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Polarographic studies of complex ions

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POLAROGRAPHIC STUDIES OF COMPLEX IONS

by

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I. INTRODUCTION

It has been known for at least fifty years that iron forms colored compounds in solution with sulfosalicylate (1). These complexes have been used for the determination of iron colorimetrically (2-26) and conductimetrically (27), and indirectly for the colorimetric determination of borate (28) and fluoride (29,30). They have also been used for the separation of iron from titanium, aluminum, manganese, magnesium, thallium, uranium and phosphates (31-35). However, very little was known about the identity and stability of these complex ions. Although the yellow colored complex (alkaline solution) has been most often used analytically, less was known about it than about the red-violet colored complex (acid solution). Some have thought that the yellow color of the alkaline solutions was caused by the breakdown of the red colored complex to form colloidal hydrous ferric oxide (30,36). This however does not seem consistent with the fact that in alkaline solutions, at the same pH and ionic strength, ferric ion is much more soluble in the presence of sulfosalicylate than in its absence.

The polarographic method has been found suitable for the study of other iron complexes by other authors, since these complexes have half-wave potentials that fall within the polarographic range (0 to -1.8 volts versus saturated calomel electrode). This method was found most applicable in this case to the study of the yellow colored complex, as here the ferric waves are more negative than the calomel electrode, so that the half-wave potentials may be used in the study of the complex ions. Also the ferrous wave is developed more completely, without the interference of the hydrogen-ion wave. For these reasons, and because there was less known about the yellow colored complex, the present research, for the most part, has been concerned with the iron-sulfosalicylate complex in alkaline solution.

The dissociation constants of sulfosalicylic acid were known only in very rough approximation (30,37,38). As the knowledge of the second constant would aid in the interpretation of the variation of the iron-sulfosalicylate complexes with pH, a short spectrophotometric study of this constant was made and the results are reported here. As this ionization is quite strong, only a rough estimate could be made from potentiometric pH curves. However, the absorption of ultraviolet light by the singly and doubly ionized sulfosalicylate ions are quite different and this permitted a determination of the second constant from this property of sulfosalicylic acid solutions.

II. REVIEW OF THE LITERATURE

A. Polarographic Method for Complex-Ion Study

The method used was essentially that first described by Heyrovský and Ilkovič in 1935 (39). The half-wave potentials of series of solutions in which all factors except concentration of complexing agent were kept constant were plotted against the logarithms of this concentration. The slope of the straight line obtained was proportional to the number of molecules or ions of complexing agent combined with the metal ion in the complex, and the intercept with the axis corresponding to the half-wave potential of the uncomplexed metal ion was a function of the instability constant of the complex ion. The method will be described in further detail in Section V.

This method was described rather completely by Tomés (40), Stackelberg (41), Stackelberg and Freyhold (42), Kolthoff and Lingane (43), Lingane (44), and most recently by Souchay and Faucherre (45). Tomes was mainly interested in the study of the dissociation of a weak electrolyte. He developed the equations for the two extreme cases with regard to the concentration of the anion of the salt. The first case was that of a weak electrolyte in solution with a supporting electrolyte that does not contain ions that are common to the weak electrolyte. In this case the concentration of the anion of the salt studied, corresponding to the complexing agent, was negligible. He found theoretically that the wave in this case is not symmetric as it is in the reduction of a free metal ion, the slope of the wave is less, and the half-wave potential varies with the concentration of the weak electrolyte, in contrast to the case of the free metal ion in which the half-wave potential was an independent constant for a given metal ion. He tested this theory successfully on mercuric cyanide.

The second case described was that in which the supporting electrolyte had the anion in common with the weak electrolyte. This was the same as the method used generally for the study of complex ions, in which the half-wave potential varied with the concentration of the total complexing agent.

Stackelberg's paper on the scientific basis of polarography had a short section on the evaluation of complex ions with the half-wave potential method (41). It was more completely treated in the later paper of Stackelberg and Freyhold (42). They listed the limitations of the method, the most serious of which is the necessity of reversibility of the reduction. If the reduction is irreversible, equilibrium is not maintained between the complex ion and its simple ion, so that an overvoltage is required. The potential is then not a true measure of the stability of the complex. The most reliable test for reversibility, according to these authors, is the comparison of the anodic wave, from the oxidation of the reduced form of the complex, with the cathodic wave caused by the reduction of the oxidized form of the complex. Reversibility is proved only if these waves coincide on the potential scale. If one of them is displaced with respect to the other, the oxidation-reduction system is irreversible and is useless for the study of the stability and composition of the complex by polarographic means. Also, usually the slope of the wave is less than the theoretical value when the reduction is irreversible, and this has been used by Lingane and others as a criterion for reversibility. Stackelberg and Freyhold stated, however, that this is not reliable, and cited the case of zincate that they studied. The reduction wave of zincate was well formed and had the theoretical slope, and its half-wave potential varied regularly with hydroxyl-ion concentration, giving the expected value of four for the number of hydroxyl ions necessary for its formation. However, the instability constant for the complex obtained polarographically differed greatly from reliable values obtained by other methods. When zinc amalgam was used in the dropping electrode, the anodic wave was found to have a considerably different half-wave potential from that of the cathodic wave. This showed irreversibility, which explained the discrepancy in the values for the instability constants.

Another limitation of this method is that the solution must be either buffered with respect to the complexing agent, or have a high concentration of complexing agent in comparison with that of the complex ion if complexing agent is liberated or taken up in the reduction. This has been neglected by some workers, causing their results to be unreliable.

A third limitation is that since a rather high concentration of supporting electrolyte must be maintained, the ionic strength must of necessity be high. This means that the activity coefficients vary considerably from 1 and the instability constants obtained are good for that ionic strength only. Also, because of departure of the polarographic wave from the ideal shape, the accuracy of the instability constant is quite low, because of uncertainty of the half-wave potentials.

Another limitation that was pointed out in the extensive study of the copper ammine complexes by Stackelberg and Freyhold is that because of the necessarily high concentration of the complexing agent in comparison with that of the complex ion, the lower complexes of the metal ion (ones with fewer molecules of complexing agent) are often not observed. Generally then only the higher complexes of the ions can be studied.

One of the systems described briefly in this paper was the zinc oxalate system. This one was found to be obviously irreversible. The polarographic treatment of this complex by Sartori (46) was reported by these authors to be incorrect.

In the investigation of the iron fluoride complexes it was found that the reduction of the ferrous complex to the metal could not be observed polarographically. Because of the great stability of the complex the half-wave potential is shifted to a value more negative than the polarographic range. The ferric-ferrous potential was investigated however, from which was obtained the ratio of the instability constants of the complexes in the two different oxidation states. Analogous conditions were observed with the iron oxalate system. A very thorough analysis of the copper chloride complexes was also reported in this paper.

Kolthoff and Lingane (43) have devoted a chapter of their monograph on polarography to the description of the interpretation of the polarographic waves of the metal-ligand complex ions and the derivation of the basic equations. Extension of the method to cases where one complex ion is reduced to another complex ion, where a complex ion is reduced in a stepwise manner, and where the complex ion consists of a neutral weak electrolyte were described in this chapter. Examples that were given of systems that had been examined by this method were the biplumbite system, studied by Lingane (44), the ferric and ferrous oxalate system, by Stackelberg and Freyhold (42) and by Lingane (44), the copper ammine system by these same authors (42,44), and the mercuric cyanide system by Toměs (40).

The paper by Lingane (44) in Chemical Reviews had essentially the same material as the chapter in Kolthoff and Lingane (43). A description was included of cases having several irreversible waves for one actual reduction stage, caused by the existence of several complex ionic species in solution that are only slowly transformed from one to the other. An example cited was the zinc-cyanide complex ions studied by Pines (47). The polarograms for these complexes have three waves at low cyanide concentration. They disappear one by one when the cyanide concentration is increased, until finally there are no waves at high cyanide concentrations. Obviously, this cannot be reduction to successive oxidation states, as zinc has no known monovalent salts. Also, there are three waves, more than could be accounted for by stepwise reduction. It was thought that the waves represent the uncomplexed zinc ion, tetracyanozinc and pentacyanozinc ions which are only slowly interconverted, and that at high cyanide concentrations only the hexacyanozinc ion, which is not reducible in the polarographic range, exists. Also mentioned were similar cases of trivalent goldcyanide complex ions studied by Herman (48) and the prewave observed by Brdička in the reduction of cobaltous chloride (49).

Souchay and Faucherre (45) described the tangent potential method of polarographic study of complex ions that was used prior to about 1935, before the thermodynamic significance of half-wave potentials was known, as well as the half-wave potential method now generally used. The former method, first used by Heyrovský (50), consists of obtaining the potential of the curve where it is tangent to a line with slope of one, both with and without complexing agent. By means of the Nernst equation the concentration of the free metal ion in the complexed solution could be determined from the difference in potentials. The concentration of the complex ion was then determined by difference. By trial and error substitution into the mass action equation the number of molecules of complexing agent per metal ion could be determined, and the average instability constant calculated. Souchey and Faucherre generalized the half-wave potential method so that the data obtained at the 45° tangent could be used instead of the half-wave potentials. Generally any desired potentials could be used, as long as all of the potentials are taken for the same ratio of current to limiting current. They illustrated this method using the tangent potentials obtained by Dobryszycki for the cadmium and zinc ammines (51) and by Pines for the cadmium-cyanide complex ions (52). They pointed out that this method has disadvantages that are not present in the half-wave potential method. The measurement of potential is in general less accurate, as it is easier to construct the half-wave potential. Also variation of the wave height may be considerable, as illustrated by the copper-tartrate complex ion in 0.1 M KOH solution which varies from 97 to 39 mm. when the concentration of tertrate is changed from 0.004 M to 0.2 M. This causes uncertainty in the measurement of tangent potentials. However, the authors of this paper recommended it in cases where there is a pronounced maximum, which makes the half-wave potential uncertain. In many of these cases the lower half of the curve is unaffected by the maximum, so that the tangent potentials are here more accurate than half-wave potentials. They illustrated this by data they obtained with bismuth-mannitol and basic antimony-mannitol complex ions. As examples of the half-wave potential method the study by Lingane of the stannous-chloride complex ion (53) and their own study of the cadmium-pyrophosphate system were cited.

It was pointed out that in the case of stepwise reduction of complex ions having more than one ionic oxidation state the data from the first wave gives only the ratio between instability constants of the complexes in the two oxidation states and likewise only the difference in the number of molecules of complexing agent in the two complexes. The absolute values may be obtained from these if the succeeding steps in the reduction are capable of treatment by the same method. Thus the final reduction to the metallic state gives the constants, for the amalgam does not contain complex ions of this nature. Neglect of this has made the results of Caglioti and Sartori on the titanic-tartrate complex ions (54) useless according to Souchey and Faucherre.

This paper also contained an extensive section on the principal causes of error in polarographic studies of complex ions. The most frequent of these is irreversibility. The criteria mentioned in the discussion of the paper of Stackelberg and Freyhold (42) were also listed by these authors.

There seems to be no way to predict whether a system will be reversible or not by analogy with very similar systems. Cited was the irreversibility of iron-citrate complex ions in alkaline medium in contrast to the iron-tartrate complex ions in alkaline medium, which are reduced reversibly. Also in alkaline solution antimony-tartrate complex ions are reduced irreversibly, while the corresponding complex ions with mannitol are reduced reversibly. However, some general rules were stated. One is that above a certain concentration of reducible ion the waves are always irreversible. This maximum concentration is a function of the individual ion, but seldom varies greatly from a few millimoles per liter. Also, the concentration of the complexing agent affects the reversibility, the reduction of the ion generally being irreversible in the presence of very large concentrations of complexing agent. Some metals, such as copper, cadmium, and lead have complex ions which are generally reduced reversibly, while the complex ions of nickel and cobalt, for example, are almost always reduced irreversibly. In the case of nickel and cobalt even the supposedly uncomplexed ions yield waves with small slopes and all the other characteristics of irreversibility. This was attributed to slowness of the aquo ion in breaking down to the unhydrated ions that are reduced at the electrode. In concentrated chloride solutions the wave is better formed, probably because the chloride complex ion is more reversibly dissociated than the aquo complex. The thiocyanate complex, however, has the best waves, with the theoretical slope and more positive half-wave potential than the aquo complex.

Several examples of published work that is incorrect because of irreversibility of the systems were described. They found that the zinc-pyrophosphate waves were obviously irreversible, showing that the work on this system by Sartori (46) is valueless. Also, the same author studied the nickel-cyanide complex ions, using concentrated chloride solutions as his uncomplexed nickel solutions (55). However, as shown above, the waves of the nickel chloride solutions are more negative than those of nickel in thiocyanate solutions, in which nickel is known to be complexed. This means that the nickel in the chloride solutions must be complexed by chloride, or else the reduction from this solution is irreversible. Also, it was later shown by Hokhshtein (56) that the cyanide ions affect the anode potential of mercury pool. Souchay and Faucherre used an external reference electrode for this system and found that the half-wave potentials did not vary with concentration of cyanide, which is an anomaly showing irreversibility. The reduction of cobalt in cyanide solutions was more evidently irreversible, as the slope was quite small. This means that the cobalt-cyanide data reported by Sartori in the same paper is also useless.

Another source of error is trying to draw conclusions from data over too limited a range. These authors stated that the concentration of the complexing agent should be varied at least by a factor of ten, so that the potential may have a range of at least 59xp/n millivolts (p is number of ions or molecules of complexing agent per metal ion, n is the number of electrons needed for the reduction of one complex ion). Here again the three cited papers by Sartori and Caglioti were in error, for in general they varied their concentration by a factor of two, giving such a short range of potentials that almost any conclusions could be drawn from the data. Solubility and reversibility difficulties often put a rather severe upper limit on the concentration of the complexing agent, while the lower limit is of necessity bounded by the concentration of complexing agent necessary to prevent appreciable variation of this concentration due to the amount of complexing agent which is liberated during the reduction at the surface of the electrode. Caglioti, Sartori, and Bianchi (57) neglected this last requisite, with solutions in which the ratio of trimetaphosphate to zinc was only about two. To further make this work inaccurate, the stability of the complex is low. These two factors combined caused the concentration of free zinc ion to be appreciable in comparison with the complex ion, making the basic equations invalid in this case.

A third common cause of error in complex ion studies is the neglect of ionic strength. Care must be taken to keep the ionic strength constant by varying the supporting electrolyte inversely as the complexing agent, or by having such a large ionic strength that the variation of the complexing agent concentration causes insignificant changes in the ionic strength. Caglioti, Sartori, and Bianchi (57) have neglected this requirement also. In their study of the trimetaphosphate complexes of lead, zinc, and manganese, they allowed the concentration of trimetaphosphate to vary from 0.05 to 0.3 M. in the presence of 0.1 M chloride as supporting electrolyte. Since the complexing agent is trivalent, a large change in the ionic strength occurred, the largest concentration having about twenty times the ionic strength of the smallest. Souchay and Faucherre used the same concentrations of trimetaphosphate and metal ion as they did, but had a supporting electrolyte of saturated potassium chloride. The potentials they obtained were essentially constant with metaphosphate concentration, which indicates that trimetaphosphate had negligible complexing action on these ions. The variation in potential that was attributed to the complexation by Sartori and coworkers was caused solely by changes in ionic strength.

Souchay and Faucherre generalized the half-wave potential method to include ions in which there are two or more different complexing agents participating, and ions which include more than one metal atom. With regard to the first case, the quantity p could readily be determined for each of the complexing agents if the concentrations of the others were kept constant. This is not always possible in practice, for example, in studying complexes in which anions of weak acids and hydroxyl ions both participate. Upon variation of the pH, the ionic species of the acid also changes in certain pH ranges.

In the second case they found that the slope of the curve of half-wave potential plotted against the logarithm of the concentration of complexing agent is $-0.059p/mn$ (m is the number of metal atoms in the complex ion), and the slope of the line of half-wave potential versus the logarithm of the metal ion concentration is $-0.059(1-1/m)/n$. This latter slope does not allow any great accuracy in the determination of m, as the difference in potential only doubles over a given concentration range when m is varied from 2 to infinity for a bivalent metal ion. This difference in potential when m is infinity is only 30 millivolts for a tenfold change in concentration of the metal ion. Also, the probability of finding a complex of this type that is reversibly reduced is very low.

Souchay and Faucherre illustrated these principles with their study of tartrate mannitol complex ions in strongly alkaline solutions, where hydroxyl ions also take part, and where it has been shown that some of the complexes contain more than one metallic atom. At pH values above 14, KOH-KCl solutions were used as supporting electrolyte. Between 10 and 14, carbonate-bicarbonate and carbonate-KOH mixtures were used. A borate buffer was used for the pH range of 8-10.

In no case was variation of the half-wave potential with metal ion concentration observed, even though it had been expected in the case of the copper-tartrate complexes, which have been shown to have ions with several copper atoms by cryoscopic methods. They explained this by saying that the cryoscopic work was done with high concentrations of copper, while the polarographic work was of necessity done with low concentrations. Evidently the multiple complex was depolymerized in more dilute solutions into single complexes.

