

7-1-1955

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Jane Bell Grinnan Gladding

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A STUDY OF THE CHELATION OF
1,3-BIS (TRIS (HYDROXYMETHYL) METHYLAMINO) 2 -
PROPANOL WITH IRON (III)

BY

JANE BELL GRINNAN GLADDING

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
OF THE UNIVERSITY OF RICHMOND
IN CANDIDACY
FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Approved by:

Wm E. Trout, Jr.

August 24, 1955

AUGUST, 1955

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I N T R O D U C T I O N

THE ELEMENT IRON is so important that a major era of history bore its name. Its magnetic and metallic properties have long been studied and used. It is also well known that iron is the central element in the oxygen-carrying compound hemoglobin and therefore essential to life. Its biological importance is also evidenced by its presence in the cytochrome oxidases. These important biochemical compounds are iron chelates.

Fundamental research with iron chelates may therefore shed light on the operations of certain enzyme systems, drugs and poisons. Analytical chemistry and the dye industry have used chelate compounds for many years. Citrates and oxalates have also been used to tie up calcium ions and prevent coagulation of blood, while polyphosphates have been used as water softeners. In recent years many new uses have been developed and interest has grown accordingly.

Such spurts of growth within a field usually come when the time is ripe, but it seems that two major impetuses have

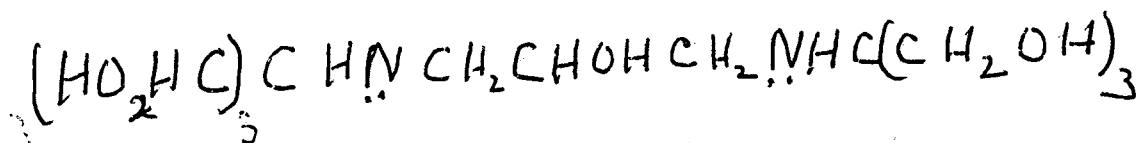
contributed to this: one fundamental, the other practical. The fundamental impetus is the development of theories of chemical bonding aided by quantum theory. Metal complexes have provided a means for testing some of this theory and the theory in turn has shed light on the complexes. A practical aid is government-sponsored research to find safe methods of removing radioactive metals from the body.

One of the most widely publicized chelating agents introduced in recent years is EDTA or ethylenediamine-tetraacetic acid. EDTA chelates a very large number of metal ions and can be used as a water softener because of its sequestering power for calcium and magnesium ions. Martell and Calvin¹ claim that it is also useful to remove harmful heavy metal ions from the body since it is not metabolized. To prevent undue lowering of the blood calcium level, it is administered in the form of the calcium chelate.

From these premises, it may be reasonable to hope that each further study of iron chelates may provide clues useful to other research projects. The chelating agent, 1,3-bis (tris(hydroxymethyl) methylamino) 2-propanol, was chosen because it was known to have a solubilizing action with respect to iron, was water-soluble, and was made in the laboratory

1 Martell and Calvin, Chemistry of the Metal Chelate Compounds, Prentice-Hall, N. Y., 1952. P. 509

of ~~the~~ The University of Richmond by Pierce and Wotiz.² It will be referred to in the future as Disec. The formula is:



Since the chelate is water-soluble and colored, spectrophotometric methods for studying complexes in solution were tried. Difficulties were encountered due to the marked absorbancy of the hydrolysis products of Fe(III) ion over the pH range where chelation occurs. Therefore potentiometric titrations have been used also and the results compared to find the common denominator.

² Pierce and Wotiz, J. Am. Chem. Soc., 66, 879, (1944)

A B S T R A C T

A short review of chelation and of the spectrum and hydrolysis of iron (III) ion is followed by a more detailed account of the methods developed for the determination of formulae and stability constants of complex species in solution.

The chelation of iron (III) with 1,3-bis (tris (hydroxymethyl) methylamino) 2-propanol has been studied both potentiometrically and spectrophotometrically. Evidence from both methods points to a 1:1 compound. Because the titration curve shows the same buffer region as the curve for the free ligand, it is postulated that the amine groups of the ligand may not be involved in chelation and alternate structures are suggested. Various methods of determining the stability constant are attempted and commented on.

H I S T O R Y

Part 1 Chelation

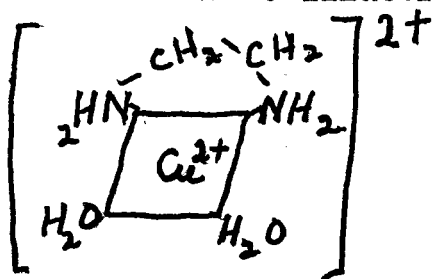
This is a study of the chelation of iron (III) and Disec, 1,3-bis (tris (hydroxymethyl) methylamino) 2-propanol. The history therefore deals with chelation and with the chemistry of iron in water solution. Since the complex was studied in solution, it is also appropriate to review the methods used to determine formulas and stability constants of complexes in solution.

A chelate compound is a metallic complex in which a heterocyclic ring is formed, the metal ion or atom being a ring member. The term is also applied to rings closed by hydrogen bonding, but it will not be used in that sense in this paper. The term was introduced by Morgan and Drew.³

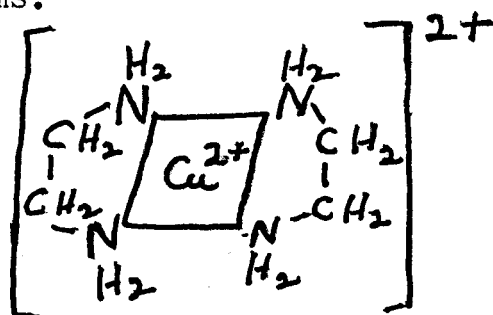
(Cu(II) en²⁺) (I) and (Cu (II) en₂²⁺) (II) , ions in which copper is chelated with one (I) and with two (II) molecules of ethylenediamine, are given as examples of

3. Morgan and Drew, J. Chem. Soc., (1920), 1457

chelation and to illustrate terms.



I



II

The rings formed are five-membered in each case and the metal ion brings about ring closure. Five and six membered rings are the most common here just as they are with organic compounds in general. In the examples shown, ethylenediamine and water are called ligands. Compound I is said to be bound to three ligand molecules and compound II to two ligand molecules. Bjerrum⁴ uses the term in this sense and the usage seems to be general. In aqueous solution, the term is usually restricted to associated groups other than water and its hydrolysis product, OH^- . The present study is confined to aqueous solution. In the example given, the ligand, ethylenediamine (en), is bidentate. A ligand which is bound to the metal by three groups is terdentate (sometimes tridentate), by four, quadridentate (sometimes tetradentate).⁵ Fernelius and Bryant⁶ give the accepted

4. J. Bjerrum, Chem. Revs., 46, 381 (1950)

5. Terms introduced by Morgan, see Harvey Diehl, Ibid., 21-39 (1937)

6. Fernelius and Bryant, J. Am. Chem. Soc., 75, 1735 (1953)

symbolism for representing ligands. Since this symbolism implies that the exact structure is known, it will not be used in this study.

Alfred Werner⁷ presented the first successful explanation of the chemistry of complex ions and molecules. He pictured metals as having inner and outer coordination spheres. Those groups bound covalently, as water and ammonia and chloride not precipitable by silver nitrate, he described as held in an inner coordination sphere, while negative ions which gave usual tests were in the outer sphere. The number of groups which could be attached in an inner sphere was accordingly called the coordination number of a metal ion. This term is still in use. Considering this coordination number and the isomers found, he developed stereochemical models for the metal complexes. These models are also in current use, an explanation having been added by Pauling⁸ and others in terms of orbitals, hybridized bonds and quantum theory. Iron's coordination number is six, its covalent complexes assuming an octahedral form.

General reviews of coordination chemistry, including chelation, have been compiled by Diehl,⁹ Bjerrum,¹⁰ Fyfe,¹¹ and Basolo.¹² In addition to these there is a book by Martell and Calvin¹³ to which frequent reference will be made.

7. Werner, Beitrag zur Konstitution anorganischen Verbindungen, Akademische Verlagsgesellschaft, M.B.H. Leipzig, 1924
8. Pauling, Nature of the Chemical Bond, pp 76 - 123, Cornell Univ. Press, Ithaca, N. Y. (1945)
9. Diehl, op. cit. this paper note 5
10. Bjerrum, op. cit. note 4
11. Fyfe, J. Chem. Soc. (1952) 2018
12. Basolo, Chem. Revs. 52, 459 (1952)
13. Martell and Calvin op. cit. note 1

The properties of metallic complexes in aqueous solution are treated in detail by Martell and Calvin.^{14,15} In this paper, the properties of greatest interest are the solubilizing of iron in neutral and basic solution and the color of the chelate compound. The iron chelate which is the subject of this paper is soluble in water and it is of general interest to know over what pH range and at what concentrations iron may be so held in solution. To find this, it is helpful to know something about the structure and stability of the compound formed. If the compound is colored, it may be possible to make a spectrophotometric study of it. When such a study was undertaken, it was found that the marked hydrolysis of iron in aqueous solution had to be taken into consideration and was of special significance when studying absorbance, since the hydrolysis products had high absorbancy in the same spectral region which apparently characterized our compound. By making this study with a different technique, potentiometric titrations, hydrolysis of iron (III) ion offered less interference. Nevertheless it seemed desirable, in reviewing the literature on iron, to inquire into its absorp-

14. Martell and Calvin, *op. cit.*

15. Martell, *J. Chem. Educ.* 29, 270 (1952)

tion spectrum and hydrolysis in addition to its complexing ability.

Part 2 Iron

Mellor¹⁶ has reviewed the chemistry of iron up to 1935. Lerner, Grove and Casey¹⁷ sum up a portion of the work done on iron complexes since then. Complexing ability is most marked among the transition elements and iron is no exception. The ferric thiocyanate and cyanide complexes are well known. Where such complexes are covalent, they are octahedral and $3d^24s4p^3$ hybrid bond orbitals are involved.¹⁸ According to Pauling,¹⁹ iron fluoride and iron aquo complexes are essentially electrostatic, while others which have been tested by magnetic criteria are covalent. Since the d^2sp^3 bonds are strong, 2.923²⁰ on Pauling's scale with 3 the maximum, it seems likely that any group capable of forming bonds with iron would have a tendency to displace water from the coordination sphere. In the present study, this displacement is thought to occur, the resulting complex being an iron chelate.

16. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vols. XII, XIII, XIV Longmans, Green and Co., N. Y. 1935

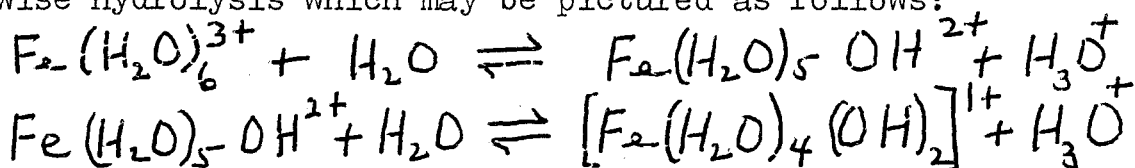
17. Lerner, Grove and Casey, J. Chem. Educ. 29, 438 (1952)

18. Pauling, op. cit. This paper, note 8

19. Pauling, ibid. pp. 113-116

20. Pauling, ibid. p. 96

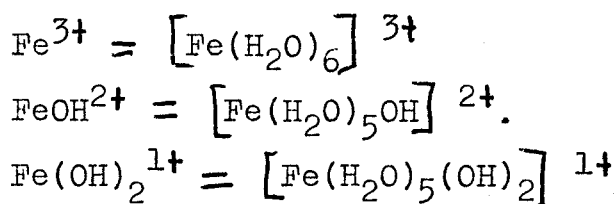
Should any such change take place, there would be a change in the electrical field within the group which would be reflected in turn by changed electron transitions and so by a difference in the absorption spectrum of the iron-containing group. Since absorption spectra are specific, their use is usually quite fruitful in the study of individual species in solution. Absorption spectra constitute one of the tools used in this study. Unfortunately, the absorption spectrum of iron (III) salts in aqueous solution is not simple. Beginning at a low pH, the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion undergoes stepwise hydrolysis which may be pictured as follows:



These three species all seem to absorb in the ultraviolet portion of the spectrum, apparently with considerable overlapping of absorption bands. Moreover this overlapping takes place in such fashion that, as pH is increased, the absorption bands due to the hydrolysis products widen into the visible portion of the spectrum and swamp the ultraviolet pattern. This means that Beer's law, usually a quantitative measure of substances in solution, cannot be applied unless the concentration distribution and molar extinction of each species present is known. Some very

interesting work has been done in an attempt to obviate these difficulties. An early spectrophotometric study of FeCl_3 in various solvents was made by Jones and Anderson.²¹ They found that solutions of the iron salt in water and in acetone did not obey Beer's law, while those in methyl and ethyl alcohol did. They surmised that the reason for the deviation in water was a change in the ratio of hydrolysis products upon dilution.

Rabinowitch and Stockmayer²² have made a careful study of the spectrum of water solutions of $\text{Fe}(\text{ClO}_4)_3$ and state that they have succeeded in separating the spectrum of Fe^{3+} and FeOH^{2+} . In the future the following abbreviations will be used:



There is little attempt to separate FeOH^{2+} and $\text{Fe}(\text{OH})_2^{1+}$. According to these workers, Fe^{3+} gives a double peak at 200-240 m μ with molar extinction ca. 5000 at 240 m μ , a small sharp peak at 407 m μ which is swamped by FeOH^{2+}

21. Jones and Anderson, The Absorption Spectra of Solutions
Carnegie Institute of Wash., pub. # 110, chap. 5 (1909)

22. Rabinowitch and Stockmayer, J. Am. Chem. Soc., 64, 335 (1942)

as pH rises, a broad low maximum at 540 m μ and another slight maximum beyond 700 m μ . There is a maximum at 330-340 m μ probably due to FeOH^{2+} and $\text{Fe}(\text{OH})_2^{1+}$. See Figures 1-6.

Olson and Simonson²³ find an isosbestic point for Fe^{3+} and FeOH^{2+} at 272 m μ (Figure 9). References will be made to the spectral interpretations of Rabinowitch and Book and Stockmayer and of Olson and Simonson later when the experimental details of this study are discussed.

Not only must hydrolysis be considered in spectrophotometric studies involving iron, but in any study of iron compounds in water. Indeed, Lerner, Grove and Casey²⁴ state that, "Unsolved problems of iron chemistry are concerned with the interaction of its compounds with solvent systems," and that, "even at 3M HClO_4 association with OH^- is still enough to interfere with spectral results." This being the case, various workers have tried to determine the equilibrium constant for each step in the hydrolysis of the iron (III) hexaquo ion. Some of these workers have used spectrophotometric methods and have therefore

23. Olson and Simonson, J. Chem. Phys., 17, 1322 (1949)

24. Lerner, Grove and Casey, op. cit. this paper note 17

determined the molar extinction of Fe^{3+} and FeOH^{2+} as well as the stability constants. The names of some who have worked in this field and their results will be tabulated below. The spectrophotometric methods will be discussed in greater detail under stability constants.²⁵

<u>Workers</u>	<u>Method</u>	<u>Results</u>
Bray and Hershey ²⁶	electrode potential	$K_1 = 6 \pm 0.5 \times 10^{-3}$ u is 0 detn. $K_2 = 2 \times 10^{-5}$ calc.
Lamb and Jacques ²⁷	electrode potential	$K_1 = 2.5 \times 10^{-3}$ 3.3×10^{-4} M sol. $K_1 = 3.5 \times 10^{-3}$ u is 0 $K_3 = 4 \times 10^{-7}$ assumed $K_{\text{sp}}\text{Fe}(\text{OH})_3 = 1 \times 10^{-37}$ assumed
Rabinowitch and Stockmayer ²⁸	spectrophotometry	K_1 ca. 10^{-3} u varied
Olson and Simonson ²⁹	" "	$K_1 = 2.8 \times 10^{-3}$
Siddall and Vosburgh ³⁰	" "	$K_1 = 6.5 \times 10^{-3}$ 25°C and u is 0
Milburn and Vosburgh ³¹	" "	$K_1 = 6.3 \times 10^{-3}$ 25°C and u is 0

25. This paper pp. 15-23

26. Bray and Hershey, J. Am. Chem. Soc., 56, 1889 (1934)

27. Lamb and Jacques, *ibid.*, 60, 1215 (1938)

28. Rabinowitch and Stockmayer, *op. cit.* this paper note 22

29. Olson and Simonson, *op. cit.*, note 23

30. Siddall and Vosburgh, J. Am. Chem. Soc., 73, 4270 (1951)

31. Milburn and Vosburgh, *ibid.*, 77, 1352 (1955)

Lamb and Jacques thought that the orange-red color which develops in ferric solutions around pH 2-3, depending on the concentration, was due to colloidal ferric hydroxide. Rabinowitch and Stockmayer take issue with this view, saying, "As soon as the concentration of $\text{Fe}(\text{OH})_3$ exceeds 2×10^{-9} moles per liter, the original molecular solution transforms itself more or less rapidly into a colloidal solution or suspension." They believe the color is due to all species and particularly to FeOH^{2+} and $\text{Fe}(\text{OH})_2^{1+}$. Other workers quoted here who have used spectrophotometric methods evidently agree with Rabinowitch and Stockmayer. Their view is accepted and followed in this paper.

Part 3 Methods in Solution

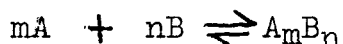
The general steps followed in studying complex and chelate compounds in solution are a repetition of those used for simpler compounds: determination of formula, calculation of stability constant and other thermodynamic functions, and comparison of stability with variations in structural groups. The methods for formulas and stability constants, however, are rather specific and deserve some detailed consideration.

One of the most commonly used methods for determining the empirical formula of a complex species in solution

was introduced by Job,^{32,33} and is known as Job's method or the method of continuous variation. It involves varying the concentrations of metal and chelating agent while the sum of the concentrations is kept constant, and then measuring some property characteristic of the chelate which should reach a maximum or a minimum at the ratio corresponding to compound formation. The property most used is light absorption, which can be measured with a spectrophotometer. It is best to use a wave length of maximum absorption. Martell and Calvin³⁴ mention other properties which have been used.

