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I hereby recommend that the thesis prepared under my supervision by John A. Stevens *entitled* Studies on Stabilities of Ferrous Ammine Sulfates

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STUDIES ON STABILITIES OF FERROUS AMINE SULFATES

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PURPOSE

This thesis attempts to clarify certain discrepancies appearing in the chemical literature concerning the oxidation of solutions of ferrous iron by air or oxygen, and to explain the favorable stability against air oxidation of the ferrous amine sulfate double salts.

PART I

INTRODUCTION

A. Scope of Thesis.

Originally the aim of this investigation was to establish the relative resistivities against air oxidation of aqueous solutions of ferrous sulfate, ferrous ammonium sulfate, and ferrous ethylenediammonium sulfate. Upon the completion of this work, if a difference had been established, the second phase of the work was the theoretical verification of this difference through the measurement of complex ion formulae and instability constants.

However, upon the publication of Nutten's[15] work on the stability of solutions of ferrous ethylenediammonium sulfate and ferrous propylenediammonium sulfate, and in view of existing work on ferrous sulfate and ferrous ammonium sulfate, it was decided that any further measurements on the rates of oxidation of these salts would be of little value in comparison with the studies on the ferrous ammino and sulfato complexes. Further, in view of Nutten's work, it was decided to include, in addition to the three salts mentioned above, ferrous propylenediammonium sulfate. Consequently the thesis had then become the problem of applying spectrophotometric and polarographic methods to the determination of complex ion formulae and instability constants of the possible complexes existing in solutions of the above salts.

B. Oxidation Studies on Ferrous Sulfate.

A survey of the literature concerned with air oxidation of ferrous sulfate contains some unresolvable discrepancies in the many systematic studies made upon the rate of oxidation and the factors affecting this rate.

1. Ferrous salts

In a study of the oxidation of ferrous sulfate to ferric sulfate by air, Reedy and Machin[1] found that ferrous sulfate is oxidized very slowly by air and that the rate of oxidation is very slow at the start and falls off rapidly with time. In neutral solutions the rate is faster than in acid solutions and increases as the temperature is increased.

In the same year, Banerjee[2] also found that the velocity of short time oxidation (2 - 5 hours) was very slow in ferrous sulfate solutions and in mixtures of ferrous sulfate and the sulfates of potassium, sodium, ammonium, magnesium, zinc, cupric, manganous, nickelous, and sulfuric acid. However, when longer periods of time were considered (1488 hours), considerable differences in oxidation rates between the pure ferrous sulfate solution and the ferrous sulfate - salt solutions were observed. From his results, he concluded that the reaction was monomolecular and that potassium sulfate accelerated the reaction while all the other sulfates mentioned above acted as retarders to a greater or lesser extent.

In their study on the effects of pH on the rate of oxidation of ferrous solutions, Cornog and Hershberger[3] utilized buffered solutions to control the pH. Weighed quantities of ferrous sulfate were dissolved in the respective buffers and then aerated for three hours. The unoxidized iron was determined by titrating with standard permanganate. At a pH less than 5.0, they found that the degree of oxidation increased with increasing concentrations of ferrous iron. On the other hand, at a pH of 10.0, the degree decreased with increasing concentration of ferrous sulfate. From their studies they formulated an equation for the rate of oxidation of ferrous iron in a solution buffered to a pH of 5.0. This rate equation is:

$$\ln t = 0.032\, x - 0.01$$

where x is the percent iron oxidized in t hours.

In 1931 Mikhelson[4] studied the effect

of sulfuric acid on air oxidation of ferrous sulfate, using a permanganic titrimetric method for the determination of the unoxidized iron. He came to the conclusion that the oxidation of ferrous sulfate followed the equation:

$$10FeSO_4 + 5O \rightleftarrows Fe_4SO_9 + 3Fe_2S_3O_{12}$$

which would be more commonly written in the form:

$$10FeSO_4 + 5O \rightleftarrows Fe_2O_3.Fe_2O_2(SO_4) + 3Fe_2(SO_4)_3$$

Further he postulated that sulfuric acid decreased the rate of oxidation through the repression of the hydrolysis of the ferrous iron. In acid solutions, when hydrolysis is repressed, the rate of oxidation is proportional to the initial concentration of ferrous sulfate.

In the same year Lamb and Elder[5] utilized electromotive force measurements to study the factors affecting the rate of oxidation of ferrous sulfate. Using a bright platinum electrode as the cathode and a saturated calomel electrode as reference electrode, they measured the change in the electrode potential as oxidation of the ferrous sulfate proceeded.

Lamb and Elder aerated their solutions through the use of vigorous stirring (1250 rpm), preventing swirling of the solution by means of a baffle which caused turbulence in the solution with a consequent mixing of air and solution. Under these conditions they found that the rate of stirring, i.e., the intimacy of contact between oxygen and solution, affected the results; increasing the rate of stirring caused an increase in the rate of oxidation. They compensated for this by using a constant rate of stirring.

In their comparison of the rates of oxidation with air and with pure oxygen, they found that the rate was proportional to the partial pressure of oxygen. Specifically, they found that air oxidized the same amount of ferrous iron in 12.7 hours that oxygen did in 2.8 hours, approximately one-fifth the time.

Over a range of concentrations of 0.169 molar to 1.36 molar in ferrous sulfate, the initial concentration of the ferrous ion affected the results, the rate increasing with increased concentration of iron.

As the concentration of the sulfuric acid was increased up to 0.23 molar, the rate of oxidation increased. However, above 0.23 molar, the rate was practically independent of the concentration of the sulfuric acid. The range of acid concentrations studied was 0.008 molar to 3.0 molar in sulfuric acid.

Using 0.1 molar solutions of neutral salts, Lamb and Elder concluded that the rate was independent of these salts. Their results are reproduced in the following table.

Salt	k x 10^5	Salt	k x 10^5
Na_2SO_4	312	Cr_2SO_4	194
K_2SO_4*	251	CH_3COONa	281
$MgSO_4$*	323	Na_3PO_4	288
$ZnSO_4$	331	$NiSO_4$	360
$MnSO_4$	257	None	287

Salts marked with (*) were 0.23 molar in sulfuric acid. All values were reported with a claimed accuracy of ± 10 per cent.

In their attempts to determine the order of the reaction, the authors found that constant values of K, the specific rate constant, were obtained when the results were substituted in both a first and a second order equation. From this they concluded that the reaction was unimolecular with respect to oxygen and bimolecular with respect to iron. However, since they were only studying relative rates, they used the equation for a second order reaction to obtain the values tabulated above.

J. R. Pound[6], in his studies on the oxidation of ferrous sulfate, found that phosphoric acid and hydrochloric acid catalyzed the reaction but that sulfuric acid had little effect. Low concentrations of nitric acid have little effect but above 0.5 molar the action becomes quite rapid, while mixed nitric acid and hydrochloric, if dilute, have little effect. Also, oxides of nitrogen accelerate the oxidation. When Pound considered the effect of acids, he found that neutral solutions were oxidized faster than acid solutions and that salts of weak acids accelerated the action more than salts of strong acids, even though the addition of neutral salts to acid solutions had little effect on the rate of oxidation. In alkaline solutions, where a precipitate of a basic ferrous sulfate is formed, the rate of oxidation is very rapid. In general, Pound found that the rate of oxidation varied as the square of the concentration of the ferrous ion. The oxidation of ferrous phosphate is very rapid but is repressed by an excess of phosphoric acid. The rate is repressed by the addition of dilute sulfuric acid, hydrochloric acid, and nitric acid, or weak acids such as boric acid and succinic acid at moderate concentrations. Citric and oxalic acids decrease the rate of oxidation markedly because they reduce the ferric iron in the presence of light, the amount of reduction depending on the concentration of the acid. Sulfuric acid inhibits the reduction of the ferric iron by oxalic and citric acids, but phosphoric acid accelerates it in the presence of light. There is little or no reduction in the dark.

Pound reached the general conclusion that oxidation is least in the presence of low concentrations of strong non-oxidizing acids, e.g. sulfuric and hydrochloric, although he does not attempt to give any explanation of his results. Pound did not report any rate constants for the oxidation of ferrous iron.

R. San Martin[7] found that changes in aqueous solutions of ferrous sulfate were due to the formation of basic ferroso-ferric sulfate, $Fe_2(SO_4)_2OH$, and an equivalent quantity of sulfuric acid. The oxidation will decrease after a definite quantity, which is dependent upon the initial concentration of the ferrous sulfate, is formed. He postulates, if the quantity of sulfuric acid is determined experimentally beforehand, the alteration of solutions of ferrous sulfate through air oxidation may be prevented. This is equivalent to postulating the addition of sulfuric acid to repress hydrolysis of the ferrous sulfate and also presumes that the oxidation process is preceded by hydrolysis of the ferrous ion.

E. Slackenstein and R. Steiger[8] investigated the autoxidation of ferrous salt solutions. They found that the ease of oxidation of neutral salt solutions of ferrous chloride, ferrous acetate, and ferrous bicarbonate increases in that order. Further, they found that the ferrous citrate, lactate, gluconate are oxidized much more rapidly than the above inorganic salts. In the absence of acid, ferric ion is precipitated as the hydroxide, causing a shift in the equilibrium towards further oxidation of the ferrous iron. Similarly, the complex forming acids react with the ferric ion causing a shift in the equilibrium towards further oxidation. As the concentration of the ferrous ion increases, they found that the degree of hydrolysis is less pronounced and, as a consequence, there was less tendency towards oxidation. Increasing the temperature caused increased oxidation because of the increased hydrolysis taking place. In agreement with other authors, they found that light had little effect upon the degree of oxidation except in the case of the citrates, which reduce the ferric ion in presence of light. As would be expected, in the absence of oxygen and in a carbon dioxide atmosphere no oxidation was observed. Also, upon the removal of carbon dioxide, a solution of ferrous bicarbonate gave a precipitate of ferric hydroxide in the presence of air and of ferrous carbonate in the absence of air.

Chrétien and Rohmer[9] found that aqueous solutions of ferrous chloride were only slowly oxidized by an air stream. When the oxidation was performed in an acetic acid medium buffered by calcium or sodium acetate, the oxidation took place more rapidly. From these results they postulated that acetate forms an easily oxidizable complex with ferrous iron. In contrast with the results of Lamb and Elder, they found that the rate of passing air through the solution had little effect on the rate of oxidation. The rate they used was one liter of air per 45 seconds through 350 ml. of solution. With increasing acetic acid concentration, the rate of oxidation decreased up to 15 weight per cent and then increased until at 30 weight per cent of acetic acid the rate of oxidation was the same as that of the free solution. Above 30 weight per cent the rate of oxidation increased still further. In a solution containing 1.8 per cent by weight of ferrous chloride, 28.6 per cent by weight of acetic acid, and 2.8 per cent calcium acetate, the authors found the amount of ferrous iron oxidized in two hours was 53.8 per cent. The amount oxidized was 84.4 per cent when this solution contained 5.7 weight per cent of calcium acetate. Upon investigating the effect of the initial concentration of iron on the rate of oxidation, they found that the rate of oxidation was inversely proportional to the initial concentration of iron. The amount of iron oxidized in a solution containing 1.8 per cent by weight of ferrous chloride, 28.6 per cent by weight of acetic acid, and 5.7 per cent by weight of calcium acetate is 16 per cent at 20 degrees centigrade, 70 per cent at 40 degrees, 92 per cent at 60 degrees and 100 per cent at 75 degrees centigrade. When the above measurements were carried out on ferrous sulfate instead of ferrous chloride, it was found that the ferrous sulfate was oxidized slower.

In a study on the effect of pressure of oxygen on the rate of oxidation of ferrous sulfate, G. Agde and F. Schimmel[10] found that the rate of oxidation decreased as the initial concentration of ferrous sulfate was increased and also increased with increasing pressure of oxygen. Further, they studied the rate of oxidation as a function of the volume of oxygen passed through the solution at different concentrations of ferrous sulfate and at different temperatures. In neutral solutions a basic salt of ferric sulfate precipitated out; when sulfuric acid was added to change this salt to pure ferric sulfate, they found that the reaction went further toward completion. Finally, they found that air at 105 atmospheres gave more complete oxidation than pure oxygen at 20 atmospheres. This they attributed to the increased surface of the solution offered to the oxygen in the air as compared to the surface of the solution offered to the oxygen.

Opposed to the results of Agde and Schimmel, Kobe and Dickey[11] found that the same partial pressure of oxygen had the same effect regardless of whether or not air or pure oxygen was used. They studied the effect of oxygen pressures of 20, 100, and 275 pounds per square inch at temperatures of 100, 145, and 175 degrees centigrade. The authors also found that the addition of sulfuric acid had an inhibiting effect upon the oxidation and that dilutions of one-half and one-quarter did not affect the rate.

2. Ferrous ammonium sulfate

Jirkovsky[12] oxidized Mohr's salt slowly in neutral solution. After a year's time, a slightly yellow crystalline powder settled out which was insoluble in cold water, cold sulfuric acid, dilute or concentrated nitric acid, soluble in aqua regia and sodium hydroxide, and analyzed to give the compound: $(NH_4)_2Fe_2(OH)_4(SO_4)_2 \cdot Fe_4(OH)_8(SO_4)_2$. From this study he concluded that normal ferric sulfate is formed in acid solutions, basic sulfate in neutral solutions and sub-basic salts from alkaline solutions.

The first comparison of the stabilities of ferrous sulfate and of Mohr's salt was made by Karpova[13]. He bubbled air through solutions of ferrous sulfate and ferrous ammonium sulfate at room temperature. The rate of oxidation was estimated by a visual observation of the color developed with potassium thiocyanate. In general he found that Mohr's salt was more stable than ferrous sulfate and that the rate of oxidation was directly proportional to the initial concentration of the iron. Although he found that the pH of the solutions changed during aeration, he made no attempt to interpret the effect this change would have on the rates of oxidation.

3. Ferrous ethylenediammonium and propylenediammonium sulfates

Oesper and Caraway[14] measured the stability of ferrous ethylenediammonium sulfate against air oxidation in the solid state. They found no measurable oxidation occurred for a period of 54 hours. This work was confirmed by Nutten[15] and by the author. The latter recrystallized ferrous sulfate, ferrous ammonium sulfate, ferrous ethylenediammonium sulfate, and ferrous propylenediammonium sulfate from air-free saturated solutions. The resultant crystals of ferrous sulfate were laminated blue plates; Mohr's salt appeared as blue monoclinic prisms; Oesper's salt and ferrous propylenediammonium sulfate were green prisms, indistinguishable from each other in appearance. Upon allowing these dried crystals to stand under ordinary laboratory conditions for a period of time it was found that the ferrous sulfate completely disintegrated to a white powder in three to four days; Mohr's salt after approximately a month gradually acquired a white coating; Oesper's salt and the ferrous propylenediammonium sulfates remained unaltered in appearance and gave no test for ferric iron with potassium thiocyanate after standing for over a year. Nutten found that the ferrous propylenediammonium sulfate remained unaltered for a period of 48 days under normal laboratory conditions and remained unaltered for 12 hours at 50 degrees centigrade.

Nutten amplified his studies to include the stabilities of solutions of Oesper's salt and ferrous propylenediammonium sulfate. He prepared solutions of the two salts containing equivalent amounts of ferrous iron. These solutions were titrated daily with freshly standardized permanganate and the results corrected to milliliters of 0.1 M potassium permanganate. From his results, Nutten reached the conclusion that the rate of oxidation of solutions of Oesper's salt and the ferrous propylenediammonium sulfate was of the same order of magnitude as that observed for other ferrous salts. As a consequence, he presumed that complexing of the ferrous iron does not stabilize it against atmospheric oxidation.