The results obtained with lead indicated that it formed a complex with carbonate which is more stable than that with tartrate, so that very little could be determined from these polarograms about lead-tartrate complexes. Three hydroxyl ions and one mannitol molecule took part in the formation of the copper complex, giving $MOCuO^-$ with the third hydroxyl ion neutralizing the hydrogen ion of the mannitol replaced by the copper. The copper-tartrate complexes seemed to have only a single dependence on hydroxyl ion below a pH of about 10, two hydroxyl ions taking part at higher pH values. There seems to be only one tartrate ion in the complex. For cadmium-tartrate complexes two hydroxyl ions take part at higher pH, none appear in the lower range. Only one tartrate appears in the complexes.

Antimony and bismuth were found to react with three hydroxyl ions and one mannitol to form dihydroxy mannitol complexes. Pyrocatechol requires only two hydroxyl ions for its antimonyl complex, as the pyrocatechol is doubly ionized at this high pH.

The ferric-tartrate complex at high pH was found to require three hydroxyl ions and three tartrate ions for its formation. The hydroxyl ions are considered to neutralize the hydrogen ion removed from one of the carbinol groups in the tartrate. The ferrous-tartrate complex contains one hydroxyl and two tartrate ions. This differs from the polarographic study of Toropova who found ferric monotartrate and ferrous ditartrate as the complexes at high pH (58).

B. Iron Sulfosalicylate and Related Complexes

Sulfosalicylic acid was first prepared by Cahours in 1845 (59) and first extensively studied by Mendius in 1857 (60). Both of these authors prepared the acid by treating salicylic acid with sulfur trioxide. Later Remsen (61) prepared it more simply by warming salicylic acid with concentrated sulfuric acid. The reaction in this way goes to completion.

The acid and some of its derivatives have been studied rather thoroughly for their pharmaceutical properties (62-65). Its mercuric and zirconyl salts have been used for theoretical studies of sols and gels (66-70). It has also been used for the precipitation of proteins (71,72) and for the determination of sulfa drugs in blood (73). Its titanium complexes have been used for the separation of this element from aluminum, chromium, magnexium, manganese, and phosphates (31-33, 74). The uses of its ferric complex for the determination of iron, boron, and fluoride have been mentioned in the introduction. Gutzeit and others have also used it for the detection of iron (75,76). The sulfosalicylate complex of thorium has been used to keep that ion from precipitating as the hydroxide in the polarographic determination of zinc (77).

Other analytical uses have been reviewed by Welcher (78). Among these were the separation of aluminum from manganese (33), of thallium from aluminum, chromium, lead, and manganese (34), of beryllium from zinc (79), and of niobium and tantalum (80,81). Determinations described were colorimetric methods for sodium (82,83), nitrate (84,85), an indirect determination of calcium or oxalate (86), and a titrimetric method for copper (87).

A few studies have been made of sulfosalicylate complexes of metal ions. Meek has investigated the beryllium sulfosalicylate complex by means of its ultraviolet absorption, and has developed from it a method for the spectrophotometric determination of beryllium in aluminum and other metals (88). He found that the complex has two sulfosalicylate ions for one beryllium ion, and that the hydrogen is displaced from the phenolic group of the sulfosalicylate, so that it is a tetravalent ion. It is most stable at a pH of about 10.5 and the instability constant for its equilibrium with whatever beryllium species is present in solution at that pH and divalent sulfosalicylate is

2.1×10^{-9} at 25°.

R. C. Anderson and co-workers have investigated the sulfosalicylate complexes of a series of metal ions spectrophotometrically by Job's method of continuous variations (89). Along with Turner he studied the cupric-sulfosalicylate complexes (90). At pH 5 one copper ion was found to be combined with one sulfosalicylate ion in the complex, which has an instability constant of 2×10^{-3} at 25°. At pH 9 they found that there are two sulfosalicylate ions for each copper in the complex, and that the instability constant is 8×10^{-7} at 25°. These instability constants are valid only at the ionic strength used, which was about 0.1.

Foley and Anderson found that the uranyl ion forms only a 1:1 complex with sulfosalicylate, which is most stable at pH 4.5 with a K' value of 1.93×10^{-4} at 25° and unspecified, but constant ionic strength (91). (When the K is primed in the present paper, it signifies that it is in terms of concentrations instead of activities, and is therefore valid only at the experimental ionic strength).

Preliminary studies have been made by Tompkins and Mayer with regard to the use of sulfosalicylate complexes of europium and promethium for the separation of these elements by ion exchange methods (92). They used radioisotopes to determine the distribution of the rare earths between the resin and the solution.

All of the previous work on the iron-sulfosalicylate complexes has been spectrophotometric or colorimetric. Alten, Weiland, and Hille claimed that only the ferric ion gave a red color with sulfosalicylate in acid solutions, but that both ferric and ferrous ions gave the alkaline yellow color (5). They used this to determine ferric and total iron. Thiel and Peter showed that the ferrous ion did not form a colored complex with sulfosalicylate, but that in alkaline solution it was almost immediately air oxidized to the ferric-sulfosalicylate complex (10). They suspected this because the yellow color of both the ferrous and ferric "complexes" had the same intensity, a fact which would be rather surprising, if each was a separate ionic species. They added hydrosulfite to a solution of the yellow complex, and the solution became colorless. If air was shaken into this solution, it rapidly turned yellow again, but slowly became colorless again on standing. This showed that the yellow ferric-sulfosalicylate complex was very stable, and there was a strong tendency for the colorless ferrous species to be oxidized. These results were confirmed by the present author.

The absorption spectra of sulfosalicylate solutions containing ferric ion was found by Kennard and Johnson to have flat regions of transmittancy at pH values of around 1.5, 5.0, and 8.2 (21), which might indicate three complexes with maximum stabilities at these pH values. Monnier, Rusconi, and Wenger, in the development of the method for the determination of fluoride using this complex, found that the full color development of the complex was obtained in acid solution when there was at least one mole of sulfosalicylate per mole of ferric ion (29), indicating a 1:1 complex.

Foley and Anderson made an extensive spectrophotometric study of this complex ion (38). Using Job's method of continuous variations they found that the complex contains one sulfosalicylate ion at pH 2.4 and below, in agreement with Monnier, Rusconi, and Wenger. K' is 1.3×10^{-5} at pH 2.38, ionic strength 0.061, and 2.1×10^{-4} at pH 0.9 and ionic strength 0.153. At higher pH values the Job's method treatment seemed to indicate that the complex had more sulfosalicylates, even up to five or more. This appearance of increase of sulfosalicylate content was attributed by the authors to hydrolysis of ferric ion and change in ionic species of the sulfosalicylic acid. They believed that these results do not represent the composition of real complexes. They found that at high pH, ferric perchlorate solutions absorb more strongly than the ferric sulfosalicylate solutions, because of the formation of hydrous oxide sols.

Lacroix and Labalade in their recent paper on the determination of fluoride using this complex (30) referred to Bertin's, as yet unpublished, work on these complexes (36). He concurs with other authors with the single 1:1 complex in acid solution. He says that the complex probably breaks down in alkaline solution to form colloidal ferric hydroxide, in the same manner as the salicylate complex.

The salicylate complexes of ferric iron might be expected to be similar to the sulfosalicylate complexes. Babko has reported his studies of these complexes in a series of papers in 1945 (93-95). He found a violet 1:1 complex in acid solution with a K of $4x10^{-17}$. At higher pH and salicylate concentration a red disalicylate complex forms, with a K of $3.5x10^{-12}$. Finally a trisalicylate complex forms at pH 10, which is yellow and has a K of $2x10^{-6}$. The last complex is in disagreement with Bertin, who says that the complex is broken down to the colloidal ferric hydroxide in alkaline solution (36).

III. MATERIALS

For the most part, reagent-grade chemicals were used in this work. A few of the chemicals that were prepared or specially tested will be described.

A. Sulfosalicylic Acid

The sulfosalicylic acid (5-sulfosalicylic acid) at first obtained (Eastman white label) was not considered to be sufficiently pure for this use. Concentrated solutions of it were dark red, indicating iron impurity, and a considerable amount of insoluble matter was visible in suspension. It was therefore thought advisable to purify this material by the method of Moser and Brukl (34), which was also recommended by Welcher (78). A saturated alcohol solution of the acid was allowed to stand for about a week, after which it was filtered on a sintered glass disc with suction. In order to recover the solid acid, about one-fifth of the alcohol was distilled off. Because of the high concentration of the sulfosalicylic acid, the boiling point was 117°. No precipitate of the acid appeared on cooling to room temperature. The viscous solution, which had an odor somewhat similar to wintergreen, was then cooled below 0°, with the result that the whole solution became white and of about the consistency of taffy. The solution again cleared when it was warmed to room temperature. Evidently much of the sulfosalicylic acid had been esterified by the alcohol at the high temperature of the boiling, if not before this during the week of standing at room temperature.

About this time some Mallinckrodt sulfosalicylic acid was obtained, which seemed to be of better quality than the previous material. The solid acid was white, instead of pink, had a much weaker pink color when dissolved, and had less insoluble matter. This acid was subjected to the tests recommended by Rosin (96) with respect to loss on drying, assay, and residue on ignition, and was found to be within the limits set in this work. It might be well to mention that in the determination of the residue on ignition, the first samples were lost because the melted acid, after bubbling quietly for about half an hour while being ignited, suddenly became very black and tarry, and quickly bubbled over the top of the platinum dishes used for the ignition. This was avoided in subsequent samples by heating the sample under an infrared lamp until this sudden transformation occurred, at which time the lamps were immediately removed before the melt had overflowed the dish. This tarry mass cooled to a hard black porous solid which could be heated again without overflowing. The

Mallinckrodt acid was pure enough that no waves were obtained polarographically, either in acid or alkaline solution, when no iron was added.

B. Iron Perchlorate Solutions

The ferric perchlorate solutions were prepared by dissolving weighed amounts of electrolytic iron wire or granulated primary standard iron in a nitric-hydrochloric acid mixture. These acids were then removed from solution by evaporating several times to fumes with a slight excess of perchloric acid. The solutions were then diluted to known volume. They contained a very small amount of excess perchloric acid, but since the iron was generally 10^{-4} molar in the final solutions, the perchloric acid introduced was negligible.

Ferrous perchlorate solutions were prepared by the method of Goetz (97). Granulated primary standard iron was dissolved in fifty per cent perchloric acid with gentle warming, until nearly all of the iron was dissolved. Long pale green needles of ferrous perchlorate formed in the solution. These were filtered off and dissolved in water, giving a blue solution when very concentrated. The solution was stored over the small amount of iron left undissolved to prevent oxidation. The ferrous salt is very soluble in water.

Ferrous iron in the solution was determined by titration of samples of the solution with ceric sulfate using ferroin, i.e., tris-(1,10- phenanthroline)-iron (II) sulfate, as the indicator. Total iron was determined by passing samples through a Jones reductor, and titrating as before.

C. Ferric Acetylacetonate

This compound was prepared by the method of Urbain and Debierne (98). The commercial acetylacetone was bright red, in color, probably from the iron and other metals dissolved from the metal cap of the bottle. Distillation yielded a product which was light yellow in color. Pure acetylacetone is water-white in color, but the distilled liquid was considered pur enough for the preparation of ferric acetylacetonate. About one-half mole of ferric ammonium sulfate was dissolved in water and precipitated as the hydrated oxide with ammonium hydroxide. This was filtered on a large glass fritted disc filter funnel and washed five times by transferring the precipitate to a beaker, mixing it well with two liters of water, allowing the hydrated oxide to settle, and filtering it. The hydrous ferric oxide, which by now was almost entirely free of the odor of ammonia, was then suspended in 1800 milliliters of water and treated with about ten per cent excess acetylacetone. This mixture was stirred for twenty-four hours with a large magnetic stirrer, the solution being kept warm by the heat of the stirring motor. At the end of this time the dark red colored needles of ferric acetylacetonate were filtered, and recrystallized twice from benzene. (Ferric acetylacetonate is very soluble in benzene). The large crystals obtained in this way were very dark red in color and had a strong odor of benzene even after air drying for several hours. On crushing these crystals in a mortar the material became orange red in color, and at first had a strong odor of benzene, which gradually disappeared. The dark red colored crystals probably had contained benzene of crystallization.

Samples were weighed out for analysis and heated to fumes with concentrated sulfuric acid. After digestion at this temperature for a while the solution became dark brown in color because of partial decomposition of the acetylacetone. This was then treated with hydrogen peroxide several times and boiled to decompose the brown colored material. After the solution cleared, there remained in the solution a precipitate of dehydrated ferric sulfate.

The solution was diluted with water and gently heated. In most cases the ferric sulfate dissolved within an hour, but one sample required treatment with hydrochloric acid to dissolve this precipitate, followed by evaporating to light fumes of sulfuric acid to remove the hydrochloric acid. The solutions were then diluted to one hundred milliliters, passed through a Jones reductor, and titrated with standard ceric sulfate using ferroin as the indicator. The results obtained were 16.07, 15.75, and 15.91 per cent, as compared to the theoretical value of 15.81 per cent iron in the compound. Urbain and Debierne found 15.6 per cent. Discarding the first result found here, as it was noticeably over-run in the titration, the average is 15.83 per cent. This value was considered to be a satisfactory check with the calculated value.

IV. APPARATUS

The Sargent Model XII Polarograph, with photographically recorded current-voltage curves, was used for preliminary work on this system. Most of the work was done using the Sargent Model XXI Polarograph, which records the curves with a Brown recorder.

The polarographic cells used were the H-type cell of Lingane and Laitinen (99) with only slight modification. This consisted of two cylindrical half-cells joined by a cross-arm about one centimeter above the bottom of each. A sintered-glass disc with an agar plug saturated with potassium chloride allowed the necessary electrical migration but prevented diffusion and convection between the half-cells. On the agar side of the disc was a saturated calomel half-cell. The other half-cell contained the dropping mercury electrode and the solution to be studied. This half-cell contained the side-arm through which the hydrogen or nitrogen used for freeing the solution of oxygen was introduced. The principal modifications introduced here were the placing of the sintered-glass disc at the dropping mercury side of the cross-arm instead of the center of it, and the introduction of a stop-cock at the bottom of the dropping mercury half-cell. Both of these facilitated draining and cleaning of the half-cell with the minimum disturbance of the calomel half-cell.

A bridge consisting of an asbestos fiber sealed into the glass cross-arm of the H-type cell was used for a while. This seemed to give results that were in agreement with those obtained with the sintered disc-agar bridge cell at first. After some use, however, the potentials obtained with the asbestos-bridged cell became more negative than those of the agar cell. This effect seemed to be proportional to the current of the polarograms. The best explanation seemed to be that the high concentration of perchlorate ion in the dropping electrode half-cell combined with the saturated potassium chloride in the calomel half-cell to cause a precipitation of sparingly soluble potassium perchlorate in the bridge, thus increasing its resistance. This caused an IR drop that was included in the apparent half-wave potential. This effect of a high resistance in causing errors in half-wave potentials that are proportional to the current at the half-wave potentials has been mentioned by Lingane and Vandenbosch (100). Miss Doris V. Stage of this laboratory, using the same cells found that the diffusion current for chromium was smaller for the asbestos cell after this effect became noticeable, as would be expected with the increased resistance.

For some of the pH work an H-type cell modified similarly to that of Meites (101) was used. The dropping mercury part of this cell was made from a tall form two hundred fifty milliliter beaker. A number 14 rubber stopper was turned down on a lathe so that it fit this beaker, and six holes were bored in it. Two were for pH meter leads, two for microburets, one was for the dropping electrode, and one, fitted with a bunsen valve, was for outlet of nitrogen. Using this cell it was possible to run several polarograms on one solution by adding various materials between polarograms from microburets, and stirring a few minutes with the nitrogen bubbler. The solutions added from the burets were previously flushed with nitrogen.

The dropping electrodes used were supplied with the polarograph, and were the conventional type first used by Heyrovsky and illustrated in Kolthoff and Lingane (43, p. 241). Temperature was controlled at 25° ± 0.5° C by a constant temperature bath with a Merc-to-Merc regulator. It was necessary to stop the stirring motor of this bath while the polarograms were being made, as the vibration caused the drops to fall too rapidly. Oxygen was removed by flushing with nitrogen for at least fifteen minutes. Ordinary commercial nitrogen was used for a while with the residual oxygen removed by an alkaline pyrogallol bubbler. Later nitrogen specially purified for gas analysis was obtained from Matheson in bottles of seventeen cubic feet capacity. This was found to be sufficiently pure that the pyrogallol was unnecessary. In fact, for most polarographic purposes ordinary commercial nitrogen is now sufficiently free of oxygen.