Harvey and Manning³⁵ have reviewed and compared some other "Spectrophotometric Methods of Establishing Empirical Formulas of Colored Complexes in Solution." These include:

1. Slope ratio method



$$\frac{\text{slope 1}}{\text{slope 2}} = \frac{n}{m}$$

$$\frac{E_d}{m} = \text{slope 1}, \quad \frac{E_d}{n} = \text{slope 2}$$

E = absorbancy, d = cell thickness

32. Job, Ann. chim., (10) 9, 113 (1928)

33. Martell and Calvin, op. cit., pp. 29-32

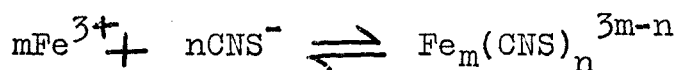
34. Martell and Calvin, op. cit., p. 72

35. Harvey and Manning, J. Am. Chem. Soc., 72, 4488 (1950)

2. Molar ratio method of Yoe and Jones³⁶

This method consists in keeping the metal ion concentration constant while varying the molar ratio of the chelating agent and measuring the absorbancy of each solution at a significant wave length. A break in the graph of absorbancy versus molar ratio corresponds to compound formation. Harvey and Manning find that these breaks are sharper when the ionic strength is controlled.

3. Method of Bent and French³⁷



$$K = \frac{(\text{Fe}^{3+})^m (\text{CNS}^-)^n}{[\text{Fe}_m(\text{CNS})_n]^{3m-n}}$$

$$\log [\text{Fe}_m(\text{CNS})_n]^{3m-n} = m \log (\text{Fe}^{3+}) + n \log (\text{CNS}^-) - \log K$$

If one ion is kept constant, the equation gives a straight line of slope m or n . According to Harvey and Manning, this is applicable only when the complex in solution is highly dissociated, which means at high dilution.

4. Molland³⁸ method

36. Yoe and Jones, Ind. Eng. Chem., Anal. Ed., 16, 111 (1944)

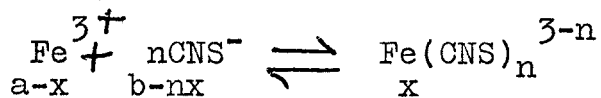
37. Bent and French, J. Am. Chem. Soc., 63, 568 (1941)

38. Molland, ibid., 62, 541 (1940)

In this method, solutions having different ratios but equal molar extinctions are related. Molland used it to find the formulas for iron and copper with 8-hydroxyquinoline 5-sulfonic acid.

5. Edmonds and Birnbaum³⁹ method

The equilibrium equation is set up for the case in which there is a large excess of the complexing species.



$$b \gg a \text{ or } x$$

$$\frac{(a-x) b^n}{x} = K$$

For a second solution where (CNS^-) is d and the complex concentration is y , we have

$$(a-x) b^n / x = (a-y) d^n / y$$

The value of n for which K is constant, is the quantity sought.

Vosburgh and Cooper⁴⁰ describe a spectrophotometric method, related to Job's method, whereby nickel is shown to combine with o-phenanthroline and ethylenediamine in 1:1, 1:2, and 1:3 proportions. In order to use this method,

39. Edmonds and Birnbaum, J. Am. Chem. Soc., 63, 1471 (1941)

40. Vosburgh and Cooper, *ibid.*, 63, 437 (1941)

there must be a marked difference in wave length of maximum absorbancy for each species and the wave length must be carefully chosen.

Martell and Calvin⁴¹ consider potentiometric titration the easiest and most accurate method for determining formulas. They describe Schwarzenbach's graphs and interpretations. It is not surprising that this is the method used by Chaberek and Martell⁴² in a series of articles on Stability of Metal Chelates. Several other methods are mentioned by Martell and Calvin⁴³, change of solubility being the only one of these which will apply to the present study.

Considering the relative merits of these methods, we find that Job's method is applicable if the solution obeys Beer's law or if the absorbancy due to any other species can be determined and subtracted from the total absorbancy. Molar ratio and slope ratio methods should apply whenever there is marked change in absorbancy with chelation. Potentiometric titrations require a break in

41. Martell and Calvin, op. cit., pp 39 - 46

42. Chaberek and Martell

I. J. Am. Chem. Soc., 74, 5052 (1952)

II. Ibid., 74, ~~5055~~ (1952) 5057

III. Ibid., 74, ~~6062~~ (1952) 6021

IV. Ibid., 74, 6228 (1952)

V. Ibid., 75, 2185 (1953)

VI. Ibid., 75, 2888 (1953)

43. Martell and Calvin, op. cit., chap. 2

the titration curve to show formula. If complexing takes place in a series of overlapping steps, such breaks will not appear but rather the curve will be characterized by a long sloping region similar to the buffer region of an acid-base neutralization graph. The choice of method depends upon the problem.

Martell and Calvin⁴⁴ devote a chapter to methods of calculating equilibrium constants. Rather than repeat their work, it would seem more fruitful to review the methods in the literature which might be applied to data collected from spectrophotometric and potentiometric determinations. These divide into:

1. Bjerrum method and modifications
2. slope-intercept method
3. method of corresponding solutions
4. substitution in the equilibrium equation if one term can be accurately measured and the others calculated by difference
5. Babko's dilution method

Bjerrum's⁴⁵ method, originally devised to find each step-wise constant for metal amines, has been adapted or

44. Martell and Calvin, op. cit., chap. 3

45. Bjerrum, J., Metal Ammine Formation in Aqueous Solution
P. Haase and Son, Copenhagen, 1941

reviewed by various investigators. Among these, Martell⁴⁶ has applied it successfully in finding the step-wise ionization constants of such chelating agents as ethylenediaminetetraacetic acid, EDTA, while Schwarzenbach⁴⁷, Calvin and Wilson⁴⁸, Chaberek and Martell⁴⁹, and Freiser Charles and Dwight⁵⁰ have used it to find chelate stability constants. All these authors give good explanations of the mathematical formulations. More general mathematical treatments of the method may be found in articles by Irving and Rossotti⁵¹ and Sullivan and Hindman⁵². In their article, Analysis of the General Mathematical Formulations for the Calculation of Association Constants of Complex Ion Systems, Sullivan and Hindman review three similar methods: Leden's, Bjerrum's and Fronaeus'. Bjerrum's is preferred.

Some of the essential points of Bjerrum's method, taken from Martell and Calvin⁵³, follow. A quantity \bar{n} is defined as the average number of ligands bound per central ion present.

46. Martell and Calvin, op. cit., pp 78-94

47. Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 31, 1029 (1948)

48. Calvin and Wilson, *J. Am. Chem. Soc.*, 67, 2003 (1945)

49. Chaberek and Martell, *ibid.*, 74, 5052 (1952)

50. Freiser, Charles and Dwight, *ibid.*, 74, 1383 (1952)

51. Irving and Rossotti, *J. Chem. Soc.*, (1954) 2905

52. Sullivan and Hindman, *J. Am. Chem. Soc.*, 74, 6091 (1952)

53. Martell and Calvin, op. cit., pp 79 - 81

$$\bar{n} = (C_A - (A)) / C_M$$

C_A = total conc. of
chelating agent

A = unbound chelating
agent

C_M = total conc. of
metal present

Omitting charges, the consecutive reactions can be shown.



$$K_1 = (MA) / (M)(A)$$



$$K_2 = (MA_2) / (MA)(A)$$

From the equation for K_1 , it is seen that when (MA) equals (M) ,

$$K_1 = 1/(A)$$

$$\log K_1 = \log 1/(A) = p(A)$$

This is true when one half the total metal has been converted to MA .

$$\text{Then } \bar{n} = (MA) / C_m = .5 / 1 = .5$$

Similarly when (MA_2) equals (MA)

$$K_2 = 1/(A)$$

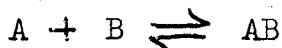
$$\log K_2 = \log 1/(A) = p(A)$$

This is true when one half the MA has been converted to MA_2 , and here \bar{n} is 1.5. Then K_1 and K_2 may be read from a graph of \bar{n} versus $p(A)$, K_1 being equal to $p(A)$ at \bar{n} equal .5 and K_2 being equal to $p(A)$ at \bar{n} equal 1.5.

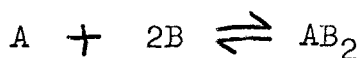
Such a graph is known as a "formation function".

Remembering that \bar{n} equals $(C_A - (A))/C_M$, it is obvious that the accuracy of this method depends upon the accuracy of the quantity (A). When A can be in large excess, errors in its determination will be less significant. Sometimes (A) can be determined from the appropriate acid dissociation constant of the chelating agent and the measured pH.

James I. Watters⁵⁴ has tabulated the slope-intercept methods for determining association constants for complex species in solution using spectrophotometric data. According to him, this method was introduced by Hildebrand and Benesi⁵⁵. Watters says, "This method is applicable if there is an extinction change due to complex formation and if the concentration of one species, B, can be established by other methods." Representing the reaction by



$$K_1 = (AB)/(A)(B)$$



$$K_2 = (AB_2)/(A)(B)^2$$

then the working equation, achieved by a series of substitutions, is in this case

$$\frac{[B]/(\epsilon - \epsilon_0)}{\text{(plot as y)}} = \frac{1}{(\epsilon_1 - \epsilon_0)K} + \frac{(\epsilon_1 - \epsilon_0)}{(\epsilon - \epsilon_0)} \frac{[B]}{\text{(plot as x)}}$$

(intercept) (slope)

54. Watters, private communication

55. Benesi and Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949)

If the function gives a straight line, the assumptions are "valid within this range of concentration,"⁵⁶ and K_1 is obtained by dividing the slope by the intercept.

$\bar{e} - e_0$ is the measured increase in molar extinction caused by complexing

In general, "The technique consists in plotting some function of the reciprocal of the extinction versus the known concentration of one reactant."⁵⁷

Most of the workers cited who determined the first hydrolysis constant for ferric ion by spectrophotometric means used this method. The equation of Rabinowitch and Stockmayer⁵⁸, also used by Milburn and Vosburgh⁶⁰, is

$$\bar{e} = d/c = e_{\text{Fe}^{3+}} + e_1 k_1 / h_0$$

\bar{e} = average molar extinction coefficient

d = A_s for 1 cm path

c = total Fe(III) conc.

$e_{\text{Fe}^{3+}}$ = extinction coefficient for Fe^{3+}

k_1 = first hydrolysis constant

h_0 = (H^+) of HClO_4 introduced

Inspecting the equation, it is seen that the average molar extinction coefficient, A_s/c , is plotted against the reciprocal of the hydrogen ion concentration. Siddall and Vosburgh⁶¹ reverse this and plot $1/A_s$ versus (H^+) .

56. Watters, op. cit.

57. Watters, ibid.

58. This paper, p 10

59. Rabinowitch and Stockmayer, op. cit., this paper note 22

60. Milburn and Vosburgh, op. cit., this paper, note 31

61. Siddall and Vosburgh, op. cit., this paper, note 30

Their equation is

$$1/d_h = 1/Ce_1 + (H^+) / C e_1 k_1$$

They make the approximation that

$$d_h = d, \quad (H^+) = h_0$$

All terms have the same meaning as above. They also state that Bjerrum's method cannot be used when polynuclear species are present. Milburn and Vosburgh⁶² believe that $(FeOH)_2^{4+}$ is present in solutions of Fe(III) more concentrated than 10^{-4} M.

For the method of corresponding solutions Bjerrum⁶³ gives

$$\bar{n} = (C'_A - A) / C'_M = (C''_A - A) / C''_M$$

If the numerator, which is MA, can be measured, the other term can be calculated and K found by Bjerrum's method or by the following equation given by Martell and Calvin.⁶⁴

$$K = (MKe) / (C_{M1} - (MKe))(C_{Ke1} - (MKe))$$

$$K = (MKe) / (C_{M2} - (MKe))(C_{Ke2} - (MKe))$$

Foley and Anderson⁶⁵ used this method for uranyl ion and Turner and Anderson used it for Cu(II) with sulfosalicylic

62. Milburn and Vosburgh, op. cit., this paper, note 31

63. J. Bjerrum, Chem. Abs., 40, 4590² (1946)

64. Martell and Calvin, op. cit., p. 98

65. Foley and Anderson, J. Am. Chem. Soc., 71, 909 (1949)

66. Turner and Anderson, ibid., 912 (1949)

acid. Turner and Anderson⁶⁷ found that FeOH^{2+} interfered with spectrophotometric data for Fe(III) and sulfosalicylic acid and were not able to calculate the equilibrium constant for that complex. This method did not give probable results in the present study, presumably for the same reason.

Hughes and Martell⁶⁸ present an interesting spectrophotometric method for calculating chelate stability constants based on Beer's law. They have applied it to EDTA chelates.

Babko's^{69,70} dilution method for K, while simple, gives results which Martell and Calvin say are approximations. The equation is

$$\Delta = \frac{\epsilon_1 - \epsilon_n}{\epsilon_1} = \left(\frac{K_d}{C_1} \right)^{1/2} (\sqrt{n} - 1)$$

$\Delta =$ fractional decrease in extinction coefficient in dilution of complex from C_1 to C_n

$K_d =$ dissociation constant

$n =$ dilution $= C_1/C_n$

It is noted that a deviation from Beer's law is used here.

The K values determined will be concentration constants and will vary with ionic strength. If stability constants are to be used to calculate other

67. Turner and Anderson, J. Am. Chem. Soc., 70, 1195 (1948)

68. Hughes and Martell, J. Phys. Chem., 57, 694 (1953)

69. Martell and Calvin, op. cit., p.99

70. Babko, Zavodskaya Lab., 13, 9 (1947)

thermodynamic properties, K_o , the true thermodynamic constant, based on activities, must be known. According to Martell and Calvin⁷¹, K_o may be calculated from the Debye-Hückel equation, or K_c may be determined at various ionic strengths and extrapolated to infinite dilution. They prefer the second method where complex ions are concerned, considering that their activities probably deviate from the equation used for simpler ions. Siddall and Vosburgh⁷² use the Debye-Huckel equation to find K_o . Their formulation is

$$\log K = 2.04\sqrt{u} / [1 + 2.5\sqrt{u}] = \log K_o + B u = \log K_o'$$

They made determinations at 26.6 degrees C and at 24.8 degrees C and corrected these for zero ionic strength. Using these K_o values, they then plotted $-\log K_o$ versus $1/T$ to find K_o at 25 degrees C. Milburn and Vosburgh⁷³, in a later paper, use the graphical method to find K_o , plotting $-\log K$ against $u^{\frac{1}{2}}$.

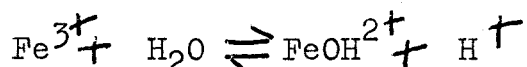
Theory demands that K_o be constant for a given ionic strength, since the activities of the species in the reaction will then be constant. There is rather persuasive evidence that this is not so for K_1 hydrolysis

71. Martell and Calvin, op. cit., pp. 131-133

72. Siddall and Vosburgh, op. cit., this paper note 30

73. Milburn and Vosburgh, op. cit., this paper note 31

of iron(III) ion. Olson and Simonson⁷⁴ have made a study of Salt Effects on Ionic Equilibria and say that they have proved, in the study of



that equilibria between ions of the same sign ~~are~~ not a function of ionic strength. The equilibrium does depend on the "concentration and character of ions of sign opposite to that of the reactants."⁷⁵ Rabinowitch and Stockmayer,⁷⁶ in their study of ferric ions already cited, seem to substantiate this view, stating that "lack of adherence to Beer's law means that K_h is not constant even when μ is constant." The best policy seems to be to state the exact conditions under which K is obtained.

Bjerrum⁷⁷ gives a formula for calculating the energy of exchange of water for a complexing ligand, saying that the free energy involved may be expressed as a function of

$$N/Z \log K + \log 55$$

N = no. of uniformly bound ligands

Z = characteristic coordination number

74. Olson and Simonson, J.Chem.Phys., 17, 348 (1949)

75. Olson and Simonson, loc. cit.

76. Rabinowitch and Stockmayer, op. cit., this paper note 22

77. Bjerrum, J., op. cit., this paper note 4

Schwarzenbach⁷⁸ says chelates have greater stability than simple complexes because the entropy term is more favorable, more water being displaced from the coordination sphere.

Various attempts have been made to predict chelate stability on the basis of the charge/radius ratio of the metal and the electron donating power of the ligand. Taylor⁷⁹ discusses the first property and Bjerrum⁸⁰ the second. Bjerrum states, however, that though these factors may play a part, "quantum-mechanical electron bonds" are also an important factor. In discussing the bond type he says "the solution lies in thermodynamics and spectra."