C. Amine Complexes.

In connection with his studies on the nature of residual valence, Ephraim[16] investigated the stability of the ammonia complexes of certain bivalent metals. More specifically, he studied the capacity of the halides and sulfates of bivalent nickel, cobalt, iron, copper, manganese, cadmium, and zinc to coordinate ammonia. According to the findings of Ephraim, bivalent nickel, cobalt, iron, and cadmium unite with 6, 4, or 2 mols of ammonia; bivalent manganese with either 6 or 2; copper with 5, 4, or 2; and zinc with 5, 4, or 3 mols of ammonia.

The criterion of stability used by Ephraim was the temperature at which the vapor pressure of the salt was 500 millimeters of mercury. Upon this basis, he found that the capacity to annex ammonia is a function of the atomic volume, and that the energy of union increases as the atomic volume decreases. This relationship is documented by a table abstracted from his article.

Ammine sulfate	Atomic vol. of metal	Temperature at 500 mm. pressure
Nickel	6.59	398
Cobalt	6.77	378.5
Iron	7.12	369
Copper	7.12	364.5
Manganese	7.43	340
Zinc	9.13	299
Cadmium	12.95	323.5

In correlating the affinity for ammonia and the electronegativities of the elements, Ephraim postulated that no simple relationship existed between these two quantities since the order of electronegativities is:

$$Cu > Ni > Co > Fe > Cd > Zn > Mn > Mg$$

and the affinity for ammonia according to the above table is:

$$Ni > Co > Fe > Cu > Mn > Cd > Zn > Mg.$$

As a natural consequence of measuring the dissociation temperature at a vapor pressure of 500 millimeters, he also calculated the heat of dissociation of the ammino salts considered above according to the formula:

$$\log p = \frac{-Q}{4.571\ T} + 1.75\ T + 3.3$$

Since his results are of some interest, they are tabulated below:

Salt	Temperature °C $p = 760$ mm.	Heat of Dissociation Kilogram Calories
$NiSO_4 \cdot 6NH_3$	407	14.67
$CoSO_4 \cdot 6NH_3$	389.5	13.98
$FeSO_4 \cdot 6NH_3$	381	13.65
$MnSO_4 \cdot 6NH_3$	346.5	12.29
$CdSO_4 \cdot 6NH_3$	334.5	11.83
$CuSO_4 \cdot 5NH_3$	360	12.83
$ZnSO_4 \cdot 5NH_3$	308	10.81
$NiSO_4 \cdot 4NH_3$	451.5	16.44
$CoSO_4 \cdot 4NH_3$	409.5	14.78
$FeSO_4 \cdot 4NH_3$	398	14.32
$CdSO_4 \cdot 4NH_3$	360	12.83
$CuSO_4 \cdot 4NH_3$	442.5	16.08
$ZnSO_4 \cdot 4NH_3$	383	13.73
$CuCl_2 \cdot 4NH_3$	395.5	14.22

Lastly, Ephraim found that the ferrous hexammino sulfate was a white powder that oxidized very easily in air. He did not report the effect of moist air as opposed to that of dry air.

Mellor and Maley[17] in their studies on the stability of the complexes of the transition elements found that the order of stability of the bivalent metals in this series was the same regardless of the nature of the ligand. The order of increasing stability they found was:

$$Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg.$$

However, if the oxidation number of any element is altered, it may change its position in this series. For example, in considering the metal bis-salicylaldehyde-ethylenediamine complexes, the following order was found:

$Cu^{II} > Ni^{II} > Fe^{III} > Zn^{II} > Mg^{II}$.

For the bivalent metals in the first transition series the above order of stability is clarified by the following tabulation of the logarithms of the instability constants.

Bivalent Metal	log K_1 (Salicylaldehyde)	log K_1 (Men_3)
Pd	-14.8	-26.9 for $Pden_2$
Cu	-13.3	-19.6
Ni	- 9.2	-18.6
Co	- 8.3	-13.8
Zn	- 8.1	-12.9
Cd	- 7.8	-12.3 for $Cden_2$
Fe	- 7.6	- 9.5
Mn	- 6.8	- 5.7
Mg	- 6.8	

Irving and Williams[18] substantiated the work of Mellor and Maley and amplified it with their studies on other complexes of these metals. In their article the authors plotted the logarithm of the stability constant versus the atomic number for the bivalent metals of the first transition series. This plot is partially reproduced in Figure I.

It is of interest to compare the findings of Ephrian with Mellor and Maley and Irving and Williams.

Ephrian: Ni > Co > Fe > Cu > Mn > Cd > Zn > Mg

Mellor and Maley
Irving and Williams: Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg

1. Preparations

G. Spacu[19] prepared some complex compounds of both ferrous iron and ferric iron with various ammine ligands. In reacting dry ammonia with ferric sulfate.x water, he obtained a red brown powder which readily lost ammonia and was decomposed by water to form ferric hydroxide. He proposed the formula for this compound as $[Fe(H_2O)_2(NH_3)_4]SO_4$. When this compound was further reacted with pyridine, he obtained the diaquo-triammono-pyridino-ferri diaquo-tetraammono ferri sulfate, $[Fe(H_2O)_2(NH_3)_3Py][(H_2O)_2(NH_3)_4Fe](SO_4)_3$. This second compound was unstable in air and decomposed in water. In the preparation of the ferrous tetra ammono sulfate, Spacu reacted dry ammonia with ferrous sulfate heptahydrate. A brown amorphous powder was formed, $Fe(NH_3)_4SO_4$.

A white amorphous powder which analyzed to give the molecular formula: $[Fe(enH_2SO_4)_2](SO_4)_3.H_2SO_4.H_2O$ was prepared. This salt would be the ferric analog of Oesper's salt. The writer tried without success to prepare a crystalline version of this salt. Despite all methods of crystallization and preparations attempted, a creamy white amorphous powder was obtained which was stable in air but which hydrolyzed completely in water to give a precipitate of ferric hydroxide.

Spacu also prepared the dianilino-ferrous sulfate, $Fe(aniline)_2SO_4$, by boiling ferrous sulfate in aniline. It is a white amorphous powder, hydrolyzed by water.

On reacting ferric chloride with excess potassium thiocyanate in a very large excess of pyridine, Spacu obtained the tetrapyridino-ferrous thiocyanate, which crystallized from solution as black needles. He found, further, that these black needles were isomeric with the crystalline yellow compound of Grossman and Hunseler[20]. On boiling in pyridine, the black compound was transformed into the yellow compound.

On the other hand, when the yellow material was treated with chloroform, it formed the black needles reported above. On treatment of this pyridino ferrous thiocyanate with ammonia, a hydroscopic product of hexammono ferrous thiocyanate was obtained which was oxidized with chlorine water to the ferric product. Spacu assumed the black and yellow needles to be cis and trans forms of the type MA_2B_4.

Despite Ephraim's[16] findings, Verhoeff[21] prepared a compound that analyzed as the pentammino-ferrous sulfate, $Fe(NH_3)_5SO_4.H_2O$, a white powder very susceptible to oxidation.

E. Weitz[22] not only prepared some interesting complex salts of ferrous iron but also devised a convenient apparatus for handling these solutions in an atmosphere of hydrogen or nitrogen. Weitz found that ferrous chloride tetrahydrate in the absence of oxygen reacted with ammonia to give a precipitate of ferrous hydroxide which dissolved in excess ammonia. On cooling the solution, greenish octahedra were formed. These were washed with alcohol and ether and stored over sodium to prevent peroxide formation. On exposure to air, the compound quickly lost ammonia, but was stable in air-free tubes. When the ferrous chloride was replaced by Mohr's salt, he obtained skewed rhombohedra instead of octahedra. The compound resulting from the use of Mohr's salt analyzed to be $[Fe(H_2O)(NH_3)_5]SO_4 \cdot (NH_4)_2SO_4$, aquo pentammino ferrous ammonium sulfate. Lastly, the hexammino perchlorate, bromide, iodide all separated as green octahedra.

Breuid[23] prepared ethylenediamine and trimethylenediamine complex compound of ferrous halides and sulfates of the general formula $Fe\ En_3\ X_2$, where X may be Cl, Br, I, or $1/2(SO_4)$. In absence of oxygen, these salts were decomposed by water to give a precipitate of ferrous hydroxide.

PART II

EXPERIMENTAL

The experimental section of this thesis is divided into three separate sections; (A) studies of the rates of oxidation by air and oxygen, (B) spectrophotometric studies on complex ions for the application of the method of continuous variations, and (C) polarographic studies on complex ion formulae and stability constants.

A. Rates of Oxidation.

The mechanism of the air oxidation of ferrous sulfate is a function of the acidity of the solution. This mechanism may be generally represented by the following equations.

Acid Oxidation

$$4Fe^{+2} + O_2 + 4H^{+} \rightleftharpoons Fe^{+3} + 2H_2O$$

Neutral Oxidation

$$4Fe^{+2} + O_2 + 2H_2O \rightleftharpoons Fe(OH)^{+2}$$

Alkaline Oxidation

$$Fe^{+2} + OH^{-} \rightleftharpoons Fe(OH)_2\downarrow$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightleftharpoons 4Fe(OH)_3\downarrow$$

After due consideration of the above mechanism and other results published in the literature, it was decided to measure the relative rates of oxidation in solutions which were 0.5 Molar in sulfuric acid. Briefly, the reasons for this choice of concentration were: (1) to prevent the precipitation of hydrated ferric oxide or basic ferric sulfate from disturbing the equilibrium unduly; (2) to minimize the change in the pH of the solution due to the hydrolysis of the ferrous and/or the ferric ions; (3) to minimize the change in pH due to the amount of hydronium ions used up in the oxidation reaction; and (4) to maintain a constant acidity in each solution without the necessity of introducing buffer solutions which might either destroy or enhance the stability of the ferrous or ferric iron present.

In order to measure the rate of oxidation through the increase in the concentration of the ferric iron, colorimetric methods for the determination of ferric iron in the presence of ferrous iron were investigated. The colorimetric reagents tried were: thiosalicylic acid for both ferric and total iron, salicylic acid and potassium ferrocyanide for ferric iron[24]. Unfortunately, it was learned that green coloration of the ferrous iron, which was in tremendous excess as compared with the ferric ion, caused a change in hue of the oxidized solution as compared with the pure ferric standard solution. Attempts to apply the Fisher Electrophotometer to these solutions also proved unsatisfactory.

The feasibility of using the decrease in the ferrous iron concentration to follow the change was investigated. Using potassium ferricyanide and dimethylglyoxime as reagents for ferrous ion, a precision of

± 1.5 per cent was obtained. However, in order to apply this reagent to the solutions being oxidized, a dilution of 1/100 was required. This caused such an amplification in the precision required for accurate determinations that the method had to be abandoned.

Further investigations into the colorimetric methods were not made because it was found that a titrimetric method could be applied with greater accuracy than either of the above. Using diphenylamine sulfonate as an indicator, the determination of iron with potassium dichromate can be made with a precision of ± 0.1 per cent.

Although the volumetric method for the determination of the decrease in the concentration of the ferrous iron proved satisfactory on a day to day basis, it had one distinct disadvantage. This was that large volumes of ferrous sulfate solution were required in order to maintain the rate studies for a sufficient length of time. For example, assuming each titration consumed 25 milliliters of ferrous sulfate solution, this would require 50 milliliters of ferrous sulfate solution for each determination in order to run duplicate titrations. Assuming further that only one determination was made each day, this would require 50 milliliters each day or a volume of 1.5 liters for a period of thirty days. This period of time was desirable because of the slow rate of oxidation of the solutions in the 0.5 Molar acid solutions. Briefly, it was found that the aeration of such large volumes of solutions was not feasible with the equipment on hand. A precision of approximately ± 15 per cent was obtained. The low precision was explained on the basis of insufficient aeration of the solution.

When the volumetric method was discarded, recourse was taken in the rate of change of the ferrous/ferric electrode potential as a measure of the rate of oxidation. Like the previous work, these investigations were also performed in solutions that were 0.5 Molar in sulfuric acid.

This electrometric method is essentially the method of Lamb and Elder[5]. However, Lamb and Elder reported values accurate to ±10 per cent, which was considered by the present author as entirely too large an error in order to differentiate properly between the relative rates of oxidation of ferrous sulfate, Mohr's salt and Oesper's salt. Therefore, an attempt was made to improve upon the method by producing more aeration of the solutions. In order to accomplish an aeration of the ferrous sulfate solution as efficiently as possible, the air or oxygen was passed through a sintered glass dispersion tube.

The electrode potential of the iron in solution was measured with a bright platinum disk electrode with a saturated calomel electrode as the reference electrode. The temperature of the system was controlled to 25 ± 0.1 degrees centigrade.

With the apparatus used in these studies, the degree of precision was ±10 per cent for low periods of oxidation (a few hours) up to ±6 per cent for a period of oxidation approximately 260 hours duration.

In general, it was found that 0.15 Molar solutions of ferrous sulfate, ferrous ammonium sulfate, and ferrous ethylenediammonium sulfate have about the same stability in 0.5 Molar sulfuric acid. Further, the data seemed to indicate that the order of increasing stability was Mohr's salt, ferrous sulfate, and Oesper's salt. For example, after 278.5 hours of air oxidation, the changes in the electrode potential for the aerated solutions were:

Salt	Mohr's Salt	Ferrous Sulfate	Oesper's Salt
Δ E (millivolts)	105.3	104.8	104.3

However, in view of the precision in measurement, it was impossible to draw any reliable conclusions concerning the stability of these salts from these measurements.

The biggest source of error in air oxidations seems to be the efficiency of contact between the gas and the liquid. This author believes that a greater precision in the above measurements could be obtained if the solution were to be sprayed through a fine nozzle into an atmosphere of oxygen in a closed system. This required apparatus that was not available.

B. Spectrophotometric Methods.

The application of the spectrophotometric method to complex ion determination lies chiefly in determining the change in optical density of the solutions as a function of ligand concentration. This method, the method of continuous variations, is discussed in section I of the appendix.

1. Materials

The ferrous sulfate used in these experiments was a commercial C.P. salt recrystallized from a sulfuric acid solution containing iron filings to keep the ferrous sulfate in the reduced state.

The ferrous ammonium sulfate was a commercial C.P. product.

Oesper's salt was prepared in accordance with the method of Grossman and Schuck as published in the article by Oesper and Caroway[14].

The ferric sulfate and ferric ammonium sulfate were commercial C.P. salts. Attempts to make the ferric analogue of Oesper's salt were, as reported above, fruitless. Despite the use of several variations of the methods of making alums, the only product obtained was a creamy white amorphous powder of doubtful composition.

2. Apparatus.

The Beckman DU spectrophotometer was used. In the visible regions this instrument uses a tungsten filament lamp as the source of light and in the ultraviolet regions it uses a hydrogen discharge lamp.

The cells used were made of quartz and were matched in respect to their thickness.

3. Results.

In Tables I through VIII, the results of the spectrophotometric measurements are tabulated. Tables II through V contain the measured optical densities, while Tables VI through VIII give the Vosburg and Cooper "Y" function as a function of wavelength.

In figures II through IV, the "Y" function of the ferro-ammono, ferro-ethylenediammono, and the ferro-propylenediammono is plotted versus "x", the molar ratio of ligand to ferrous iron.