Beckman models M, G, and H-2 pH meters were used at various times for pH control of the solutions studied. At high pH type E glass electrodes were used or corrections were made for sodium ion error when ordinary glass electrodes were employed. Considerable trouble was experienced with pH measurements of solutions with high perchlorate ion concentration. There was a rapid drift of meter readings to lower pH values with time of immersion of the electrodes in the solutions. The source of trouble seemed to be in the calomel electrode of the pH meter, since the reading went back to its original value after that electrode had been soaked in water for a short time. The ordinary bridge used in the calomel electrodes is an asbestos fiber sealed in glass. It was thought that this type of bridge might be the source of trouble. Some readings were taken with a Leeds and Northrup pH meter that had a calomel electrode with a sintered glass bridge. The readings drifted as badly with this bridge as with the asbestos fiber bridge. A special Leeds and Northrup calomel electrode was obtained that had a bridge that consisted of a ground glass joint that could be flushed out by turning the two parts thus joined with respect to each other. The readings obtained with this electrode did not drift as rapidly as the ones from the other types of bridge. Most of the pH values used in this research were obtained using the asbestos fiber bridge with the reading obtained as soon as possible after the electrodes were immersed in the solutions.

For the spectrophotometric study the Beckman model DU spectrophotometer with a hydrogen discharge ultraviolet source was used. Cuvettes used varied from 0.998 to 1.000 centimeters in cell length.

V. METHODS

The method of treating the data which are obtained from polarograms of complex ions that is outlined below is essentially that described by Kolthoff and Lingane (43).

The reduction of a complex ion to another complex ion of a lower valence state may be considered to consist of three processes. The first is the dissociation of the oxidized complex into its simple ions:

$$MX_p^{n+pb} = M^n + pX^b \qquad (1)$$

where n is the charge of the oxidized free metal ion, p the number of molecules of complexing agent included in the complex ion, and b the charge of the ion of the complexing agent. Letting a_{M_O} be the activity of the oxidized free ion, a_X that for the complexing agent, and a_{MX_O} the value for the complexing agent, the instability constant K_O of this complex ion then becomes:

$$K_O = \frac{(a_{M_O})\ (a_X)^p}{(a_{MX_O})} \qquad (2)$$

The second process is the reduction of the simple oxidized ion to the simple reduced ion at the electrode:

$$M^n + (n-m)e = M^m \qquad (3)$$

where m is the charge of the reduced free metal ion. At 25° C the Nernst equation for this reduction is:

$$E = E° - \frac{0.0591}{n-m} \log \frac{(a_{M_R})}{(a_{M_O})} \qquad (4)$$

where a_{M_R} is the activity of the free metallic ion in the reduced state. The third process is the formation of the complex of the reduced metal ion:

$$M^{m} + qX^{b} = MX_{q}^{m+bq} \qquad (5)$$

where q is the number of molecules of complexing agent in the reduced complex. The instability constant of this complex ion is:

$$K_R = \frac{(a_{M_R})\ (a_X)^q}{(a_{MX_R})} \qquad (6)$$

where a_{MX_R} is the activity of the complex ion of the metal in the reduced state. Combining these equations by the elimination of the simple oxidized and reduced, we obtain upon replacing the activities by (C) (γ):

$$E = E° - \frac{0.0591}{n-m} \log \frac{(K_R)(C_{MX_R})(\gamma_{MX_R})(C_X\gamma_X)^{p-q}}{(K_O)(C_{MX_O})(\gamma_{MX_O})} \qquad (7)$$

At the dropping mercury electrode the concentrations of the complex metal ions that enter into this relationship are those at the surface of the drop, which we shall denote as C''_{M_O} and C''_{M_R}. Assuming that the complex ions are sufficiently stable that the concentrations of the simple metal ions in the main body of the solution are negligibly small, only the two complex ions are brought to the electrode by diffusion. Under these circumstances the concentration of the reduced complex ion at the electrode is proportional to the current and the decrease of the concentration of the oxidized form is likewise proportional to the current, or:

$$k_{MX_R} C''_{MX_R} = i, \text{ and } k_{MX_O}(C_{MX_O} - C''_{MX_O}) = i \qquad (8)$$

where the k's are a function of the diffusion coefficients of the complex ions and are characteristic of these ions. However, the concentration of the reducible substance in the body of the solution is proportional to the diffusion current, a fact that is so useful in the determination of ions by polarography. The second of these relationships becomes then:

$$k_{MX_O} C''_{MX_O} = (i_d - i) \qquad (9)$$

Substituting into the equation for the potential this gives:

$$E - E^\circ = \frac{0.0591}{n-m} \log \frac{(K_R)(\gamma_{MX_R})(C_X \gamma_X)^{p-q}(i)(k_{MX_O})}{(K_O)(\gamma_{MX_O})(i_d - i)(k_{MX_R})} \qquad (10)$$

At the half-wave potential $i_d - i = i = \frac{1}{2}i_d$, and the above expression reduces to

$$(E_{\frac{1}{2}})_c = E^\circ - \frac{0.0591}{n-m}\log\frac{(K_R)(\gamma_{MX_R}(C_X\gamma_X)^{p-q}(k_{MX_O})}{(K_O)(\gamma_{MX_O})(k_{MX_R})} \qquad (11)$$

The half-wave potential of the simple ion may be derived similarly to be:

$$(E_{\frac{1}{2}})_s = E^\circ - \frac{0.0591}{n-m}\log\frac{(\gamma_{M_R})(k_{M_O})}{(\gamma_{M_O})(k_{M_R})} \qquad (12)$$

The difference of the half-wave potentials of the complex and simple ions is then:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n-m}\log\frac{K_O}{K_R} - \frac{0.0591(p-q)}{n-m}\log C_X$$

$$- \frac{0.0591}{n-m}\log\frac{(\gamma_{MX_R})(\gamma_X)^{p-q}(k_{MX_O})(\gamma_{M_O})(k_{M_R})}{(\gamma_{MX_O})(k_{MX_R})(\gamma_{M_R})(k_{M_O})} \qquad (13)$$

If this difference of the half-wave potential of the complex and simple ions is plotted against the logarithm of the concentration of the complexing agent it is readily seen from equation 12 that a straight line with the slope -0.0591 (p-q)/(n-m) should result. This may be used for the calculation of the difference of the number of molecules or ions of complexing agent in the oxidized and reduced complexes.

The sum of the first and third terms of the right side of equation 13 is the intercept of this straight line. If it is assumed that the ratio $k_{MX_O} k_{M_R}/k_{MX_R} k_{M_O}$ in the last term is approximately one and if molarities are used instead of activities, equation 13 becomes:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n-m}\log\frac{K'_O}{K'_R} - \frac{0.0591(p-q)}{n-m}\log C_X \qquad (14)$$

in which K'_O and K'_R are the molar instability constants for the oxidized and reduced complexes respectively. The intercept then becomes $0.0591/(n-m)\log K'_O/K'_R$. These ratios of diffusion current constants may in some cases be determined from the ratio of the cathodic to the anodic diffusion currents for the same concentration of oxidized as reduced form. In the case studied here it was not possible to investigate this relationship for the simple ion because the anodic wave could not be observed with mercury electrodes. The half-wave potential for the ferric wave was more positive than the potential of the saturated calomel electrode, so that for a solution of both ferric and ferrous ions there was only the cathodic wave that began at zero potential.

The thermodynamic equilibrium constants cannot be determined by this method without knowledge from some other source as to the variation of activity coefficients of the participating species with ionic strength. The usual method of determining this absolute constant without data on individual activity coefficients consists of determining the K' values at various ionic strengths approaching infinite dilution. On plotting these constants against the square root of the ionic strength, an extrapolation to zero ionic strength gives an approximate value of the true instability constant, since by the Debye-Huckel limiting law the activity coefficients are proportional to the square root of the ionic strength at very low ionic strengths. In the polarographic method the requirement of a supporting electrolyte prevents the determination of the constant at ionic strengths low enough to approach the limiting law straight line.

In the case where the complex ion is reduced to a metallic state that forms an amalgam, equation 13 becomes:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n}\log K_O - \frac{0.0591p}{n}\log C_X$$

$$- \frac{0.0591}{n}\log \frac{(\gamma_M)(\gamma_X)^p(k_{MX})}{(\gamma_{MX})(k_M)} . \qquad (15)$$

If the metal is not soluble in mercury, the equation becomes:

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{0.0591}{n}\log K_O - \frac{0.0591p}{n}\log C_X$$

$$- \frac{0.0591}{n}\log \frac{(\gamma_X)^p(\frac{1}{2}C_M)(\gamma_M)}{(\frac{1}{2}C_{MX})(\gamma_{MX})} \qquad (16)$$

It will be noticed that in equation 16 the half-wave potentials are not independent of concentration of the metal ion.

Since iron is not soluble in mercury equation 16 would apply for the reduction of the ferrous complexes, and equation 13 applies for the reduction of a ferric complex to a ferrous complex. However, all evidence seems to indicate that complexation of ferrous ions by sulfosalicylate is negligible. If the ferric complex is reduced to the simple ferrous ion, the situation is similar to the reduction of the complex metal ion to the amalgam, and equation 15 can be used, with the modification that "n-m" is substituted for "n" in the denominators for the coefficients for the logarithm terms.

The slopes and intercepts of the lines obtained by plotting the difference of the half-wave potentials of the complex and simple ions against the logarithm of the concentration of the complexing agent were determined by the least squares method. The line obtained by this method has the minimum value of the sum of the squares of the deviations of the experimental points.

The general formula of a straight line is:

$$y = a + bx \tag{17}$$

If X and Y are respectively the individual values of x (in this case the logarithm of the concentration of complexing agent) and y (here, the difference of the half-wave potentials of the complex and simple ions), the deviation of an experimental Y value from a straight line is:

$$d = Y - (a + bX) \tag{18}$$

The sum of the squares of the deviations is:

$$\Sigma d^2 = \Sigma(Y - (a + bX))^2 \tag{19}$$

For this to be a minimum the partial derivatives with respect to a and b must be zero.

$$\frac{\partial \Sigma d^2}{\partial a} = -2\,\Sigma(Y - (a + bX)) = 0 \tag{20}$$

$$\Sigma Y = na + \Sigma b\,X \tag{21}$$

$$\frac{\partial \Sigma d^2}{\partial b} = -2\,\Sigma(\;X\;)\;\;(Y - (a + bX)) = 0 \tag{22}$$

$$\Sigma XY = a\Sigma X + b\Sigma X^2 \tag{23}$$

where n is the number of individual pieces of data used (n must be greater than 2). Solving equations 21 and 23 for a and b we obtain:

$$b = \frac{\Sigma X \Sigma Y - n\Sigma XY}{(\Sigma X)^2 - n\Sigma X^2} \qquad (24)$$

and

$$a = \frac{\Sigma Y - b\Sigma X}{n}\ . \qquad (25)$$

VII. EXPERIMENTAL

The ferric and ferrous complexes will be considered separately, even though the data from the two ionic states were generally taken from the same polarograms.

A. Ferric Complex

Since some have doubted the presence of a sulfosalicylate complex of ferric iron in alkaline solution (30,36), it might be well to cite evidence for its existence. The explanation of the yellow color of the alkaline solutions as caused by colloidal ferric hydroxide does not explain the properties of these solutions very well. The yellow color was much stronger in these solutions than in similar solutions with the same concentration of iron, ionic strength, and pH, but without sulfosalicylate. Also, the sulfosalicylate solutions were much more stable, showing no precipitation after months of standing, while the solutions without sulfosalicylate had almost complete precipitation in about an hour. The phenomenon of almost instantaneous oxidation of ferrous ions by air in the presence of alkaline sulfosalicylate, which was first described by Thiel and Peter (10) and confirmed polarographically in the present investigation, would also indicate that the ferric ion species is much more stable than in the absence of sulfosalicylate, as in the latter case no such rapid oxidation was observed. Polarographically also ferric iron behaved differently in sulfosalicylate solutions. In the absence of sulfosalicylate only a wave at 0 and one -1.45 volts with respect to the saturated calomel electrode, were obtained when polarograms were made a few minutes after the solutions were prepared. These waves were the same ones observed for ferric iron in acid solutions. If the solutions were allowed to stand until the hydrous oxide had been precipitated, the same waves were obtained, but they are very small. In the presence of sulfosalicylate no wave was obtained at 0 volt, but there were waves at -0.6 volt, -1.0 volt and -1.45 volts. The last wave, attributed to the ferrous ion was the same for the two types of solutions, but the first one, which evidently represented a ferric species, showed a strong negative shift of potential from +0.51 volt vs. the saturated calomel electrode the half-wave potential of the aquo ferric ion. This indicated a strong stabilizing effect of the sulfosalicylate on ferric iron. There is no reason to believe a colloid of hydrated ferric oxide should be so much more stable toward both reduction and precipitation in the presence of sulfosalicylate than in its absence, especially at the high ionic strengths used. This would seem to be rather strong evidence that the ferric ion is complexed by the sulfosalicylate ion.

1. Effect of pH

As most of the work with this complex was done in solutions of pH in the vicinity of 9, a pH study was made over a pH range of 8.38 to 10.22, with 0.35 M boric acid present as a buffering agent. The solutions were 0.0001 M in ferric ion and 0.02 M in sulfosalicylate. The ionic strength of the solutions was brought to 0.6 by the addition of sodium perchlorate. The data from this experiment are found in Table 1. Some trouble was encountered with a maximum that occurred at a constant potential of -0.84 volt, which became merged with the ferric wave at higher pH values. It was finally decided to construct the diffusion current plateau through the minimum that follows the maximum, for the sake of uniformity. This made the half-wave potentials more negative and the diffusion currents slightly greater than if the plateau was constructed at a potential more positive than the maximum.

Three waves were observed in the polarograms of these solutions. They occurred approximately -0.6, -1.0, and -1.4 volts with respect to the saturated calomel electrode.

TABLE 1

Variation of Half-Wave Potential and Diffusion Current with pH

pH	Half-Wave Potential, volts *vs.* S. C. E.	Diffusion Current, microampere
8.38	-0.479	0.155
	-1.059	0.054
	-1.404	0.364
8.51	-0.488	0.113
	-1.094	0.061
	-1.417	0.370
8.65	-0.505	0.145
	-1.112	0.024
	-1.422	0.342
8.65	-0.521	0.154
	-1.034	0.076
	-1.433	0.483
8.88	-0.540	0.137
	-1.061	0.064
	-1.428	0.383
9.09	-0.561	0.106
	-1.086	0.047
	-1.446	0.352
9.26	-0.561	0.131
	-1.088	0.052
	-1.456	0.357
9.48	-0.596	0.103
	-1.093	0.023
	-1.463	0.314
9.70	-0.624	0.092
	-1.093	0.072
	-1.483	0.358
9.77	-0.624	0.112
	-1.103	0.059
	-1.490	0.288
10.05	-0.639	0.093
	-1.120	0.077
	-1.502	0.296
10.22	-0.663	0.121
	-1.081	0.061
	-1.502	0.352

The first wave represented the reduction of the ferric sulfosalicylate complex. The best line for the relationship between the half-wave potential and pH for this wave, as determined by the method of least squares, was as follows:

$$E_{\frac{1}{2}} = 0.3390 - 0.0985 \text{ pH} \qquad (26)$$

The calculated value of p/n, which in this case was equal to p, was 1.67. This would probably indicate that the complex contains two more hydroxyl ions than the ferrous complex. On the assumption that the ferrous complex contained one hydroxyl ion, the number of hydroxyl ions associated with the ferric complex is then three.

The second wave was of uncertain origin. It was nearly independent of pH. The equation of the straight line that corresponded best with the data on the variation of half-wave potential with pH is:

$$E_{\frac{1}{2}} = -0.948 - 0.0149 \text{ pH}. \qquad (27)$$

The calculated p/n value for this wave is 0.26. This means that n would have to be four for p to be equal to one.

The ferrous wave is considered in the section on the ferrous complex. Experiments with the variation of half-wave potential with pH over a larger range with nitrate and sulfate as supporting electrolyte are described in the section on effect of anions.

2. Effect of sulfosalicylate concentration.

In acid solutions of pH less than 4.5 the only wave appearing in the polarograms was at a potential more positive than the saturated calomel electrode, so that the current increases to almost its full value as soon as the circuit is completed. These waves could not then be studied by the method used here because the true half-wave potential could not be observed. For this reason the study of the variation of the half-wave potential with sulfosalicylate concentration has been restricted mainly to the yellow alkaline complex. From pH 4 to about pH 10 sulfosalicylate did not act as a buffer at all. Since the half-wave potential changed with pH above pH 8, indicating liberation of hydroxyl ions on reduction, it was essential for the solutions to be buffered to obtain reliable half-wave potentials. Otherwise there would have been local changes in pH at the dropping mercury electrode, which would have caused the half-wave potential to be erroneous. Boric acid was decided upon as a buffer, since it seemed to have little complexing effect on iron. With this buffering agent the optimum theoretical pH was 9.2, as the first ionization constant of boric acid is 6.4 x

10^{-10} (102). For this reason pH 9 was taken as the one at which most of the work would be done. The solutions were 0.5 M in total borate, 0.0001 M in iron, and had an ionic strength of 1. The sulfosalicylate concentration was varied from 0.00486 to 0.2067 M. The half-wave potentials and diffusion currents obtained from polarograms of these solutions are found in Table 2.