Whatever the explanation of stability in terms of bond type may be, structural changes which influence it have been studied and the results applied by analogy to other problems. The series of articles by Chaberek and Martell⁸¹ on Stability of Metal Chelates is closely related to this study. Our chelating agent is a polyhydroxydiamine; they are testing various compounds related to ethylenediaminetetraacetic acid. On testing the chelating ability of β -hydroxyethylimino diacetic

78. Schwarzenbach, *Helv.Chim.Acta*, **35**, 2344 (1952)
Chem. Abs., **47**, 3092^b (1953)

79. Taylor, *Va.J.Sci.*, **1**, 145 (1950)

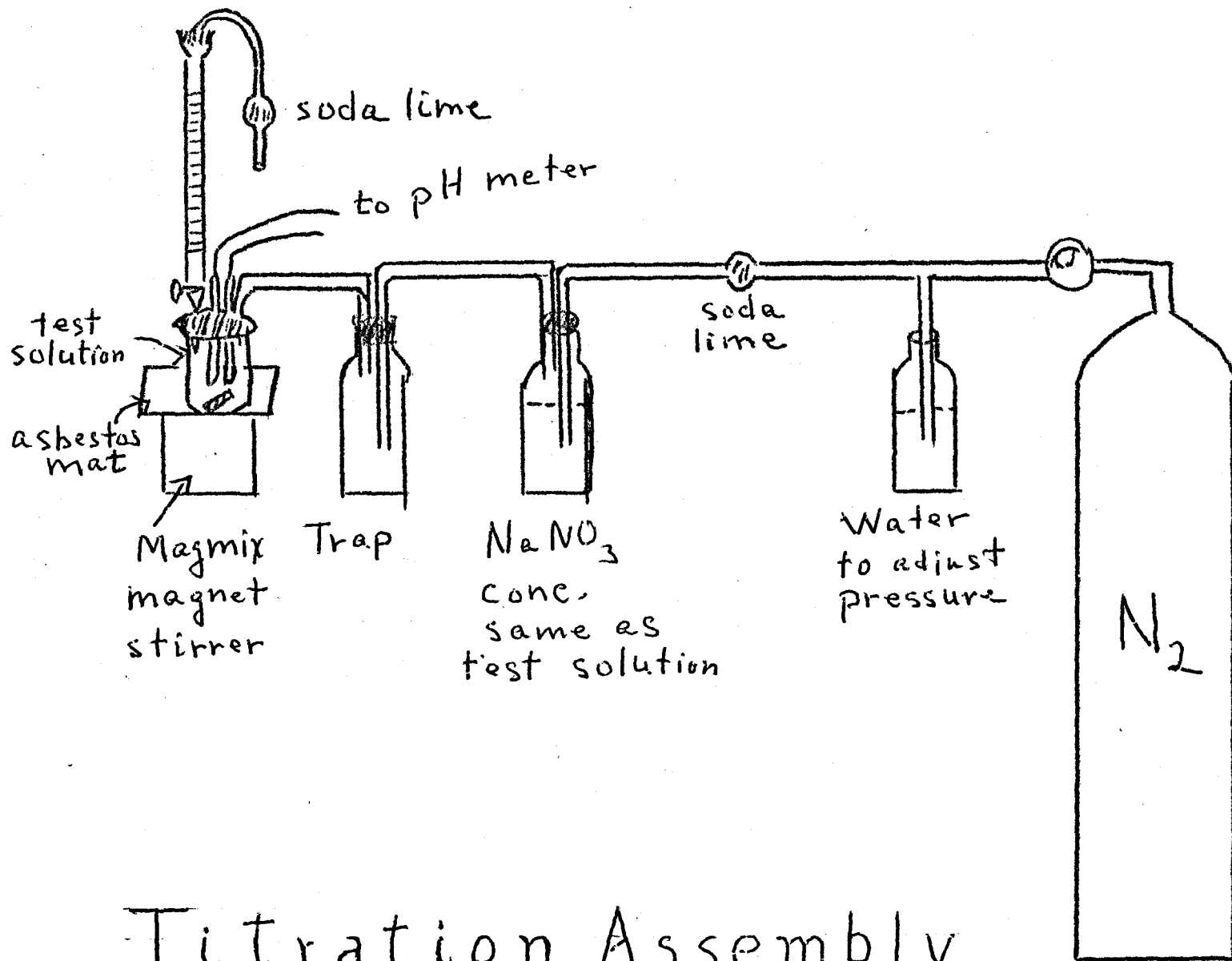
80. Bjerrum, *op. cit.*, This paper note 4

81. Chaberek and Martell, *op. cit.*, this paper note 42

E X P E R I M E N T

Potentiometric titrations were conducted in a beaker through which a stream of nitrogen gas was being passed. The nitrogen was pre-treated by passage first through a soda lime tube and secondly through a pre-saturator containing sodium nitrate of the same concentration as that in the test solutions. Carbon dioxide free sodium hydroxide solution was used in a 5 ml burette fitted with a soda lime tube. The Beckman G pH meter used was standardized frequently against a Beckman buffer solution, not diluted, and rated at pH $7.00 \pm .01$ at 25 degrees C, "based on U. S. Natl. Bureau of Standards Certified Buffers." The titration assembly is shown on the next page.

Spectrophotometric measurements were made in 1 cm cells, silica and corex, calibrated against each other throughout the wave lengths used. A section clarifying spectrophotometric terms is given on page 29.



Titration Assembly

86

Spectrophotometric terms according to Boltz:

Symbols suggested by the National Bureau of Standards and given below will be used in the discussion which follows.

$$A_s = \log I_0/I_s = a_s bc, \quad \log I_0/I = a_s bc$$

$T_s = T \text{ solution} / T \text{ solvent} =$ transmittance of solution

$A_s =$ absorbancy \approx D on instrument panel

$a_s =$ absorbancy index

$b =$ cell thickness (here in cm)

$c =$ conc. (here in moles per liter)

$a_m = \epsilon = A_s / bc_m =$ molar absorbancy index

$\epsilon =$ molar extinction and is more frequently used in the literature than a_m . It is included here because it may be necessary to refer to it when discussing the literature.

Conditions:

Water was all redistilled with $KMnO_4$ in a pyrex glass still.

Ionic strength was controlled by adding $NaNO_3$.

The highest ionic strength was .2 from .2 M $NaNO_3$.

Temperature varied from 25 - 30 degrees C. This

86. Boltz, David F., "Selected Topics in Modern Instrumental Analysis", Prentice-Hall, N.Y. 1952
p.112

variation has been compensated as ~~far~~ as possible by making comparisons under the same conditions or by running reference solutions along with the test solutions.

Apparatus:

Beckman G pH meter

Beckman D. U. spectrophotometer

Reagents:

$\text{Fe}(\text{NO}_3)_3$ B&A reagent grade, standardized by the Zimmermann-Reinhardt procedure

HNO_3 Mallinckrodt analytical reagent
.1 N dilution standardized against standard NaOH

NaOH reagent grade, made up CO_2 free, standardized against potassium acid phthalate, primary standard analytical reagent, Mallinckrodt

NaNO_3 Mallinckrodt analytical reagent

Disec Prepared and recrystallized according to directions of Dr. J. Stanton Pierce (87) quoted below

Preparation of 1,3-bis(tris(hydroxymethyl) methylamino) 2-propanol dihydrochloride

"Place 964 grams of tris(hydroxymethyl) methylamine (8 mols) and 800 ml of 95% alcohol in a 5 liter flask, fitted with a reflux condenser. A 3-neck flask is desirable and since epichlorhydrin is toxic, it is desirable to carry

87. Pierce, J.S., private communication

out the reaction under the hood. Add 280 ml epichlorhydrin through the side arm of the three-neck flask or through the condenser if the flask has only one neck. Heat on a water bath for six hours. Transfer contents to a 4 liter beaker. Add 500 ml 95% ethyl alcohol and 500 ml HCl conc., latter slowly, with stirring, since the product may foam vigorously. Cool. Filter with suction. Wash the precipitate with 95% ethyl alcohol.

Recrystallize from hot dilute alcohol. To do this, dissolve in the minimum quantity of hot water~~and~~ add hot alcohol. Complete precipitation takes place slowly so it is desirable to let the mixture stand for several hours before filtration. Disec can be recovered from the filtrate by adding approximately 70% by volume of acetone."

Disec is a white solid with melting point 184 - 186 degrees C, uncorrected. It is extremely soluble in water but not in alcohol.

Fresh solutions were prepared at frequent intervals.

Procedure:

Potentiometric titrations were conducted in a nitrogen atmosphere as already described and at total iron(III) concentrations from $5 - 25 \times 10^{-4}$ M. The ferric nitrate stock solution was .05 M with nitric acid added to make a solution approximately .1 N in nitric acid. An equal amount of concentrated nitric acid was added to the same total volume of water and standardized against standard NaOH. Its titer was .0906 N. This nitric acid solution was used to add to the solution of Disec alone and to add to the solutions of lower iron concentration so that the amount of nitric acid present at the beginning of each titration would be constant. Sample solutions will illustrate this.

Stock solutions	Test solutions		
	#1	#2	#3
Fe(NO ₃) ₃ .0505 M	2 ml	1 ml	0 ml
Disec .0505 M	2 ml	2 ml	2 ml
HNO ₃ .0906 M	0 ml	1 ml	2 ml
NaNO ₃ 2 M	4 ml	4 ml	4 ml
H ₂ O	32 ml	32 ml	32 ml

Such solutions were titrated with approximately .1 N NaOH solutions which had been standardized. Ionic

strength was varied. Comparisons were made between solutions containing Disec alone, as in #3, and ones containing Disec and ferric nitrate, as in #1 and #2, when sodium nitrate was constant.

Spectrophotometric readings were made on solutions of total iron concentration from 1×10^{-4} M to 5×10^{-3} M. The solutions were diluted a little below the final mark and pH was adjusted using a pH meter and a 1 N NaOH solution to a little below the desired pH if on the acid side and a little above if on the basic side. Final dilution was then made and a negligible volume of 1N base was used to effect the exact pH desired. Sample solutions will illustrate this.

Stock solutions	Test solutions		
	#1	#2	#3
Fe(NO ₃) ₃ .002 M	1 ml	1 ml	1 ml
Disec .002 M	0 ml	1 ml	3 ml
NaNO ₃ 2 M	2 ml	2 ml	2 ml
H ₂ O	17 ml	16 ml	14 ml

Solution #1, containing Fe(NO₃)₃ alone, could be prepared only at pH values less than 3.5. At wave lengths shorter than 360 mμ, nitrate absorbancy is measurable. Therefore its absorbancy was determined, using a solution of known NaNO₃ concentration, and absorbancy readings on test solutions were corrected accordingly.

T A B L E S A N D G R A P H S

T A B L E 1

Data for graph in Figure 1

Total iron (III) is 5×10^{-3} M No NaNO_3 added

Fe(III)/ Disec is 1/3

Absorbancy read on D.U.

$\lambda = \mu$	#1 pH 3.0	#2 pH 6.5	#3 pH 9.0
320	3.00	3.00 +	3.00 +
325	3.00	3.00 +	3.00 +
335	3.00 +	3.00 +	3.00 +
345	3.00 +	3.00 +	3.00 +
355	2.46	3.00 +	3.00 +
365	1.604	∞	∞
375	.924	∞	∞
385	.519	3.00 +	3.00 +
395	.279	3.00 +	2.81
405	.308	3.00 +	2.21
415	.088	2.37	1.51
425	.056	1.96	1.16
450	.028	1.18	.600
500	.009	.611	.294
550	0	.215	.100
600	0	.072	.041
700	0	.013	.011
950	.002	.015	.018

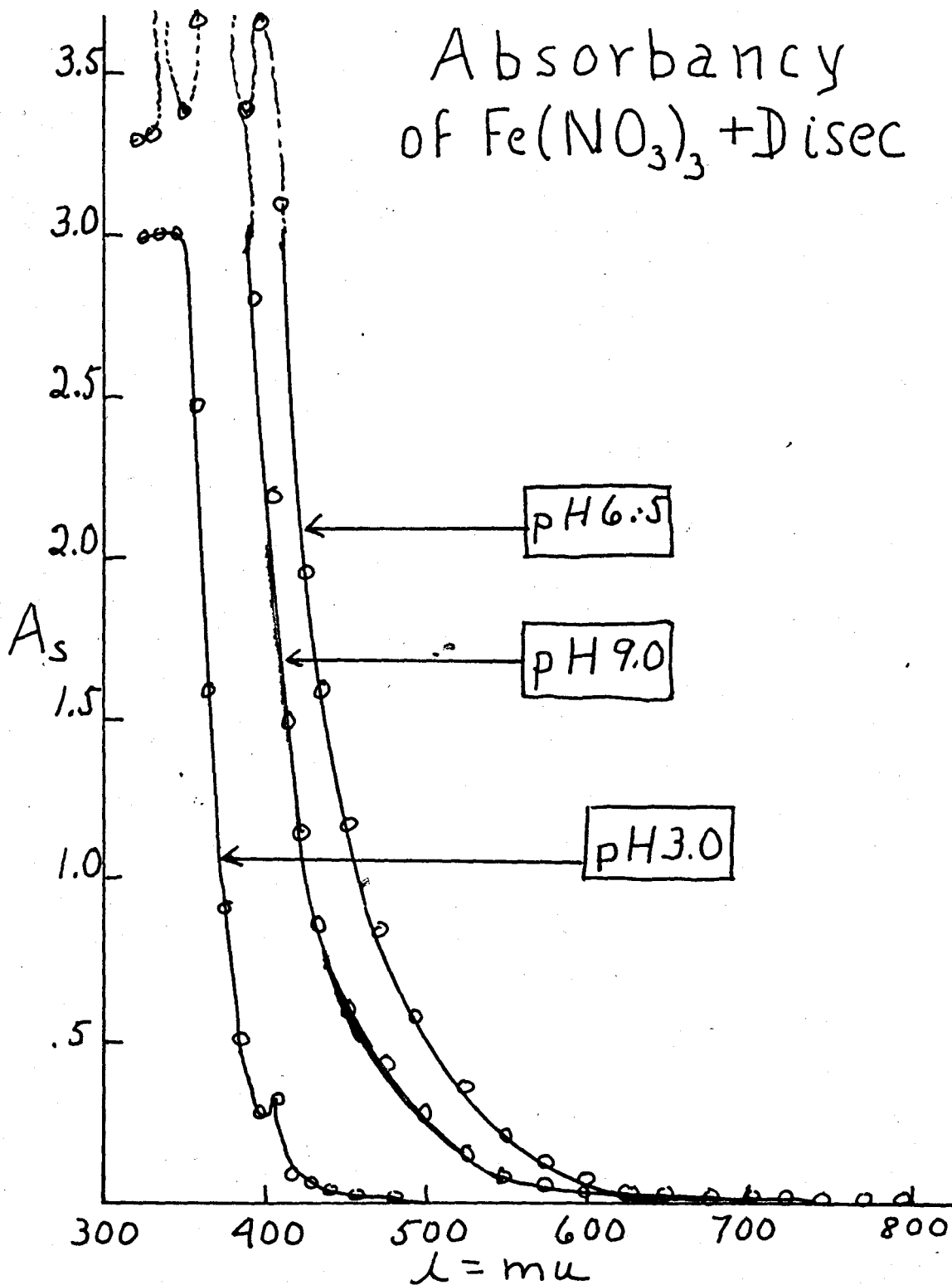


Figure. 1

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ and
 $\text{Fe}(\text{NO}_3)_3 + \text{Disec}$ pH=2.5

x = $\text{Fe}(\text{NO}_3)_3$ alone
o = $\text{Fe}/\text{Disec} = 1/1$
 $\Delta = \text{Fe}/\text{Disec} = 1/3$
 $\text{Fe}^{3+} = 10^{-4} \text{ M}$

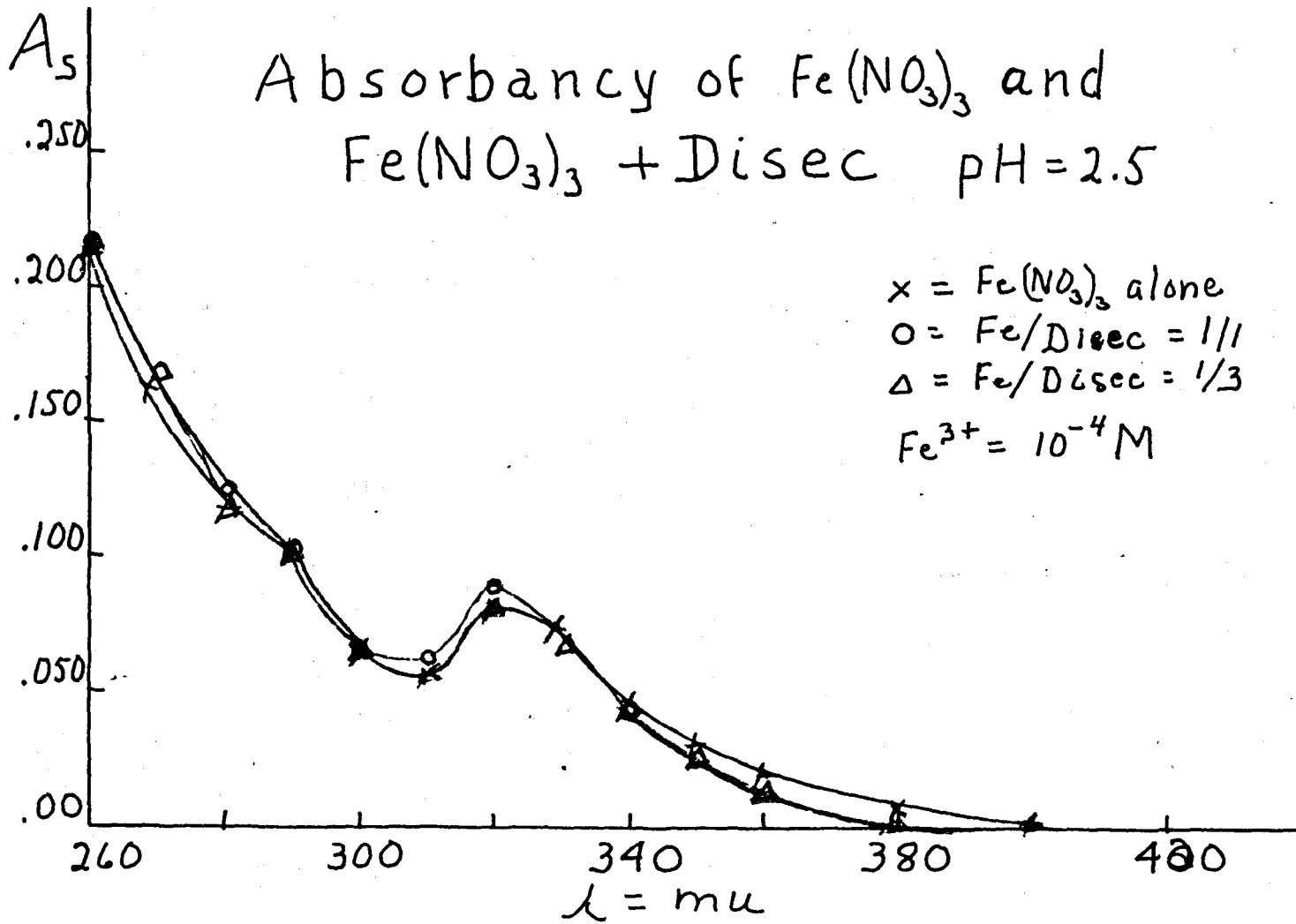


Figure 2

T A B L E 2

Data for graph in Figure 2.