Figure V is a graphical representation of an extension of the results in Tables IV and VII.

Table I

Determination of Cell Equivalence ($\alpha \times 10^3$) using Distilled Water. Reference Cell = 9163. Corrections to be added.

Wavelength	Cell 8668	 8713	 9162
201	-70	-3	-50
210	-50	-3	-50
220	-44	-3	-37
230	-38	0	-32
240	-32	-5	-26
250	-28	-4	-26
260	-24	-2	-26
270	-20	-3	-24
280	-10	-3	-23
290	-16	-2	-21
300	-12	-2	-21
310	-12	-1	-21
320	-12	-1	-19
330	-12	-2	-19
340	-10	-2	-17
350	-10	-2	-17

Table II

Optical Density x 10^3 of 0.0128 Molar Ferrous Sulfate (pH = 3.78)

Wavelength mu	x	0.8	0.6	0.5	0.4	0.2
	Cell	9162	8713	8668	8668	9162
	pH	4.30	4.01	3.93	3.87	3.76
201		233	388	377	618	528
210		167	269	245	410	355
220		140	206	198	311	294
230		120	169	172	253	257
240		104	151	158	222	236
250		93	132	137	194	212
260		75	94	89	138	138
270		60	59	48	86	73
280		51	44	33	62	49
290		44	37	27	48	43
300		41	32	26	42	42
310		39	28	23	36	38
320		35	25	19	33	35
330		32	20	15	26	29
340		28	16	13	21	26
350		25	13	12	18	24

Table III

Optical Density of 0.0128 M $FeSO_4$/0.01 M $(NH_4)_2SO_4$ Mixtures

	x	0.8	0.6	0.5	0.4	0.2
Wavelength	Cell	9162	8713	8668	8668	9162
mu	pH	4.60	4.35	4.31	4.21	4.10
201		231	368	426	496	608
210		159	242	283	334	429
220		148	203	239	278	362
230		138	184	214	247	322
240		127	174	201	228	298
250		118	155	180	203	270
260		98	113	130	145	198
270		79	79	87	96	132
280		72	69	72	76	112
290		68	60	69	70	98
300		64	55	65	64	92
310		60	48	55	58	86
320		56	44	50	52	77
330		51	37	47	44	72
340		47	33	39	38	62
350		43	28	34	33	54

Table IV

Optical Density of 0.0128 M Ferrous Sulfate/0.01 M Ethylenediammonium Sulfate

	x	0.8	0.6	0.5	0.4	0.2
Wavelength	Cell	9162	8713	8668	8668	9162
mu	pH	4.95	4.60	4.45	4.32	4.15
201		229	372	491	575	626
210		149	248	325	389	438
220		134	205	265	317	368
230		121	180	230	270	320
240		109	168	212	245	294
250		101	151	188	222	264
260		81	108	138	162	194
270		62	73	93	110	128
280		52	59	72	87	101
290		48	50	64	75	92
300		44	43	57	66	85
310		40	37	50	58	77
320		37	32	44	50	66
330		32	26	38	41	58
340		30	23	32	35	50
350		28	19	28	28	45

Table V

Optical Density of 0.0128 M $FeSO_4$/0.01 M $PnSO_4$

Wavelength mu	x Cell pH	0.8 9162 4.53	0.6 8713 4.20	0.5 8668 4.28	0.4 8668 4.22	0.2 9162 4.09
201		193	302	358	502	520
210		126	198	257	333	396
220		119	171	222	278	344
230		115	158	204	248	313
240		107	154	195	234	294
250		100	138	175	208	266
260		79	98	125	151	196
270		62	64	84	100	126
280		53	53	67	79	108
290		51	50	64	72	102
300		50	48	64	68	96
310		48	45	57	60	89
320		45	42	53	59	84
330		42	37	51	53	78
340		39	34	45	48	70
350		36	29	39	42	63

Table VI

"Y" Function for Ammonium Sulfate

Wavelength mu	x 0.8	0.6	0.5	0.4	0.2
201	- 2	-20	49	-122	80
210	-8	-17	37	- 76	74
220	8	- 3	41	- 33	68
230	18	15	42	- 6	65
240	23	23	43	6	62
250	25	23	43	9	58
260	23	19	41	7	60
270	19	20	39	10	59
280	21	25	39	14	63
290	24	23	42	22	55
300	23	23	39	22	50
310	21	20	32	16	48
320	21	19	31	16	42
330	19	17	32	11	33
340	19	17	26	12	36
350	28	15	22	12	30

Table VII

"Y" Function for Ethylenediammonium Sulfate

Wavelength mu	x 0.8	0.6	0.5	0.4	0.2
201	- 4	-16	114	8	188
210	-18	-21	80	-21	83
220	- 6	- 1	67	6	74
230	1	11	58	17	53
240	5	17	54	23	58
250	8	19	41	28	52
260	6	14	49	24	56
270	2	14	45	24	55
280	1	15	38	25	52
290	4	13	37	27	49
300	3	11	31	24	43
310	1	9	27	22	39
320	2	7	25	17	31
330	0	6	23	15	29
340	2	7	19	14	24
350	3	6	16	10	21

Table VIII

"Y" Function for Propylenediammonium Sulfate

Wavelength mu	x 0.8	 0.6	 0.5	 0.4	 0.2
201	-40	-66	-29	-116	- 8
210	-41	-71	13	- 77	41
220	-21	-35	24	- 33	50
230	- 5	-11	32	- 5	56
240	3	3	37	12	58
250	7	6	38	14	54
260	4	4	11	13	58
270	2	5	36	14	53
280	2	9	34	17	59
290	7	13	37	24	59
300	9	16	38	26	57
310	9	17	34	24	51
320	10	17	34	26	49
330	10	17	36	27	49
340	11	23	32	27	44
350	11	16	27	14	39

4. Discussion of spectrophotometric results

The application ofthe "method of continuous variations" to the study of the ferro-ammino complexes gives definite proof for the existence of the monoammino complex in each case studied. On the other hand, although no evidence is existent for the higher complexes, their presence is not necessarily disproven.

The existence of the di-, tri-, tetra-, penta-, and hexa-ammino complexes would be indicated by a maximum (or minimum) at values of x equal to 0.66, 0.75, 0.80, 0.833, and 0.857 respectively. Of course, these maxima or minima may or may not occur at a wavelength of 240 mu. From a consideration of analogous work with other metallic ions, it would be predicted that the maxima for the higher complexes would appear at different wavelengths. However, since no measurements were made at the "x" values corresponding to the di-, tri-, penta- and hexa- ammino complexes, no statements can be made concerning their existence. On the other hand from the shape of the curves in figures II, III, and IV, the existence of the tri-ammino complex would be predicted.

In summary, the application of the "method of continuous variations" gives proof of the mono-ammono, mono-diethylenediammono-, and the mono-dipropylenediammono-ferrous complexes. Further, the existence of the tri-ammino complexes is indicated by the shape of the curves for ammonia and propylenediammine.

Figure V illustrates the existence of the ferro-di and tri ethylenediammino complexes. This data was obtained from further measurements on these complexes.

C. Polarographic Determinations.

1. Apparatus

The instrument used in these studies was the Leeds & Northrup "Electro-chemograph". This instrument utilizes the principle of the "Micromax" recorder to produce current-voltage curves which are drawn directly and visually with pen and ink on a recording chart. This direct and visual recording of current-voltage curves is one of the distinct advantages of the electrochemograph over the photographic recording of the "Polarograph". For the continuous application of a voltage to the cell, the instrument utilizes a potentiometer whose rate of voltage application is synchronized with the speed of advance of the chart.

Briefly, in addition to the cell, the electrochemograph contains three parts: (1) the Micromax recorder, (2) the potentiometer, and (3) the thermionic amplifier, which amplifies the small currents involved in polarography.

In order to test the instrument for satisfactory electrical performance, a fixed resistance of known value was connected in place of the cell and a current-voltage curve recorded.

When the instrument was operating satisfactorily, in accordance with Ohm's law, a straight line was obtained whose slope was equal to the value of the fixed resistance.

Though several means of recording polarograms are employed, the successful applications of polarography lie within the cell used, more specifically, the dropping mercury electrode.

As reference anodes, two saturated calomel electrodes were used. One calomel electrode was used as a reference electrode while the other was used as a working reference anode in the cell. These calomel electrodes were checked against each other periodically in order to insure that no change in the working calomel electrode had taken place because of the currents flowing within the cell.

A 50 ml. weighing bottle was used as a container for the solution to be polarographed. This was fitted with a rubber stopper into which the following tubes were inserted: (1) the capillary of the dropping mercury electrode with outside diameter 6 mm. and inside diameter of 0.05 to 0.07 mm.; (2) a capillary, flared at the end, and fitting the rubber stopper just loosely enough so that it could be rotated rather easily. This tube was bent into an "L" shape and was used to collect drops of mercury for the purpose of calibrating the electrode during electrolysis. Whenever the drops of mercury were to be collected, the "L" shaped capillary was rotated so that the flared end was directly below the dropping mercury electrode. When the capillary was in this position, the drops of mercury would fall into the funnel shaped end of the capillary. Conversely, after about 25 drops of mercury were collected the "L" shaped tube was rotated out of the path of the falling mercury, and no more mercury could be collected. This tube was also used as an inlet through which the nitrogen was passed in order to deoxygenate the solution. Further, whenever ligand solution was added to the cell, it was mixed with the solution in the cell by passing nitrogen through the solution. This had the dual effect of deoxygenating the added solution and also mixing the solutions.

(3) A 6 mm. glass tube which extended slightly below the rubber stopper, through which nitrogen was passed over the surface of the solution in order to keep oxygen from reentering the solution.

(4) A 6 mm. capillary glass tube with inside diameter of 0.1 mm. extended just below the rubber stopper, for the purpose of providing an outlet for the nitrogen. (5) A 10 mm. glass tube containing a 2.5 per cent agar-agar saturated potassium chloride gel was the salt bridge connecting the cell to an intermediate vessel containing saturated potassium chloride. Liquid saturated potassium chloride salt bridges led from the saturated calomel electrodes into this intermediate vessel. (6) A 10 ml. burette graduated in 0.05 ml., was led through the stopper by means of a 6 mm. glass tube drawn to a capillary.

2. Materials

The source of ferrous iron used in these experiments was prepared by reacting C.P. 60 per cent perchloric acid with iron filings. The reaction was allowed to go to completion so that a saturated or very nearly saturated solution of ferrous perchlorate was maintained. Ten milliliters of this solution, which gave no test for ferric iron with a 1 per cent potassium thiocyanate solution, was then diluted to a liter with distilled water to provide the solution of ferrous iron that was used in the following experiments. Since the stock solution of ferrous perchlorate was very nearly saturated at all times, its concentration was very nearly constant and, as a result, known concentrations of ferrous iron could be made up purely by dilution of this stock solution. However, all solutions of ferrous perchlorate were standardized with potassium dichromate (0.0537 N) using sodium diphenylamine sulfonate as the indicator. Duplicate titrations were made in all determinations.

The ammonium perchlorate used in these studies was made by adding the equivalent amount of 60 per cent C.P. perchloric acid to 28 per cent C.P. ammonia. Upon cooling a white solid separated out which was filtered and air dried by drawing air through the salt. The percentage yield was 56 per cent of theoretical.

The ethylenediammonium perchlorate used in these experiments was prepared by reacting 60 per cent C.P. perchloric acid with 98 per cent recrystallized ethylenediamine. The ethylenediamine was purified by fractional recrystallization in an ice-salt bath. Because of the high heat of reaction and the very nature of perchlorates, the reaction mixture was kept cool in an ice-salt bath at -10 degrees centigrade and all additions were made dropwise. In all cases, the perchloric acid was added to the base in order to prevent an excess of perchloric acid being present at any time during the reaction. As the equivalence point was neared in the neutralization of the ethylenediamine, a white solid began to precipitate out. This was filtered, washed with ether, and air dried. The percentage yield was 78 per cent of theoretical.

The propylenediammonium perchlorate was prepared in the same manner as the ethylenediammonium perchlorate. However, in this case it was found that an excess of perchloric acid of 1 per cent was required to cause precipitation of the white solid. The white solid was air dried, washed with alcohol and ether and air dried. The percentage yield was 73 per cent of theoretical.

The buffer solutions used were those of Clark and Lubs. However, in the case of the boric acid buffer, it was found that it was necessary to increase the capacity of the buffer in order to prevent a change in the pH due to the hydrolysis and precipitation of the ferrous ion as ferrous hydroxide. This boric acid buffer was 0.5 Molar in boric acid, 0.25 Molar in sodium hydroxide, and 0.1 Molar in potassium chloride.

The impure mercury was prepared in accordance with the recommendations of Wichers[25]. The impure mercury was washed in a solution of 5 per cent nitric acid containing a trace of mercuric nitrate. The solution was agitated from two to four days by bubbling air through it. Further, since there was some indication that the mercury had been fouled with sulfide, a few milliliters of 3 per cent hydrogen peroxide was added to aid in the cleansing. The reasons that the air was bubbled through the mercury are: (1) to expose as much surface of the mercury as possible to the oxidizing action of the cleaning solution, and (2) to aid in the oxidation of any base metals by the oxygen in the air.

After a thorough treatment with the nitric acid solution, the mercury was washed very thoroughly with distilled water, dried, and filtered through a filter paper with a pinhole in the tip of the cone. The resultant product had a very clean surface, showed no tailing, and, when polarographed in a solution of potassium chloride at maximum sensitivity of the electrochemograph, gave no waves on the polarogram. On the basis of this, the mercury was considered to be pure.

3. Polarographic procedure

Before any measurements were made, the instrument was given an electrical check using a 200,000 ohm resistance with a 50,000 ohm resistor as the shunt. If the slope of the resultant straight line current-voltage curve was 200,000 ± 500 ohms, the instrument was obeying Ohm's law and satisfactory electrical performance was indicated.

The dropping mercury electrode was set into operation and the height adjusted to a constant value. The value used throughout all of these determinations corresponded to a reading of 35 cm. on the meter stick mounted in a fixed position relative to the electrode.

All tubes entering into the cell were washed with distilled water and dried thoroughly. The cell itself was treated similarly.

The Beckman pH meter, Model G, used to measure pH throughout these determinations, was standardized with a commercial buffer solution. This setting was checked before each measurement of pH.

All solutions were tested for purity by polarographing a blank. The absence of any polarographic waves indicated that the solutions were of sufficient purity to be used.

The temperature throughout all determinations was maintained at 25 ± 0.5 degrees centigrade by means of a water bath.

The stock solution of ferrous perchlorate was kept in the reduced state by adding iron filings and sixty per cent C.P. perchloric acid to the solution and allowing the reaction to proceed until a one per cent solution of potassium thiocyanate gave no test for ferric iron. Ten milliliters of this stock solution was then diluted to a liter with distilled water and the solution standardized with standard potassium dichromate using sodium diphenylamine sulfonate as the indicator. This standard solution of ferrous perchlorate was then used in preparing all solutions to be polarographed. Although a fresh standard ferrous perchlorate solution had to be made for each series of polarograms, the concentration of the standard solutions was in the range of 0.0225 ± 0.0025 Normal, since the stock solution of ferrous perchlorate was always a saturated solution.

a. Procedure for sulfate complexes

The solutions for the investigations into the sulfate complexes of ferrous iron were prepared in the following manner. A known volume of the standard ferrous perchlorate solution was pipetted into a 100 ml. volumetric flask. One milliliter of 0.1 per cent gelatin was added and 25 ml. of a Clark and Lubs phthalate buffer (pH 6.01) was added and the solution diluted up to the mark of the flask. Twenty milliliters of this solution were pipetted into the previously dried cell and deoxygenated with nitrogen for twenty minutes. The instrument was then balanced in the usual manner and the polarogram of the solution drawn.