The least squares equation for the first wave was calculated to be:

$$E_{\frac{1}{2}} = -0.896 - 0.1660 \log (T_{SS}) \qquad (28)$$

where (T_{SS}) is total sulfosalicylate concentration. This gives a calculated value of p of 2.8, indicating three sulfosalicylate ions in the complex above the number in the ferrous complex. Assuming that the ferrous complex has one hydroxyl ion and no sulfosalicylate ions, the ferric complex then has three sulfosalicylate ions and three hydroxyl ions. The dissociation of the complex may be written as follows:

$$Fe(HSS)_3(OH)_3^{-6} = Fe^{+3} + 3HSS^{-2} + 3\ OH^- \qquad (29)$$

and:

$$K_1^1 = \frac{(Fe^{+3})\ (HSS^{-2})^3\ (OH^-)^3}{(Fe(HSS)_3(OH)_3^{-6})} \qquad (30)$$

TABLE 2

Half-Wave Potentials and Diffusion Currents with Different Sulfosalicylate Concentrations

(Tss) mole/l	log (Tss)	Half-Wave Potential, volts *vs.* S.C.E.	Diffusion Current, microampere
0.00486	-2.313	-0.520	0.186
		-1.392	0.310
0.01043	-1.982	-0.568	0.420
		-1.308	0.518
0.01077	-1.968	-0.588	0.258
		-1.382	0.322
0.02047	-1.689	-0.586	0.280
		(-0.98)*	
		-1.416	0.381
0.0499	-1.302	-0.647	0.235
		-0.974	0.054
		-1.441	0.433
0.1002	-0.999	-0.764	0.138
		-1.027	0.069
		-1.502	0.408
0.2067	-0.685	(-0.83)*	
		-1.083	0.091
		-1.536	0.558

* Half-wave potentials in parenthesis were estimates for waves that were too small or too poorly formed for accurate measurement.

Ignoring activity coefficients and diffusion current constants we may modify equation 12 for the present case as follows:

$$(E_{\frac{1}{2}})_c - 0.51 = 0.0591 \log K_1^1/K_2^1 - 0.0591 \times 3 \log T_{SS} - 0.0591(2)(pH-14) \qquad (31)$$

where K_2^1 may be represented as:

$$K_2^1 = \frac{(Fe^{+2})(OH^-)}{(FeOH^+)} \qquad (32)$$

If the nearest theoretical slopes were used and intercepts recalculated by the least squares method, using these slopes, equations 26 and 28 become respectively:

$$E_{\frac{1}{2}} = 0.521 - 0.1182 \text{ pH} \qquad (33)$$

$$E_{\frac{1}{2}} = -0.915 - 0.1773 \log (T_{SS}) \qquad (34)$$

From the intercepts of these equations the ratio K_1^1/K_2^1 may be determined. The values obtained for this ratio from these equations were -32.76 and -34.11 respectively. The value of the constant K_2^1 was not available, but it would seem to be of the order of magnitude of one. K_1^1 is then very probably around 10^{-33}.

The wave at -1.0 volt with respect to the saturated calomel electrode was very elusive. Only at the three highest concentrations of sulfosalicylate in Table 2 was this wave distinct enough to be measured. It did not appear below pH 4 nor in sulfosalicylate solutions that contain no iron. Moreoever, it did not appear in 0.5 M solutions of sulfosalicylate at any concentration of iron from 10^{-5} to 0.01 M. In chloride solutions at pH 9 it appeared only at the very lowest concentration of sulfosalicylate used (0.02 M). The wave was sometimes seen as only a small deflection of the polarogram. At best the wave was quite small and flat, a condition indicative of considerable irreversibility. Its relationship to the iron sulfosalicylate system is quite uncertain. It was most likely caused by some impurity, by-product or side reaction in the solution. It did not seem to be caused by another ferric species in slow equilibrium with the first one, as the latter was shown to be reversibly reduced in this work. It would not seem to be a ferrous complex as its potential is more positive than other half-wave potentials observed for ferrous species. The only factors causing positive shift in potentials of uncomplexed materials are increased reversibility or a strong complex of the reduced form of the substance. The latter may be eliminated because of the impossibility of complexes with the metallic iron, and the increased reversibility was hardly probable because of the greatly reduced slope of this wave, which of course indicated considerable irreversibility of the reduction.

The three points obtained for this wave fell as nearly as could be determined on a straight line, the equation of which was

$$E_{\frac{1}{2}} = -1.204 - 0.1766 \log (T_{SS}) \qquad (35)$$

The slope of this line coincided almost exactly with the theoretical one for a reducible complex containing three more sulfosalicylate ions than the reduced form.

B. Ferrous Complex

No ferrous complex of sulfosalicylate has been found and very little has been said in the literature on the possibility of existence of such a complex. It was erroneously believed by Lorber and others (2, 4, 5, 8, 9) that the ferrous ion as well as the ferric ion formed a yellow complex with sulfosalicylate in ammoniacal solutions. It was shown by Thiel and Peter (10) that ferrous-sulfosalicylate solutions were colorless even at high pH, and the apparent coloration of the ferrous complex when the solution was made alkaline was caused by the almost instantaneous air oxidation of the ferrous ion to ferric ion in alkaline solution. The experiments carried out by these authors to show this, made use of the very strong reducing properties of sodium hydrosulfite. Their experiments are described in the Literature Survey of the present work.

The evidence for the existence of a ferrous-sulfosalicylate complex was preponderantly negative. The solutions, both at acid and alkaline pH values, were colorless in contrast to most of the known ferrous complexes, which are highly colored (*e.g.*, 1,10-phenanthroline and 2, 2' bipyridyl complexes). The alkaline solutions were very unstable with respect to both oxidation and hydrolysis to the hydrated oxide. Hydrosulfite was the only reducing agent tried that successfully reduced the ferric complex to the ferrous state. Reduction with sulfite, hydrazine, hydroxylamine, zinc, formaldehyde and manganese were all unsuccessful in alkaline solutions. The yellow ferric complex was evidently reduced all the way to the metallic state by magnesium, as the colorless solution resulting gave no coloration with 1,10-phenanthroline. In acid solutions the red complex was readily decolorized by sulfur dioxide. These solutions became yellow very rapidly when neutralized with sodium hydroxide. It was noticed when the work of Thiel and Peter on the reduction of the yellow complex with hydrosulfite was repeated, that in a short time a black colored precipitate of ferrous hydroxide formed in the solution. This precipitation in cases where the solubility product of ferrous hydroxide was exceeded only slightly showed that if there was any complexing action of sulfosalicylate on ferrous iron, it was very weak indeed.

The polarographic evidence was also negative. The wave for the reduction of the ferrous ion to the metal appeared at -1.4 volts with respect to the saturated calomel electrode. The best line for the variation of half-wave potential of this wave with sulfosalicylate as calculated by the least squares method from the data in Table 2 was:

$$E_{\frac{1}{2}} = -1.616 - 0.0789 \log (T_{SS}) \qquad (36)$$

The value of p calculated from this slope for n equal to two was 2.7, which indicated a ferrous complex with three sulfosalicylate ions. However, there was no displacement of the half-wave potential from that of the ferrous ion in the absence of sulfosalicylate. This potential was found to be -1.45 volts which was just about the median value of the data of Table 2. The variation of the half-wave potential with sulfosalicylate concentration was probably caused by the strong irreversibility that is so evident from the flattened slope of the wave and the strong negative displacement of its half-wave potential from the standard electrode potential.

The effect of the pH on this ferrous wave may be seen from the data of Table 1. The straight line best fitting the data from Table 1, as determined by the method of least squares was:

$$E_{\frac{1}{2}} = -0.9607 - 0.0535 \text{ pH} \qquad (37)$$

This gives 1.8 for p. Of course this is not reliable because of the irreversibility mentioned above. If this complex is the simple aquo ferrous ion, as seems probable, it would be expected to have one hydroxyl ion associated with it at the high pH values at which the ferrous wave appeared.

C. Other Experiments

In this section are grouped miscellaneous experiments that are pertinent to this research but were not conveniently described elsewhere.

1. Effect of borate.

Since borate was used as a buffering agent in the studies at pH 9, it was a matter of concern whether the borate had a complexing action on the iron that might compete with the sulfosalicylate reaction. If borate competed with sulfosalicylate, a variation of the half-wave potentials and probably of the diffusion currents with borate concentration would be observed.

TABLE 3

Variation of Half-Wave Potential and Diffusion Current with Borate Concentration

Total Borate, mole/liter	Half-Wave Potential, volts *vs*. S. C. E.	Diffusion Current, microampere
0.5	-0.53	0.29
	-1.44	0.48
0.2	-0.57	0.21
	-1.45	0.46
0.1	-0.54	0.25
	-1.41	0.58

Table 3 shows the results obtained when the boric acid added was varied by a factor of five in solutions of 10^{-4} M ferric ion in the presence of 0.005 M sulfosalicylate in solutions adjusted to ionic strength 2 and pH 9 by sodium chloride and sodium hydroxide. No trend was noticeable either in half-wave potential or diffusion current for ferric or ferrous waves.

2. Sodium borate precipitation

In many of the solutions used for polarographic study of the ferric sulfosalicylate complex at pH 9 a white crystalline precipitate formed on the sides and bottom of the flask. This precipitate sometimes formed on the dropping mercury electrode, causing erratic drop rates and therefore greatly malformed waves. It was at first thought to be potassium perchlorate formed by diffusion of the potassium ion from the calomel electrode of the pH meter, as the precipitate always showed up on neutralization. This possibility was eliminated by neutralizing the solutions to a pH of 9 as indicated by pH paper, with the result that the precipitate still appeared. It was not a sulfosalicylate salt, since it appeared even in the absence of sulfosalicylate. This left only sodium perchlorate and sodium borate as possibilities. It was found to be sodium borate, since the supernatant liquid from one of these precipitates was found to dissolve sodium perchlorate readily without precipitation, but when boric acid was added followed by neutralization, almost immediate precipitation of the same character of the original precipitate occurred.

In testing the range of concentrations that are free from precipitation, it was found that precipitation just occurred in solutions that were 0.02 molar in sulfosalicylate, 0.4 molar in total borate and had ionic strengths of 0.7 and pH of 9. If the sodium ion was decreased by decreasing sulfosalicylate concentration or ionic strength or pH or if borate ion is decreased, no precipitation was observed.

3. Effect of anions on the polarograms

Most of the common anions except perchlorate seemed to form complexes with ferric iron. Perchlorate was therefore used in most of these experiments as the supporting electrolyte, to avoid complications from competing complexes. However, because of the drifting of the pH meter readings in the presence of perchlorate it was desirable, and in some cases almost necessary, to use some other anion. In the pH study using the large polarographic cell in which increments of alkali were added directly to the cell, it would be impossible to obtain accurate pH readings without soaking the calomel electrode in distilled water between readings, which would have necessitated a very much longer flushing with nitrogen before each polarogram to eliminate the oxygen absorbed by the solution during these manipulations. Even the ground glass sleeve bridge showed some drifting if the sleeve was not occasionally turned to provide fresh potassium chloride in the bridge. For this reason it was decided to test the possibility of using other anions as supporting electrolytes. Accordingly, solutions were prepared with perchlorate, nitrate, chloride, and sulfate individually as supporting electrolyte at pH 2, 4, and 9. The concentrations of iron and sulfosalicylate were 10^{-3} M and 0.025 M respectively, and the ionic strength was 0.685 ± 0.005. The data from this investigation are summarized in Table 4.

The chloride, perchlorate, and sulfate solutions had only one wave at pH 2, which fell at 0 volt, and was therefore not usable. The nitrate solution, however, had a wave at -0.245 and another at -0.553 volt. It seemed from this that the presence of the nitrate ion stabilized the ferric complex with the singly ionized sulfosalicylic acid that predominates in this pH range. This agreed with the observations made in the preparation of these solutions. After the iron, sulfosalicylate, and acid of the supporting electrolyte solutions had been added, and before the addition of the sodium hydroxide to bring the pH to the desired value, the solutions had a pH of about 0.5. The hydrochloric acid solutions were still rather yellowish from the ferric chloride complex, the sulfuric and perchloric acid solutions were faintly pink and of about the same shade, but the nitric acid solutions had a very

TABLE 4

Effect of Anions of the Supporting Electrolyte

pH	Anion	Half-Wave Potential volts *vs.* S.C.E.	Diffusion Current, microamperes
1.98	chloride	(greater than 0)	2.229
2.03	nitrate	(greater than 0)	2.496
		-0.245	0.144
		-0.553	0.120
2.04	perchlorate	(greater than 0)	2.236
2.03	sulfate	(greater than 0)	2.788
4.00	chloride	(greater than 0)	0.568
		-0.124	0.220
		-0.47	maximum
		-1.458	3.762
3.83	nitrate	(greater than 0)	1.864
		-0.14	maximum
		-0.46	maximum
		-1.416	4.104
3.98	perchlorate	(greater than 0)	0.880
		-0.076	0.400
		-0.46	maximum
		-1.105	0.616
		-1.431	2.752
4.03	sulfate	(greater than 0)	2.152
		-0.12	maximum
		-1.415	4.380
8.90	chloride	-0.648	0.912
		-1.061	0.369
		-1.457	1.926
		-1.663	0.240
9.08	nitrate	-0.626	0.960
		-1.063	0.516
9.01	perchlorate	-0.643	0.810
		-1.056	0.366
		-1.446	1.764
		-1.659	0.888
8.88	sulfate	-0.584	0.510
		-1.094	0.759
		-1.456	2.079
		-1.704	0.675

strong pink color. This indicated that in these strongly acid solutions more of the iron was complexed by sulfosalicylic acid in nitric acid solutions than in hydrochloric, perchloric, or sulfuric acid solutions. Hydrochloric acid and possibly sulfuric acid to a lesser extent would be expected to form complexes with iron which would compete with sulfosalicylic acid complexes. However perchloric acid is supposed to have no complexing action on metal ions, so that it would be expected that the wave at -0.25 volt in perchloric acid would have a more negative half-wave potential and would probably have a greater step height. This was not the case at all. On the contrary, no wave appears in perchloric acid at pH 2 except the one that begins at 0 volt. This would indicate that nitrate took part in the complex. That sulfosalicylic acid also participated was shown by the polarograms of ferric nitrate in the absence of sulfosalicylic acid. These showed only the wave at 0 volt that was characteristic of uncomplexed and weakly complexed ferric ion. It was quite evident then that the complex must contain both nitrate and sulfosalicylate ions. Thus the three waves for the nitrate solution at pH 2 probably indicated three ferric complexes in rather slow equilibrium with each other. The first wave represented the reduction of the aquo ferric ion, the second a complex of ferric ion with both nitrate and singly ionized sulfosalicylic acid, and the third a complex of ferric ion with doubly ionized sulfosalicylic acid. This latter sulfosalicylate species comprised about one-third of the total sulfosalicylate present at pH 2 and ionic strength 0.1 when the sulfosalicylic acid concentration was 0.006 M, according to the brief study made on the ionization of sulfosalicylic acid that is reported elsewhere in this work. This phenomenon of separate polarographic waves for different complex ions of the same oxidation state of a metal in slow equilibrium with each other has been observed by Pines (47), Herman (48), and Brdicka (49) as mentioned in the Literature Survey. It was also found in the case of ferric tartrate complexes by Toropova (58) and Lingane (104). In a recent series of papers Meites has shown that copper citrate, tartrate, and oxalate complexes have two waves for the cupric state in certain pH ranges (101, 103, 105).

The variation of the polarograms of the nitrate solutions with pH at constant sulfosalicylic acid concentration, and also the variation with sulfosalicylic acid at pH 2 were investigated. The pH study was carried out on solutions that were 3 M in nitric acid, 0.05 M in sulfosalicylic acid and 0.001 M in ferric ion. The polarograms were made using a Sargent-Heyrovsky Model XII photographic recording polarograph. Some of the results were later checked with the Model XXI polarograph used for the rest of the work reported in this paper. The results of this investigation are listed in Table 5. The two initial waves were present in these polarograms up to pH 3. At pH 5 both of these waves had disappeared. This indicated that the second wave represented a complex with the singly ionized species of sulfosalicylic acid, since this species was also decreased to a negligible concentration by the time this pH was reached. The fact that the first wave had also disappeared indicated that the complex with the doubly ionized sulfosalicylic acid was stable enough so that there was a negligible concentration of uncomplexed ferric ion in the solution. It was also shown in the reversibility studies that this complex was reversibly reduced, so that of course in this case there was only one wave for this oxidation state. The polarogram of the complexes in the presence of nitrate at pH 4 that appears in Table 4 had a small maximum at -0.46 volt so that it could not be determined whether there was a wave at this point, which would fall in a straight line with the points from Table 5 for the second wave. There did seem to be a slight deflection of the residual current at about this point, indicating that there might have been just a hint of a wave, which might be expected since nearly all of the sulfosalicylic acid is in the doubly ionized state at this pH. The fact that the ratio of the second wave to the first was much greater for the polarogram at pH 2 in Table 5 than the corresponding one in Table 4 also indicated the participation of nitrate in the complex represented by the second wave, since the large excess of nitrate in the former would be expected to shift the equilibrium toward the complex that contained the nitrate ion.

