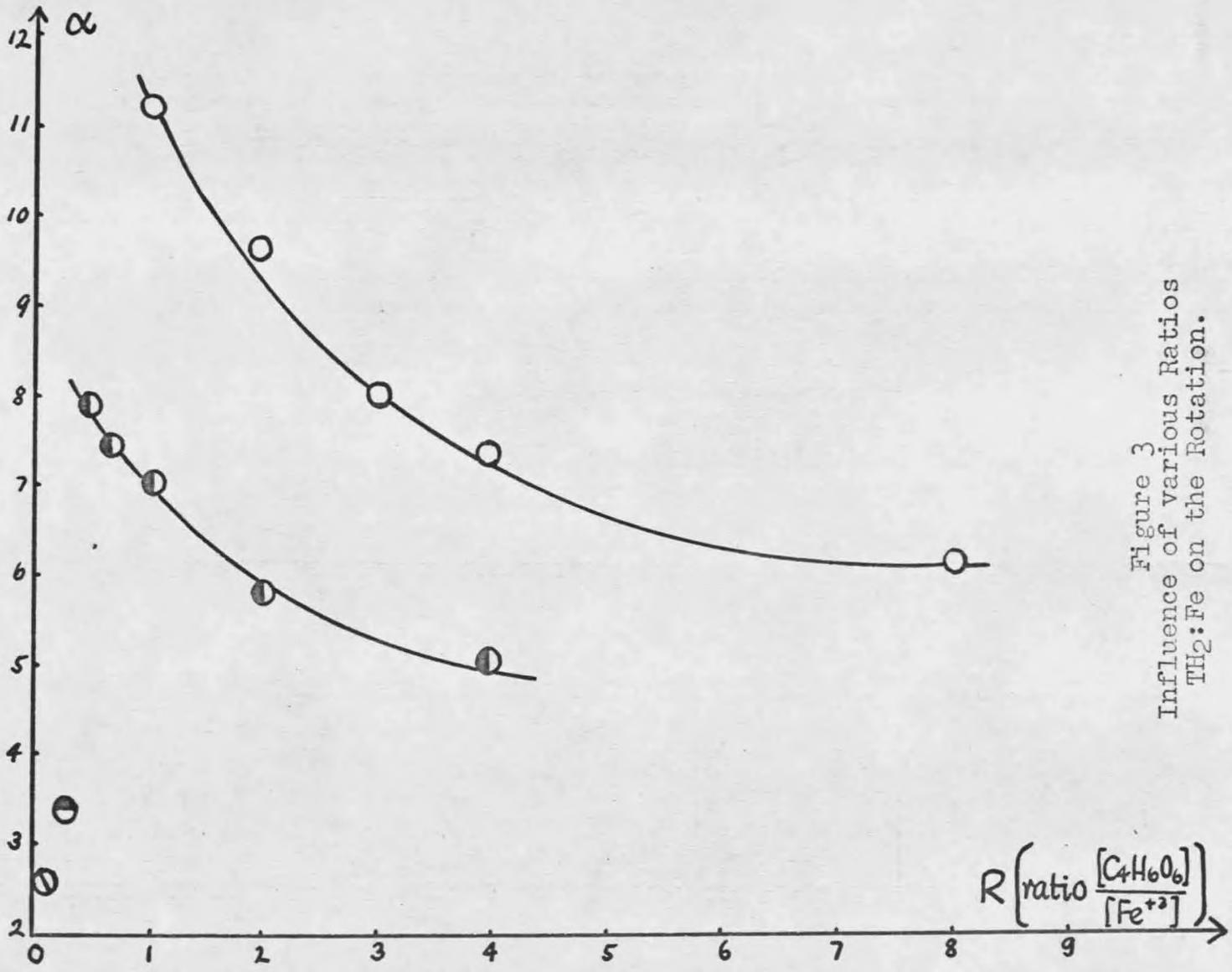
Figure 3
Influence of various Ratios
TH$_2$:Fe on the Rotation.