After the polarogram of the ferrous solution had been made, the cell was disconnected from the electrochemograph and the resistance of the cell measured with the commercial wheatstone bridge, Model RC-1B.

By means of a burette, increments of

0.5 Molar potassium sulfate solution were added to the cell, and a polarogram for each increment determined.

In order to obtain higher concentrations of the sulfate ion in the solution, it was necessary to add known volumes during the preparation of the solutions to be polarographed.

The pH of solutions was measured before and after polarographing in order to insure that no shift in pH had occurred due to the addition of the potassium sulfate solution.

In addition to drawing polarograms for the ferrous solutions, polarograms of blank solutions were made under the same conditions. These polarograms were used to correct for the residual current in the analysis of the polarograms.

b. Procedure for ammine complexes

The procedure for these solutions is essentially the same as for the sulfate complexes with some minor variations.

A known volume of the standard ferrous perchlorate solution was pipetted into a 100 ml. volumetric flask and one milliliter of 0.1 per cent gelatin solution added. The resulting solution was then diluted up to the mark with the boric acid buffer (pH 8.60). Twenty milliliters of this prepared solution were then pipetted into the previously dried cell and deoxygenated immediately for twenty minutes.

Known increments of the ammine perchlorate solution, buffered to a pH of 8.60 with the ammine, were added from the 10 ml. burette.

As in the case of the sulfate complexes, the cell resistance was measured for each increment added, and the pH of the solutions was determined before and after polarographing. The pH was found to remain constant in all cases.

4. Polarographic data

The data measured in the polarographic investigation is tabulated in Tables IX through XVIII. Table XIX shows the root mean square error, average error, and probable error, which were calculated from the deviations (D) reported in Tables IX through XVIII.

In order to find the best slope and intercept for each complex, the method of least squares was applied to the respective data for each complex. The results of this treatment are reported in Table XX. The calculations with the method of least squares are reported in section III of the Appendix.

Figures VI and VII give the results of the test for reversibility of the electrode reaction. The theoretical equation, which is used for this test, is the equation for the polarographic wave of a metal insoluble in mercury. (Cf. section II, Appendix)

In section II of the Appendix, the equation which is used for the determination of the results tabulated in Table XX is derived.

Table IX

Half Wave Potential of Ferrous Iron at pH 6.00

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$ volts meas.	$-E_{\frac{1}{2}}$ volts corr.
1	25.8	1600	20.6	1.392	1.371
2	6.2	1450	4.5	1.385	1.380
3	28.0	1580	22.1	1.400	1.378
4	28.6	1580	22.6	1.400	1.377
5	5.9	1450	4.0	1.393	1.389
6	28.4	1580	22.0	1.400	1.378
7	25.8	1600	21.0	1.400	1.379
8	27.6	1580	21.8	1.392	1.370

Average

1.377 ± 0.003

Table X

Formation of Ferro-monosulfate

Polarogram Number	I_D amps	Rcell ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. $SO_4^=$ moles per liter	D
9	6.0	1450	4.5	1.392	1.387	10	1.988	+7.0
10	25.0	1550	19.4	1.398	1.379	2	1.889	+1.7
11	5.68	1450	4.0	1.385	1.381	4	1.784	+0.5
12	5.64	1450	4.0	1.388	1.384	7	1.644	-0.6
13	24.60	1525	18.8	1.408	1.381	4	1.604	-5.0
14	5.6	1425	4.00	1.396	1.392	15	1.555	+4.0
15	5.48	1425	4.0	1.392	1.388	11	1.482	-2.0
16	23.0	1500	17.3	1.407	1.390	13	1.429	-1.0
17	5.5	1425	4.0	1.396	1.392	15	1.412	+0.5
18	5.3	1400	4.0	1.400	1.396	19	1.359	+3.0
19	22.8	1475	16.8	1.409	1.392	15	1.331	-2.0
20	5.5	1400	4.0	1.399	1.395	18	1.305	0.0

Table XI

Formation of Ferro-disulfate

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. $SO_4^=$ moles per liter	D
21	27	1440	19.4	1.419	1.400	23	1.301	- 3
22	25.2	1440	18.0	1.423	1.405	28	1.301	- 9
23	23.0	1440	16.6	1.415	1.398	21	1.266	+ 1
24	5.24	1375	4.0	1.404	1.400	23	1.248	0
25	22.0	1450	15.9	1.415	1.399	22	1.226	+ 3
26	5.20	1375	3.6	1.400	1.396	19	1.224	+ 6
27	5.12	1350	3.4	1.407	1.404	27	1.198	0
28	21.8	1425	15.5	1.422	1.406	29	1.165	0
29	25.4	1400	17.8	1.423	1.405	28	1.150	+ 2
30	5.0	1350	3.	1.410	1.407	30	1.141	0
31	21.3	1400	15.0	1.426	1.411	34	1.096	- 1
32	4.98	1325	3.0	1.408	1.405	28	1.078	+ 6
33	21.0	1375	14.4	1.428	1.414	37	1.057	- 2
34	24.0	1370	16.4	1.430	1.414	37	1.040	0
36	20.8	1350	14.0	1.431	1.417	40	1.015	- 2

Table XI (Continued)

35	4.8	1325	3.0	1.408	1.405	28	1.030	+ 9
37	20.5	1350	14.5	1.430	1.415	38	1.006	+ 1
38	20.0	1325	13.0	1.431	1.418	41	0.972	0

Table XII

Formation of Ferro-trisulfate

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2} I_D R$ m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. $SO_4^=$ moles per liter	D
39	4.48	1300	3.0	1.415	1.412	35	0.964	+ 7
40	23.0	1350	15.5	1.438	1.422	45	0.961	- 2
41	19.8	1300	13.0	1.431	1.418	41	0.937	- 4
42	19.4	1275	12.3	1.434	1.422	45	0.914	+ 1
43	22.0	1350	14.9	1.439	1.424	47	0.907	0
44	18.6	1280	11.9	1.435	1.423	46	0.895	- 2
45	18.5	1275	12.4	1.439	1.427	50	0.887	+ 1
46	17.8	1250	11.0	1.441	1.430	53	0.861	+ 1
47	21.0	1320	13.9	1.442	1.428	51	0.856	0
48	16.6	1260	12.7	1.446	1.433	56	0.855	+ 4
49	4.16	1275	2.6	1.423	1.420	43	0.851	- 9
50	17.8	1250	11.0	1.441	1.430	53	0.845	+ 1
51	17.4	1250	11.0	1.441	1.430	53	0.829	- 1
52	4.08	1250	2.5	1.422	1.419	45	0.827	- 9

Table XII (Continued)

53	16.8	1250	10.5	1.447	1.436	59	0.814	+ 4
54	20	1300	13.0	1.446	1.433	56	0.813	+ 1

Table XIII

Formation of Ferro-tetrasulfate

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. $SO_4^=$ moles per liter	D
55	3.7	1250	2.3	1.430	1.428	51	0.783	+9
56	19.4	1280	12.4	1.442	1.430	53	0.778	+7
57	18.5	1280	12.5	1.446	1.433	56	0.748	+8
58	17.5	1260	11.0	1.454	1.443	66	0.722	+1
59	16.6	1260	11.0	1.466	1.455	78	0.700	-9
60	26.0	1250	16.2	1.462	1.446	69	0.699	+1
61	26.1	1250	16.4	1.466	1.450	73	0.699	-3
62	24.6	1220	15.1	1.466	1.451	74	0.644	-3
63	24	1220	14.6	1.469	1.454	77	0.641	-7

Table XIV

Formation of Ferro-hexasulfate

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. $SO_4^=$ moles per liter	D
64	20	1200	12.0	1.477	1.465	88	0.571	+0.2
65	20.5	1200	13.0	1.477	1.464	87	0.579	-0.2
66	18.5	1180	11.6	1.480	1.469	92	0.550	+0.2
67	17.4	1180	10	1.484	1.474	97	0.524	-0.1

Table XV

Half Wave Potential of Ferrous Iron at pH 8.60

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2} I_D R$ m.volts	$-E_{\frac{1}{2}}$ volts meas.	$-E_{\frac{1}{2}}$ volts corr.
68	1.52	1360	0.97	1.412	1.411
69	1.20	1480	0.89	1.400	1.399
70	0.90	1480	0.66	1.400	1.399
71	1.36	1400	0.95	1.400	1.399
72	0.632	1340	0.38	1.408	1.407
73	0.616	1340	0.40	1.407	1.406

Average

1.404 ± 0.005

Table XVI

Formation of Ferrous-ammono Complex

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. NH_3 moles per liter
74	1.40	1330	0.93	1.419	1.418	14	2.231
75	1.15	1280	0.73	1.415	1.414	10	1.717
76	1.08	1270	0.69	1.415	1.414	10	1.494
77	0.98	1260	0.63	1.413	1.412	8	1.376
78	0.82	1240	0.51	1.415	1.414	10	1.245
79	0.86	1220	0.53	1.415	1.414	10	1.186
80	0.80	1220	0.49	1.419	1.419	15	1.131
81	0.90	1200	1.03	1.416	1.415	11	1.092
82	0.70	1200	0.91	1.418	1.417	13	1.054

Table XVII

Formation of Mono- and Tri- ethylenediammino Ferro Complexes

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2}$ I_DR m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. ethylenediamine m./l.	D
83	1.35	1480	1.00	1.431	1.430	26	3.527	-1.2
84	1.92	1450	1.39	1.450	1.449	45	3.110	+2.9
85	2.96	1420	2.14	1.459	1.457	53	2.679	-4.6
86	3.60	1380	2.48	1.469	1.467	63	2.609	+3
87	3.28	1370	2.24	1.480	1.479	75	2.465	+2.4
88	3.60	1360	2.45	1.500	1.498	94	2.343	-5
89	4.40	1340	2.95	1.508	1.505	101	2.191	+2.6
90	3.50	1340	2.35	1.515	1.513	109	2.118	+1.6
91	4.00	1320	2.64	1.527	1.525	121	2.034	-2.4
92	4.00	1280	2.56	1.535	1.532	128	1.931	0

Table XVIII

Formation of Mono- and Tri- propylenediammino Ferro Complexes

Polarogram Number	I_D amps	R_{cell} ohms	$\frac{1}{2} I_D R$ m.volts	$-E_{\frac{1}{2}}$meas. volts	$-E_{\frac{1}{2}}$corr. volts	$-\Delta E$	-log conc. propylenediamine m./l.	D
93	1.30	1400	0.91	1.481	1.480	76	2.656	+0.4
94	1.58	1400	1.11	1.489	1.488	84	2.358	-0.8
95	1.97	1400	1.38	1.497	1.496	92	2.128	+0.2
96	4.00	1400	2.80	1.522	1.519	115	1.409	+1.2
97	4.12	1380	2.80	1.522	1.521	117	1.304	0
98	4.20	1380	2.84	1.526	1.523	119	1.208	-1, -1
99	4.08	1380	2.82	1.535	1.533	129	1.128	+1.6
100	3.80	1380	2.62	1.542	1.539	135	1.053	+1.0
101	3.60	1380	2.48	1.545	1.542	138	0.993	-1.3

Table XIX

Precision of Polarographic Results

Ferrous Complex	Root mean square error millivolts	Average error millivolts	Probable error millivolts
Sulfato			
mono-	3.2	2.4	2.2
di-	3.9	2.7	2.6
tri-	4.1	3.0	2.8
tetra-	6.6	5.7	4.4
hexa-	0.2	0.2	0.13
Ethylenediammono			
mono-	3.7	3.4	2.5
tri-	3.0	2.6	2.0
Propylenediammono			
mono-	0.66	0.66	0.44
tri-	1.4	1.40	1.00

Table XX

Instability Constants

Complex	-log K_n	K_n	Per cent error
Sulfate			
mono-	2.21838	6.05×10^{-3}	13.0
di-	3.78821	1.63×10^{-4}	8.0
tri-	4.50151	3.15×10^{-5}	7.0
tetra-	5.39030	4.07×10^{-6}	7.0
hexa-	6.86642	1.36×10^{-7}	2.5
Ethylenediammono			
mono-	5.50383	3.14×10^{-6}	6.0
tri-	10.93306	1.17×10^{-11}	2.5
Propylenediammono			
mono-	5.61885	2.41×10^{-6}	4.0
tri-	8.00176	9.96×10^{-9}	3.2

5. Discussion of polarographic results

The reversibility of the electrode reaction is a critical point in the application of the polarographic method to the determination of complex ion formulae and instability constants. When the reversibility of the electrode reaction has been established, the accuracy of the calculated results are dependent only upon the tolerances and precision of the experimental method. In view of the importance in establishing the reversibility of the electrode reaction, the evidence supporting the reversibility of the reaction will be discussed before an evaluation of the results are made.

a. Reversibility of electrode reaction

The theoretical equation for the reduction of a metallic ion to the metal, which is insoluble in mercury, (e.g., Fe) is

$$E_{d.e.} = E_m^o + \frac{RT}{nF}\ln K_m + \frac{RT}{nF}\ln (I_D - I) \qquad (1)$$

where E_m^o is the standard electrode potential of the metal/metal ion, K_m is a proportionality factor derived from the Ilkavic equation and is equal to $605nD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}$; I_D is the diffusion current, and I is the current at the potential, $E_{d.e.}$, along the curve. The quantities $\frac{RT}{nF}$ have the usual significance.

At a temperature of 25°C, with a constant drop time, the values of E_m^o and K_m will be a constant, e. Consequently the equation may be simplified to the form:

$$E_{d.e.} = e + \frac{RT}{nF} \ln(I_D - I) \qquad (1a)$$

This equation was derived on the basis of two important assumptions: (1) the reaction is reversible, (2) the activity of the deposited metal is independent of the current density, i.e. is equal to unity.

If this equation is valid, a plot of E versus $\log(I_D - I)$ should give a straight line with a slope equal to 0.059/n volts. The equation was tested in this manner and the results are plotted in figure VI (for pH 6.00) and figure VII (for pH 8.60). The results of this plot clearly indicate that equation (1) does not hold for the reduction of ferrous iron to the metal. The reasons for this may be either (1) the reaction is irreversible or (2) the activity of the deposited metal is not independent of the current density, i.e. is not unity. It shall be shown below that the reaction is reversible and that it is the second assumption that invalidates the above method of testing.

Kolthoff and Lingane[28] postulated that for a reversible reduction of a metallic ion to a metal insoluble in mercury, the following relationship for the half wave potential should hold.

$$E_{\frac{1}{2}} = E^{o}_{m} + \frac{RT}{nF} \ln K_{m} + \frac{RT}{nF} \ln \frac{C}{2} \qquad (2)$$

In order to test this equation, a plot of $E_{\frac{1}{2}}$ versus concentration of the metal ion should yield a straight line with a slope equal to 0.059/n volts. Kerlinger and Laitinen[29] tested this equation for ferrous iron in 1 Molar ammonium perchlorate medium and found that $E_{\frac{1}{2}}$ decreased uniformly from -1.48 volts to -1.44 volts versus saturated calomel electrode when the concentration of ferrous iron was increased from 2 x 10^{-4} up to 0.01 Molar. This shift in 0.04 volts is in good agreement with the 0.05 volts predicted by equation (2) for a fifty fold concentration change and a value of n, the number of electrons entering into the electrode reaction, equal to two.