TABLE 5

Data of Polarograms of Solutions with Varying pH at Constant Sulfosalicylate, Ferric, and Nitrate Concentration

pH	Half-Wave Potential, volts vs. S.C.E.	Diffusion Current, microamperes
0.70	(greater than 0)	2.28
	-0.17	1.78
2.18	(greater than 0)	2.31
	-0.24	2.74
2.97	(greater than 0)	1.87
	-0.31	1.00
	-0.59	0.44
4.87	-0.69	3.61
9.90	-0.73	3.65
10.40	-0.79	2.46

The least squares method was used to determine the best equation for the relationship of the half-wave potentials of the second wave to the pH. The line obtained was:

$$E_{\frac{1}{2}} = -0.123 - 0.0599 \text{ pH} \tag{38}$$

If this result were reliable, which is doubtful because of the irreversibility, it would indicate that one hydrogen ion is used up in the reduction of this complex. This could be either by releasing a hydroxyl ion from the complex or by the acid radical released from the complex taking up a hydrogen ion. Neither of these seem probable at this pH for this complex. Very likely the variation of the half-wave potential with pH was caused by the irreversibility of the reduction of this complex.

The wave at -0.6 to -0.8 volt, which was attributed to a ferric complex with the doubly ionized sulfosalicylic acid appeared at pH 2 in the data in Table 4, but not until pH 3 in the data of Table 5. This might also be caused by the very high concentration of nitric acid in the latter case, which shifts the equilibrium toward the complex containing the nitrate. The wave at pH 3 was small but very distinct when the polarogram was prepared with the Model XII polarograph, but was not visible in polarograms of the same solution taken with the Model XXI instrument. Possibly the stability of this complex at this low pH and high concentration of nitrate was not great enough to give a permanent complex, so that it had decomposed by the time (two months later) the latter polarogram was made. The half-wave potentials were more negative than those for corresponding pH values in the perchloric acid study, of which the data are listed in Table 1. This was no doubt caused by the high ionic strength rather than by the nitrate, as may be seen from the data in Table 4 in which the half-wave potential of this complex in nitrate solution was slightly more positive than that of the complex in perchlorate solution of the same pH and ionic strength.

As is shown later in this section in the discussion of the pH study with sulfate as supporting electrolyte, there was a break in the curve of half-wave potential versus pH at about pH 8, with the curve becoming steeper above this pH. Thus the four points obtained in this present investigation are half in one region and half in the other. Thus there is little meaning to a line drawn so that it best fits all four of the points. However, the slope of this line, which was 0.02, was only about twice as large as the slope of the low pH branch of this curve in sulfate solutions.

The ferrous wave at -1.4 volts did not appear in these polarograms at all, and only at pH 4 in the nitrate solutions in Table 4. This was true for all supporting electrolytes for pH values less than 4, because of the strong wave of the hydrogen ion reduction. This wave was very large because of the high mobility of the hydrogen ion. Above pH 4, however, the ferrous wave appeared in the solutions of the other three electrolytes but not in nitrate solutions, as nitrate is reduced at potentials more positive than this. That it should appear at pH 4 in Table 4, but not in Table 5 was to be expected, as the greater quantity of nitrate caused the reduction of the latter to begin at a lower potential. At pH 9 in Table 4 the wave had again disappeared, since it shifted to more negative potentials with increasing pH.

The polarograms of this system with varying sulfosalicylic acid concentration at pH 2 with nitrate supporting electrolyte were carried out with solutions that had ionic strength of one and concentration of iron equal to 0.001 M. These data are listed in Table 6. Two sets of polarograms were made for these solutions and both sets are listed in this table.

If the equilibrium between the first two waves was sufficiently slow that there was negligible interconversion during the running of the polarogram, the step heights of

TABLE 6

Half-Wave Potentials and Diffusion Currents at Varying Concentrations of Sulfosalicylate at pH 2 in Nitrate Solution

(Tss) mole/l	log (Tss)	Half-Wave Potential, volts *vs*. S.C.E.	Diffusion Current, microamperes
0.0324	-1.490	(greater than 0) -0.24	2.53 0.44
0.0324	-1.490	(greater than 0) -0.23	2.68 0.65
0.0572	-1.243	(greater than 0) -0.25	2.67 0.94
0.0572	-1.243	(greater than 0) -0.24	2.91 1.34
0.0693	-1.159	(greater than 0) -0.26	2.47 1.47
0.0693	-1.159	(greater than 0) -0.26	2.61 1.92
0.0932	-1.031	(greater than 0) -0.31 -1.13	2.87 1.71 1.26
0.0932	-1.031	(greater than 0) -0.26 (-1.1)	2.32 2.50
0.1089	-0.963	(greater than 0) -0.26	2.51 2.31
0.1089	-0.963	(greater than 0) -0.25	2.53 3.55

the two waves should be proportional to the concentrations of the two species being reduced at these waves. Then at constant pH and ionic strength the ratio of the diffusion current of the first wave to that of the second multiplied by the concentration of total sulfosalicylate, raised to the p power should be equal to a constant, or:

$$(\mathrm{Tss})^{p} i_{d_1}/i_{d_2} = K \qquad (39)$$

This is not the equilibrium constant because (1) activity coefficients of the three ions involved were not included, (2) the diffusion currents would have to be divided by their individual diffusion current constants to obtain the concentrations of the aquo ferric and the ferric monosulfosalicylic acid complex, (3) a factor would be needed for hydroxyl ion activity as shown by the dependence of half-wave potential on pH, and (4) total sulfosalicylate instead of singly ionized sulfosalicylic acid was used (equation 37). The first two factors were kept constant by working at constant ionic strength. The third factor did not vary if the pH was kept constant. At constant ionic strength and pH the singly ionized sulfosalicylic acid is proportional to the total sulfosalicylate. This may be readily seen if the concentration of the doubly ionized sulfosalicylic acid is eliminated between the following two simultaneous equations:

$$K_2 = \frac{(H^+)(HSS^{-2})}{(H_2SS^-)} \qquad (40)$$

and

$$(H_2SS^-) + (HSS^{-2}) = (TSS) \qquad (41)$$

This gives the equation for the concentration of the singly ionized sulfosalicylic acid as:

$$(H_2SS^-) = \frac{(H^+)(TSS)}{(K_2 + (H^+))} \qquad (42)$$

Since diffusion currents are very susceptible to such capillary characteristics as drop rate and height of reservoir that are changed from one experiment to the other, the data of the two sets of polarograms were here considered separately in calculating K. Tables 7 and 8 list the calculated K for each solution.

In both sets of data the value for K increased with concentration of sulfosalicylate for p equal to two and decreased for p equal to one. However, the variation was not as great for p = 1. The ratio of the largest K to the smallest K was 1.6 for one and 2.4 for two sulfosalicylates per ion from Table 7.

TABLE 7

Calculated K Values (Equation 39). First Set of Polarograms

(TSS) mole/l	K(p=1)	K(p=2)
0.0324	0.186	0.00604
0.0572	0.162	0.00929
0.0693	0.116	0.00807
0.0932	0.156	0.01455
0.1089	0.118	0.01289

TABLE 8

Calculated K Values (Equation 39). Second Set of Polarograms

(TSS) mole/l	K(p=1)	K(p=2)
0.0324	0.134	0.0043
0.0572	0.124	0.0071
0.0693	0.094	0.0065
0.0932	0.086	0.0080
0.1089	0.078	0.0085

The difference was not as great in Table 8 where the ratios are 1.7 and 2.0 respectively. Also the K for one sulfosalicylate decreases with sulfosalicylate concentration as expected if the equilibrium was rapid enough that there was some shift of species during the preparation of a polarogram. This evidence then pointed to a single sulfosalicylate ion in the complex. This agreed with the work of Foley and Anderson, who found that the complex in this pH range contained one sulfosalicylate (38).

A least squares calculation of the line for the variation of half-wave potential with sulfosalicylate concentration gave the equation:

$$E_{\frac{1}{2}} = -0.303 - 0.0442 \log (Tss) \qquad (43)$$

This gave a value of p of 0.75 or approximately one, which corroborated the results from the ratios of the step heights as well as Foley and Anderson. It must be admitted that any conclusions from equation 41 alone would be open to serious doubt, both because of the irreversibility that was evident in the existence of two waves of the same oxidation state of the metal in the same polarograms, and because of the short range of concentrations that the study covered, which, combined with the low degree of accuracy with which the half-wave potentials were measured, allowed only a very rough estimate of the slope and intercept of this line.

Polarograms were also made of nitrate solutions of the ferric sulfosalicylate complex at pH 4. The ionic strength was kept at one and the concentration of iron was 0.001 M. Table 9 contains the data from this investigation.

The waves at -0.4 volt were very small and only appeared in two of the solutions, so they will be ignored here. Table 10 shows the results obtained by multiplying the diffusion current ratio of the first two waves by the sulfosalicylate concentration raised to the p power, after equation 37. In this case values of p of zero, one, and two were used. A p value of two may be readily eliminated because of the great increase of K with concentration of sulfosalicylate. The value of K for p equal to 2 increased by a factor of 9.9 while the sulfosalicylate concentration was only changing by a factor of 2.7. The ratios of the largest to the smallest K values for zero and one for values of p are respectively 2.2 and 2.3, which are quite close together and are both reasonable values. However, the K values decreased with concentration of sulfosalicylate for p equal to zero, as might be theoretically expected for an equilibrium that was rapid enough that there was some interconversion of the ions while the polarogram was being run, while the variation for p equal to one was in the opposite direction.

This would indicate that there were no sulfosalicylate ions in the complex whose reduction is represented

TABLE 9

Half-Wave Potentials and Diffusion Currents at Varying Concentrations of Sulfosalicylate at pH 4 in Nitrate Solution

(Tss) mole/l	log (Tss)	Half-Wave Potential, volts *vs.* S.C.E.	Diffusion Current, microamperes
0.00983	-2.007	(greater than 0)	0.44
		-0.460	maximum
		-0.759	0.47
		-1.080	0.65
0.02040	-1.690	(greater than 0)	0.23
		-0.470	maximum
		-0.769	0.79
		-1.094	0.54
0.04080	-1.389	(greater than 0)	0.41
		-0.470	maximum
		-0.783	0.59
		-1.080	0.49
0.05660	-1.247	(greater than 0)	0.90
		(-0.11)	
		-1.069	0.36
		(-1.39)	
0.07790	-1.108	(greater than 0)	0.80
		-0.133	1.33
		-1.405	4.45
0.09740	-1.011	(greater than 0)	0.66
		-0.163	0.95
		-1.031	0.35
		-1.389	3.95
0.20700	-0.684	(greater than 0)	0.64
		-0.163	1.58
		-0.394	0.33
0.34100	0.467-	(greater than 0)	0.56
		-0.163	1.80
		-0.400	0.25
		-1.409	4.84

by the wave at -0.16 volt. At least there were no more sulfosalicylate ions in this complex than there were in the complex ion reduced at 0 volt. This would agree with the half-wave potential dependence on concentration of sulfosalicylate which seemed to be zero, at least at concentrations of this ion above 0.1 M. This indicated that there was the same number of sulfosalicylate ions in the ferric complex as in the ferrous complex. As mentioned elsewhere in this paper, the ferrous complex seemed to contain no sulfosalicylate ions. These conclusions from half-wave potential measurements of course were subject to gross error because of the irreversibility as shown by the two waves for the same oxidation state. However it agrees with the diffusion current calculations. Neither of these methods gave unequivocal indications

TABLE 10

Calculated K (equation 39) Values for nitrate electrolyte at pH 4.

(TSS) mole/1	K(p=0)	K(p=1)	K(p=2)
0.0779	0.602	0.0469	0.00365
0.0974	0.694	0.0656	0.00639
0.2070	0.405	0.0838	0.01736
0.3410	0.311	0.1061	0.03620

as to the nature of this complex.

The wave at -0.75 volt, which appeared only in polarograms of solutions with the lowest concentrations of sulfosalicylate, evidently represented the reduction of the ferric complex with the doubly ionized sulfosalicylate, even though the half-wave potential was about 0.1 volt more negative than expected at this pH range. The equation best fitting the relationship of the half-wave potential to the concentration of sulfosalicylate was:

$$E_{\frac{1}{2}} = -0.832 - 0.0363 \log (Tss) \qquad (44)$$

The p value calculated from this was 0.6 or about one sulfosalicylate per complex ion. This did not at all agree with the value of three obtained from the variation of half-wave potential with concentration of sulfosalicylate at pH 9 in perchlorate supporting electrolyte. However in the rather complete study of the dependence of half-wave potential on pH in the presence of sulfate as supporting electrolyte reported in the present section, it was found that there was a sharp change in slope for the half-wave potential pH curve at a pH of 8, indicating a change in ionic species of the complex at this point. The complex ion had one less hydroxyl ion below pH 8, and could very well also have had fewer sulfosalicylate ions.

Also the validity of any conclusions from the half-wave potential sulfosalicylate concentration relationship from the data on this wave in Table 9 was made very doubtful by the irreversibility of this wave under these conditions as shown by the presence of two waves of the same oxidation state. This irreversibility might also account for the half-wave potential being more negative than expected. The range of sulfosalicylate concentrations in which the wave was observable was also quite short, with only about a four-fold change in concentration where there should be at least a change by a factor of ten. The appearance of this wave only at low concentrations of sulfosalicylate, while the wave at -0.16 volt appears only at high concentrations was not explainable from apparent compositions of the complex ions.

The unidentified wave at -1.0 volt had a half-wave potential sulfosalicylate concentration relationship of

$$E_{\frac{1}{2}} = -1.003 + 0.0465 \log (Tss) \qquad (45)$$

This would indicate a first degree dependence of the reduction of the unknown species on pH if it required one electron per ion for reduction.

The ferrous wave at -1.4 volts appeared only at high concentrations of sulfosalicylate. The relationship between sulfosalicylate concentration and half-wave potential for this wave was:

$$E_{\frac{1}{2}} = -1.415 - 0.0167 \log (Tss) \qquad (46)$$

This gave a calculated value for p of 0.565. This was rather inconclusive, probably indicating one hydroxyl ion per iron. Again it must be emphasized that ferrous reductions are almost invariably irreversible, so there was little significance to equation 44.

The half-wave potentials of the chloride solutions in Table 4 agreed very well with those for the perchlorate solutions. The greatest differences were in the ferrous wave, in which the chloride solutions gave waves that were 27 millivolts more negative at pH 4 and 11 millivolts more negative at pH 9. Also the diffusion currents agreed quite well, except for the much larger wave for chloride solutions at -1.7 volts.

Polarograms were made of solutions with varying sulfosalicylate concentration at pH 9 in chloride medium, the data from which were listed in Table 11. The ionic strength of these solutions was 2 ± 0.1, the iron concentration was 10^{-4} M, and the total borate concentration of these solutions was 0.5 M.

The half-wave potential sulfosalicylate concentration equation of the wave for the reduction of ferric ions to ferrous ions, as determined by the method of least squares was as follows:

$$E_{\frac{1}{2}} = -0.862 - 0.1529 \log (Tss) \qquad (47)$$

This agreed well with equation 26, which was the corresponding equation for polarograms of solutions under similar conditions except that perchlorate was the supporting electrolyte. In the present case the slope was a little less steep, giving a calculated value for p of 2.6 as compared to 2.8 for the perchlorate solutions. Thus the presence

TABLE 11

Half-Wave Potentials and Diffusion Currents
at pH 9 for Various Concentrations of Sulfosalicylate
in Sodium Chloride Supporting Electrolyte

mole/l	Log (Tss)	Half-Wave Potential, volts vs. S.C.E.	Diffusion Current, microampere
0.01009	-1.996	-0.550	0.264
		-1.443	0.412
0.01971	-1.705	-0.611	0.256
		-1.452	0.358
0.0485	-1.314	-0.652	0.758
		-1.468	0.308
0.0999	-1.000	-0.717	0.258
		-1.517	0.442
0.3130	-0.504	-0.780	0.174
		-1.555	0.537
0.5180	-0.286	-1.613	0.488

of three more sulfosalicylate ions in the ferric complex than in the ferrous ion was confirmed.