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ at 27 degrees CFe(III) is 10^{-4} M, NaNO_3 is .2 M pH 2.5

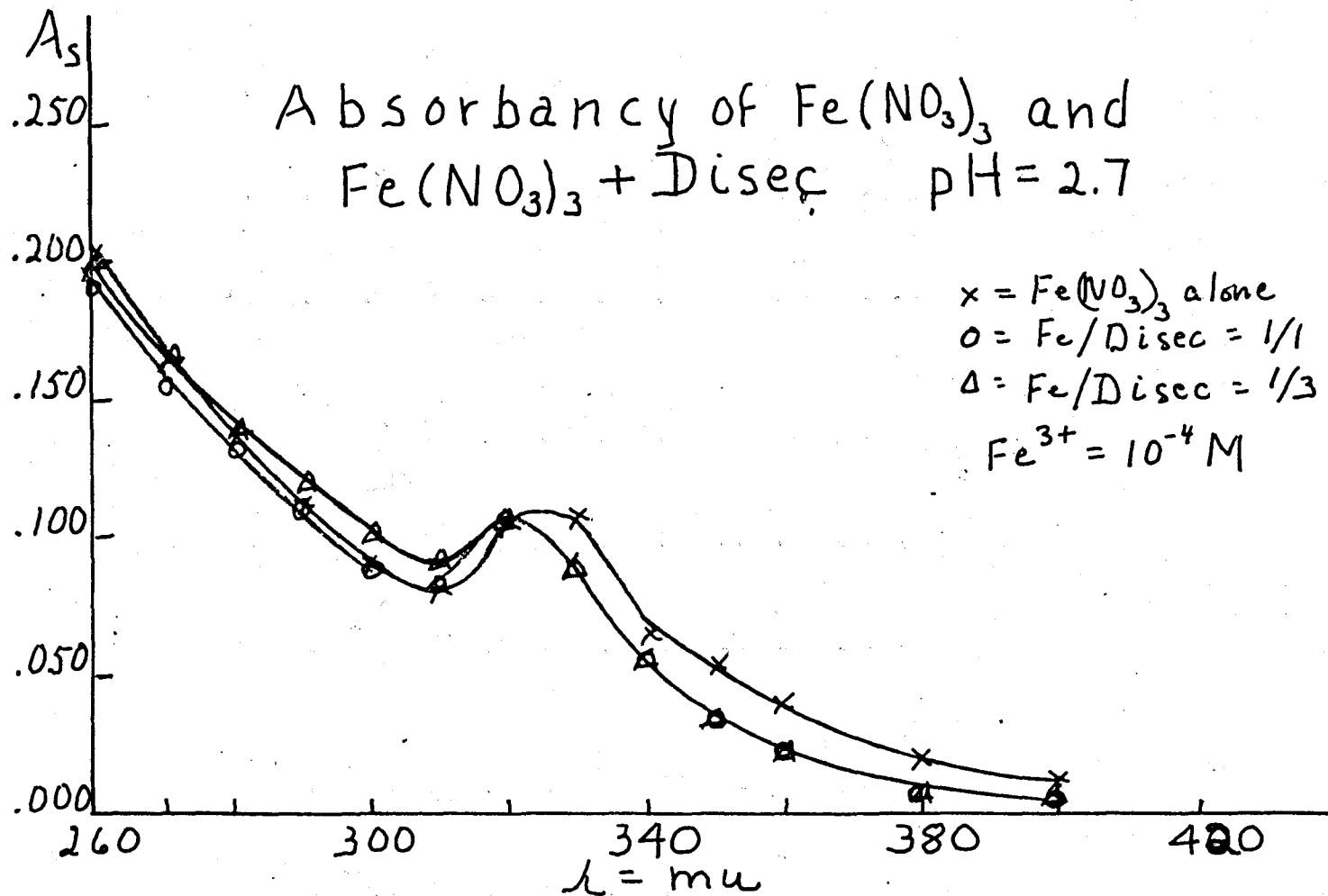
1 Fe(III) alone

#2 Fe(III) plus Disc 1/1

#3 Fe(III) plus Disc 1/3

<u>mu</u>	A_s	# 1		A_s	#2		A_s	#3	
		corrected	-		corrected	-		corrected	-
		cell	NO_3		cell	NO_3		cell	NO_3
260	.540	.539	.220	.541	.538	.219	.538	.537	.218
270	.578	.578	.166	.582	.580	.168	.571	.582	.170
280	.865	.866	.117	.873	.872	.123	.863	.865	.116
290	1.267,1.267,	.103		1.267,1.265,	.101		1.259,1.261,	.097	
300	1.540,1.540,	.064		1.540,1.539,	.063		1.540,1.542,	.066	
310	1.335,1.336,	.056		1.342,1.341,	.061		1.335,1.337,	.057	
320	.788	.784	.083	.788	.790	.089	.780	.783	.082
330	.269	.269	.075	.269	.266	.072	.263	.261	.067
340	.084	.084	.048	.081	.078	.042	.076	.074	.038
350	.038	.038	.031	.035	.032	.025	.031	.029	.022
360	.023	.022	.022	.019	.016	.016	.016	.016	.014
380	.009	.008	.008	.007	.005	.005	.004	.004	.002
400	.003	.004	.004	.001	.000	.000	.001	.000	.000

Figure 3



T A B L E 3

Data for graph in Figure 3.

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ at 27 degrees C

$\text{Fe}(\text{III})$ is 10^{-4} M, NaNO_3 is .2M pH is 2.71

#1 $\text{Fe}(\text{III})$ alone

#2 $\text{Fe}(\text{III})$ plus Disec 1/1

#3 $\text{Fe}(\text{III})$ plus Disec 1/3

The first column under each number shows absorbancy readings.

The second column gives the readings corrected for cell.

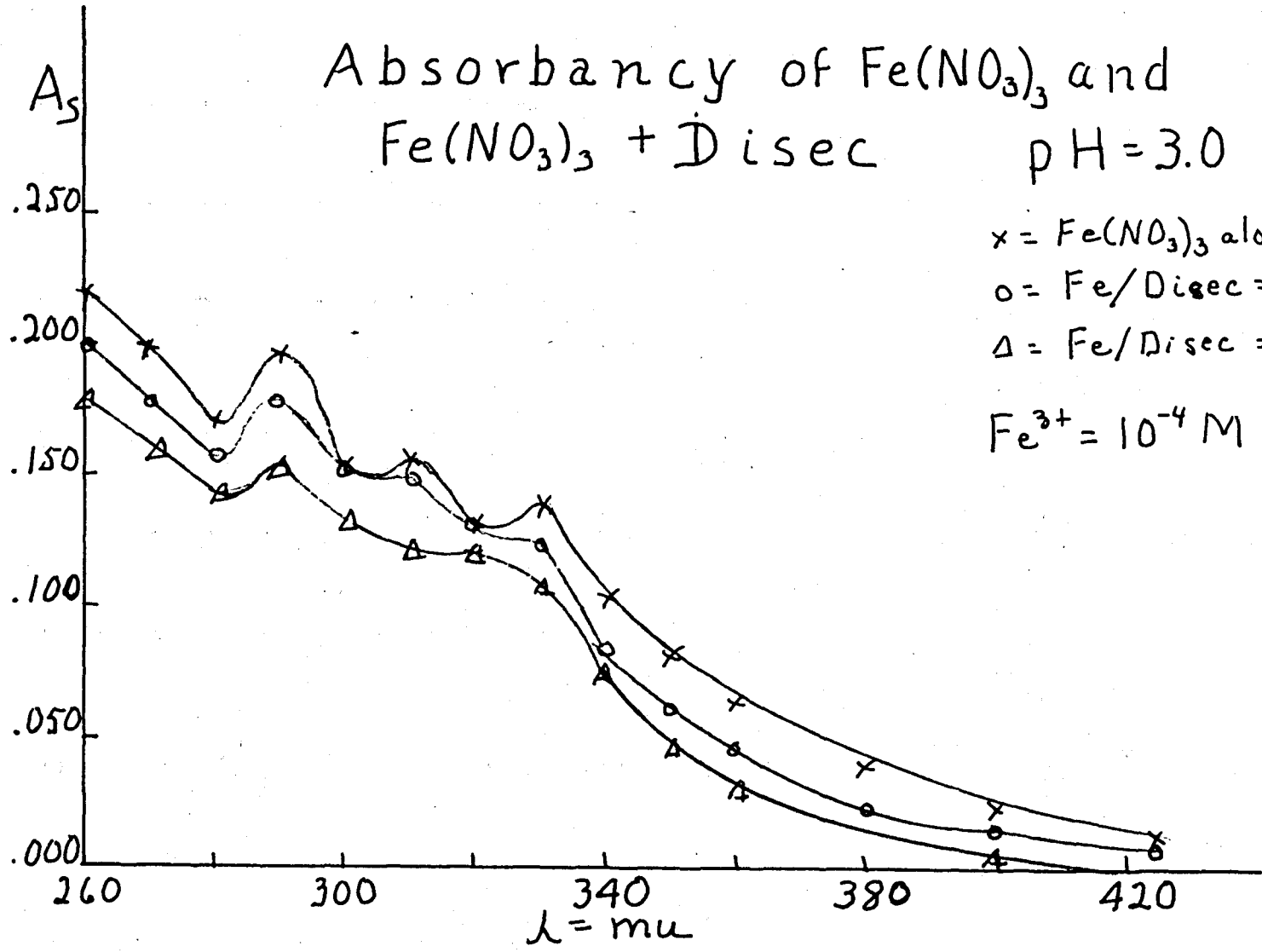
The third column gives the readings corrected for nitrate.

<u>mu</u>	<u>#1</u>			<u>#2</u>			<u>#3</u>		
260	.520	.519	.201	.517	.514	.196	.519	.518	.200
270	.577	.577	.165	.569	.567	.155	.569	.572	.160
280	.890	.891	.140	.886	.885	.134	.889	.891	.140
290	1.277	1.277	.113	1.277	1.275	.111	1.281	1.283	.119
300	1.561	1.561	.090	1.561	1.560	.089	1.571	1.573	.102
310	1.362	1.363	.081	1.366	1.365	.083	1.371	1.373	.091
320	.804	.801	.106	.800	.792	.107	.802	.799	.104
330	.302	.301	.109	.286	.281	.089	.283	.283	.091
340	.100	.099	.065	.092	.088	.055	.088	.089	.056
350	.062	.062	.055	.043	.040	.033	.039	.041	.034
360	.042	.042	.042	.025	.022	.022	.021	.023	.023
380	.022	.022	.022	.009	.007	.007	.006	.008	.008
400	.011	.013	.013	.006	.007	.007	.004	.007	.007

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ and
 $\text{Fe}(\text{NO}_3)_3 + \text{Disec}$ $\text{pH} = 3.0$

x = $\text{Fe}(\text{NO}_3)_3$ alone
 o = $\text{Fe}/\text{Disec} = 1/1$
 Δ = $\text{Fe}/\text{Disec} = 1/3$
 $\text{Fe}^{3+} = 10^{-4} \text{ M}$

Figure 4



T A B L E 4

Data for graph in Figure 4.

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ at 27 degrees C

$\text{Fe}(\text{III})$ is 10^{-4} M, NaNO_3 is .2 M pH is 3.00

#1 is $\text{Fe}(\text{III})$ alone

#2 is $\text{Fe}(\text{III})$ plus Disec 1/1

#3 is $\text{Fe}(\text{III})$ plus Disec 1/3

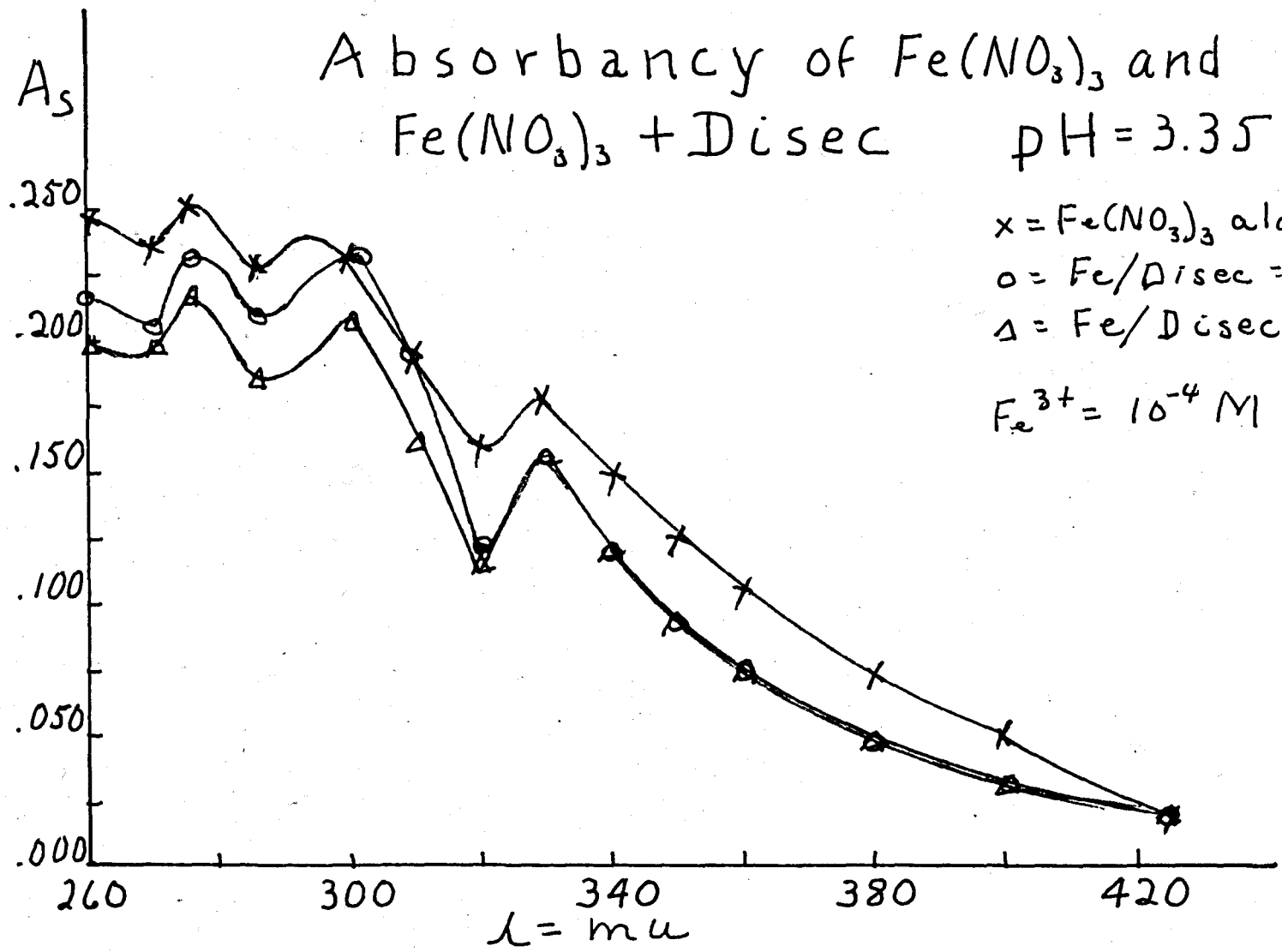
The first column under each number shows absorbancy readings.

The second column gives the readings corrected for the cell.

The third column gives the readings corrected for nitrate.

μ	#1			#2			#3		
260	.538	.537	.218	.518	.515	.196	.497	.496	.177
270	.610	.610	.198	.591	.589	.177	.569	.572	.160
280	.919	.920	.169	.909,	.908	.157	.890	.892	.141
290	1.359,1.359		.195	1.344,1.342		.178	1.316,1.318		.154
300	1.629,1.629		.153	1.628,1.627		.151	1.596,1.598		.132
310	1.437,1.438		.156	1.432,1.431		.149	1.400,1.402		.120
320	.830	.826	.131	.822	.824	.129	.811	.814	.119
330	.333	.333	.141	.317	.314	.122	.302	.300	.108
340	.137	.137	.103	.121	.118	.084	.112	.110	.076
350	.087	.084	.081	.068	.065	.058	.054	.052	.045
360	.065	.064	.064	.048	.045	.045	.033	.031	.031
380	.039	.038	.038	.025	.023	.023	.013	.011	.011
400	.023	.024	.024	.012	.013	.013	.003	.004	.004
425	.012	.013	.013	.005	.006	.006	.000	.000	.000

Figure 5



T A B L E 5

Data for graph in Figure 5.

Absorbancy of $\text{Fe}(\text{NO}_3)_3$ at 25 degrees C

$\text{Fe}(\text{III})$ is 10^{-4} M, NaNO_3 is .2 M pH is 3.35

#1 $\text{Fe}(\text{III})$ alone

#2 $\text{Fe}(\text{III})$ plus Disec 1/1

#3 $\text{Fe}(\text{III})$ plus Disec 1/3

The first column under each number shows absorbancy readings.

The second column gives the readings corrected for cell.

The third column gives the readings corrected for nitrate.