The shift in potential with change in the concentration of the ferrous ion was also investigated by Heyrovsky and Součeck[30] in their studies on the electrolytic potential of iron amalgams.

Heyrovsky and Součeck[30] prepared a solution of iron amalgam by the electrolysis of aqueous ferrous sulfate and measured the E.M.F. which was -0.750 volts versus the normal calomel electrode at 18 - 20°C. They postulated from their results that a "hyperactif" amalgam of iron was formed and was transformed into a suspension of crystalline iron in mercury.

In order to measure a fresh amalgam, they used a periodic polarizing current and determined the potential of the amalgam after formation. The frequency of polarization was 20 times a second and measurements were made after each polarization. This is essentially the same type of polarization that occurs with the dropping mercury electrode. However, the frequency of polarization in the case of the dropping mercury drop falls to about once every three seconds.

Using the dropping mercury electrode, they studied the shift of the potential with concentration of ferrous sulfate. They found that the potential increased uniformly from -1.122 ± .003 for a 1.0 Normal ferrous sulfate, to -1.150 ± .005 for 0.1 Normal, to -1.193 ± .005 volts versus the Normal Calomel electrode for a 0.01 Normal solution of ferrous sulfate. This shift of 0.70 volts is in fair agreement with the theoretical shift of 0.60 volts for a 100 fold concentration change.

The above potentials reported by Heyrovsky were not half wave potentials, but were tangent potentials, which was the earlier method of measuring polarographic potentials.

Further, Heyrovsky states "these potentials are reversible and prove that the fresh 'hyperactif' and metastable amalgam of iron has a very negative potential and is equal to that potential of deposition of iron on the dropping mercury cathode."

It is important to note that Kerlinger and Laitinen found that the half wave potential, which is the mid-point of thewave, shifted by 0.029 volts for a ten-fold change in concentration. On the other hand, Heyrovsky and Součeк found that the decomposition potential, which is at the start of the wave, also shifted by approximately 0.029 volts for a ten-fold change in concentration. Consequently, two independent studies found that on the ferrous iron polarogram two points, wholly unrelated, obeyed equation (2).

In summary, it was concluded that the electrode reaction was reversible because (a) equation (2) was found to hold (b) Heyrovsky[30] found the potential of $Fe^{+2}/Fe(Hg)$ was reversible, and (3) Heyrovsky and Souček[30] found that iron deposited in mercury is "hyperactif" and metastable. This last reason shows that the assumption (2) in the derivation of equation (1) was not valid. Further this author tested equation (2) over a limited range and found that it applied.

b. Evaluation of results

The precision in measuring the half wave potential of ferrous iron is ± 5 millivolts. The root mean square error of the various complexes are given in Table XIX. The magnitude of the intercepts are given in section III of the

Appendix. Since the value of the intercept is the value of $\Delta E_{\frac{1}{2}}$ when the concentration of the ligand is unity, the error in determination of $\Delta E_{\frac{1}{2}}$ is a direct measure of the error in the determination of the instability constant from the intercept. Consequently, the percentage error in the determination of the instability constants is reported in Table XX.

The values of the ferro-sulfato complexes cannot be evaluated with respect to the sulfato complexes of the other metals in the first transition series because the instability constants of the sulfato complexes of the other metals have not been reported in the literature.

However, in view of the work of Irving and Williams (Cf. figure I) it is possible to evaluate the order of magnitude of the ferro-ammino complexes.

First, it is impossible to compare the complexes of ammonia and ferrous iron because, within the concentration range investigated in this thesis, no complex was formed.

On the other hand, Bjerrum[3/] measured the stability complexes of ferrous iron and ethylenediamine. He reported values of log $K_n = 4.3$ for the mono and 9.6 for the triethylenediammono ferrous complexes. Both of these values differ from this author's values by 1.2 (mono) and 1.3 for the tri-complex. Regardless, in view of the respective methods, favorable agreement is obtained. Bjerrum also found evidence for the diethylenediammono complex with log $K_n = 3.2$ However, in his derivation, he assumed that the complexes were formed in a stepwise manner. Consequently, he had assumed the existence of the di-complex and, as a result, obtained a value of the stability constant. On the other hand, this author made no assumptions concerning the possible complexes present. Therefore, the detection and determination of the diethylenediammono complex depends upon the number of determinations made as well as the width of the concentration range in which it is stable. Reference must be made to figure V, curve C, which shows the presence of the di-complex.

In summary, the instability constants for the mono and triethylenediammono complexes agree favorably with those of Bjerrum. The diethylenediammono complexes were not detected by the polarographic method but were detected by means of the spectrophotometer.

The propylene complexes of ferrous iron are not reported in the literature. Referring to figure I, one would predict that the magnitude of the stability complexes would be less than those of ethylenediamine, i.e. the instability complexes would be greater than those for ethylenediamine. Further, comparing the results of copper, it would be expected that the mono-propylene complex would be of the same order of magnitude as the mono-ethylenediamine complex. An examination of the values in Table XX shows this to be the case.

In conclusion, the order of magnitude and stability of the complexes investigated are found to agree favorably with literature values and to follow the general order of stability exhibited by the bivalent metals in the first transition series, as reported by Irving and Williams[18].

PART III

CONCLUSION

A. Summary

The purpose of this thesis was to attempt to clarify certain discrepancies in the chemical literature concerning the oxidation of ferrous sulfate by air or oxygen and to explain the favorable stability against air oxidation of the ferrous ammine sulfate double salts.

The effect of acidity on the air oxidation has been investigated. In general, it was found that the rate was faster in neutral than in acid solutions[1,2,4,5,6,7] but that, in solutions of a weak acid, the rate of oxidation was accelerated[6,9,8].

The retarding effect of acids has been explained by the repression of hydrolysis. On the other hand, the effect of the weak acids has been explained through the formation of an easily oxidizable complex of ferrous iron with the anion of the weak acid (e.g., acetic acid)[9]. In general, complexing stabilizes the metal ion, except in those cases where the ligand itself acts as an oxidizing agent (e.g., cobaltic complexes). There is no evidence for the oxidation of ferrous complexes to the ferric complex by the ligand when the ligand is the anion of a weak acid.

Mellor and Maley[17] have reported that the relative stability of complexes, irrespective of the ligand, are:

$$Cu^{+2} > Ni^{+2} > Fe^{+3} > Co^{+2} > Zn^{+2} > Cd^{+2} > Fe^{+2}.$$

On the basis of this order, the effect of weak acids, which are stronger complex formers than strong acids, may be explained through the greater stability of the ferric complex as compared to the ferrous complex. However, if the weak acid is in sufficient excess, it should stabilize the ferrous iron, since it will take a higher potential to oxidize the complexed ferrous ion as compared with the uncomplexed ferrous ion. On the other hand, if the weak acid is not in sufficient excess to fully complex the ferrous iron, it may act as an accelerator by unduly disturbing the equilibrium through the complexing of the ferric ion as it is formed from the uncomplexed ferrous iron. No evaluation of these postulates can be given until the stability constants of both the ferrous and ferric complexes with anions of weak acids are reported in the literature.

Considering sulfuric acid, ferrous ion complexes with the sulfate ion to form the mono-, di-, tri-, tetra-, and hexa- sulfato complexes. The stability constants of the ferric-sulfato complexes have not been reported, however, it would be expected that they are greater than those reported for the ferrous ion in these investigations. Regardless, it would be predicted that the above considerations for weak acids also apply here. This would explain the fact that dilute solutions of sulfate ion, in acid solution, accelerate the oxidation[2] while concentrated solutions of sulfate ion act as retarders[2,4,6]. At some concentration of sulfate intermediate between these two extremes, the rate of oxidation should not be altered[5].

Pound[6] in his sutides on the relative rates of oxidation found that ferrous sulfate was more slowly oxidized than ferrous chloride. This may be explained by the increased stability of the sulfate complexes as compared with the stability of the chloride complexes.

The order of decreasing stability of the ferrous ammine sulfate double salts has been reported as ferrous ethylenediammonium sulfate, ferrous propylenediammonium sulfate, and ferrous ammonium sulfate[15,13].

This order of stability would be predicted from the instability constants reported in these investigations. (Table XX) It would be expected that, in acid solutions, only the mono-ammino complex would exist because of the low concentrations of the free ammine existing in solutions of high acidity. As a result, ferrous ethylenediammonium sulfate and ferrous propylenediammonium sulfate would have the same order of stability.

In conclusion, the results of these investigations may be summarized as follows:

1. The rates of air oxidation were measured, but inconclusive results were obtained.

2. The application of the spectrophotometric

method of continuous variations gave evidence for the existence of the ferro-mono-ammino complexes in solutions of ferrous sulfate-ammine sulfates. Further, evidence for the existence of the di-, tri-, and tetra ethylene diammono complexes was found.

3. The polarographic method was applied to the study of the ferro-ammono and ferro-complexes. Instability constants and formulae were reported for complexes.

4. An explanation for the relative stability of the ferrous ammine sulfate double salts was proposed.

B. Suggestions for Further Research

1. The stability of the ferri-sulfato and ammino- complexes should be investigated. The spectrophotometric method and polarographic method should be applicable.

2. The stability of the ferro-ammino complexes and the ferri-ammino complexes should be investigated through the application of the solubility method. These results would be a good check on the ferro-ammino results contained in this thesis.

3. The stability of complexes of ferrous and ferric iron with other anions of weak and strong acids, as well as with other ammines should be investigated. This would provide an admirable extension to the work

of Irving and Williams.[18]

PART IV

APPENDIX

I. Spectrophotometric Method

The "method of continuous variations" was first proposed by Job[26] for the determination of complex formation between two components in solution. Recently, it was extended by Vosburg and Cooper[27] to those cases in which more than one complex ion is formed by the reaction of two components in solution.

The formation of a complex ion may be represented by the general equation:

$$M^{+n} + nB \rightleftharpoons MB_n^{+n}$$

where M is the metal ion and B is the molecular or anionic ligand. The optical density of mixtures of equimolar mixtures of M and B is measured. This value is subtracted from the optical densities of M and B, calculated on the basis of no reaction between M and B. The value of n is then determined from a plot of this difference, Y, versus composition of the solutions. The resultant curve will have a maximum if the optical density of the complex ion is greater than either M or B and, conversely, a minimum if it is less.

More specifically, the experimental determinations were performed in the following manner. Mixtures of equimolar solutions of M and B (Concentration of S moles per liter) are made by mixing x liters of B to (1 - x) liters of M, where x is a value less than unity. For any mixture, the following equations will apply.

$$C = S(1 - x) - C_3$$

$$C = Sx - nC_3$$

$$C_1C_2^n = KC_3$$

where the subscripts 1, 2, and 3 refer to the metal ion (M), ligand (B), and complex ion (MB_n) respectively.

The condition for a maximum in the curve of C_3 plotted against x is

$$dC_3/dx = 0.$$

Upon the completion of the indicated differentiation, it is found that the condition for a maximum is given by the relationship

$$n = x/(1 - x) \qquad (5)$$

Consequently, the determination of the value of x for which C_3 is a maximum allows the calculation of n by equation (5).

It can also be shown that a maximum in Y corresponds to a maximum in C_3 if E_3 is greater than E_1 and, conversely, to a minimum if E_3 is less than E_1, where E is the extinction coefficient of the substance denoted by the subscript. This relationship is obtained by differentiating Y with respect to x, where Y is given by the following relationship:

$$Y = L(E_1C_1 + E_2C_2 + E_3C_3 - E_1S(1 - x) - E_2Sx) \qquad (6)$$

L is the length of cell used in the determination of the optical density.

When a second complex is formed, denoted by subscript 4, the condition for a maximum in C_3 is

$$n = \frac{x}{1 - x} + \frac{q(n + q)}{S(1 - x)} \cdot C_4 \qquad (7)$$

where q is the coordination number of the second complex.

If the stability of the two complexes is such that, when C_3 is a maximum, C_4 is small, n can be determined from the maximum in the C_3 curve and $(n + q)$ can be determined from the maximum in the C_4 - composition curve.

When three complex ions are formed in solution, it is assumed that when C_3 is a maximum, C_4 and C_5 should be at a minimum. Consequently, the treatment of three complexes is essentially the same as if only two complexes were formed.

Assuming that the extinction coefficient of the ligand (E_2) is zero and assuming that two complexes are formed, the condition for a maximum in Y becomes

$$\frac{dY}{dx} = L\left[(E_3 - E_1) \cdot \frac{dC_3}{dx} + (E_4 - E_1) \cdot \frac{dC_4}{dx}\right] \qquad (8)$$

Two conclusions are obvious from equation (8), (a) a maximum or minimum in Y does not have to coincide with a maximum in C_3 or in C_4 since dC_3/dx or dC_4/dx need not be zero for dY/dx to be zero; (b) the values of x at which Y is a maximum will vary with the values of the extinction coefficients of the complex ions and, consequently, with the wave length of the light used.

As a result of these conclusions, certain specific cases become of importance in the application of this method. Firstly, if the wave length of light is chosen so that E_4 equals E_1 and E_3 does not equal E_1, then a maximum in Y will correspond to a maximum in C_3. Secondly, if the wave length of light is so chosen that E_3 equals E_4, the same condition will result. Thirdly, if E_4 is much greater than E_3, Y will be a maximum when C_4 is a maximum, if the complexes are sufficiently stable, i.e. if C_3 is small when C_4 is large.

When three complexes are formed in solution, the same considerations are applied as above assuming, as is usually the case, that the complexes are sufficiently stable. This is assuming that C_3 is a maximum when C_5 is very small and, conversely, when C_5 is a maximum, C_3 is small. In conclusion, it must be pointed out that, in actual practice, the proper choice of wavelengths in accordance with the above criteria is a critical consideration.

II. Polarographic Method.

In the reduction of metal ions at the dropping mercury electrode, there are four possibilities that must be considered. Firstly, the reduction to a metal soluble in mercury; e.g. $Cu^{+2} \longrightarrow Cu(Hg)$. Secondly, the reduction to a metal insoluble in mercury, e.g. $Fe^{+2} \longrightarrow Fe$. Thirdly, the reduction from a higher oxidation state to a lower oxidation state, e.g. $Fe^{+3} \longrightarrow Fe^{+2}$. Fourthly, a combination of case three with case one, e.g. $Cu^{+2} \longrightarrow Cu^{+1}$ and $Cu^{+1} \longrightarrow Cu$, or case three with case two, e.g. $Fe^{+3} \longrightarrow Fe^{+2}$, $Fe^{+2} \longrightarrow Fe$. The fourth possibility will appear on the polarogram as two distinct polarographic waves. In these studies, we are concerned only with the second possibility.

The following derivation is taken from Kolthoff and Lingane.[28]

The electrode reaction for the reduction of a metal ion to a metal insoluble in mercury (e.g. Fe^{+2}) may be represented by the equation

$$M^{-n} + ne \longrightarrow M_{(s)}$$

If this reaction is reversible and very rapid compared to the rate of diffusion of the metal ions to the electrode, the dropping mercury electrode will be subject only to concentration polarization and, accordingly, its potential at every point on the polarographic wave should be given by the equation:

$$E_{d.e.} = E_m^{\circ} + \frac{RT}{nF} \log \frac{c_m^{\circ} f_m}{c_s\ f_s} \qquad (1)$$

where E_m° is the standard potential of the solid metal, c_m° is the concentration of the metal ion at the surface, and f_m is the corresponding activity coefficient.