The only other wave appearing in these solutions was the wave for the reduction of ferrous ion to the metal that appeared at -1.4 volts. The half-wave potential sulfosalicylate concentration equation, which has little meaning because of irreversibility, was calculated by the least squares method to be as follows:

$$E_{\frac{1}{2}} = -1.616 - 0.0952 \log (Tss) \qquad (48)$$

This gave a calculated p/n value of 1.6 indicating, if the results were reliable, that the ferrous complex ion contained three sulfosalicylate ions. This of course was contrary to all the other evidence.

The results obtained with sulfate supporting electrolyte in Table 4 were appreciably different from those for perchlorate, especially for the wave at pH 9 representing the reduction of the ferric complex to the ferrous state. In this case the half-wave potential was 59 millivolts more positive for the sulfate supporting electrolyte, indicating competition between sulfosalicylate and sulfate as complexing agents.

In Table 12 were recorded the data of an extensive study of the variation of half-wave potential and diffusion

TABLE 12

pH Variation of Half-Wave Potential and Diffusion Current in Sodium Sulfate Supporting Electrolyte

pH	Half-Wave Potential, volts *vs*. S.C.E.	Diffusion Current, microamperes
2.37	-0.074	0.792
2.53	-0.038	0.296
2.53	-0.052	0.507
2.92	-0.066	0.608
2.94	0.012	0.406
4.00	(greater than 0)	0.360
	(-1.06)	
	(-1.4)	
4.13	(greater than 0)	0.465
	(-1.38)	
4.59	-0.066	0.408
	-1.396	1.090
4.93	(-0.4)	
	-1.413	1.029
5.53	-0.442	0.140
	-1.124	0.194
	-1.426	0.864
5.89	(-0.44)	
	(-1.14)	
	-1.414	0.660
6.00	-0.406	0.174
	-1.182	0.189
	-1.425	0.488
6.50	-0.444	0.177
	-1.134	0.159
	-1.469	0.999
7.22	-0.448	0.261
	-1.151	0.117
	-1.436	0.816
8.07	-0.478	0.159
	-1.130	0.219
	-1.464	0.866
8.66	-0.505	0.166
	-1.142	0.222
	-1.440	0.975
	(-1.76)	

TABLE 12
(continued)

pH	Half-Wave Potential, volts *vs*. S.C.E.	Diffusion Current, microamperes
9.21	-0.555	0.174
	-1.129	0.290
	-1.443	0.840
	(-1.74)	
9.55	-0.570	0.150
	-1.151	0.136
	-1.455	0.910
	-1.727	0.149
10.12	-0.630	0.180
	-1.147	0.162
	-1.460	0.771
	-1.743	0.151
11.35	-0.712	0.198
	-1.139	0.106
	-1.492	0.459
	-1.745	0.354

current with pH in the presence of sulfate as supporting electrolyte.

In this study the two hundred fifty milliliter capacity polarographic cell was used. The dropping electrode chamber was filled with a solution that was 0.200 M in sodium sulfate, 0.01044 M in sulfosalicylic acid, and 0.0002 M in ferric ion. After thirty minutes of flushing with nitrogen, a polarogram was made of this solution. Then a small amount of 0.370 M sodium hydroxide, previously flushed with nitrogen, was added through the stopper by means of a microburet. After the solution in the dropping electrode chamber had again been flushed with nitrogen for about a minute to insure thorough mixing, another polarogram was made, and the pH determined with a Beckman model G pH meter by means of electrodes set in the rubber stopper. Polarograms were made of this solution over a pH range 2.3 to 11.3 by addition of successive increments of sodium hydroxide in this manner.

As shown in Table 12, five distinct waves appeared in these polarograms at various pH values. The ranges of their half-wave potentials with respect to the saturated calomel electrode were as follows: greater than -0.052 volt, -0.406 to -0.712 volt, -1.124 to -1.182 volts, -1.396 to -1.492 volts, and -1.727 to -1.745 volts.

Below pH 4 only the wave at about 0 volt was present. This was the wave for the reduction of the one to one complex ion of ferric ion with singly ionized sulfosalicylic acid, corresponding to the similar waves observed in perchlorate and chloride solutions. Very little could be done with this wave, as in all cases the wave began at potentials more positive than the saturated calomel electrode. The half-wave potentials could thus be only roughly estimated. As in the other supporting electrolytes, the waves had disappeared when the pH of the solution had reached five. There seemed to be some tendency for the half-wave potential to become more positive with increasing pH, as would be expected under circumstances where the concentration of the complexing agent was increasing.

The second wave, as well as the third and fourth waves, began to appear at pH 4.5. This wave represented the reduction of the complex ion of ferric ion with doubly ionized sulfosalicylic acid. This wave had a very sharp change in slope at pH 8. Below this pH, the wave was nearly independent of pH. Above this value the half-wave potentials became more negative with pH. The equations determined by the least squares method for this wave in the two pH regions were respectively:

$$E_{\frac{1}{2}} = - 0.366 - 0.0109 \text{ pH} \qquad (49)$$

and

$$E_{\frac{1}{2}} = 0.1281 - 0.0741 \text{ pH} \qquad (50)$$

The calculated p/n values were 0.18 and 1.25 for the two equations respectively. This indicated the same number of hydroxyl ions associated with the complex ion below pH 8 as with the ferrous ion, and one more for the ferric complex above pH 8. As the ferrous ion was assumed to contain one hydroxyl ion, the ferric complex ion would have one hydroxyl ion below pH 8 and two hydroxyl ions above this pH. This latter value was one less than the number obtained from the data on the pH study over the range eight to ten in perchlorate supporting electrolyte, as recorded in Table 1.

The half-wave potential of the third wave was almost completely independent of pH. The equation determined by the method of least squares for this was:

$$E_{\frac{1}{2}} = - 1.151 + 0.00104 \text{ pH} \qquad (51)$$

The calculated value of p/n for this wave was less than 0.02.

The ferrous wave appeared at pH 4.5 and above, having been masked by the hydrogen wave at lower pH values. The equation obtained by the least squares method was:

$$E_{\frac{1}{2}} = - 1.365 - 0.0101 \text{ pH} \qquad (52)$$

The calculated value for p in this case was 0.33, or approximately zero for the ferrous ion (probably the aquo ion). This did not agree with the more probable value of one, obtained from the data in Table 1 on polarograms of solutions with perchlorate as supporting electrolyte.

The wave at -1.7 volts appeared only above pH 9. Because only three half-wave potentials of this wave were obtained in the study of Table 12, no least squares determination was carried out. That this wave was caused by the reduction of a ferrous complex ion was indicated by the decrease of the diffusion current of the wave at -1.4 volts that accompanied the increase of the diffusion current of the wave at -1.7 volts with pH. The fact that this latter wave did not appear until this high pH and that it increases in height with pH might indicate that this wave was caused by the reduction of a complex ion of ferrous iron with triply ionized sulfosalicylic acid that was in slow equilibrium with the aquo ferrous ion. The third ionization of sulfosalicylic acid first becomes significant in this pH region. The dependence of the concentration of the complexing agent on the pH in this region would be as follows:

$$\log a_{SS} = \log K_3 + \log a_{HSS} + \text{pH} \qquad (53)$$

where a_{SS} and a_{HSS} were respectively the activities of the triply and doubly ionized sulfosalicylic acid ions and K_3 the third ionization constant of sulfosalicylic acid. If the pH is less than $pK_3 - 1$, a_{HSS} is approximately constant and equal to the total sulfosalicylate (101). Under these circumstances log a_{SS} is proportional to pH and the slope of the line of the half-wave potential plotted against pH should be 0.0296, since n is 2 for the reduction of ferrous ion to the metal. The slope of the straight line through the first two of the three experimental points obtained was 0.032 which is in good agreement with this. As the pH increases, the slope should decrease until it reaches zero when the pH becomes greater than about $pK_3 + 1$. The pH studies were not extended to high enough values to observe this.

On comparison of equations 26, 27 and 37 with equations 50, 51 and 52 respectively, it was seen that in every case the slope for the wave in perchlorate solutions was more negative than that for the corresponding wave in sulfate solutions. The most plausible explanation for this seemed to be that there were complex ions formed between sulfate and the iron species strong enough that the slope became less negative because of their competition with ferric sulfosalicylate and ferrous aquo ions. Other possible reasons for this seemed to be inadequate. The discrepancies of the slopes of the waves at -1.0 and -1.4 volts might possibly have been caused by differences in the degree of irreversibility of these reductions under the different conditions of the two experiments. These two waves were definitely irreversible. However this did not explain the great difference in the slopes for the wave of the reduction of the ferric complex ion to the ferrous ion, which is shown in this paper to be reversible. The difference in the concentration of sulfosalicylate between these two experiments should cause only a difference in intercepts of the corresponding equations with no change in slope. The dilution of the complexing agent by the addition of the sodium hydroxide solution would be expected to shift half-wave potentials to more positive values than theoretical at high pH values, and this was the direction of the difference in results. However, in the case of the sulfate experiment, where this dilution occurred, the volume change of the solution was only about eight per cent for the highest pH, giving a maximum correction of about two millivolts, which was entirely negligible. In both cases the pH values were obtained by means of a model G pH meter, the ordinary glass electrode, and the asbestos fiber calomel electrode. In addition, in the perchlorate solutions the pH values were also checked with a Leeds and Northrup pH meter, both with the ordinary calomel electrode with a bridge consisting of a small sintered glass disc in the electrode wall, and also the calomel electride with the ground glass sleeve for a bridge. If the difference were caused by the uncertainty of measurement of the pH in the presence of perchlorate, there should have been no trend with pH. The pH values observed would have nearly uniformly less than the true pH values. Ahother possibility for the discrepancy of the slopes of the equations might be the change of ionic strength. In the titration experiment the ionic strength increased slightly with pH, as the sulfosalicylic acid became more highly charged and the excess sodium hydroxide increased. On the other hand in the other experiment where the borate buffer was used, the ionic strength would decrease somewhat with concentration if the ion formed on ionization of boric acid was tetraborate instead of dihydrogen borate as assumed, since the contribution of the former ion to the ionic strength was only about three-fourths of the latter. One would expect, however, that the effect of these minor variations in ionic strength would be small.

4. Reversibility studies.

According to Stackelberg and Freyhold (42) and

Souchay and Faucherre (45) the only reliable test for reversibility is the coincidence of the anodic and cathodic waves of the system in question. The criterion used by Kolthoff and Lingane (43, p. 154) was that the slope of the straight line obtained by plotting the potential at any given point on the polarographic wave against $1/i_d-i$ should be equal to $-0.0591/n-m$ at 25° C. This relationship is readily seen from equation 10 and the text immediately following. The equation for the variation of the potential at the dropping electrode with current becomes:

$$E = E_{\frac{1}{2}} - \frac{0.0591}{n-m} \log \frac{i}{i_d - i} \qquad (54)$$

Kolthoff and Lingane stated that if the reduction was irreversible the plot may or may not give a straight line, but if it does, the slope will differ from the theoretical. This has been disputed by Stackelberg and Freyhold, who have shown that in some cases of irreversibility the theoretical slope of this line has been obtained. However it may be still used as an indication, if not as an infallible test, of reversibility.

Tomes (40) has derived from this a rapid test for reversibility that was used generally in this present work. At points on the wave corresponding to one-fourth and three-fourths of the diffusion current the quantity i/i_d-i becomes 1/3 and 3 respectively. Substituting these values into equation 52, and taking the difference of the two equations obtained gives the following equation:

$$E_{3/4} - E_{\frac{1}{4}} = - \frac{0.0591}{n-m} \log 9 \text{ or } 0.0564/n-m \quad (55)$$

By this test the waves for the reduction of the ferric complex ion to the ferrous ion was reversible, except at the extreme concentration limits, but the waves for the reduction of ferrous ions to metallic iron, as well as the wave occurring at -1.0 volt were irreversible. That this test is not entirely reliable as indicated by the fact that the waves for ferric reduction in acid solution passed the test, even though irreversibility was shown by the fact that there was more than one wave for the reduction of the different ions of the same oxidation state.

In order to be certain of the reversibility of the reduction of the ferric-sulfosalicylate complex ion to the ferrous species in alkaline solutions, it was necessary to obtain polarograms of both the anodic and cathodic wave of this couple. This required special precautions because of the very rapid air oxidation of the ferrous ion in the presence of sulfosalicylate in alkaline solutions. The two hundred fifty milliliter capacity cell was almost completely filled with a solution that was 0.0005 M in iron, 0.153 M in sodium sulfate, 0.0104 M in sulfosalicylate, and 0.35 M in total borate concentration, with ionic strength 0.6 and pH 9.02. The solution in the cell was flushed for thirty minutes with nitrogen, after which the polarogram of the solution was made. This polarogram contained only the cathodic wave of the ferric-ferrous couple and the wave of the reduction of ferrous ion to metal. To the solution in the cell was then added 1.5 milliliters of a ferrous perchlorate solution that was about 0.08 M in ferrous ion. After the solution had been bubbled with nitrogen again for about two minutes, another polarogram was made. This contained both the anodic and the cathodic waves of the ferric-ferrous couple, as well as a very large wave for the reduction of ferrous ion to metallic iron. These polarograms were reproduced in Figure 1. It can readily be seen that the ferric-ferrous couple is reversible under these conditions. The cathodic wave is a continuation of the anodic wave, with no leveling off between the two waves. The half-wave potential of the composite wave is only slightly displaced from that of the cathodic wave alone.

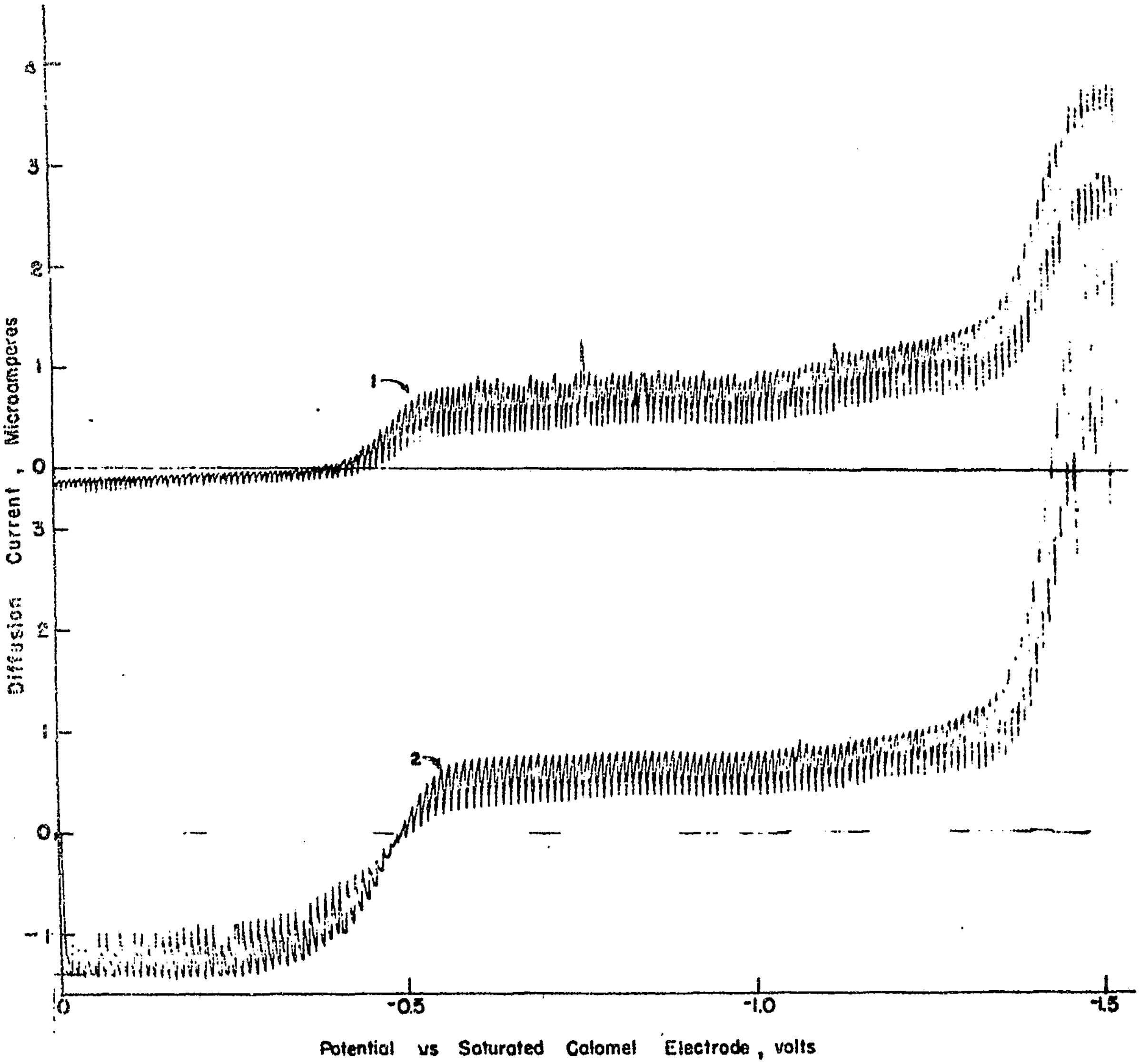

Fig.1—Proof of reversibility of Ferric-Ferrous couple in Alkaline solution.
Curve 1 — Polarogram of solution containing ferric ion, but negligible ferrous ion.
Curve 2 — Polarogram of solution from Curve 1 with ferrous ion added.