μ	#1			#2			#3		
260	.568	.565	.246	.534	.534	.215	.518	.519	.200
270	.650	.648	.236	.618	.617	.205	.603	.606	.194
275	.795	.793	.253	.771	.771	.231	.757	.757	.217
285	1.190,1.188		.288	1.168,1.168		.208	1.143,1.145		.185
300	1.710	1.709	.233	1.710	1.710	.234	1.682	1.684	.208
310	1.480	1.479	.197	1.470	1.471	.189	1.442	1.444	.162
320	.858	.853	.158	.821	.818	.123	.809	.806	.111
330	.378	.373	.181	.350	.349	.157	.344	.344	.152
340	.185	.181	.147	.153	.152	.118	.149	.150	.116
350	.134	.131	.124	.099	.099	.092	.096	.098	.091
360	.110	.107	.107	.076	.076	.076	.071	.073	.073
380	.076	.074	.074	.045	.045	.045	.043	.045	.045
400	.050	.051	.051	.030	.032	.032	.026	.029	.029
425	.031	.033	.033	.018	.020	.020	.016	.019	.019

Absorbancy of
 NaNO_3 .216M

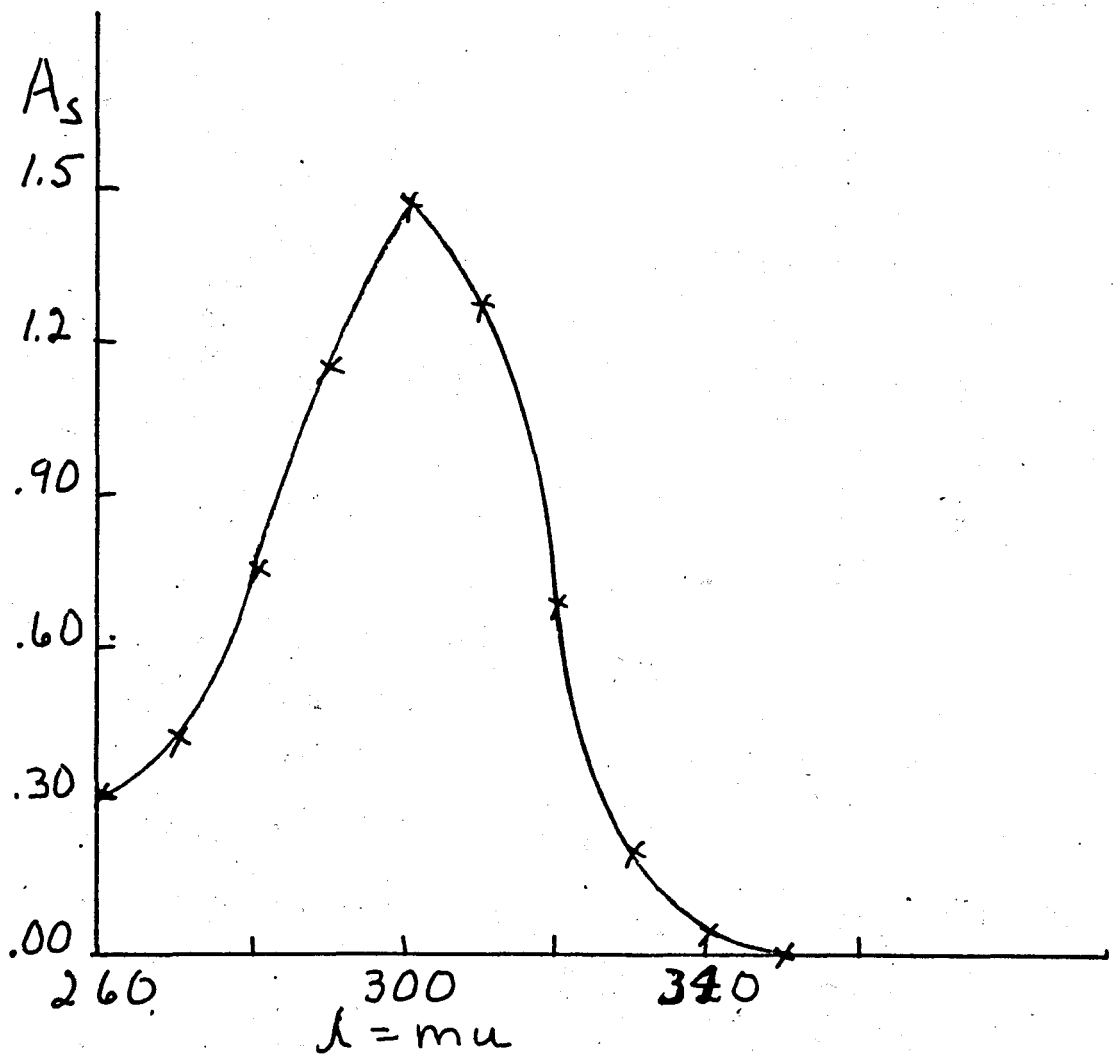


Figure 6

T A B L E 6

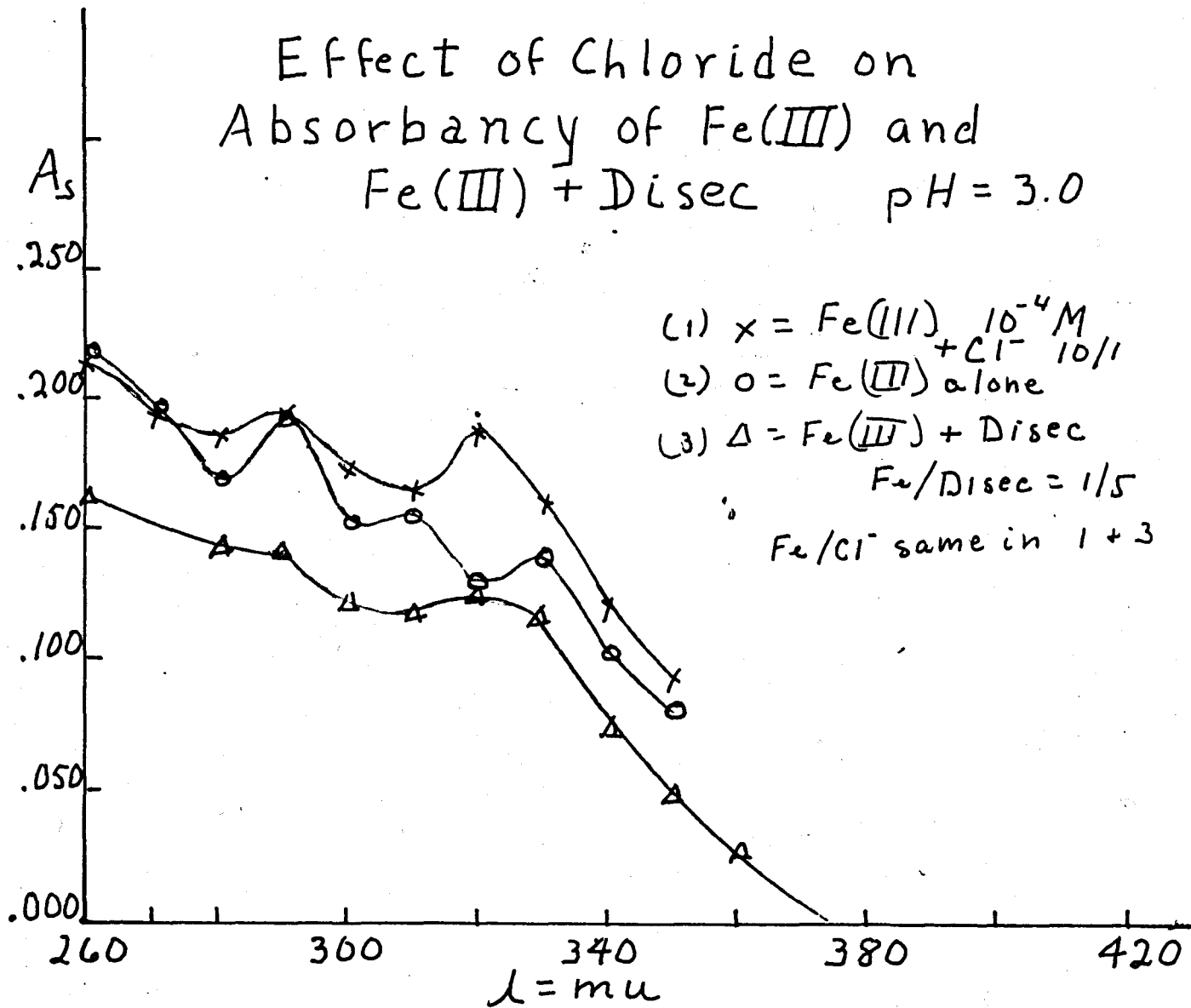
Data for graph in Figure 6.

Absorbancy for .2157 M NaNO_3 which is equal to the total nitrate content of the test solutions from $\text{Fe}(\text{NO}_3)_3$, HNO_3 and NaNO_3 . T is 27 degrees C

<u>mu</u>	<u>A_s</u>	<u>A_s - cell correction</u>
260	.320	.319
270	.412	.412
280	.750	.751
290	1.164	1.164
300	1.476	1.476
310	1.281	1.282
320	.698	.695
330	.193	.192
340	.035	.034
350	.007	.007
360	0	0

Effect of Chloride on
Absorbancy of Fe(III) and
Fe(III) + Disec pH = 3.0

Figure 7



T A B L E 7

Data for graph in Figure 7.

#1 Fe(III) alone $10^{-4}M$

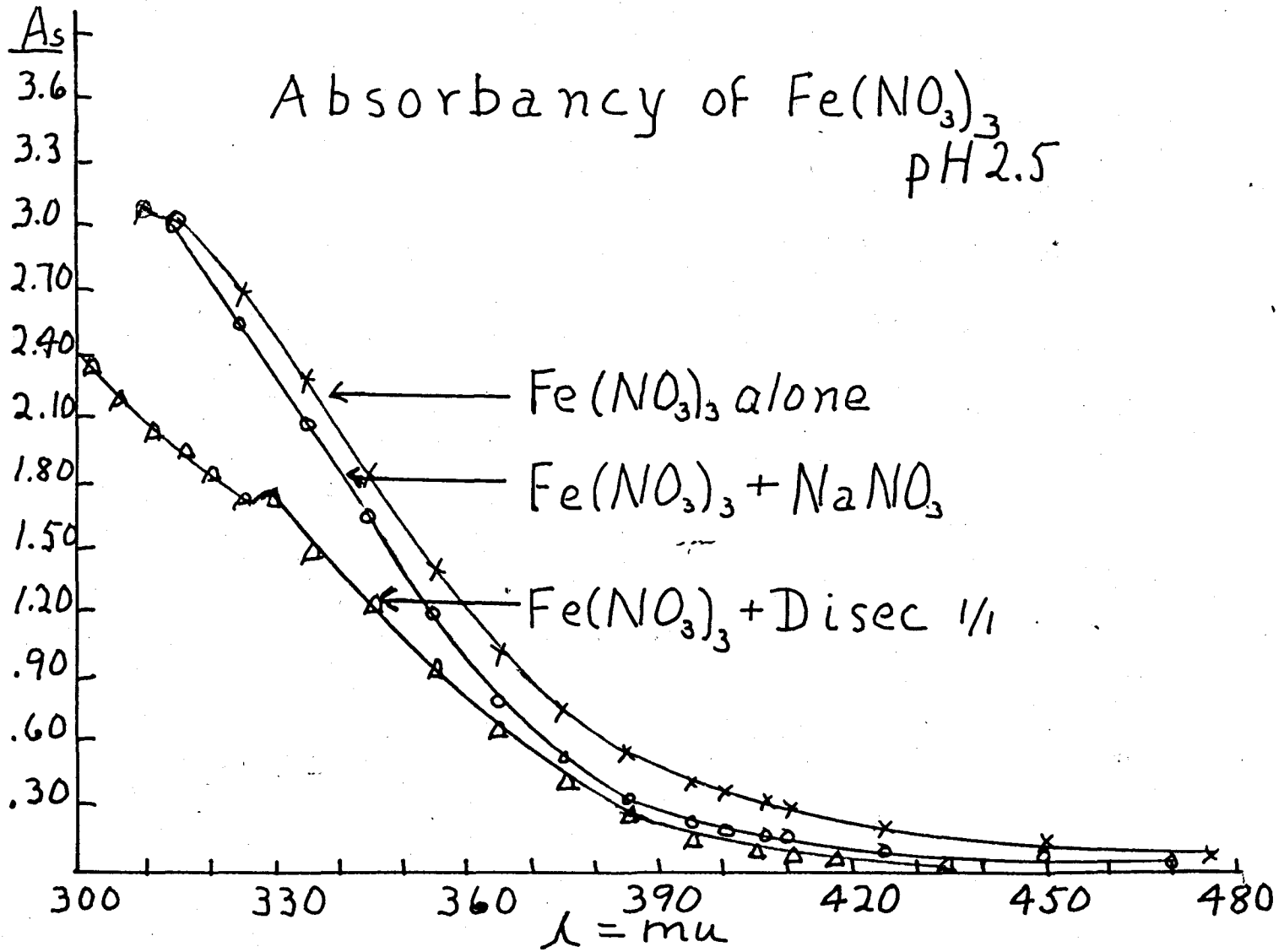
#2 Fe(III) plus Disec 1/5

#3 Fe(III) plus chloride 1/10

Absorbancy readings corrected for cell calibration and for nitrate absorbancy.

<u>mu</u>	<u>#1</u>	<u>#2</u>	<u>#3</u>
260	.218	.163	.213
270	.198	.155	.194
280	.169	.143	.186
290	.195	.142	.195
300	.153	.123	.174
310	.156	.117	.167
320	.131	.124	.189
330	.141	.118	.163
340	.103	.074	.121
350	.081	.048	.093

Figure 8



T A B L E 8

Data for graph in Figure 8.

A comparison of the effect of Disec with that of NaNO_3 on the absorbancy of $\text{Fe}(\text{NO}_3)_3$, 2.48×10^{-3} M at pH 2.5.

#1 $\text{Fe}(\text{NO}_3)_3$ alone

#2 $\text{Fe}(\text{NO}_3)_3$ plus NaNO_3 .125 M

#3 $\text{Fe}(\text{NO}_3)_3$ plus Disec 1/1

Nitrate absorbancy has not been subtracted but is zero at wave lengths longer than 350 μ .

<u>mu</u>	<u>#1</u>	<u>#2</u>	<u>#3</u>
305	> 3	> 3	1.94
315	3	3	1.71
325	2.54	2.7	1.72
335	2.08	2.28	1.42
345	1.65	1.86	0.93
355	1.20	1.42	0.64
365	.79	1.03	0.41
375	.503	.758	0.28
385	.327	.558	0.13
395	.222	.421	.073
407	.149	.313	.034
425	.096	.213	.012
450	.058	.131	.006

ABSORPTION OF $\text{Fe}(\text{NO}_3)_3$ -EFFECT OF PH

$\text{Fe}(\text{NO}_3)_3 = 1.24 \times 10^{-3} \text{ M}$

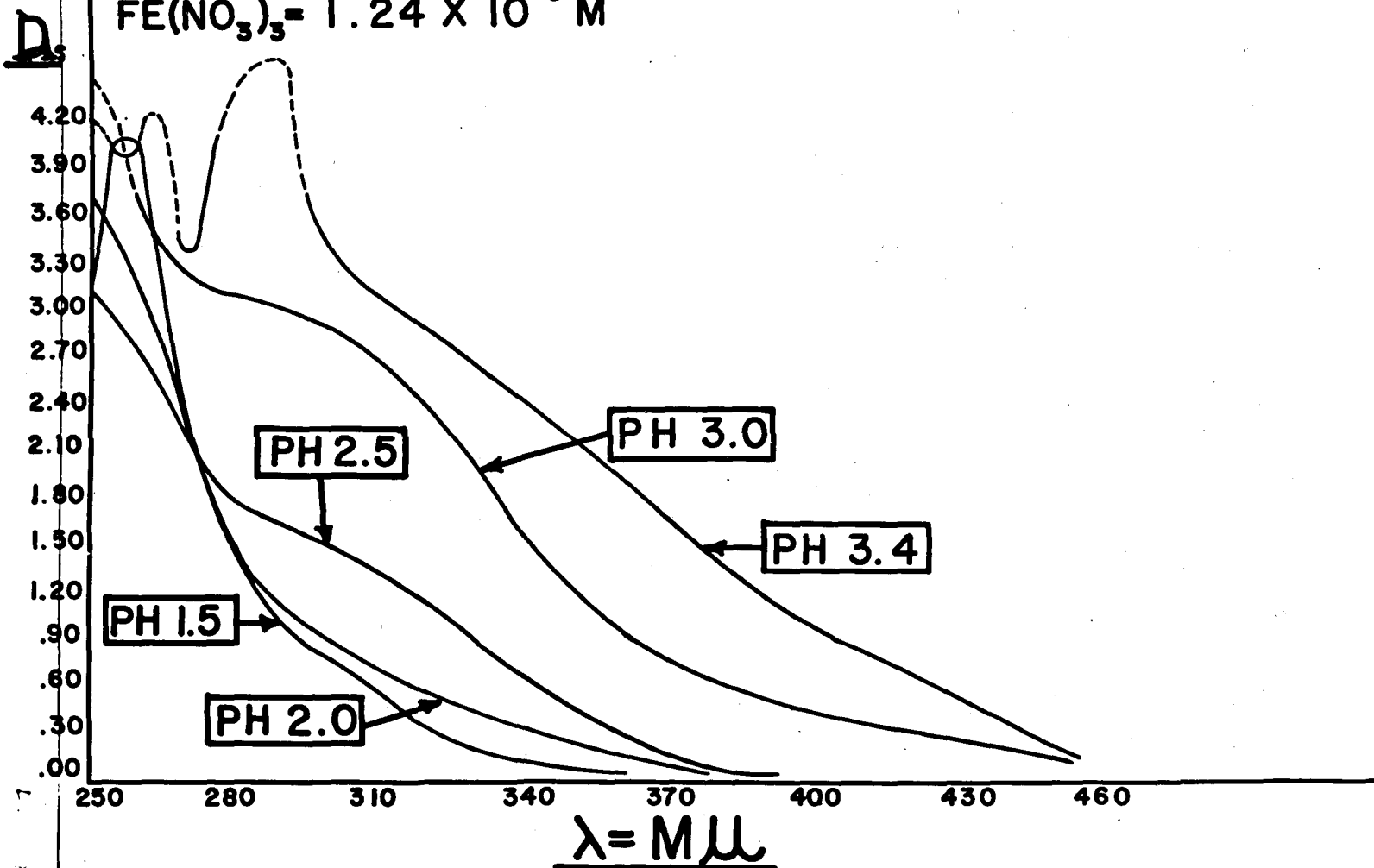


Figure 9

T A B L E 9

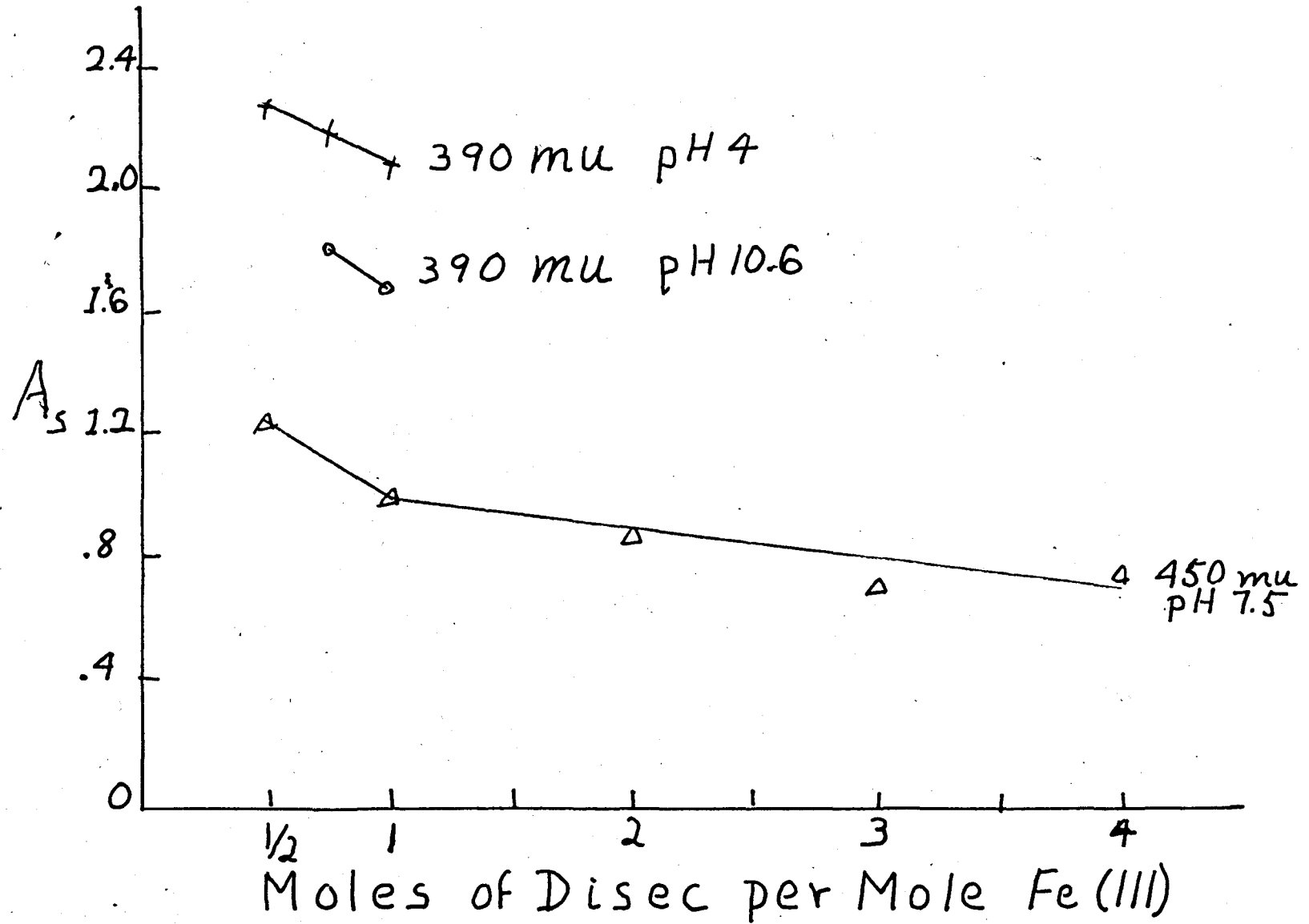
Data for graph in Figure 9.