If we assume that the activity of the deposited insoluble metal is constant (unity) and independent of the current density, the equation of the wave becomes

$$E_{d.e.} = E_m^{\circ} + \frac{RT}{nF} \log c_m f_m \qquad (2)$$

Equation (2), moreover, presupposes that the solid metal is completely insoluble in the mercury.

On the basis of the assumption that the current at any point on the wave is proportional to the concentration gradient between the surface of the drop and the body of the solution, we have the relationship

$$i = K_m(c_m - c_m^{\circ}) \qquad (3a)$$

where K_m is defined by the Ilkavic equation and is equal to $605\ nD^{\frac{1}{2}}m^{\frac{2}{3}}\ t^{\frac{1}{6}}$. n is the number of electrons taking part in the electrode reaction, D is the diffusion coefficient of the metal ion in solution, $m^{\frac{2}{3}}\ t^{\frac{1}{6}}$ is the capillary constant. When the diffusion current has reached a maximum, i.e. when $i = i_d$, the value of c_m° is negligible when compared with that of c_m, and we have:

$$i_d = K_m c_m \qquad (4a)$$

Solving equations (3a) and (4a), we find

$$c_m^{\,o} = \frac{i_d - i}{K_m}$$

Substituting this value into equation (2), we obtain:

$$E_{d.e.} = E_m^{\,o} + \frac{RT}{nF} \log \frac{f_m}{K_m} + \frac{RT}{nF} \log (i_d - i) \qquad (5)$$

In this case the half wave potential ($E_{d.e.} = E_{\frac{1}{2}}$ when $i = \frac{1}{2} i_d$) will be given by the relationship

$$E_{\frac{1}{2}} = E_m^{\,o} + \frac{RT}{nF} \log \frac{f_m}{K_m} + \frac{RT}{nF} \log \frac{i_d}{2} \qquad (6)$$

On substituting equation (4) into equation (6), we can relate the half wave potential to the concentrations.

$$E_{\frac{1}{2}} = E_m^{\,o} + \frac{RT}{nF} \log f_m + \frac{RT}{nF} \log \frac{c_m}{2} \qquad (7)$$

The applicability of this equation to the reduction of ferrous iron at the dropping mercury electrode is discussed in the section concerned with the discussion of the polarographic results. It is sufficient to say here, that it has been applied to the reduction of ferrous iron by Kerlinger[29] and Heyrovsky and Soũcek[30], and was found to be valid.

The dissociation of a complex metal ion may be represented by the equation

$$MX_p^{(n\,-\,pb)+} \rightleftarrows M^{n+} + pX^{-b} \qquad (8a)$$

where M is the metal, with oxidation number of n^+, and p is the coordination number of the metal ion with ligand X, which has an oxidation number of $-b$, where b may be 0, 1, 2, etc.

The instability constant for this complex may then be written as:

$$K_i = \frac{c_m c_x^{\,p}}{c_{comp.}} \cdot \frac{f_m f_x^{\,p}}{f_{comp.}} \tag{9}$$

where c is the concentrations, f the activity coefficients of the respective constituents, and K_i the instability constant for the complex.

Solving equation (9) for c_m and substituting the result into equation (7) we have:

$$E_{\frac{1}{2}comp.} = E_m^{\,o} + \frac{RT}{nF} \log \frac{f_s f_{comp.}}{f_m f_x^{\,p}} . K_i + \frac{RT}{nF} \log \frac{c_{comp.}}{2c_x^{\,p}} \tag{10}$$

Subtracting equation (7) from equation (10) we get

$$E_{\frac{1}{2}comp.} - E_{\frac{1}{2}metal} = \frac{RT}{nF} \log \frac{f_{comp.}}{f_m f_x^{\,p}} . K_i + \frac{RT}{nF} \log \frac{c_{comp.}}{2c_x^{\,p} . c_m} \tag{11a}$$

This equation may be rewritten in the form

$$E_{\frac{1}{2}comp.} - E_{\frac{1}{2}metal} = \frac{RT}{nF} \log K_i + \frac{RT}{nF} \log \frac{f_{comp.}}{f_m f_x^{\,p}} + \frac{RT}{nF} \log \frac{c_{comp.}}{c_x^{\,p} . c_m} + \frac{RT}{nF} \log 2 \tag{11b}$$

Assuming that the activity coefficient of the complex equals that of the metal and assuming further, that the activity of the ligand is very close to unity, we can write:

$$\Delta E_{\frac{1}{2}} = \frac{RT}{nF} \log \frac{K_i}{2} + \frac{RT}{nF} \log \frac{c_{comp.}}{c_m . c_x^{\,p}} \tag{12}$$

If we assume (1) that the reactions

$$MX_p^{(n\ -\ pb)+} \rightleftarrows M^{n+} + pX^{-b} \qquad (8a)$$

$$M^{n+} + ne \rightleftarrows M_{(s)} \qquad (8b)$$

are rapid and reversible at the dropping mercury electrode, and (2) that the metal ion in the body of solution exists entirely as the complex, i.e. the ligand is in excess, the following relationships become valid.

$$i = K_{comp.}(c_{comp.} - c^o{}_{comp.}) \qquad (3b)$$

where $c_{comp.}$ is the concentration in the body of the solution, $c^o{}_{comp.}$ is the concentration at the surface of the electrode, and $K_{comp.}$ is defined by $605\ n\ D^{\frac{1}{2}}{}_{comp.} \cdot m^{\frac{2}{3}}\ t^{\frac{1}{6}}$. When $i = i_d$, the $c^o{}_{comp.}$ is negligible and we can write

$$i_d = K_{comp.} \cdot c_{comp.} \qquad (4b)$$

Equations (4a) and (4b)

$$i_d = K_m c_m \qquad (4a)$$

$$i_d = K_{comp}{:}c_{comp.} \qquad (4b)$$

show that the ratio

$$\frac{c_{metal}}{c_{comp.}} = \frac{K_{comp.}}{K_{metal}} = \frac{n\ D_{comp.} m^{\frac{2}{3}}\ t^{\frac{1}{6}}}{n\ D_{metal}\ m^{\frac{2}{3}}\ t^{\frac{1}{6}}}$$

Consequently, for a constant drop time with the same capillary, the ratio of $c_{comp.}/c_{metal} = \dfrac{D^{\frac{1}{2}}\ metal}{D^{\frac{1}{2}}\ comp.}$.

Substituting this ratio into equation (12), we have

$$E = \frac{RT}{nF} \log \frac{K_i}{2} + \frac{RT}{nF} \log \frac{D^{\frac{1}{2}}metal}{c_x{}^p . D^{\frac{1}{2}}{}_{comp.}} \qquad (13)$$

Assuming further, that the ratio $D^{\frac{1}{2}}_{metal}/D^{\frac{1}{2}}_{comp.}$ is unity, which is a valid assumption, we can write equation (13) in the form

$$\Delta E_{\frac{1}{2}} = \frac{RT}{nF} \log \frac{K_i}{2} - \frac{RT}{nF} \log c_x{}^{p} \qquad (14)$$

Transforming this equation to logarithms to the base 10, and substituting for $\frac{RT}{F}$ the values at 25°C, we have the final equation for the determination of the formula and instability ion of a complex of a metal insoluble in mercury.

$$\Delta E_{\frac{1}{2}} = \frac{0.059}{n} \log_{10} \frac{K_i}{2} - \frac{0.059}{n} P \log_{10} c_x \qquad (15)$$

Equation (15) is of the form $y = mx + b$, or the equation of a straight line. Consequently, a plot of E as ordinate and $\log_{10} c_x$ as abscissa will give us a straight line of slope $-\frac{0.059}{n} P$, and an intercept of $\frac{0.059}{n} \log_{10} \frac{K_i}{2}$.

Since there were many assumptions in the above derivation, and an equation is only as good as the assumptions made in its derivation, the above assumptions are collected and listed below. This will allow of a more rapid and sounder evaluation of the above assumptions.

Assumption 1. The solubility of iron in mercury is neglibible.

Assumption 2. The electrode reaction is reversible and rapid as compared with the rate of diffusion.

Assumption 3. Activity of the deposited metal is constant and independent of the current density.

Assumption 4. Current at any point on wave is proportional to concentration gradient.

Assumption 5. c_m^o is negligible as compared to c_m when $i = i_d$.

Assumption 6. The equation for the half wave potential for the reaction $Fe^{+2} + 2e \longrightarrow Fe$ obeys the equation $E_{\frac{1}{2}} = E^o + \frac{RT}{nF} \log f_m + \frac{RT}{nF} \log \frac{c}{2}$. This assumption is a culmination of assumptions 1 through 5. Consequently, if this equation is found to be valid for the reduction of ferrous iron to the metal, then assumptions 1 through 5 must either be valid or cause errors which tend to cancel each other. This equation has been found to be valid by Heyrovsky and Souček,[30] and Kerlinger and Laitinen[29].

Assumption 7. The metal ion exists in the body of the solution completely as the complex. This is a valid assumption in the presence of an excess of ligand, which is the usual case in the polarography of complex ions.

Assumption 8. $D^{\frac{1}{2}}_{metal}/D^{\frac{1}{2}}_{comp.}$ is unity. Since the values are raised to the one-half power, this assumption should be valid.

Table XXI A

Mono-sulfato Complex

N	-Y	-X	XY	X^2
1	2	1.889	3.778	3.568321
2	4	1.784	7.136	3.182656
3	7	1.644	11.508	2.702736
4	11	1.489	16.302	2.196324
5	13	1.429	18.577	2.042041
6	15	1.412	21.180	1.993744
7	18	1.305	23.490	1.703025
	70	10.952	101.971	17.388847

Table XXI B

Di-sulfato Complex

N	-Y	-X	XY	X^2
1	23	1.248	28.704	1.557504
2	27	1.198	32.346	1.435204
3	29	1.165	33.785	1.357225
4	28	1.150	32.200	1.322500
5	30	1.141	34.230	1.301881
6	34	1.096	37.264	1.201216
7	37	1.040	38.480	1.081600
8	38	1.006	38.228	1.012036
	246	9.044	275.237	10.269166

Table XXI C

Tri-sulfato Complex

N	-Y	-X	XY	X^2
1	45	0.961	43.245	.923521
2	45	0.914	41.130	.835396
3	47	0.907	42.629	.822649
4	46	0.895	41.170	.801025
5	53	0.861	45.633	.741321
6	51	0.856	43.656	.732736
7	53	0.845	44.785	.714025
8	41	0.972	39.852	.944784
	381	7.211	342.100	6.515457

Table XXI D

Tetra-sulfato Complex

N	-Y	-X	XY	X^2
1	56	0.814	45.584	.662596
2	66	0.722	47.652	.521284
3	69	0.699	48.231	.488601
4	73	0.699	51.027	.488601
5	74	0.644	47.656	.414736
6	77	0.641	49.357	.410881
	415	4.219	289.507	2.986697

Table XXI E

Hexa-sulfato Complex

N	-Y	-X	XY	X^2
1	88	0.571	50.248	.326041
2	87	0.579	50.373	.335241
3	92	0.550	50.600	.302500
4	97	0.524	50.304	.274576
	364	2.224	202.049	1.238358

Table XXI F

Summary

Complex	-m	p	-b	-log K/2
1	29.76	1.00	56.561	1.91735
2	63.7966	2.16	102.87229	3.48718
3	84.6332	2.87	123.9143	4.20048
4	115.147	3.90	150.13368	5.08927
6	184.674	6.26	193.67916	6.56539

Table XXII A

Mono-ethylenediammono Complex

N	-Y	-X	XY	X^2
1	26	3.527	91.702	12.439729
2	45	3.110	139.95	9.67210
3	53	2.679	141.987	7.177041
4	63	2.609	164.367	6.806881
	187	11.925	538.006	36.095751

Table XXII B

Tri-ethylenediammono Complex

N	-Y	-X	XY	X^2
1	75	2.465	184.875	6.076225
2	94	2.343	220.242	5.489649
3	101	2.191	221.291	4.800481
4	109	2.118	230.862	4.485924
5	121	2.034	246.114	4.137156
6	128	1.931	247.168	3.728761
	628	13.082	1350.552	28.718196

Table XXII C

Summary

Ethylene-diamine	-m	p	-b	-log K/2
1	35.80	1.213	153.47981	5.20270
2	95.8469	3.249	313.64502	10.63203

Table XXIII A

Mono-propylenediammono Complex

N	-Y	-X	XY	X^2
1	76	2.656	201.856	7.054336
2	84	2.358	198.072	5.560164
3	92	2.128	195.776	4.528384
4	115	1.409	162.035	1.985281
5	117	1.304	152.568	1.700416
6	119	1.208	143.752	1.459264
	603	11.063	1054.059	22.287845

Table XXIII B

Tri-propylenediammono Complex

N	-Y	-X	XY	X^2
1	119	1.208	143.752	1.459264
2	129	1.128	145.512	1.272384
3	135	1.053	142.155	1.108809
4	138	0.993	137.034	.986049
	521	4.382	568.453	4.826506

Table XXIII C

Summary

Propylene diamine	-m	p	-b	-log K/2
1	30.57527	1.036	156.87572	5.31782
2	88.4726	2.999	227.17175	7.70073