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

general characteristics of curve
at higher concentrations

general characteristics of
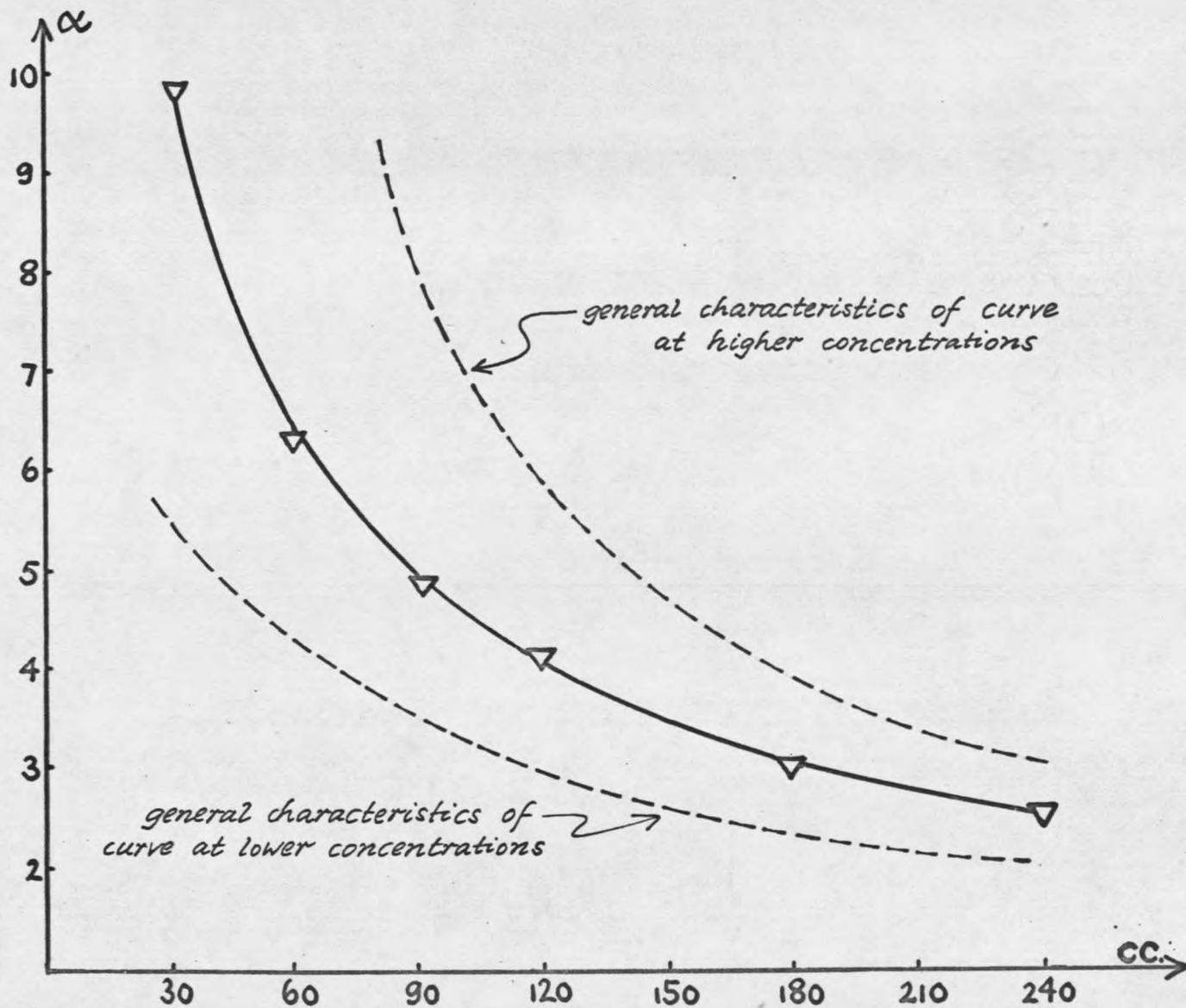curve at lower concentrations

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d) Influence of Temperature.