5. Maximum suppression

A small maximum was observed following the first wave in alkaline solutions of ferric-sulfosalicylate complex. This maximum interfered with the measurement of half-wave potential and diffusion current for this wave at higher pH values. Buckley and Taylor have recommended 0.01% gelatin as a maximum suppressor for most metal ions, and state that there is no observed reduction of diffusion currents at ordinary concentrations of metal ions (106). Concentrations of 0.001 to 0.02% gelatin were tried. The gelatin seemed to be more effective in reducing the diffusion currents than suppressing maxima in this case. In 0.01% solution the ferric wave was entirely disappeared, and in 0.02% solution there are no waves at all. Even at the lowest concentrations of gelatin some reduction of the diffusion current was observed, with practically no selective suppression of the maximum.

Kolthoff and Lingane (43, p. 117) quoted Heyrovsky (107) as saying that the Schulze-Hardy rule applies to maximum suppression, in that cations of highest charge are most effective in suppression of negative maxima, *i. e.*, maxima with potentials more negative than the potential of the electrocapillary maximum or about -0.6 volt *vs.* the saturated calomel electrode. Lanthanum was found to be ten thousand times as effective as potassium ion for suppression of this type of maxima. Since the maximum in the present case occurs at about -0.75 volt, lanthanum was tried, but with no appreciable effect.

6. Ionization constants of sulfosalicylic acid

a. Potentiometric titration - Titration of sulfosalicylic acid with standard sodium hydroxide with a pH meter gave no break at all before two equivalents of alkali had been added. At two equivalents, a break exactly like that of a moderately strong monobasic acid was observed. No break was found for the phenolic group. This titration curve has since been confirmed by Meek (88). The first two ionizations seem to be almost as strong as those of sulfuric acid. The ionization of the phenolic group must be less than 10^{-11}. Osaka's rule can not be used accurately here, as there is no distinction between the first and second ionizations. However, if it may be assumed that half of the first ionization has occurred and none of the second after addition of one-half equivalent of alkali, a rough estimate of the first constant may be obtained by assuming that it is equal to the hydrogen ion concentration at this point. An estimate may be made of the second constant by similar assumptions for the point in the curve where one and one-half equivalents had been added. The constants calculated in this manner are 0.02 and 0.004 in a solution about 0.05 molar in this acid. Actually, the sulfonic group is probably much stronger than the first ionization would indicate, and is essentially completely ionized up to very concentrated solutions of the acid. Ionic strength was not considered in this titration, and it is likely that the first ionization seems to be weaker because of interionic attraction.

b. Spectrophotometric method - Meek (88) reported that the absorbancy of sulfosalicylic acid is constant over a range of 4.5 to 9.5 in solutions of ionic strength 0.1 at 317.0 millimicrons. Outside these pH limits the absorbancy increases, indicating changes in ionic species in this region. He suggested that the spectrophotometric method of Crouthamel, Meek, Martin, and Banks (108) might be used for the determination of the second and third constants of sulfosalicylic acid. In the present work the author was concerned only with the second ionization constant, as in the pH range of interest here only the mono- and divalent ions exist in appreciable quantities. Also, a complete study necessary to establish the thermodynamic constant was not made. The constant obtained here is in terms of hydrogen ion activity and the concentrations of singly and doubly ionized sulfosalicylic acid at ionic strength 0.1 and 25°. This of course is strictly applicable at this ionic strength only.

Solutions were prepared that were 0.1 molar in perchloric acid and 0.006 molar in sulfosalicylic acid with enough sodium hydroxide added to bring the pH to the desired values. Table 13 and Figure 2 show the results of absorbancy measurements of these solutions at 317.0 millimicrons. The absorbancy is essentially constant at 0.425 at pH values above 4. At pH 1, the minimum pH possible at this ionic strength, the absorbancy curve had not leveled off completely. It was assumed that in concentrated acid solutions all of the sulfosalicylic acid was in the singly ionized state, and the absorbancy would therefore be independent of ionic strength. To determine

TABLE 13

Absorbancies of 0.006 M Sulfosalicylic Acid at Ionic Strength 0.1 and 317.0 Millimicrons

pH	Absorbancy	Average Absorbancy
0.97	0.917,0.918,0.919,0.918	0.918
2.12	0.776,0.779,0.780,0.780	0.779
3.08	0.533,0.536,0.538,0.538	0.536
3.90	0.447,0.449	0.448
6.10	0.424,0.425	0.425

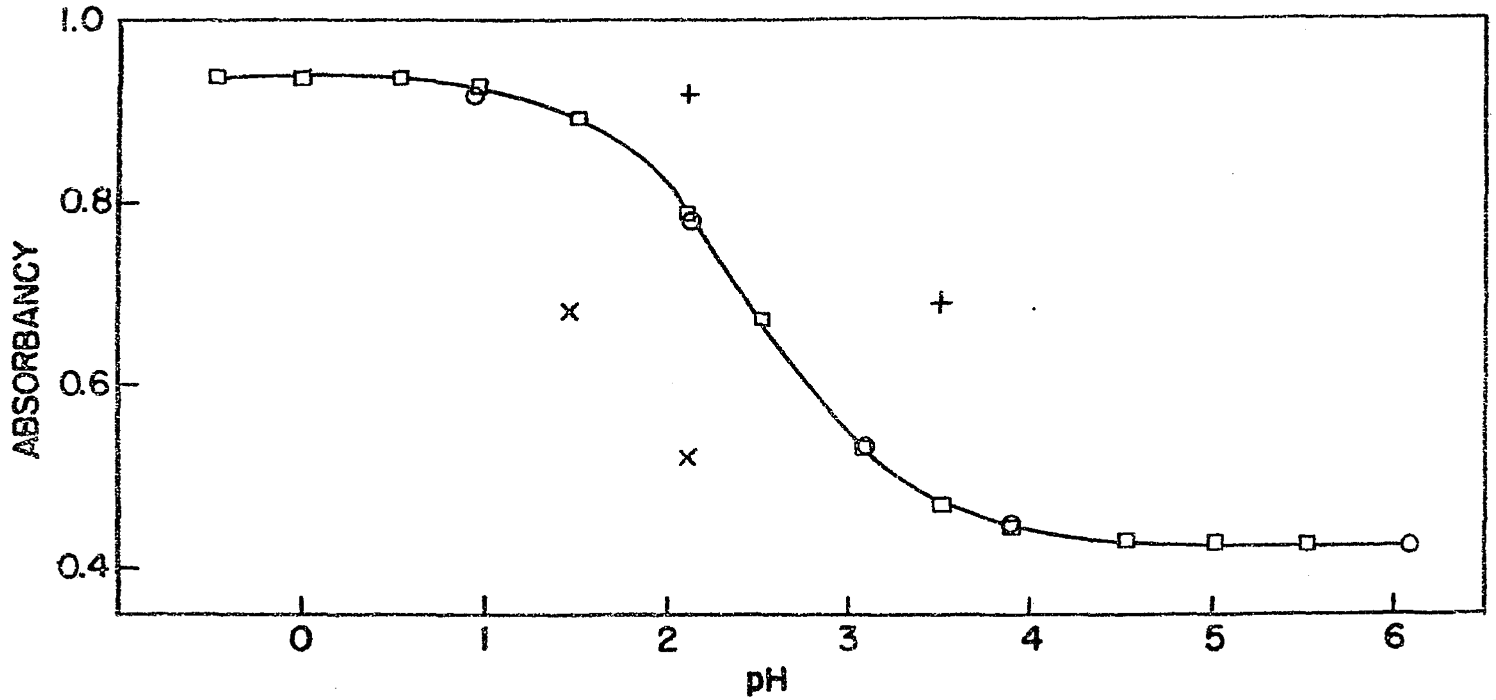

Fig. 2 — Absorbancy of sulfosalicylic acid with varying pH. Sulfosalicylic Acid, 6×10^{-4} M., $\mu = 0.10$, 0.1 M $HClO_4$ adjusted to desired pH with NaOH, 25°C. Absorbancies measured on Beckman D.U. spectrophotometer, $\lambda = 317.0\ m\mu$, band width $0.97\ m\mu$.
○ Observed points □ Calculated points for $K_2' = 3.23 \times 10^{-3}$ (pH = 2.49)
× Points calculated for $K = 3.23 \times 10^{-2}$ and + for 3.23×10^{-4}.

$$K_2' = \frac{a_{H^+}(C_6H_3OHCO_2SO_3^{-2})}{(C_6H_3OHCO_2HSO_3^{-})}$$

the absorbancy of the pure singly ionized sulfosalicylate, perchloric acid was added to 0.006 M sulfosalicylic acid, giving perchloric acid concentrations up to 5 molar. The absorbancies did not exhibit a trend either to increase or decrease in this range, and the average value for the absorbancy of 0.006 M sulfosalicylic acid for radiation of wavelength of 317.0 millimicrons was found to be 0.941.

From this and the data obtained at ionic strength 0.1, the best fitting curve was found when the second ionization constant was taken as 3.23×10^{-3}. This is in remarkably good agreement with the potentiometric estimate reported in the previous section. The curve drawn is the theoretical curve for this value of ionization constant. The plus signs above and crosses below this curve illustrate the position of the curve if the ionization constant was one-tenth and ten times as large respectively.

7. Potentiometric pH study

The pH dependence of the ferric-sulfosalicylate complex at pH 9, as determined polarographically, was verified by a titration of 0.316 millimoles of ferric acetylacetonate in the presence of six times that number of millimoles of sulfosalicylic acid with 0.1265 N sodium hydroxide solution. The titration curve for these data is found in Figure 3. The vertical line of this figure was the calculated equivalence point, assuming double ionization of sulfosalicylic acid, no ionization of acetylacetone, and three hydroxyl ions per ferric complex ion. It is readily seen that this fell at the steepest part of the curve, thus verifying the number three for the hydroxyl ions in the complex ion.

Up to pH 4 the slope gradually increased, following closely the curve for the titration of sulfosalicylic acid alone. At this pH the curve deviated from the titration curve of the acid. In contrast to the steep rise of the latter from pH 4 to 10, the slope of this wave decreased again, and the steep rise did not occur until after another 2.5 milliliters of the sodium hydroxide solution had been added. This evidently means that up to pH 4 the complex ion contained only two hydroxyl ions, but at that pH the third one began to enter the complex. The 2.5 milliliters of alkali added from pH 4 to the point where the curve is the steepest was just the amount required for one additional hydroxyl ion per complex ion. The slope began to decrease very sharply again at pH 8, instead of rising rapidly to pH 10 before leveling off. This decrease in slope is easily seen to be caused by the

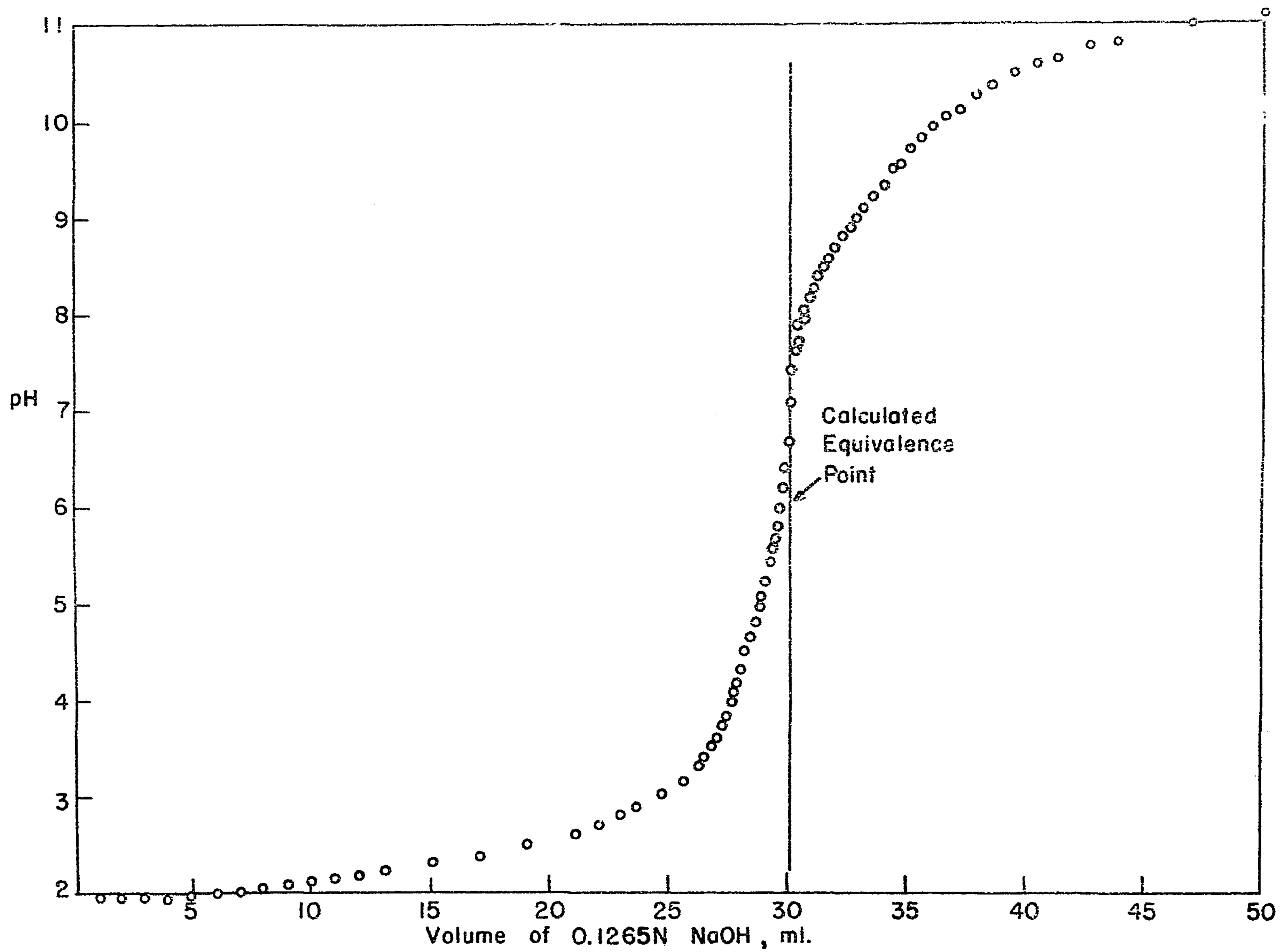

Fig. 3 — Titration of 0.316 millimoles of Ferric Acetylacetonate plus 1.898 millimoles of Sulfosalicylic acid.

ionization of the acetylacetone at this high pH. A sample of the acetylacetone was titrated with sodium hydroxide of this same concentration, and it was found that it required 4.3 milliliters of the 0.1265 N sodium hydroxide solution to bring the pH of the same amount of acetylacetone from 7 to 9, which is reasonably close to the 3.2 required in Figure 3 to go from pH 7 to 9. It is thus seen that at pH 9 the polarographic and potentiometric data agree on three as the number of hydroxyl ions associated with the ferric sulfosalicylate complex at pH 9.

VII. SUMMARY AND CONCLUSIONS

The sulfosalicylate complexes of iron in aqueous colution were studied polarographically by means of the half-wave potential method. In the pH range 8 to 11 a ferric complex with doubly ionized sulfosalicylic acid was found that was reduced to ferrous ion at half-wave potentials between -0.4 and -0.8 volt with respect to the saturated calomel electrode. This reduction was shown to be reversible by two different methods. From polarographic data it was determined that this complex ion contained three sulfosalicylate and three hydroxyl ions. The number of hydroxyl ions was confirmed by the potentiometric pH study of this complex. The molar instability constant was found by the polarographic method to be about 10^{-33} at an ionic strength of one.

An alternative to the presence of three hydroxyl ions combined with iron in the complex is the ionization of the phenolic hydrogen of the sulfosalicylic acid when it enters the complex. This would allow chelation of the ferric ion with the carboxylic and phenolic groups. These two possible structures are indistinguishable by the polarographic and titrimetric methods, as both require the same number of equivalents of hydroxyl ion for their formation. They both have the same charge, also, a value of six which seems incredibly high, except that this is a large ion with considerable space for distribution of charge. In both structures the iron has its usual number of six covalent bonds. The phenolic chelation has strong precedent in the highly colored complexes of ferric ion with phenols that are characteristic of the latter type of compounds. However, in the present case, it may be seen by the titrimetric data that this third ionization would have to begin below pH 3 for this structure to be valid, as by this pH all of the alkali required for the neutralization of the sulfosalicylic acid has been added. It is a little difficult to believe that the complex at that low pH is so stable that it would cause a seven-fold decrease in the concentration of hydroxyl ion necessary for this third ionization. This makes the hydroxyl ion structure seem more probable in this case.