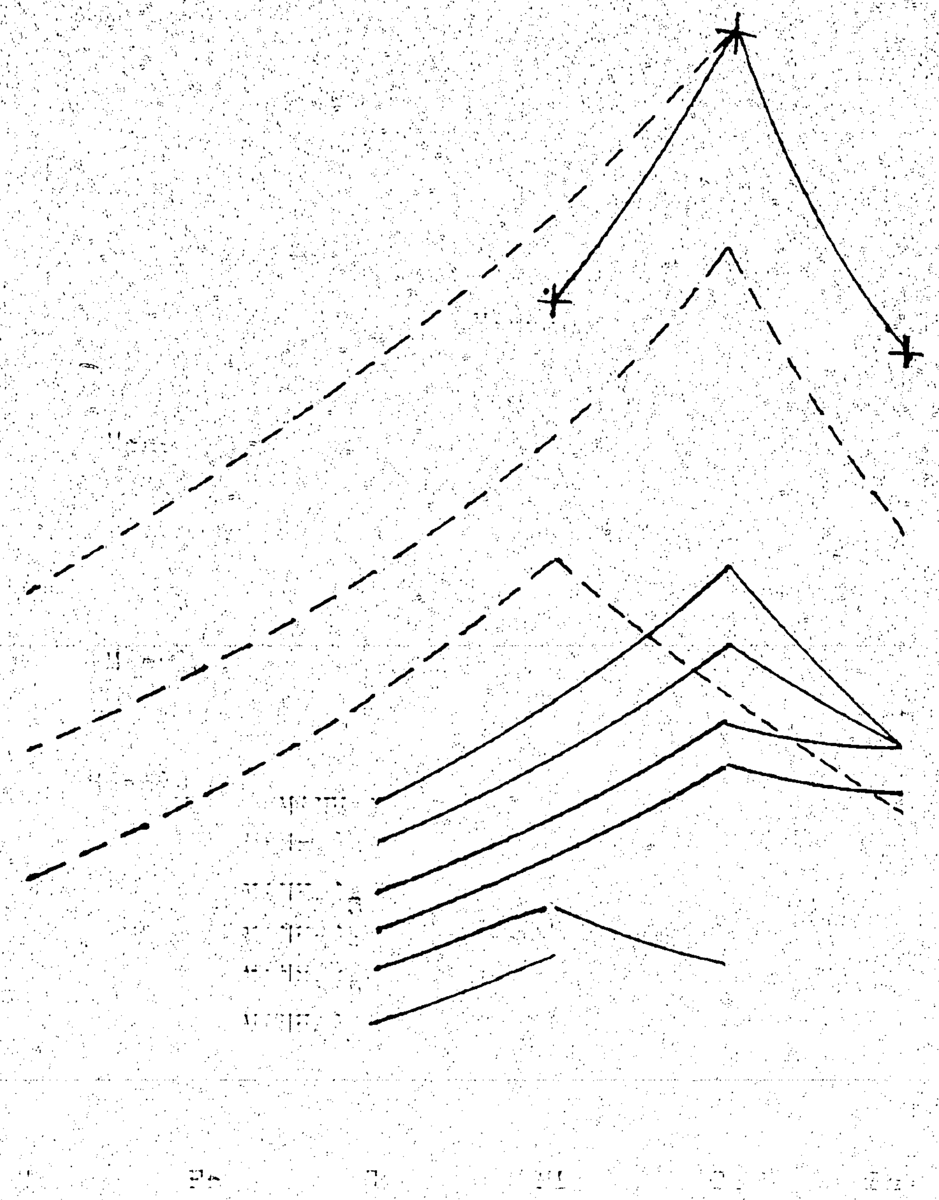


FIGURE II
FERRO-AMMONO COMPLEXES

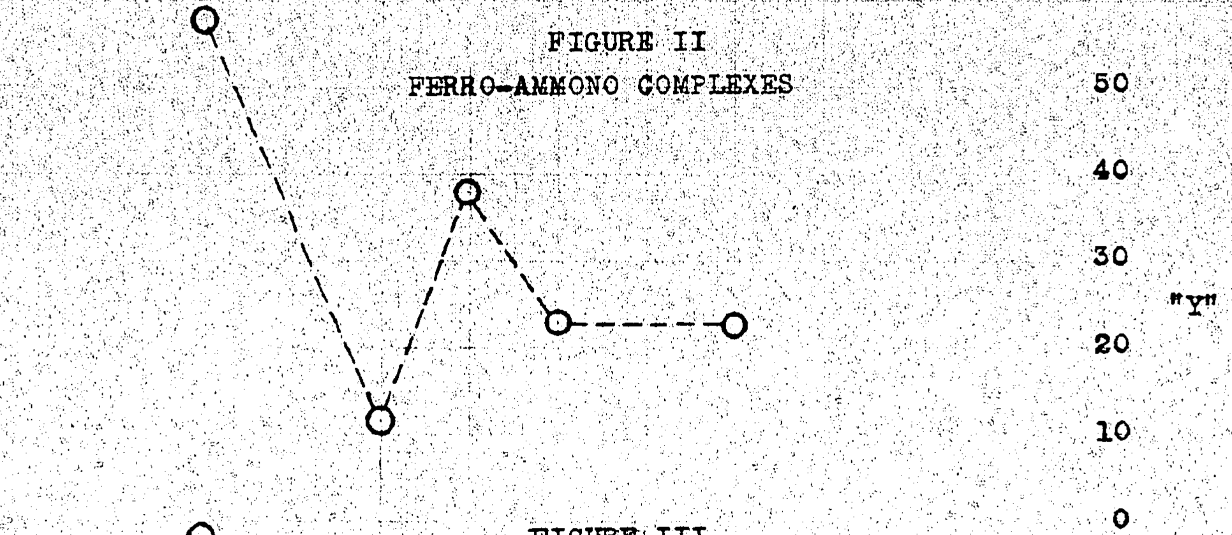


FIGURE III
FERRO-ETHYLENEDIAMMONO COMPLEXES

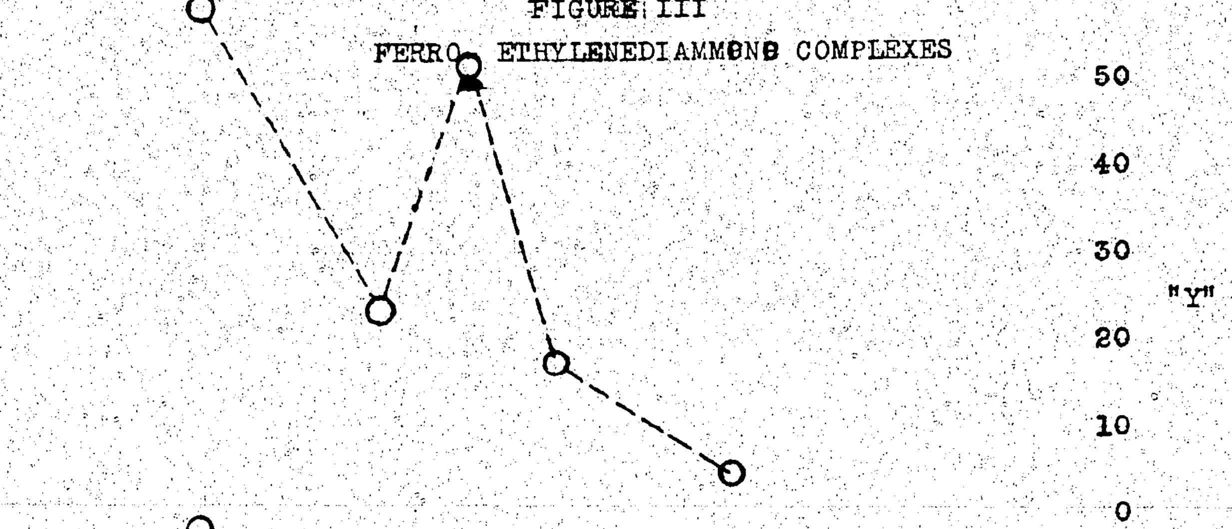


FIGURE IV
FERRO-PROPYLENEDIAMMONO COMPLEXES

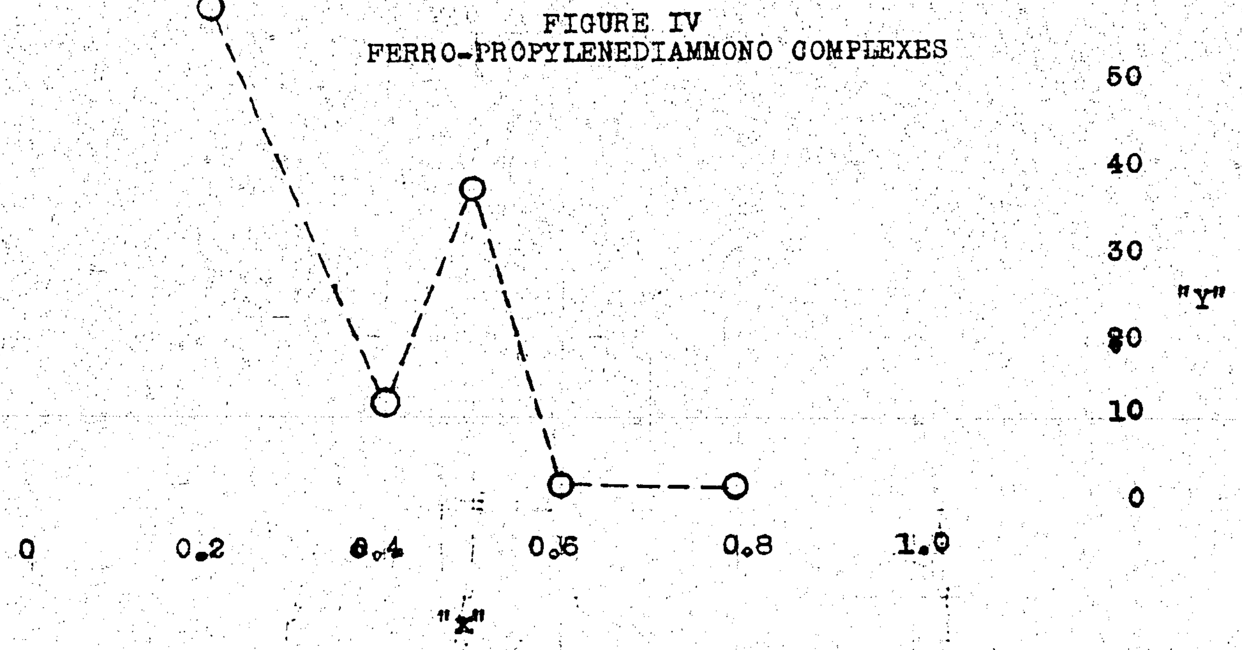


FIGURE V

(A) "Y" determined at 300 mu
(B) "Y" determined at 280 mu
(C) "Y" determined at 243 mu

FERRO-ETHYLENEDIAMMONO COMPLEXES

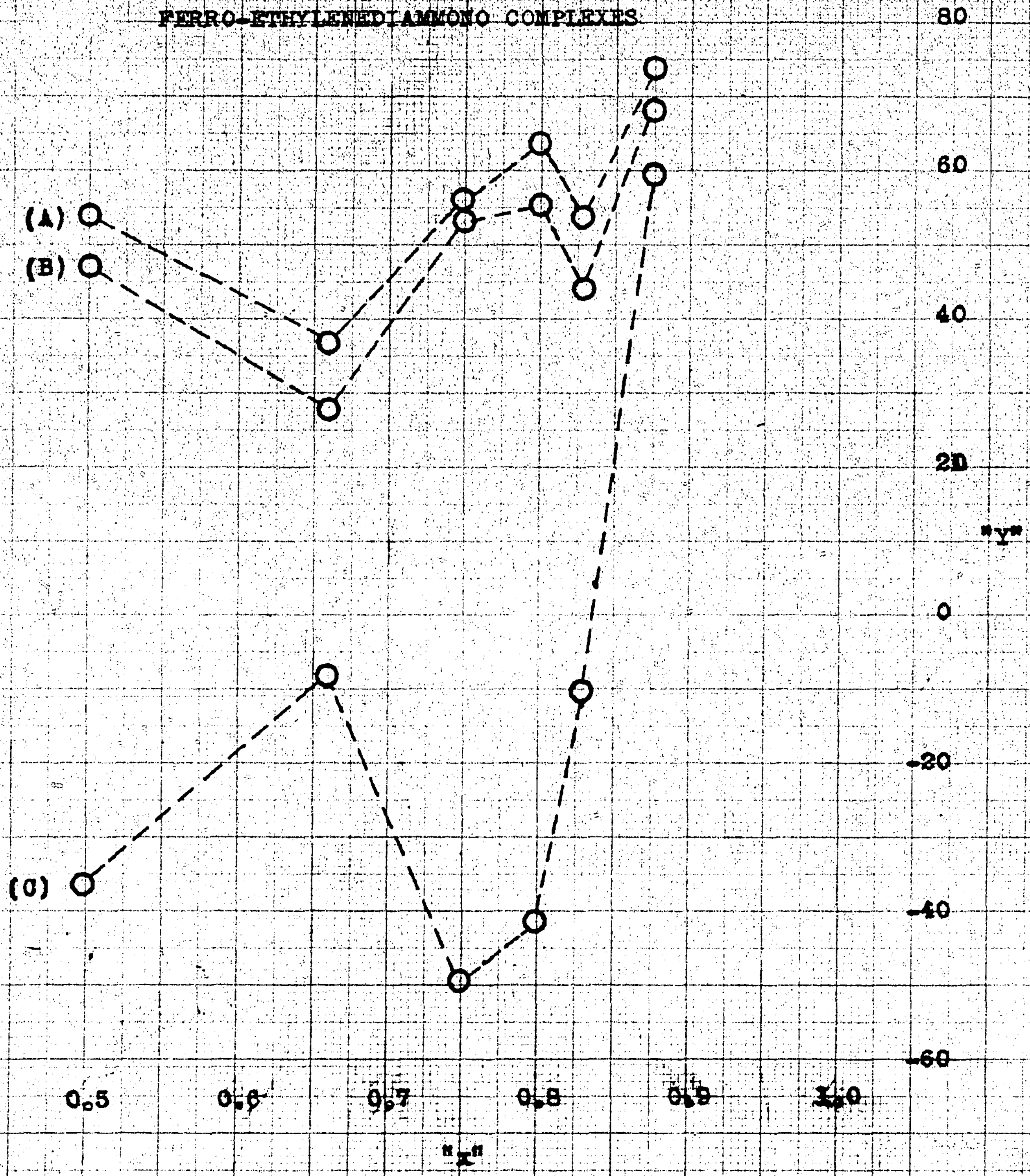
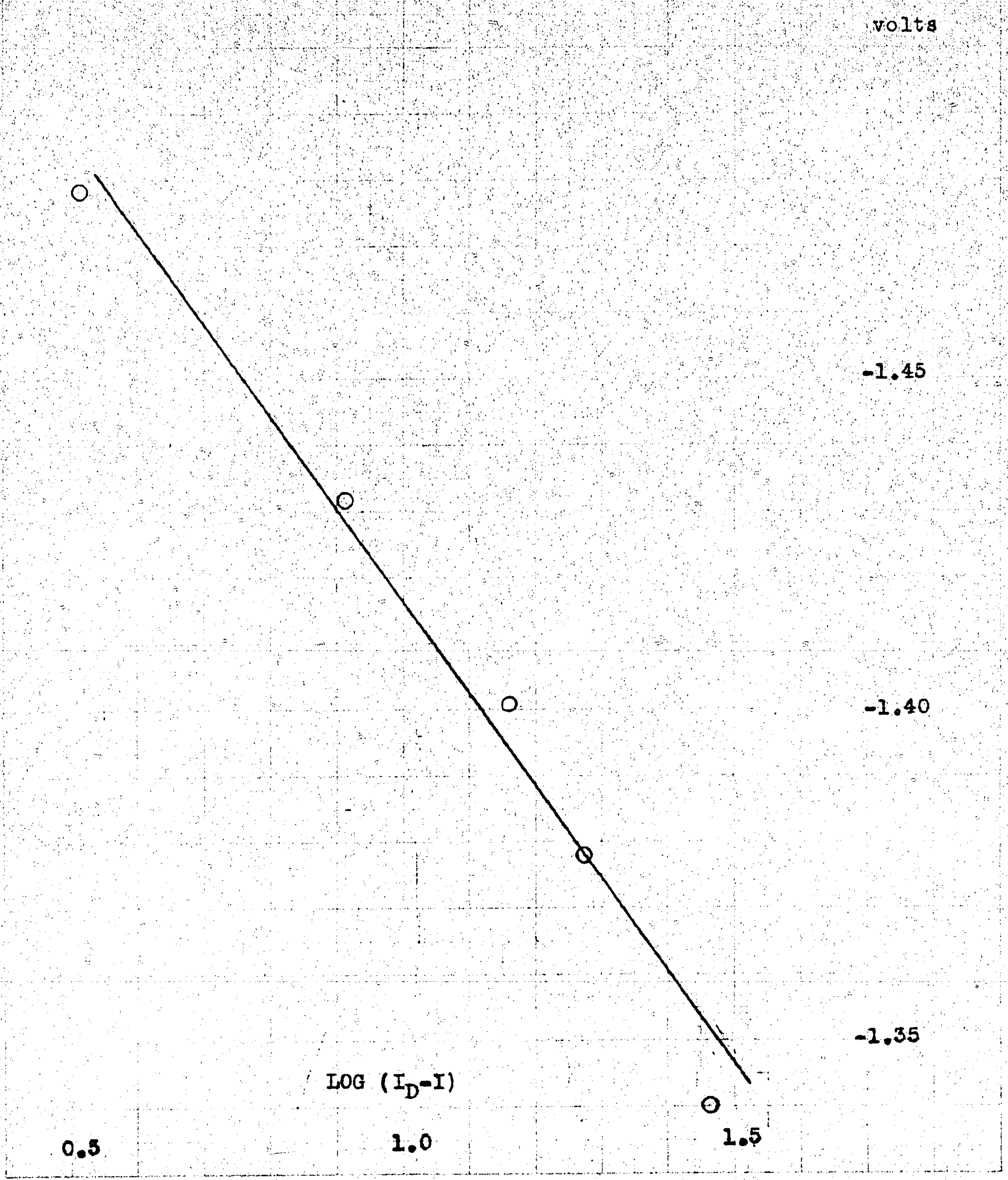