Ferritartaric acid as well as tartaric acid (15) shows an in-
crease of rotation with an increase in temperature. The reason
for this is most often explained, at least where charged com-
plexes 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 $Fe(NO_3)_3$	$t^{\circ}C.$	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 solu-
tions are as 2.33 and 6.66 to each other. The slopes of the
two curves given in Fig. 5 are:

$$\frac{\Delta\alpha}{\Delta t} = 0.025 \text{ and } 0.077 \qquad \left[\frac{\text{degrees of rotation}}{\text{degree C.}}\right]$$
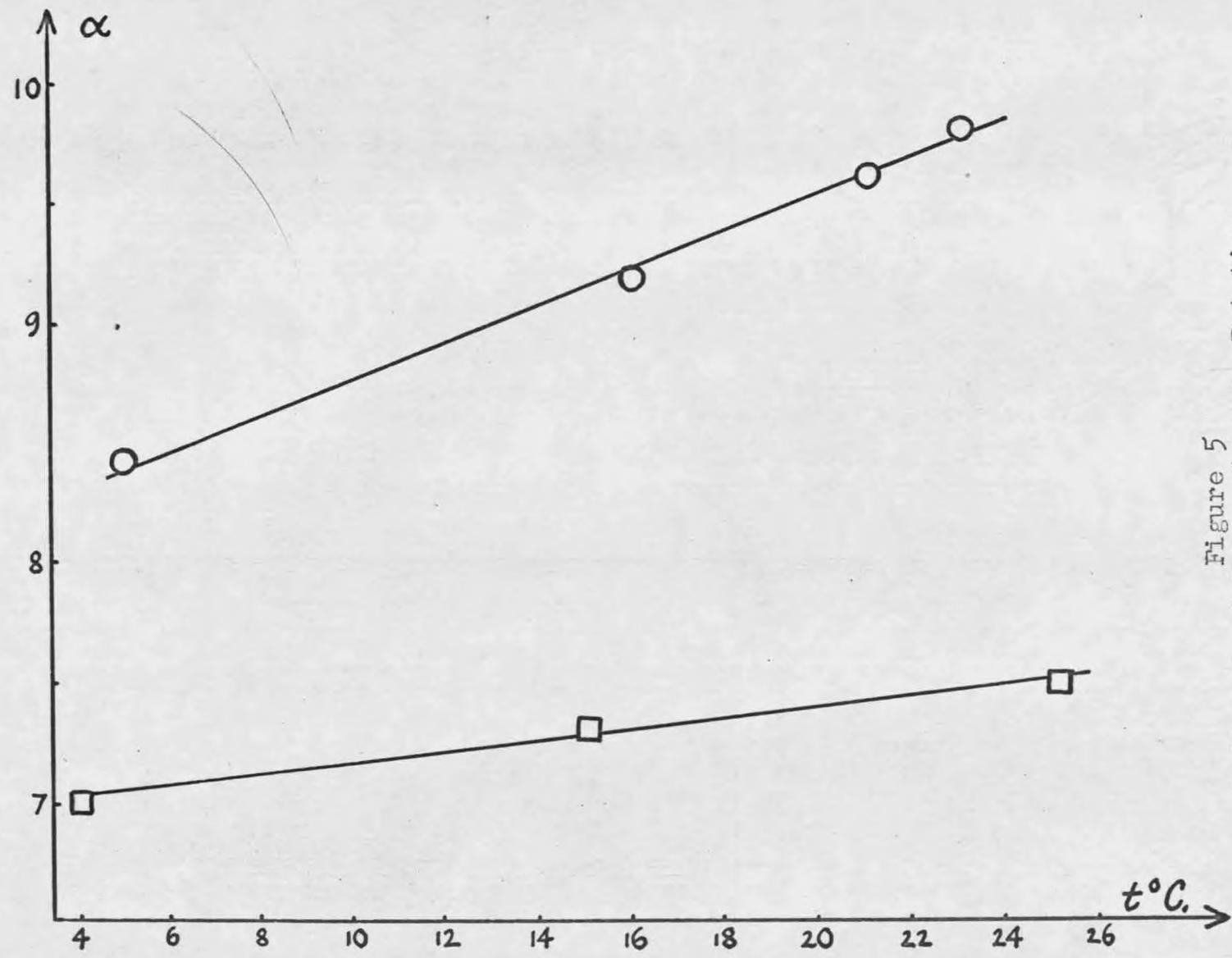
Figure 5
Influence of Temperature on Rotation

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, $NaHC_4H_4O_6$. 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 $Fe(OH)_3$ 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