In the pH range 4 to 8 evidence was found for a ferric complex with doubly ionized sulfosalicylate containing only one or two hydroxyl ions. This complex ion was not further studied.

At pH values less than four the ferric species was reduced at 0 volt with respect to the saturated calomel electrode in sulfate, chloride, and perchlorate supporting electrolyte, so that the half-wave potential method could not be applied here. In nitrate supporting electrolyte two polarographic waves were observed for ferric species at pH 4 or less, one at 0 volt and the other at about -0.2 volt. Both the application of the half-wave potential method to the second wave and the comparison of the ratios of the diffusion current of the first wave to that of the second at different concentrations of sulfosalicylate seemed to indicate that at pH 2 the complex reduced at -0.2 volt contained one singly ionized sulfosalicylate ion, in agreement with the published results of other workers, but that at pH 4 there was no sulfosalicylate in the complex ion. The first wave was considered to have been caused by the reduction of the aquo ferric ion that was in slow equilibrium with the complex of the second wave. The results obtained for the second wave were doubtful because of the irreversibility of the reduction. That this reduction of the ferric species in nitric acid was irreversible was shown by the fact that two waves were obtained for a single oxidation state of the metal. The results obtained by the diffusion current were not decisive. The presence of nitrate in the complex ion was postulated to explain the difference in the behavior of nitrate solutions.

No evidence was found for complex formation between doubly ionized sulfosalicylic acid and ferrous ion. The half-wave potential of the ferrous wave was displaced only slightly by the addition of sulfosalicylate. This wave was very irreversible. At pH values below 4, at which the singly ionized sulfosalicylic acid exists, the hydrogen wave was so large that the ferrous ion reduction wave was masked. At pH 9 and above a small wave appeared at -1.7 volts as compared to the potential of the known ferrous wave at -1.4 volts. That this wave at -1.7 volts tended to increase with pH in this region might indicate that it is caused by the reduction of a complex between ferrous iron and triply ionized sulfosalicylate.

An irreversible wave appeared in many of these solutions at -1.0 volt. It could not be identified as a reduction wave of any iron species. This wave was nearly independent of pH.

The second molar ionization constant of sulfosalicylic acid was determined spectrophotometrically to be 0.0032 at ionic strength 0.1. This was roughly corroborated by potentiometric titration with a pH-meter.

VIII. SUGGESTIONS FOR FUTURE WORK

In this work we were unable to study the ferric complex with singly ionized sulfosalicylic acid by the half-wave potential method because the wave for the reduction of this ion was found at potentials greater than that of the saturated calomel electrode. At potentials very much more positive than the latter, the waves are masked by a very strong anodic wave caused by the dissolving of the mercury of the dropping electrode. (43, p. 322). It might be possible to study these waves at potentials up to about 0.45 volt with respect to the saturated calomel electrode, especially if a saturated mercurous sulfate reference electrode was used instead of the calomel electrode. Potentials greater than this could possibly be studied by means of a rotating platinum microelectrode substituted for the dropping electrode.

In the study of the variation of the half-wave potentials with pH in sulfate solution, it was observed that below pH 8 the slope of the line formed by plotting log (Tss) against the half-wave potential was less than it was above this pH. This seemed to indicate that in the pH range 4 to 10 there was a complex of ferric ion with doubly ionized sulfosalicylic acid that had fewer hydroxyl ions than the complex ion studied in the pH range 8 to 11. If a buffering agent was found that was effective in the region of pH of 4 to 10 and that had negligible complexing action on ferric ion, the complex ion in this pH range could be studied by the half-wave potential method.

The second ionization constant of sulfosalicylic acid as determined in this work was valid only at ionic strength 0.1. The thermodynamic constant of this step could be determined by a more complete spectrophotometric study on the order of that carried out with periodic acid by Crouthamel, Meek, Martin, and Banks (108). It is conceivable that the third ionization constant of sulfosalicylic acid might also be determined in this manner.

IX. LITERATURE CITED

1. Cohn, G., *J. prakt. Chem.* (2) *61*, 544-553 (1900).
2. Lorber, L., *Biochem. Z.* *181*, 391-394 (1927).
3. Paviot, J., Chevallier, R., and Revol, L., *Compt. rend. soc. biol.* *99*, 1749-1750 (1928).
4. Lapin, L. N. and Kill, W. E., *Z. Hyg. Infektionskrankh.* *112*, 719-723 (1931). Original not available, cited *Z. anal. Chem.* *92*, 128 (1933).
5. Alten, F., Weiland, W., and Hille, E., Z. *anorg. allgem. Chem.* *215*, 81-91 (1933).
6. Korenman, I. M., *Mikrochemie* *15*, 315-318 (1934).
7. Klinov, I. Y. and Arnold, T. I., *Zavodskaya Lab.* *3*, 894-895 (1934). Original not available, cited *C. A.* *29*, 2475 (1935).
8. Urbach, C., *Mikrochemie* *15*, 207-226 (1934).
9. Rozanov, S. N., Markova, G. A., and Fedotova, E. A., *Z. Pflanzenernähr.*, *Düngung u. Bodenk.* *41*, 59-74 (1935)
10. Thiel, A. and Peter, O., *Z. anal. Chem.* *103*, 161-166 (1935).
11. Peshkova, V. M. and Egorov, A. D., *Zavodskaya Lab.* *4*, 885-887 (1935). Original not available, cited *C. A.* *30*, 984 (1936).
12. Ginsberg, H., *Metallwirtschaft* *16*, 1107-1112 (1937). Original not available, cited *C. A.* *32*, 1601 (1938).
13. Thiel, A. and Hengel, E. v., *Ber.* *70B*, 2491-2497 (1937).
14. Miloslavskiĭ, N. M., Vavilova, E. G., and Daĭkhes, I., *Novosti Tekhniki* *1939*, No. 7, 14 (1939). Original not available, cited *C. A.* *33*, 6748-6749 (1939).

15. Zusser, E. E., *Zavodskaya Lab*. *8*, 1182-1183 (1939).

16. Urech, P., *Helv*. *Chim*. *Acta* *22*, 322-330 (1939).

17. Bauer, R. and Eisen, J., *Angew*. *Chem*. *52*, 459-463 (1939).

18. Nikitina, E. I., *Zavodskaya Lab*. *9*, 629-630 (1940). Original not available, cited *C*. *A*. *37*, 1669 (1943).

19. Alimarin, I. P. and Frid, B. I., *Zavodskaya Lab*. *10*, 252-253 (1941). Original not available, cited *C*. *A*. *35*, 7316 (1941).

20. Pfeiffer, H., *Z*. *anal*. *Chem*. *126*, 81-88 (1943).

21. Kennard, M. and Johnson, C. R., *Proc*. *Trans*. *Texas Acad*. *Sci*. *27*, 45-51 (1944).

22. Kniphorst, L. C. E., *Chem*. *Weekblad* *42*, 311-316 (1946).

23. Kniphorst, L. C. E., *Chem*. *Weekblad* *42*, 328-334 (1946).

24. Kuznetsov, V. I., *Zavodskaya Lab*. *12*, 278-283 (1946). Original not available, cited *C*. *A*. *40*, 7053-7054 (1946).

25. Fogel'son, E. I. and Kalmykova, I. V., *Zavodskaya Lab*. *12*, 973-974 (1946). Original not available, cited *C*. *A*. *41*, 5812-5813 (1947).

26. Snell, F. D. and Snell, C. T., Colorimetric Methods of Analysis, 3d ed., vol. 2, p. 322-324, D. Van Nostrand, Inc., New York, (1949).

27. Corwin, J. F. and Moyer, H. V., *Ind*. *Eng*. *Chem*., *Anal*. *Ed*. *18*, 302-304 (1946).

28. Monnier, D., Rusconi, Y., and Wenger, P., *Anal*. *Chim*. *Acta* *1*, 13-18 (1947).

29. Monnier, D., Rusconi, Y., and Wenger, P., *Helv*. *Chim*. *Acta* *29*, 521-525 (1946).

30. Lacroix, S. and Labalade, M., *Anal. Chim. Acta* *4*, 68-90 (1950).

31. Moser, L. and Irányi, E., *Monatsh.* *43*, 679-684 (1922).

32. Moser, L., *Monatsh.* *44*, 91-95 (1923).

33. Moser, L., Brukl, A., and Vén, I., *Ber.* *58B*, 380-385 (1925).

34. Moser, L. and Brukl, A., *Monatsh.* *47*, 709-725 (1927).

35. Prodinger, W., Organic Reagents, p. 141-148, Elsevier, New York, 1940.

36. Bertin, C., *Bull. soc. chim. France* *1949*, 489-495 (1949). Original not available, cited *C. A.* *44*, 5256 (1950); also by Lacroix and Labalade, ref. 30.

37. Okahara, K., *Science Repts. Tohoku Imp. Univ.* (4) *6*, 573-595 (1931).

38. Foley, R. T. and Anderson, R. C., *J. Am. Chem. Soc.* *70*, 1195-1197 (1948).

39. Heyrovkeý, J. and Ilkovič, D., *Collection Czechoslov. Chem. Communs.* *7*, 198-214 (1935).

40. Toměs, J., *Collection Czechoslov. Chem. Communs.* *9*, 81-103 (1937).

41. Stackelberg, M. v., *Z. Elektrochem.* *45*, 466-491 (1939).

42. Stackelberg, M. v. and Freyhold, H. v., *Z. Elektrochem.* *46*, 120-129 (1940).

43. Kolthoff, I. M. and Lingane, J. J., Polarography, p. 161-183, Interscience Publishers, Inc., New York, 1941.

44. Lingane, J. J., *Chem. Rev.* *29*, 1-35 (1941).

45. Souchay, P. and Faucherre, J., *Bull. soc. chim. France* *1947*, 529-546 (1947).

46. Sartori, G., *Gazz. chim. ital.* (2) *64*, 3-16 (1934).

47. Pines, I., Collection Czechoslov. Chem. Communs. 1, 429-442 (1929).

48. Herman, J., Collection Czechoslov. Chem. Communs. 6, 37-53 (1934).

49. Brdička, R., Collection Czechoslov. Chem. Communs. 3, 396-405 (1931).

50. Heyrovský, J., Bull. soc. chim. France (4) 41, 1224-1241 (1927).

51. Dobryszcyki, M., Collection Czechoslov. Chem. Communs. 2, 134-144 (1930).

52. Pines, I., Collection Czechoslov. Chem. Communs. 1, 387-391 (1929).

53. Lingane, J. J., J. Am. Chem. Soc. 67, 919-922 (1945).

54. Caglioti, V. and Sartori, G., Gazz. chim. ital. (2) 66, 741-744 (1936).

55. Sartori, G., Gazz. chim. ital. (2) 66, 688-692 (1936).

56. Hokhšhtein, J. P. and Pokrovskii, V. A., Zhur. Obshchei Khim. 8, 1465-1469 (1938).

57. Caglioti, V., Sartori, G. and Bianchi, E., Gazz. chim. ital. (2) 72, 63-68 (1942).

58. Toropova, V. F., Zhur. Obshchei Khim. 15, 603-607 (1945).

59. Cahours, A., Ann. chim. et phys. (3) 13, 87-115 (1845).

60. Mendius, O., Ann. 103, 39-80 (1857).

61. Remsen, I., Ann. 179, 107-111 (1875).

62. Liebermann, T. V., Arch. klin. Chir. 125, 482-489 (1923). Original not available, cited C. A. 18, 1159-1160 (1924).

63. Berning, H., Arch. exptl. Path. Pharmakol. 168, 206-216 (1932).

64. Göpfert, K., Arch. exptl. Path. Pharmakol. 189, 387-396 (1938).

65. Weil, R. and Weil, O. to Chem.-pharmazeutische Fabrik., Ger. Pat. 556,143, March 5, 1934. Original not available, cited C. A. 28, P3529 (1934).

66. Prakash, S., J. Indian Chem. Soc. 9, 193-202 (1932).

67. Prakash, S., J. Phys. Chem. 36, 2483-2496 (1932).

68. Herzog, R. O., Kratky, O., and Petertil, E., Trans. Faraday Soc. 29, No. 1, 60-64 (1933).

69. Prakash, S., J. Indian Chem. Soc. 10, 281-285 (1933).

70. Robinson, J. R., Proc. Royal Soc. (London) A170, 519-550 (1939).

71. Roche, G., Pharm. Ztg. 72, 1263 (1927).

72. Miguel, E. J. and Miret, A. R., Ph 10, 17-18 (1938). Original not available, cited C. A. 33, 8656 (1939).

73. Schlenker, F. S., Military Surgeon 95, 502-505 (1944).

74. Moser, L., Neumayer, K. and Winter, K., Monatsh. 55, 85-97 (1930).

75. Gutzeit, G., Helv. Chim. Acta 12, 713-740, 829-850 (1929).

76. Wenger, P. and Duckert, R., Helv. Chim. Acta 27, 757-770 (1944).

77. Patterson, J. H. and Banks, C. V., Anal. Chem. 20, 897-900 (1948).

78. Welcher, F. J., Organic Analytical Reagents, vol. 2, p. 130-142, D. Van Nostrand Co., Inc., New York, 1947.

79. Moser, L. and List, F., Monatsh. 51, 181-9 (1929)

80. Schwarz, V., Angew. Chem. 47, 228-230 (1934).

81. Chernikhov, I. A. and Karsaevska, M. P., *Z. anal. Chem.* *99*, 398-402 (1934).

82. Parks, R. Q., Hood, S. L., Hurwitz, C., and Ellis, G. H., *Ind. Eng. Chem., Anal. Ed.* *15*, 527-533 (1943).

83. Darnell, M. C. and Walker, B. S., *Ind. Eng. Chem., Anal. Ed.* *12*, 242-244 (1940).

84. Caron, H. and Raquet, D., *Bull. soc. chim. France* *7*, 1026-1027 (1910).

85. Vasil'eva, L. A., *Trans. Kirov Inst. Chem. Tech. Kazan* *8*, 48-51 (1940). Original not available, cited *C. A.* *35*, 2442 (1941).

86. Jendrassik, L. and Takács, F., *Biochem. Z.* *274*, 200-204 (1934).

87. Tananaev, I. V. and Litvinenko, M. S., *Zavodskaya Lab.* *9*, 963-970 (1940). Original not available, cited *C. A.* *35*, 1345-1346 (1941).

88. Meek, H. W., Doctoral Dissertation, Iowa State College, 1950.

89. Job, P., *Ann. chim.* (10) *9*, 113-203 (1928).

90. Turner, S. E. and Anderson, R. C., *J. Am. Chem. Soc.* *71*, 912-914 (1949).

91. Foley, R. T. and Anderson, R. C., *J. Am. Chem. Soc.* *71*, 909-912 (1949).

92. Tompkins, E. R. and Mayer, S. W., *J. Am. Chem. Soc.* *69*, 2859-2865 (1947).

93. Babko, A. K., *Zhur. Obshchei Khim.* *15*, 745-757 (1945). Original not available, cited *C. A.* *40*, 7041-7042 (1946).

94. Babko, A. K., *Zhur. Obshchei Khim.* *15*, 758-765 (1945). Original not available, cited *C. A.* *40*, 7042 (1946).

95 Babko, A. K., *Zhur. Obshchei Khim.* *15*, 874-883 (1945). Original not available, cited *C. A.* *40*, 6359 (1946).

96. Rosin, J., Reagent Chemicals and Standards, 2nd ed., p. 448, 449, D. Van Nostrand Co., Inc., New York, 1946.

97. Goetz, C. A., Doctoral Dissertation, Univ. of Ill., 1938.

98. Urbain, G. and Debierne, A., *Compt. rend.* *129*, 302-305 (1899).

99. Lingane, J. J. and Laitinen, H. A., *Ind. Eng. Chem., Anal. Ed.* *11*, 504-505 (1939).

100. Lingane, J. J. and Vandenbosch, V., *Anal. Chem.* *21*, 649 (1949).

101. Meites, L., *J. Am. Chem. Soc.* *71*, 3269-3275 (1949).

102. Lange, N. A., Handbook of Chemistry, 4th ed. p. 1220, Handbook Publishers, Inc., Sandusky, Ohio, 1941.

103. Meites, L., *J. Am. Chem. Soc.* *72*, 180-184 (1950).

104. Lingane, J. J., *J. Am. Chem. Soc.* *68*, 2448-2453 (1946).

105. Meites, L., *J. Am. Chem. Soc.* *72*, 184-189 (1950).

106. Buckley, F. and Taylor, J. K., *Trans. Electrochem. Soc.* *87*, 463-478 (1945).

107. Heyrovsky J., *Actualites sci. et ind.* No. *90*, 1-48 (1934).

108. Crouthamel, C. E., Meek, H. V., Martin, D. S., and Banks, C. V., *J. Am. Chem. Soc.* *71*, 3031-5 (1949).

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