Absorbancy readings, nitrate not subtracted but no NaNO_3 added.

$\text{Fe}(\text{NO}_3)_3$ 1.24×10^{-3} M at various pH

<u>mu</u>	<u>#1</u> <u>pH 1.5</u>	<u>#2</u> <u>2.0</u>	<u>#3</u> <u>2.5</u>	<u>#4</u> <u>3.0</u>	<u>#5</u> <u>3.4</u>
250	> 3	> 3	3	∞	∞
260	> 3	> 3	∞	> 3	> 3
270	2.35	2.19	∞	> 3	> 3
280	1.42	1.46	> 3	3	∞
290	0.95	1.10	> 3	3.00	∞
300	0.75	0.88	3	2.86	> 3
310	0.58	0.73	2.80	2.68	3.00
320	0.34	0.56	2.45	2.40	2.8
330	0.17	0.42	2.0	2.2	2.6
340	0.99	0.30	0.64	1.5	2.4
350	0.06	0.14	0.45	1.2	1.9
375	0.03	0.07	0.12	0.68	1.55
400	0.01	0.023	0.02	0.38	0.98
425			.003	0.23	0.63
450				0.15	0.40

Figure 10



T A B L E 10

Data for graph in Figure 10.

Absorbancy readings for molar ratio

$\text{Fe}(\text{NO}_3)_3$ 2.48×10^{-3} M

NaNO_3 .125 M

#1 pH 4 390 mu

1/½ 2.27

1/.75 2.21

1/1 2.07

#2 pH 10.6 390 mu

1/.75 1.808

1/1 1.677

#3 pH 7.5 450 mu

1/½ 1.25

1/1 1.02

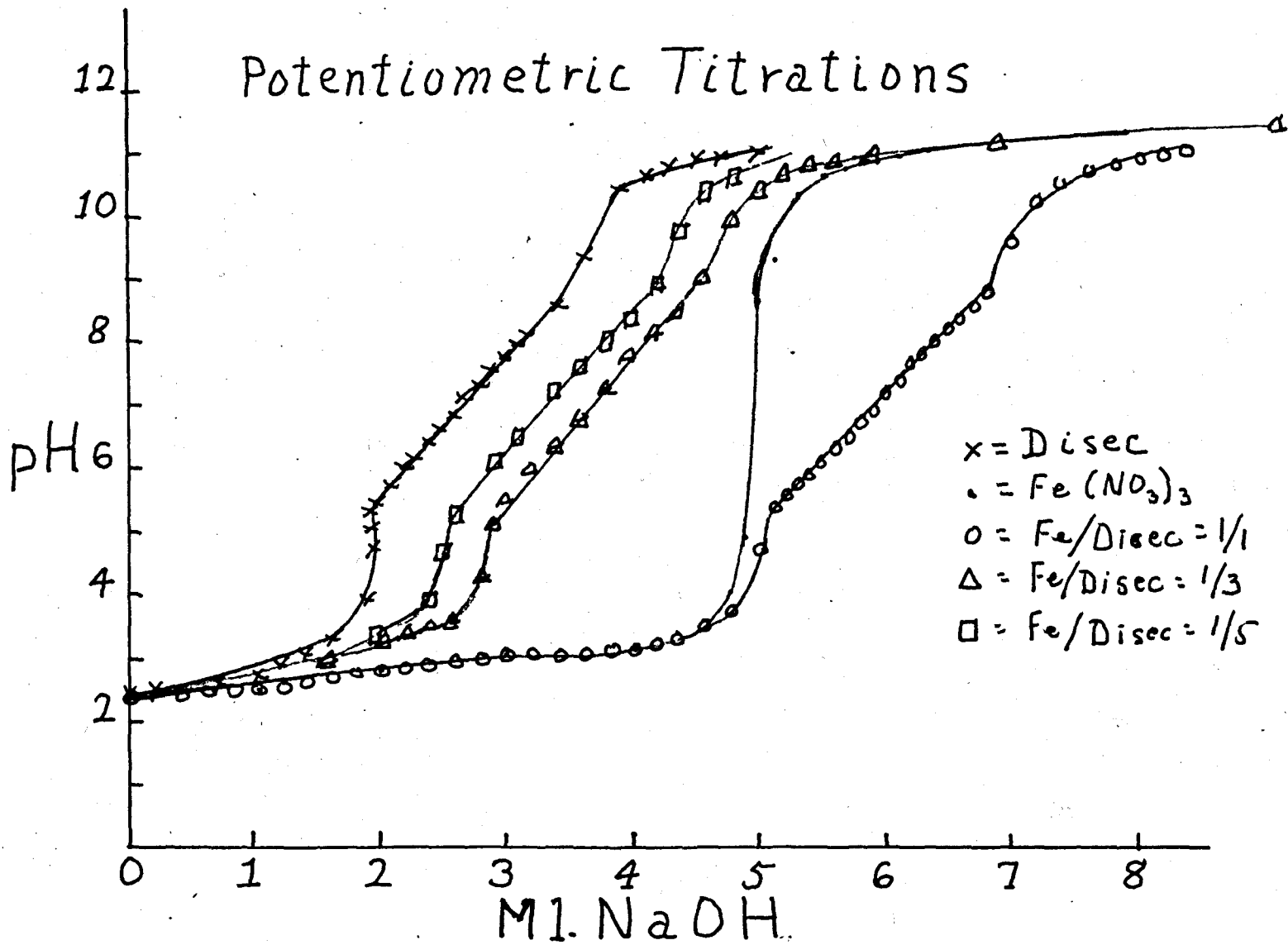
1/2 0.86

1/3 0.70

1/4 0.76

Potentiometric Titrations

Figure II



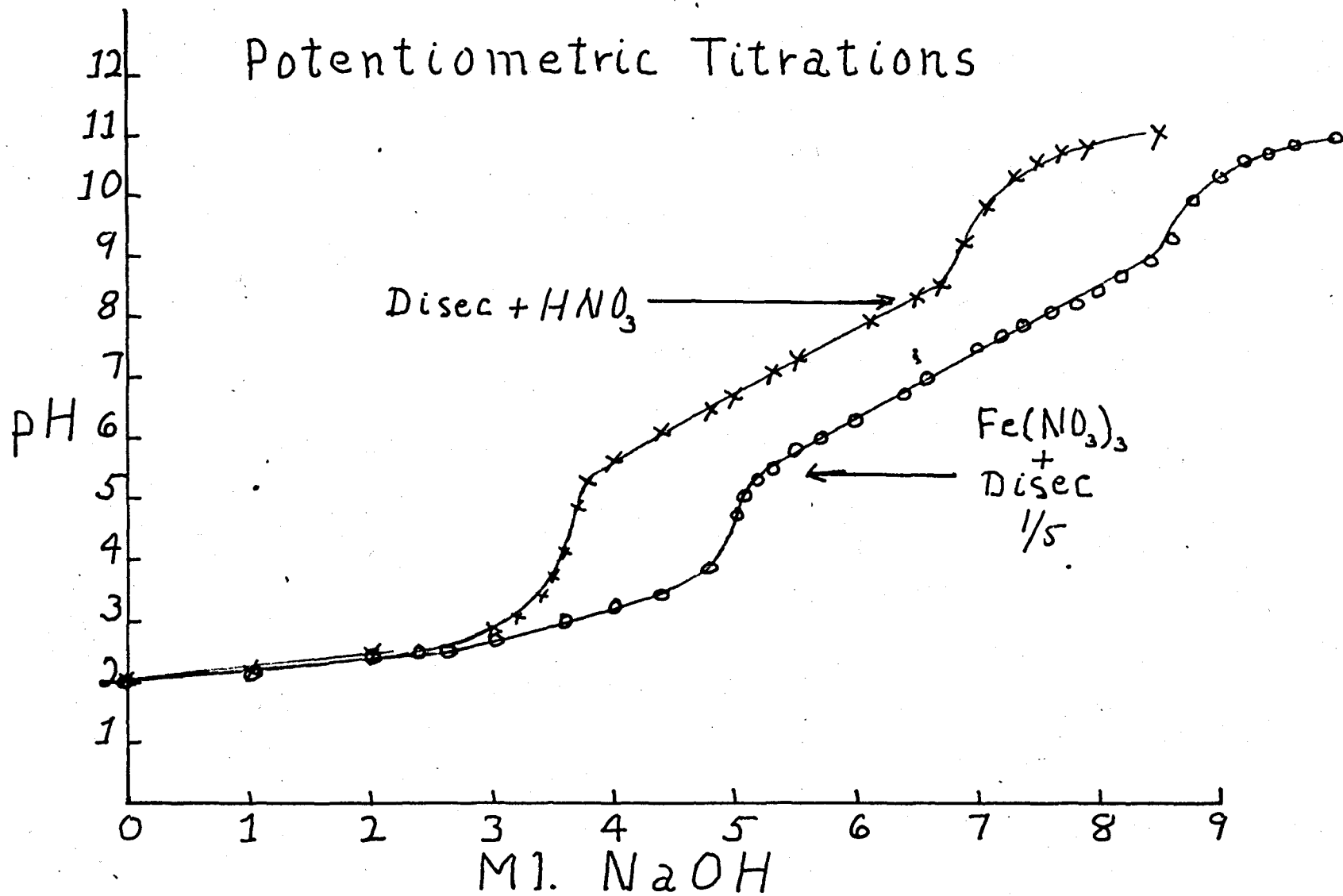
T A B L E 11

Data for graph in Figure 11.
 N_2 atmosphere $NaNO_3$.2 M

Readings are pH		Ratios are Fe(III)/ Disec			Fe is 2.5×10^{-5} M
<u>ML NaOH</u>	<u>Disec</u>	<u>Fe(NO₃)₃</u>	<u>1/1</u>	<u>1/3</u>	<u>1/5</u>
0	2.42	2.33	2.33	2.42	2.36
.2 0	2.48	2.38	2.35	2.46	2.40
.4 0	2.54	2.40	2.40	2.51	2.45
.60	2.61	2.42	2.43	2.57	2.52
.80	2.68	2.48	2.47	2.62	2.58
1.00	2.76	2.50	2.51	2.70	2.64
1.20	2.89	2.52	2.55	2.78	2.73
1.40	3.06	2.58	2.61	2.87	2.85
1.60	3.32	2.62	2.71	2.99	3.01
1.80	3.94	2.65	2.75	3.12	3.18
2.00	5.52	2.70	2.78	3.30	3.41
2.20	6.03	2.75	2.82	3.41	3.56
2.40	6.41	2.80	2.90	3.51	3.94
2.60	6.81	2.84	2.94	3.62	5.31
2.80	7.33	2.89	3.00	4.28	5.85
3.00	7.81	2.92	3.02	5.52	
3.20	8.12	2.98	3.03	6.00	6.71
3.40	8.53	3.01	3.04	6.37	7.26
3.60	9.35	3.06	3.08	6.82	7.66
3.80	10.4	3.09	3.09	7.35	8.06
4.00	10.5	3.16	3.12	7.80	8.38
4.20	10.7	3.22	3.21	8.16	8.88
4.40	10.85	3.30	3.30	8.49	9.82
4.60	10.95	3.50	3.48	9.02	10.40
4.80	11.00	4.00	3.78	9.98	10.62
5.00		8.64	4.59	10.43	10.8
5.20		9.75	5.47	10.68	10.88
5.40		10.5	5.91	10.82	10.95
5.60		10.7	6.29	10.90	11.02
5.80			6.70	10.98	
6.00			7.18		
6.20			7.60		
6.40			7.98		
6.60			8.37		
6.80			8.80		
7.00			9.55	11.2	
7.20			10.20		
7.40			10.49		
8.00			10.88		

Potentiometric Titrations

Figure 12



T A B L E 12

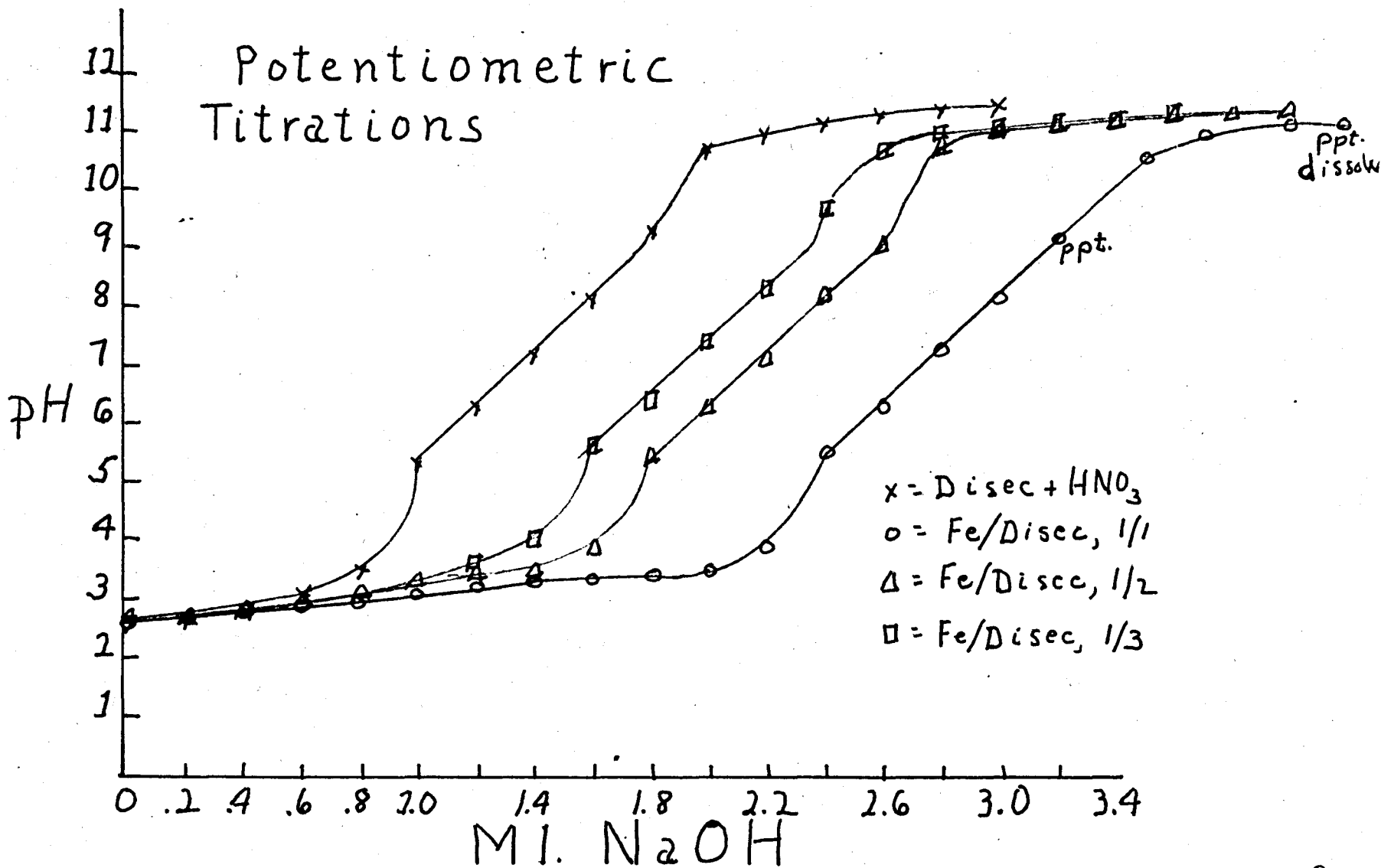
Data for graph in Figure 12.