FIGURE VI (A)

POLAROGRAM 4



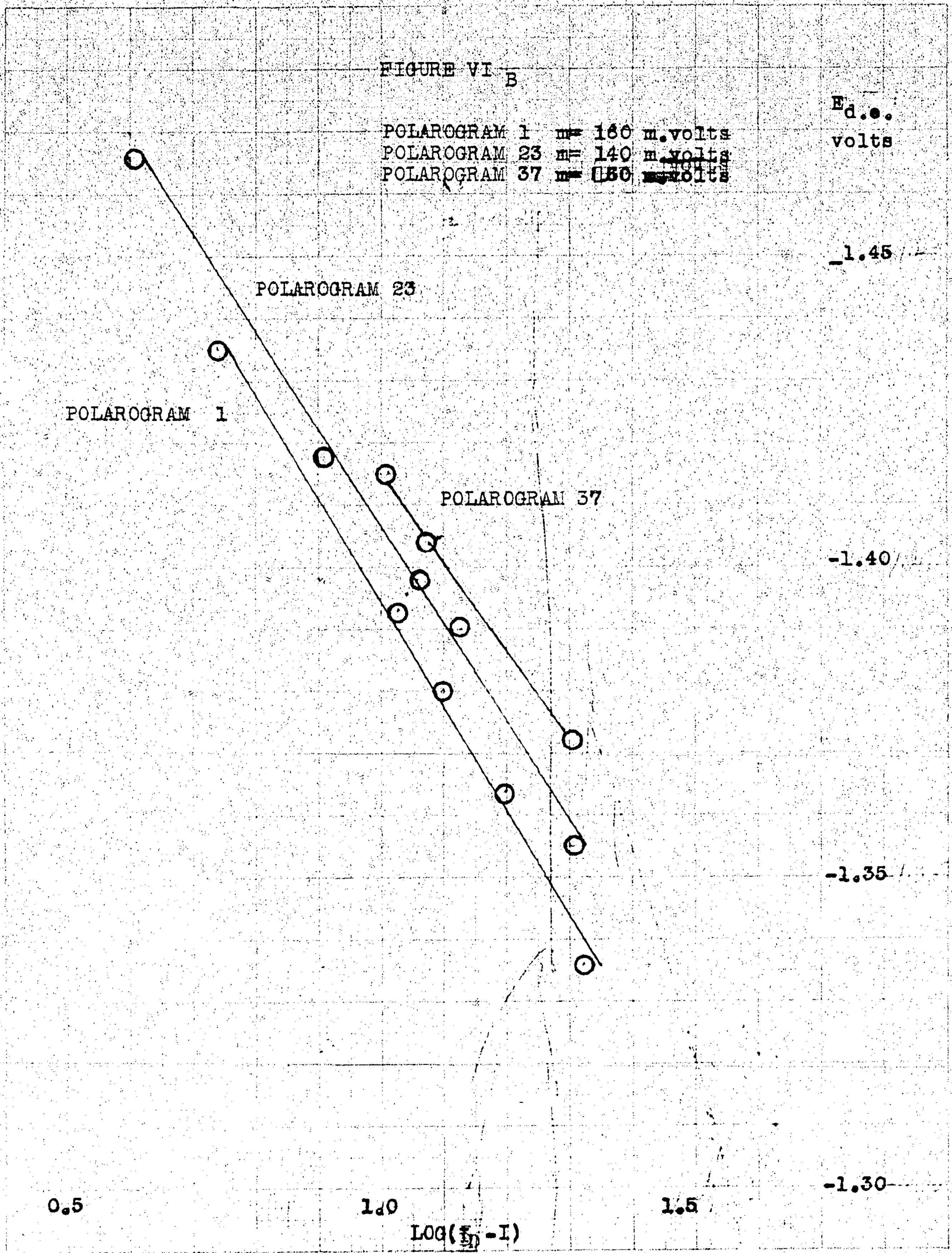


FIGURE VI_B

POLAROGRAM 1 m= 160 m.volts
POLAROGRAM 23 m= 140 m.volts
POLAROGRAM 37 m= 150 m.volts
$E_{d.e.}$
volts
-1.45
-1.40
-1.35
-1.30
POLAROGRAM 23
POLAROGRAM 1
POLAROGRAM 37
0.5
1.0
1.5
LOG(I_D-I)

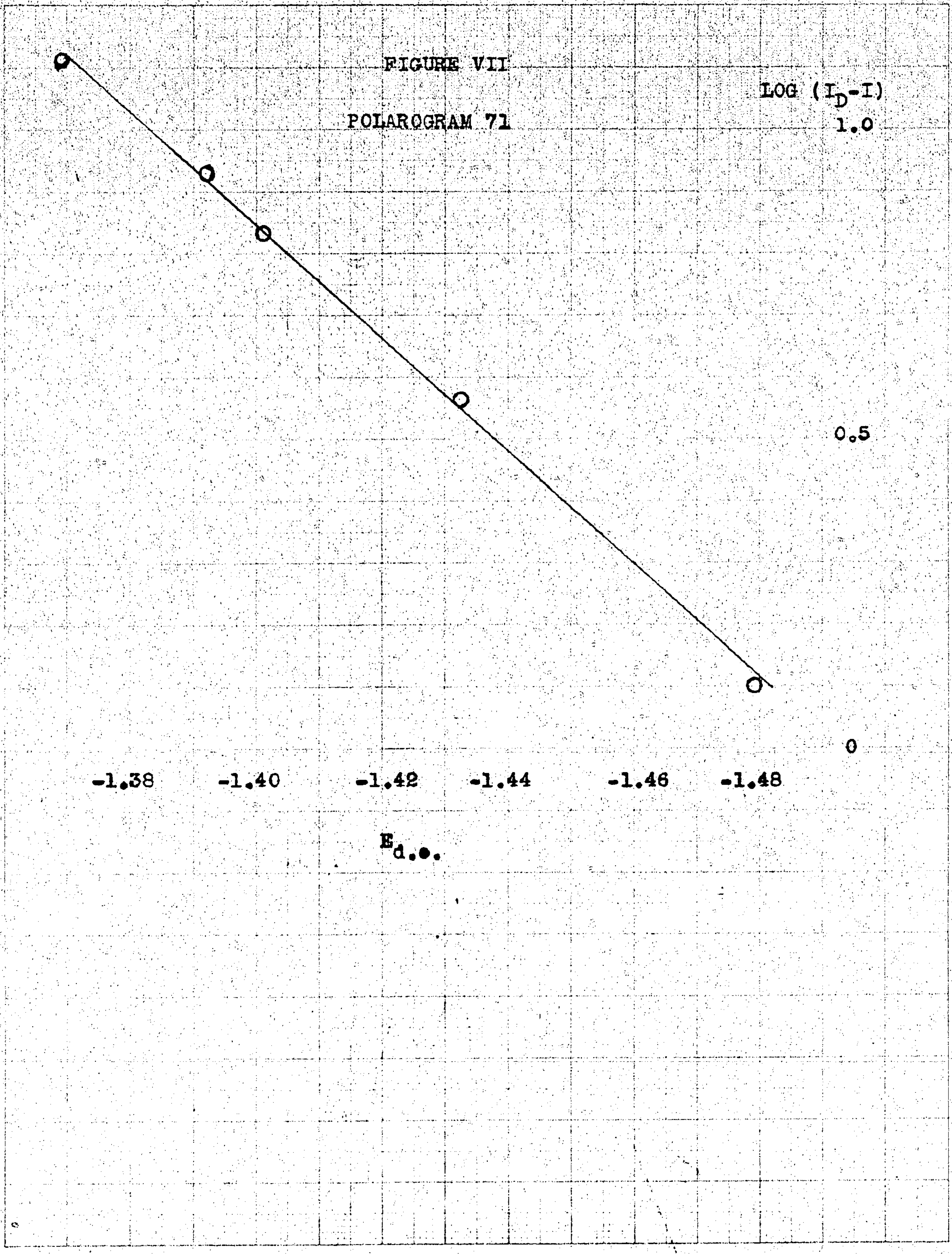
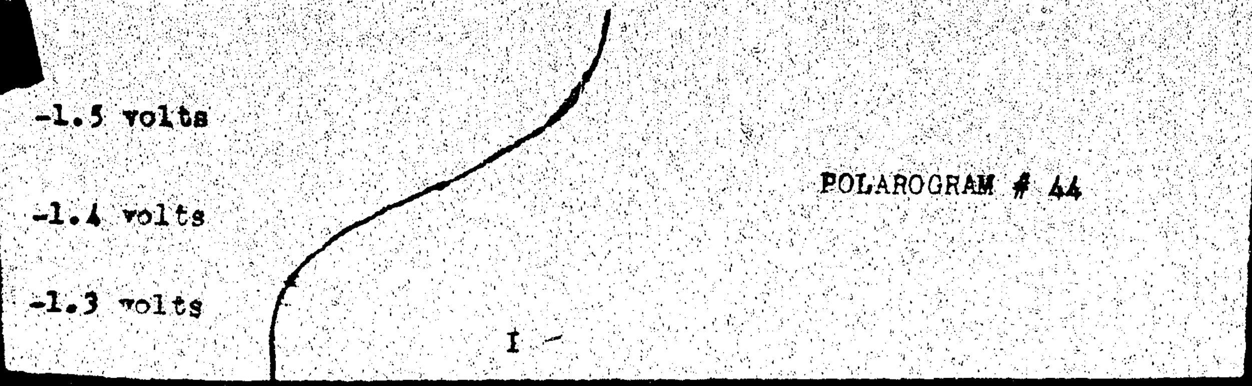


FIGURE VII

POLAROGRAM 71

FIGURE VIII



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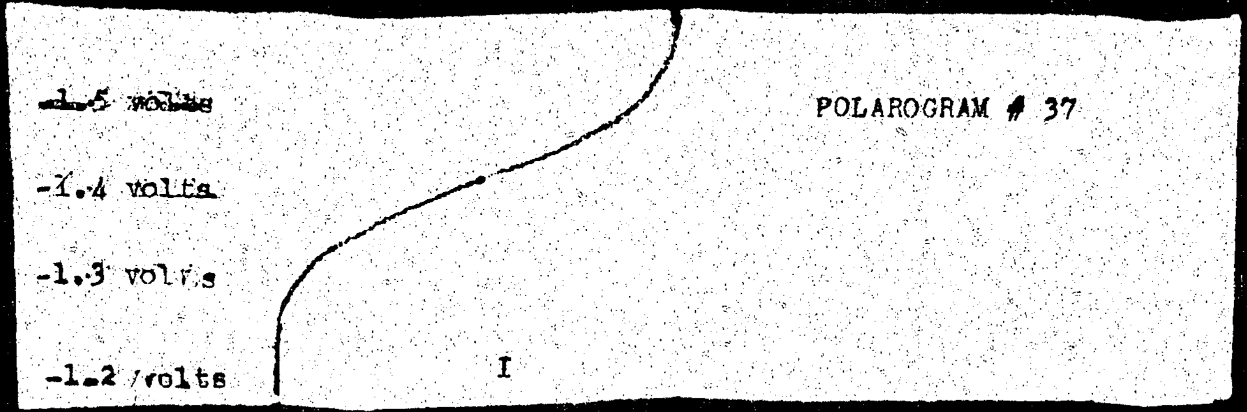

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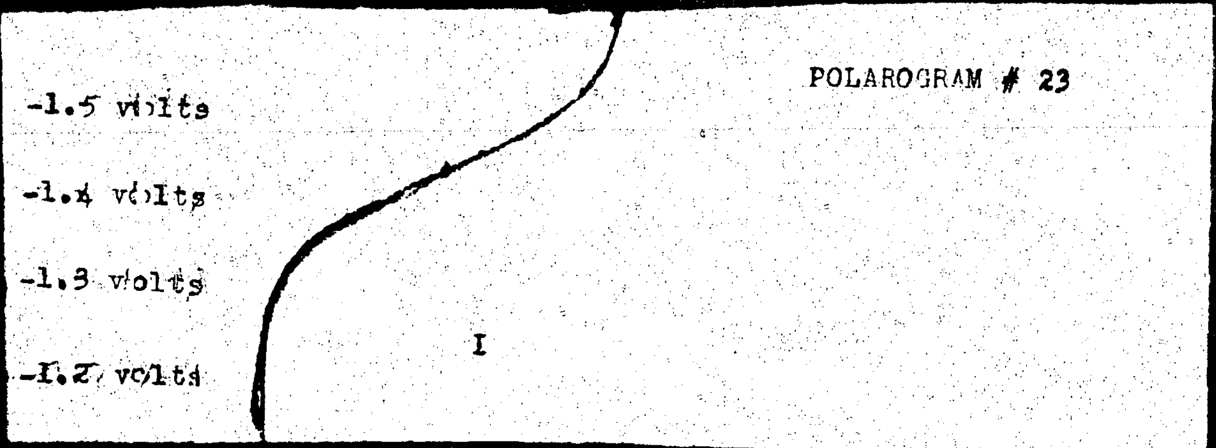

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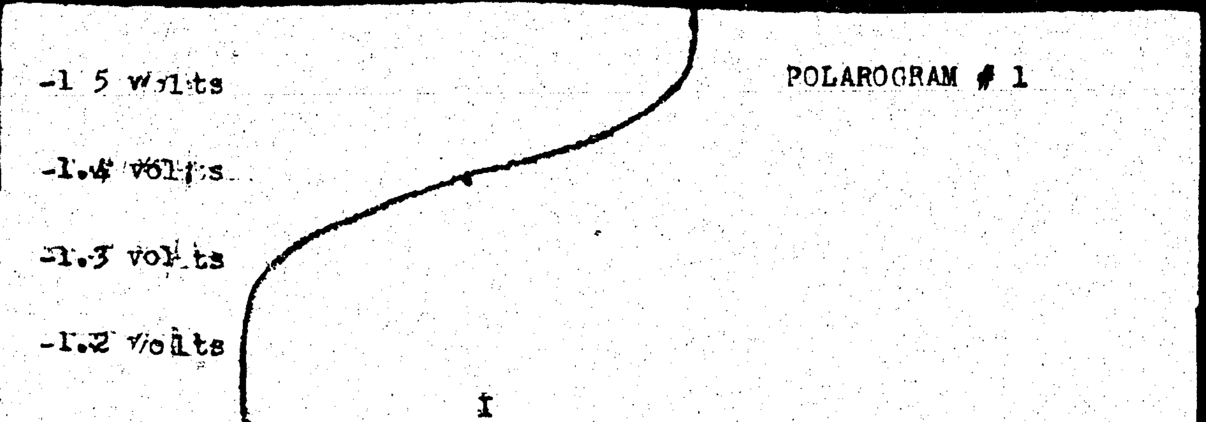

POLAROGRAM # 1

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