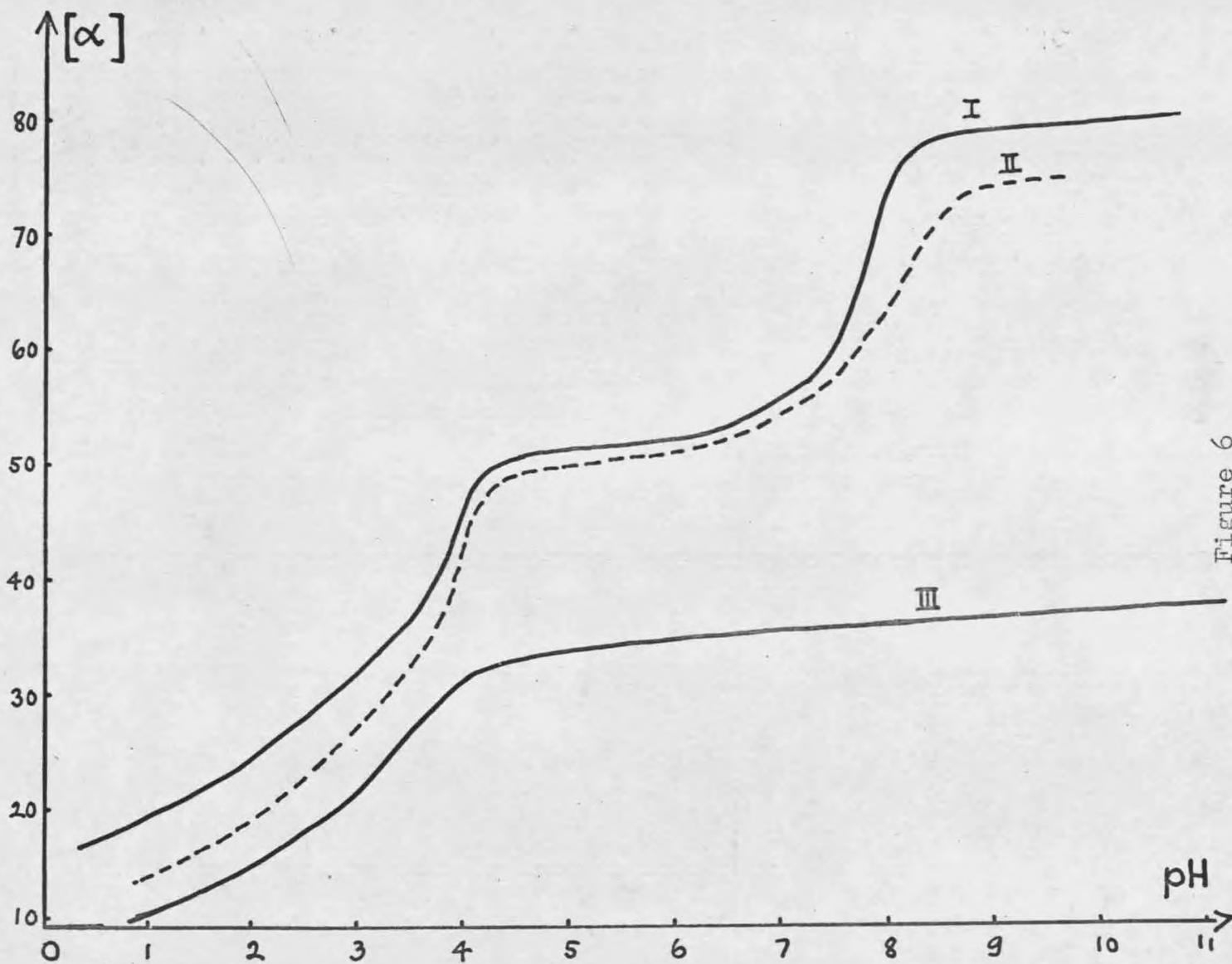| 4 M Tartaric Acid	Total Volume	pH	α observ.	$[\alpha]$
15 cc.	30 cc.	0.9	7.0	11.6
	50	2.3	6.4	17.7
	90	2.9	4.8	24.0
	130	3.4	4.0	28.8
	170	4.25	3.5	33.1
	180	6.7	3.5	35.0
	180.5	8.75	3.5	35.2
	181.5	11.2	3.5	35.4

Figure 6
Change of Rotation with pH

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