N_2 atmosphere $NaNO_3$ is .2 M Fe(III) is ^{5.0}~~2.5~~ $\times 10^{-3}$ M

Readings are pH ratio is Fe(III)/ Disc

<u>Ml NaOH</u>	<u>Disc</u>	<u>1/5-</u>
0	2.10	2.11
.40	2.16	2.16
.80	2.22	2.21
1.00	2.25	2.23
1.40	2.32	2.30
1.60	2.39	2.32
2.00	2.47	2.41
2.40	2.60	2.51
2.80	2.78	2.62
3.00	2.90	2.70
3.40	3.40	2.89
3.60	4.15	3.01
3.80	5.24	3.13
4.00	5.60	3.27
4.20	5.85	3.35
4.40	6.06	3.42
4.80	6.44	3.83
5.00	6.67	4.75
5.10	6.78	5.05
5.30	7.06	5.50
5.50	7.32	5.80
5.70	7.54	6.00
6.00	7.85	6.29
6.20		6.46
6.30	8.12	
6.40		6.72
6.50	8.29	
6.60		6.97
6.70	8.49	
6.80		7.18
6.90	9.18	
7.00		7.46
7.10	9.82	
7.20		7.64
7.30	10.32	
7.40		7.84
7.60		8.02
8.00		8.40
8.40		8.87
9.00		10.32

Figure 13



ABSORPTION OF $Fe(NO_3)_3$ + DISEC. EFFECT OF PH.

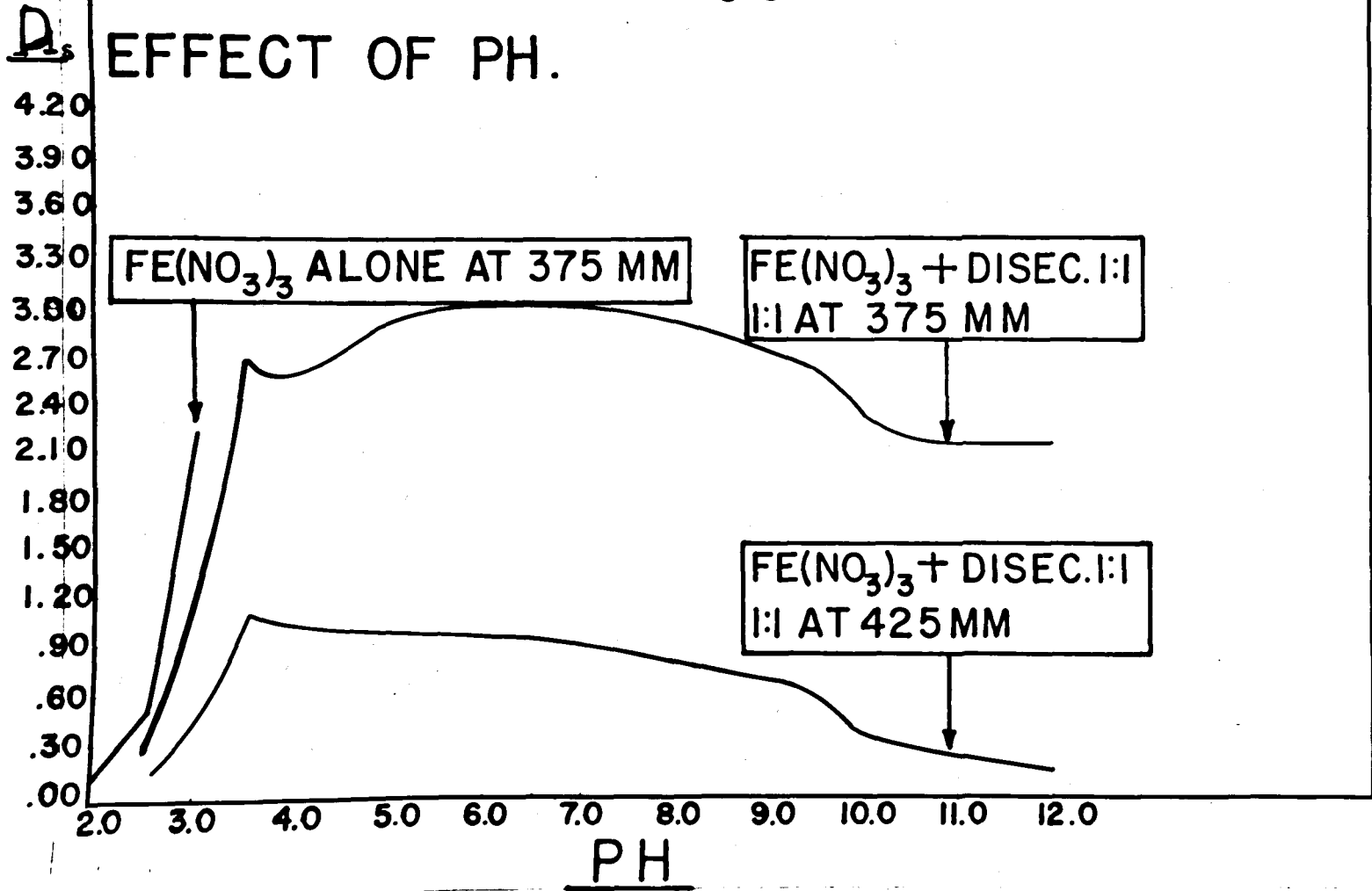


Figure 14

McE ALBERT 1947

EFFECT OF CHANGE OF PH ON ABSORPTION OF $Fe(NO_3)_3 + DISEC. 1:1$

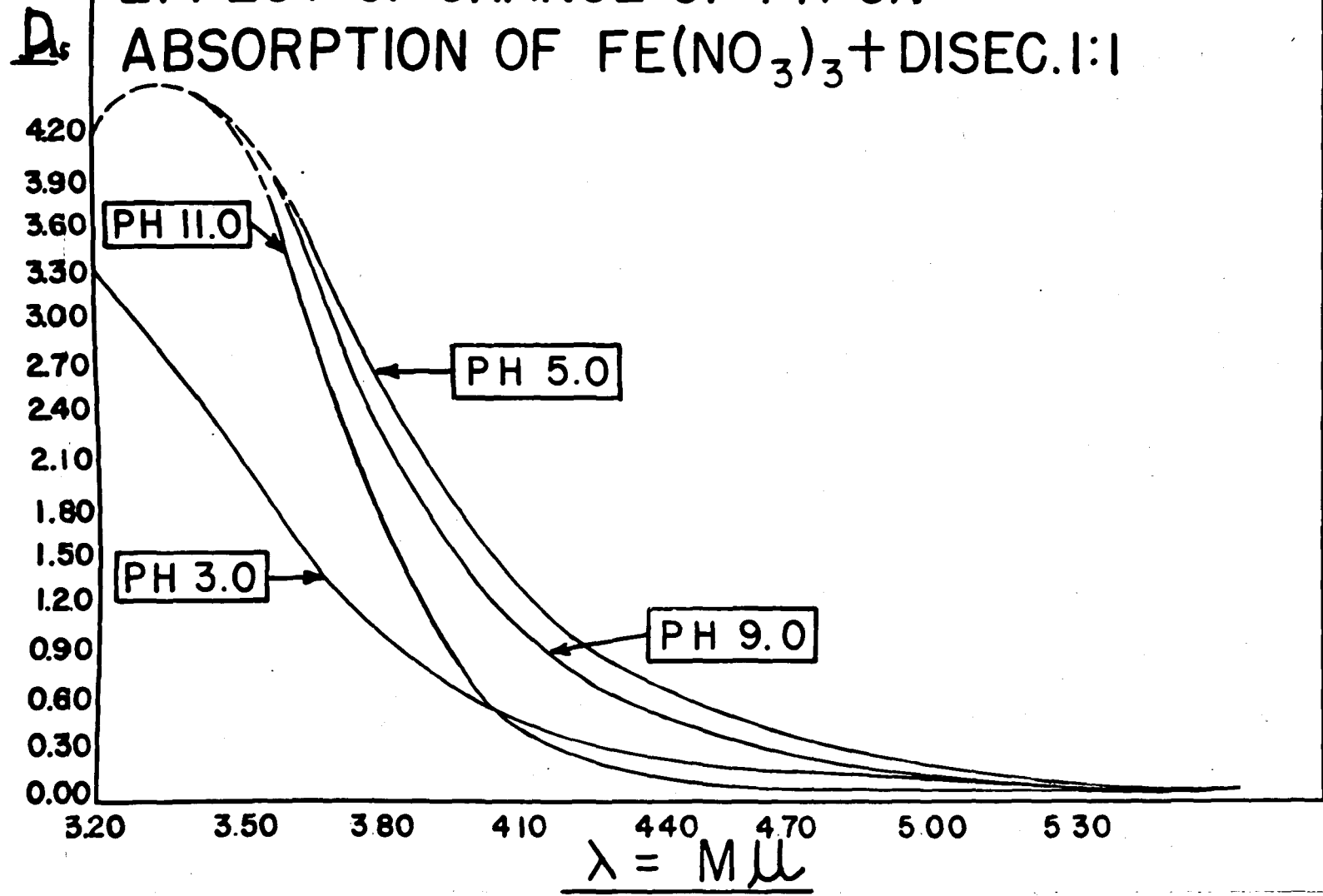


Figure 15

ICE ALBANY 1987

Figure 16

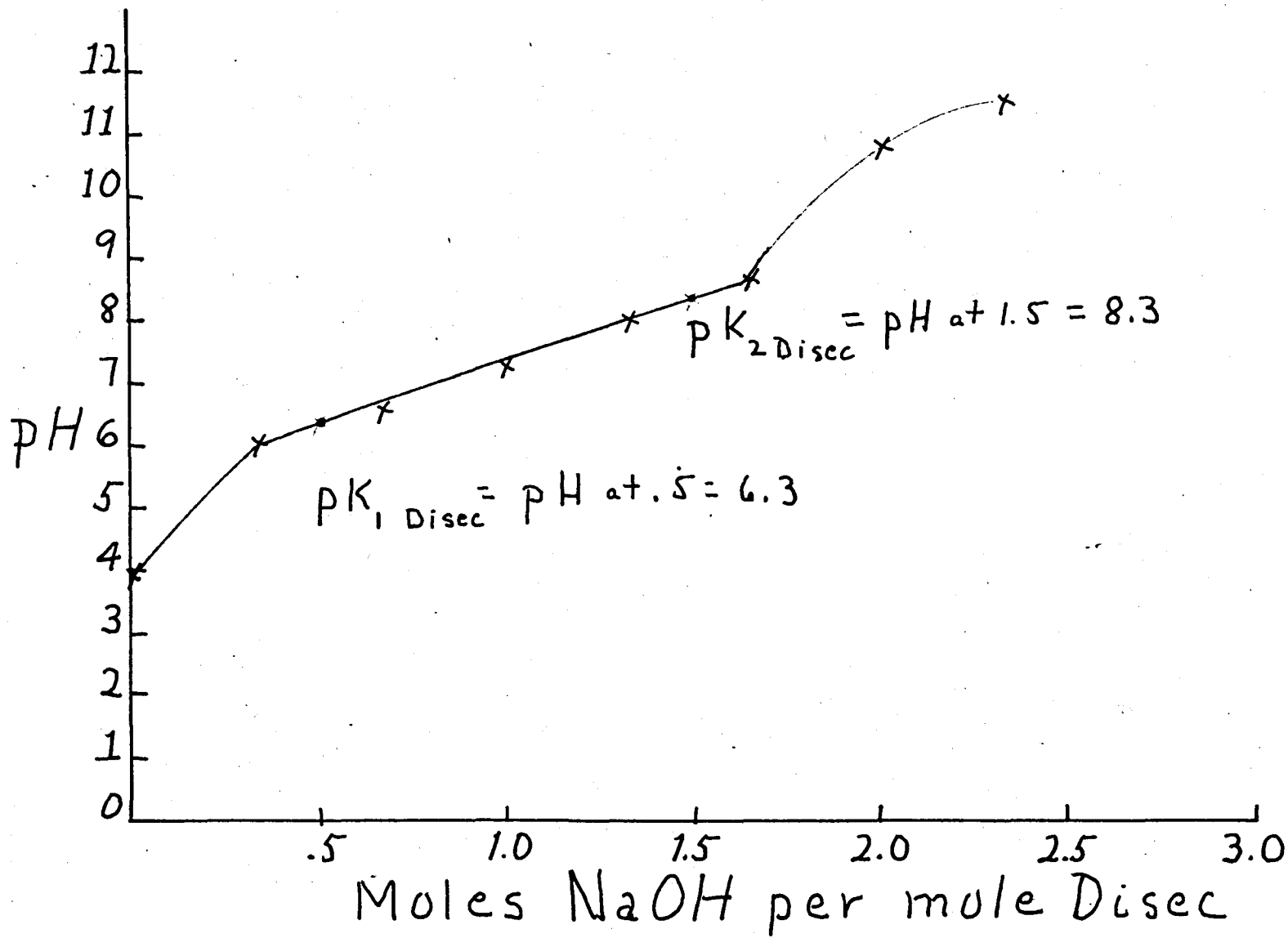


TABLE 13

Calculations for \bar{n} using graph in Figure 11 and Table 11.

pH	ml. base for Fe+Di	ml base for Di	ml base diff.	diff.	moles OH ⁻	\bar{n} E/3
	A	B	A-B = C	$C \times N_b$ D	D/.0338 E	
2.5	.36	.27	.09	.0089	.263	.088
2.7	1.00	.86	.14	.0138	.408	.136
2.9	1.45	1.19	.26	.0256	.707	.236
3.0	1.61	1.33	.28	.0276	.815	.272
3.2	1.88	1.50	.38	.0375	1.11	.370
3.4	2.18	1.62	.56	.0552	1.63	.543
3.5	2.38	1.74	.64	.0631	1.87	.623
3.8	2.65	1.76	.89	.0880	2.60	.866
4.0	2.71	1.80	.91	.0898	2.77	.923
4.3	2.80	1.82	.98	.0967	2.86	.953

Fe/ Di is 1/3

T A B L E 14

Calculations for p_{Di} ($-\log(\text{Disec})$) at various values of \bar{n} taken from Table 13.

\bar{n}	$\frac{A}{\bar{n} C_{Fe}}$	$\frac{B}{C_{Di} - A}$	Vol. % C	$\frac{(Di) \times 10^3}{B/C}$	$p(Di)$
.0888	.00297	.0990	40.36	2.45	2.61
.136	.00460	.0964	41.00	2.35	2.63
.236	.0080	.0930	41.45	2.24	2.65
.272	.0092	.0918	41.61	2.21	2.66
.370	.0125	.0885	41.88	2.12	2.67
.543	.0184	.0826	42.18	1.96	2.71
.623	.0211	.0779	42.38	1.87	2.73
.866	.0293	.0717	42.65	1.68	2.78
.923	.0312	.0698	42.71	1.63	2.79
.953	.0322	.0688	42.80	1.61	2.79

C_{Fe} is total moles Fe present in all forms

C_{Di} is total moles Disec present in all forms

$\bar{n} C_{Fe}$ is moles of Fe chelated or FeDi

$C_{Di} - \bar{n} C_{Fe}$ is moles of Disec not chelated

$$\log K = 2.70 \quad \text{here}$$

T A B L E 15

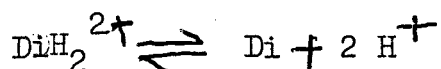
Calculations for $p(\text{Di})$ from $K_{\text{Disec}} = k_1 k_2 = 2.56 \times 10^{-15}$

\bar{n} from Table 14

\bar{n}	$\log(\text{DiH}_2^{2+})$	$\log K$	$2 \log (\text{H}^+)$	$p(\text{Di})$
.272	-2.66	-14.6	-6.0	11.26
.370	-2.67	-14.6	-6.4	10.87
.543	-2.71	-14.6	-6.8	10.51
.623	-2.73	-14.6	-7.0	10.31

At \bar{n} is .5 $p(\text{Di})$ is 10.60

$\log K_{\text{chelate}}$ is 10.60 from these figures



$$K = (\text{Di})(\text{H}^+)^2 / (\text{DiH}_2^{2+})$$

$$\log (\text{Di}) = \log K + \log (\text{DiH}_2^{2+}) - 2 \log (\text{H}^+)$$

For K_1 and K_2 of Disec, see Fig. 16

T A B L E 16

Calculations for Babko's dilution method for K using data from molar ratio, Table 10.

At pH 4.0 and 425 mu

$$\#1 \quad a_m = A_S/c = .519/1.24 \times 10^{-3} = 418$$

$$\#2 \quad a_m = A_S/c = .945/2.48 \times 10^{-3} = 381$$

$$\#3 \quad a_m = A_S/c = 1.815/4.96 \times 10^{-3} = 365$$

Using #3 and #1 and reversing the equation because molar extinction increases rather than decreasing with dilution, gives

$$(418 - 365)/418 = Kd^{\frac{1}{2}}/(1.24 \times 10^{-3})^{\frac{1}{2}} (4^{\frac{1}{2}} - 1)$$

$$Kd = 1.9 \times 10^{-5}$$

$$\underline{K = 5.3 \times 10^4}$$

At pH 10.5 and 400 mu

$$\#1 \quad a_m = 557 \quad c = 4.96 \times 10^{-3}$$

$$\#2 \quad a_m = 530 \quad c = 3.72 \times 10^{-3}$$

$$\#3 \quad a_m = 482 \quad c = 2.48 \times 10^{-3}$$

$$\#4 \quad a_m = 420 \quad c = 1.24 \times 10^{-3}$$

Formula not reversed here as a_m decreases with dilution.

$$(557 - 530)/557 = Kd^{\frac{1}{2}}/(4.96 \times 10^{-3})^{\frac{1}{2}} (1.33^{\frac{1}{2}} - 1)$$

$$\underline{K \cong 10^4}$$

See terms pp 22 and 29

Discussion of Data:

The questions to be considered are:

1. What is the empirical formula of the complex?
2. What functional groups of the chelating agent are involved in chelation and how many?
3. What is the stability constant of the chelate?

To find the formula, we might apply one or more of the methods discussed in the historical portion of this paper. Recalling that spectrophotometric methods are best applied at a wave length of maximum absorbancy, of the chelated species, such a wave length was sought by scanning the spectrum using solutions containing $\text{Fe}(\text{NO}_3)_3$ alone and $\text{Fe}(\text{NO}_3)_3$ with Disec at various concentrations and at various pH values. Also the absorbancy of solutions containing Disec alone was measured and found to be negligible. See Figures 1-5 for graphs of these results and Tables 1-5 for data. Figure 1 has not been corrected for nitrate; figures 2-5 have been.

When iron is 5×10^{-3} M, as in figure 1, absorbancy in the ultraviolet was so heavy that the maxima could not be measured at higher pH values. This absorbancy was measurable, though continually decreasing in the visible range, up to 500 mu. Since Milburn and Vosburgh⁸⁷

87. Milburn and Vosburgh, op. cit., this paper, note 29.

believe that the molar extinction of Fe (III) solutions at such concentrations is influenced by the presence of the dimer $(\text{FeOH})_2^{4+}$, which is not present at 10^{-4} M total iron (III) concentration, readings were taken at the lower concentration (figures 2-5) between 260 and 400 mu. Absorbancy was heaviest in the lower wave lengths, but unfortunately nitrate also showed heavy absorbancy here and it was found that iron-chloride complexes also interfered when Disec was five times the iron concentration. The Disec was a dihydrochloride salt, so this represented an iron/chloride ratio of 1/10.

Figure 6 shows the nitrate correction.

Figure 7 shows the effect of chloride.

Tables 6 and 7 give the corresponding data.

Inspection of these graphs shows that there is least interference, and that the results are most regular, when the spectra of iron alone and the iron-Disec chelate are compared at 330 mu and above. The main effect of Disec on the solutions seems to be the lowering of absorbancy at almost every wave length but no change in pattern of absorbancy over iron (III) alone at the pH values 2.5, 2.7, 3.0 and 3.35. This lowering increases with increasing pH. It is unlikely that this is a salt effect for two reasons. Sodium nitrate was .2 M in the solutions

represented in Figures 2-5. In Figure 8 it is shown that the lowering of absorbancy due to Disec is much greater than that due to the added sodium nitrate solution, even though the concentration of sodium nitrate is .125 M and that of Disec 2.48×10^{-3} M.

Before proceeding to try to use this knowledge of the spectrum in determining formula, it is of interest to compare the spectral pattern with the results of others. In Figure 1, at pH 3, the small sharp peak, mentioned by Rabinowitch and Stockmayer⁸⁸ as due to $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is evident at 407 mu and the maxima mentioned by them as occurring at 330-340 mu and at 375 mu due to FeOH^{2+} and $\text{Fe}(\text{OH})_2^{1+}$ are also apparent in this graph, at pH 6.5. The maximum at 330 mu, also present on graphs of Figures 2-5, is ascribed by Milburn and Vosburgh⁸⁹ to FeOH^{2+} and used by them to determine the first hydrolysis constant of iron (III). Another interesting spectral result is shown in Figure 9, the isosbestic point at 272 mu for Fe^{3+} and for FeOH^{2+} mentioned by Olson and Simonson.⁹⁰

88. Rabinowitch and Stockmayer, op. cit. supra, note 20

89. Milburn and Vosburgh, op. cit., note 2931

90. Olson and Simonson, op. cit., note 21

Having found that 330 mu and above are apparently the optimum wave length values to use in studying formula by a spectrophotometric method, which of the methods should be tried? Job's method was attempted at various wave lengths and at various pH values and found unsatisfactory for this problem. The change in absorbancy due to changing iron concentration obscured smaller changes due to chelation. It did serve to show that precipitation of $\text{Fe}(\text{OH})_3$ occurred whenever the ratio of Fe/Disec exceeded 1/1 by a significant amount.

Molar ratio method (Figure 10) shows a definite decrease in absorbancy to a 1/1 ratio, a break there and a more gradual decrease to 1/3. This might be interpreted as compound formation at 1/1 iron (III)/Disec and at 1/3. However, other data make it seem more probable that the formula is best represented as 1/1 and the slight extra decrease in absorbancy at 1/2 and at 1/3 ratios is due to an increased stability at the higher ratios. A series of spectrophotometric measurements was made at .5 pH intervals between pH 2.5 and pH 12 (meter readings not corrected) and at 1/1, 1/2 and 1/3 ratios of Fe (III)/Disec. The total Fe (III) concentration in each solution was 2.48×10^{-3} M. The readings were made between 320-550 mu. At each pH value

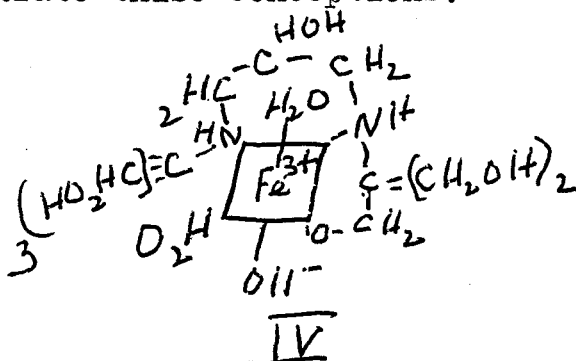
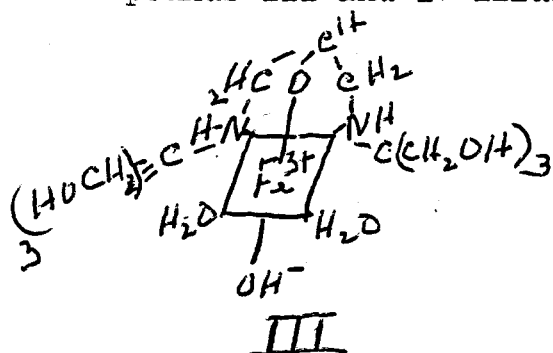
the absorbancy for 1/1, 1/2 and 1/3 ratios showed exactly similar patterns. Sometimes they coincided; sometimes there was slightly less absorbancy at the 1/2 and 1/3 ratios than at 1/1. Results from titration also are in agreement with this interpretation. Not only are the titration graphs the same shape at 1/1, 1/2, 1/3 and 1/5 ratios, but the extra base consumed by the iron-Diseac solutions, when compared with a solution containing Diseac alone with the same amount of nitric acid, is approximately the same, per mole of iron present, at all ratios studied.

See Figures 11-13 for titration graphs and tables 11-13 for the data.

To sum up, precipitation, molar ratios, titration and spectrophotometric pattern all point to a 1/1 compound.

The second question is concerned with the structure of the chelate. Diseac has two secondary amine groups, six primary alcohol groups, and one secondary alcohol group. Through which of these is it attached to iron? Using the horizontal distance at the same pH value between the titration curve for Diseac alone and for Diseac plus $\text{Fe}(\text{NO}_3)_3$, the amount of base used per metal ion present was calculated for each curve over the chelating area.

The results show that 3.03-3.37 moles of base were used per mole of iron. This would indicate a terdentate chelate. The excess base might be involved in further hydrolysis. If terdentate, what groups are chelated? An obvious choice is the two amine groups plus the propandiol group or one of the other alcohol groups. Compounds III and IV illustrate these conceptions:



The amine groups appeal because they are much more highly ionized than the alcohol groups. An OH^- group is shown on one coordination position of iron because calculations from the first hydrolysis constant show that at pH 2.33 and total iron concentration 2.5×10^{-3} M and $\alpha = .2$, FeOH^{2+} is 1.015×10^{-3} M. The hydrolysis constant was taken from Milburn and Vosburgh's⁹¹ graph of $K_1 \text{FeOH}^{2+}$ versus ionic strength. It was calculated to

91. Milburn and Vosburgh, op. cit., this paper, note 29

be 3.16×10^{-3} at $u = .2$. The pH value 2.33 was chosen as it was the lowest at which a titration was started. Apparently $\text{Fe}(\text{OH})_2^{1+}$ forms above pH 2.5, as the isosbestic point, which Olden and Simonson⁹² claim means that the two species Fe^{3+} and FeOH^{2+} are the main ones present, is lost above this pH. See Figure 9, 272 mu. Calculations for FeOH^{2+} present in 2.5×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ solution at pH 2.33:

$$K_1 = \frac{(\text{FeOH}^{2+})(\text{H}^+)}{(\text{Fe}^{3+})}$$

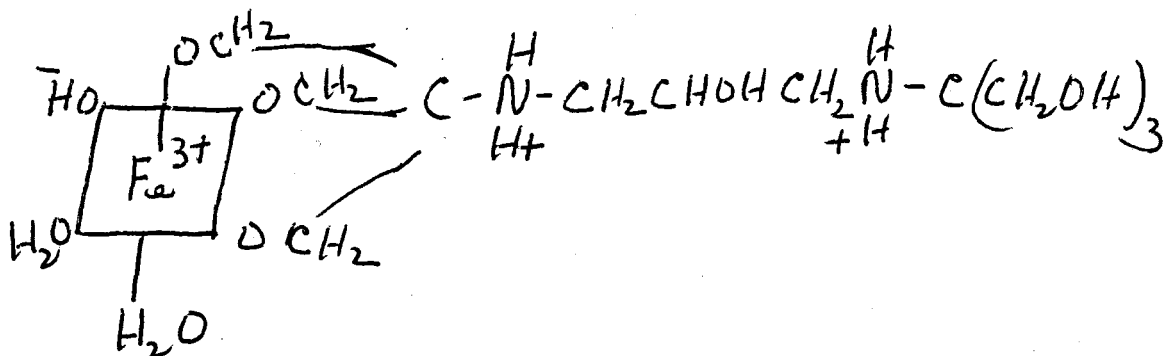
$$(\text{FeOH}^{2+}) = \frac{(3.16 \times 10^{-3})(2.5 \times 10^{-3} - (\text{FeOH}^{2+}))}{4.66 \times 10^{-3}}$$

$$(\text{FeOH}^{2+}) = 1.015 \times 10^{-3}$$

While it is possible that OH^- rather than water might be displaced by the chelating group, it seems far more likely that water will be, as it is ~~best~~ known that iron has a great affinity for OH^- .

Careful study of the titration curves, leads to another structure as a possibility. Chelation takes place at a low pH and is apparently complete by pH 5 at the highest. The presence of Disec in water makes a buffer solution. The buffer action is due to the presence of the amine groups. This buffer region is seen on the titration graph for Disec alone as the sloping section between pH 5.3 and 8.8. More-

over the slope of this buffer region is proportional to the concentration of Disec (Figures 11 and 12). When iron is present with Disec, this same slope is evident and it has not been changed by the presence of the iron, even at 1/1 ratios (figures 11-13). Now if iron and Disec combine in a 1/1 ratio, and if this compound is formed by pH 5.0, one would expect that the amine groups would be tied up and the slope would then be infinite, or at least changing. The continued presence of this buffer region might be explained in one of two ways: the amine groups are present in the original concentration because they are not involved in chelation, or the chelate formed with the amine groups has a stability which exactly parallels the stability of hydrogen ion with these amine groups. Therefore structure V is proposed as a possibility.



V

If structure V is formed, why not a Fe/Diseac ratio of 2/1? No evidence points to this, but it might be that Fe and Diseac are joined consecutively through the end hydroxyl groups to form a small polymer, increasing possibility of Diseac being on both ends accounting for the slightly higher ratio of base to Diseac at 1/3 and 1/5 ratios as compared with 1/1. Would such structures mean a change in the absorbancy? It will be recalled that the only change in the absorbancy with higher ratios of Diseac was a slight decrease.

At this point, it may be of interest to examine figures 14 and 15 which show the change in absorbancy with pH. Figure 14 shows a gradual decrease in absorbancy over Fe^{3+} alone at the same concentration and wave length up to pH 3.5 where a sharp break occurs, usually denoting a change of species. This is also the same pH at which the titration curve for Fe^{3+} plus Diseac diverges from that for Fe^{3+} alone. A less sharp break occurs at pH 9.0 to 9.5. The colors corresponding to these breaks are: yellow becoming orange in the section below pH 3.5, red-orange or yellow, depending upon the total iron concentration, and the ratio of Diseac, in the horizontal portion, between pH 3.5 and 9.0, and decidedly yellow with a decrease in color above pH 9.0. It seems possible

that the chelate is forming over the low pH range and is practically complete at the first break. What does the second break denote? Is there a change of charge at this high pH or is the difference due to the presence of free amine groups? If structure V is the correct one, it has a charge of plus one in acid solution, becoming neutral as one amine group ionizes and changing to minus one as the second amine group ionizes. The buffer region of Disec ends at pH 8.8; therefore it must become free base above this pH. It has sometimes been observed that a precipitate may form at 1/1 ratio around pH 8.5 to 9.0 and that this precipitate dissolves at higher pH values if titration is continued (see Figure 13). Also, if a solution containing Disec and iron, which has been made as basic as possible, is allowed to stand for several days, a slight yellowish precipitate forms, and the pH, when tested with the meter, is found to be around 8.8. These solutions were in beakers exposed to the air so the change in pH could be due to absorption of CO₂. The significant point here, which fits the above interpretation, is that our chelate might be neutral, and therefore less soluble, at this particular pH and dissolve again as the sodium salt at the higher pH value.

Structures III and IV would be negatively charged when formed, and therefore reasons for change with pH are less apparent.

Solutions of the iron-Disec chelate do not give good agreement with Beer's law. At pH 4.0, molar absorptancy index increases with dilution, while at pH 10.5 there is a decrease. This is shown in the data for Babko's method. An explanation for this at the lower pH might be found in the much higher absorptancy of the increased proportion of the FeOH^{2+} and other hydrolysis species produced on dilution. An explanation of the opposite behaviour at the higher pH is more difficult to find.

Three structures have been presented as possibilities: the alternate compounds III, IV or V. While V is most plausible in the light of all the data, it is difficult to discard the possibility of chelation through the amine groups.

The third question deals with stability constants. Spectrophotometric methods are not very reliable with solutions which do not obey Beer's law, have no unique spectral pattern, and where other species have high absorptancy at the same wave lengths. Nevertheless, Watters'⁹² method of graphing change in absorptancy versus hydrogen ion concentration was attempted. Titration methods would seem better in this case as the above

92. Watters, op. cit., note 52

difficulties would not be present. An equally serious difficulty presented itself here. How should the concentration of the reactive species of the chelating agent be calculated? If structures III and IV are correct and chelation takes place through nitrogen, then the ionization constants of Disec should be used to calculate the concentration of free amine which would be the chelating agent. Since chelation seems to take place mainly between pH 2.5 and 3.5, the concentration of free amine is very small and this leads to a high constant. If, on the other hand, structure V is the correct one, how can the concentration of the reactive species be determined? Both methods have been tried without obtaining results whose agreement seems reliable.

Using Watters' ⁹³ slope-intercept method, the following equation was developed $Di = D_{sec} c$

$$7 \quad \frac{1}{(e_0 - \bar{e})} = \frac{1}{(e_0 - e_1)} + \frac{1}{(e_0 - e_1)K} (H^+)^3 (Di)$$

This equation must be used below pH 3.5 as $Fe(NO_3)_3$ must be in solution. Also it is necessary to know what value to use for Di.

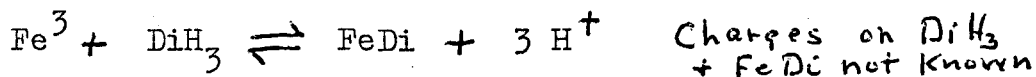
Taking values from Tables 2 - 5 to get $1/(e_0 - \bar{e})$, this was graphed against $(H^+)^3 / (Di)$. Values of (Di) were

93. Watters' method, see pp. 19 and 20, this paper

$$7 \quad \frac{1}{(e_0 - \bar{e})} = \frac{1}{(e_0 - e_1)} + \frac{1}{(e_0 - e_1)K} \cdot \frac{(H^+)^3}{(Di)}$$

determined in the two ways shown in Tables 14 and 15.

By either method, the graph gives a straight line except at pH 2.5. Using (Di) from K_{Disec} , K_{chelate} is 35.5, which seems too low to keep iron in solution. The alternate method of calculating (Di) gives K as 10^{-6} which is certainly not possible. Does the straight line mean that the formula



is valid but the difficulty lies in the value chosen for (Di) ?

Tables 13, 14, and 15 give the calculations for Bjerrum's⁹⁴ method. Similar calculations gave values from $\log K = 2.66 - 2.93$ when $\text{Di} = C_{\text{Di}} - \bar{n} C_{\text{Fe}}$. It was obvious that this was not a constant, but varied with each different Disec concentration taken. Also, the values became lower as Disec was increased, which does not seem logical and does not agree with experiment.

When (Di) was calculated from K_{Di} , as in Table 15, $\log K = 10.6 - 10.98$. These values are in better agreement and vary in the right direction with concentration change, but the agreement could be due to the heavy weight of the constant quantity 10^{-15} , which is Disec's constant.

When (Di) is calculated from $\text{Di} = C_{\text{Di}} - \bar{n} C_{\text{Fe}}$, and the equilibrium equation is stated as



there is no pH dependent term and this must constitute an error. Writing the equation as above on this page to

94. Bjerrum, pp. 17 - 19, this paper

include (H^+) , values for the \bar{n} method were corrected to include $(H^+)^3$. The results were worse, log K being -6.13 - -6.68. While this result does not seem possible, it does agree with the spectrophotometric result (Watters' method) using the same equation.

Babko's⁹⁵ dilution method shown in Table 16 gave values from 4.3×10^3 to 3.6×10^4 . The lower value was obtained at pH 10.5 where the solution is yellow and $FeOH^{2+}$ is less likely to interfere than at the lower pH values. While this method is admittedly an approximation, still the results obtained seem most probable in the present instance. The reliability of these results does not depend on the form of Disec involved in chelation.

95. Babko's method, see p. 22, this paper

S U M M A R Y

Iron (III) apparently chelates with 1,3-bis (tris (hydroxymethyl) methylamino) 2-propanol in a 1/1 ratio. This is indicated by absorbancy results using molar ratio method, by titration graphs, and by precipitation below this ratio.

Chelation takes place between pH 2.6 and 3.6 with the consumption of three moles of base per mole of metal ion. Alternate possibilities of chelation through the two amine and one of the hydroxyl groups of Disec, or through three hydroxyl groups, are considered.

Watters', Bjerrum's, and Babko's methods for determining complex stability constants are applied and the results criticized.

A P P E N D I X

A C K N O W L E D G E M E N T

I am very grateful to Dr. William E. Trout, Jr. for invaluable aid and patient and understanding guidance and to Dr. J. Stanton Pierce for allowing me to work with "Disec" and for his advice and help in its synthesis and purification. I am also indebted to Dr. W. Allan Powell, Dr. Thomas C. Franklin, and Dr. James E. Worsham, Jr. for helpful suggestions and encouragement.

I also wish to express my appreciation to the Research Corporation for a Frederick Gardner Cottrell grant through which this investigation was partly supported.

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A U T O B I O G R A P H Y

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