

POLAROGRAPHY OF FLUORIDE COMPLEXES

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POLAROGRAPHY OF FLUORIDE COMPLEXES

INTRODUCTION

Complex ions have an indispensable role in analytical chemistry. Without them, many of the now common analytical techniques would be impossible or at least much less versatile. In order to obtain the optimum benefit from the analytical application of complex ions, an understanding of the nature of complex forming systems is imperative.

Perhaps the most common use of complex ions is in separations. By forming a complex, one metal can be kept in solution while another is removed. For example, the addition of cyanide prevents copper from being precipitated with hydrogen sulfide but does not prevent the precipitation of cadmium or zinc. The separation of aluminum and zirconium by ion exchange depends upon the complexes formed by these two metals in a fluoride solution (8). Cadmium can be deposited electrolytically from a cyanide solution in the presence of copper because the reduction potential of the cadmium cyanide complex is less negative than that of the copper cyanide complex (26,p.61).

Complex formation may also be used to suppress the reaction of an ion. Thus interference from the fluoride ion can be eliminated in many cases by the addition of boric acid, which forms a very stable complex with the fluoride. In the iodometric determination of copper,

interference from iron (III) can be eliminated by complexing the iron with fluoride.

Complex ions are extensively used in colorimetric methods of analysis. An excellent example of this is the use of a thiocyanate complex for the colorimetric determination of niobium (7).

The fluoride ion has an important and in some ways unusual position in the field of complex formers. According to covalency rules, which can be used to predict the formation and stability of most complex ions, the fluoride ion should form very few complexes. However, it forms many more complexes than the other halide ions. In fact, the analytical chemistry of the fluoride ion is in a large measure the chemistry of complex ions (26,p.115), and the complexes that fluoride forms are among the strongest that are known.

An explanation for this unusual behavior is obtained by investigating the structure of fluoride complexes. Instead of containing covalent bonds, the complexes are held together by electrostatic forces (26,p.115). The extreme electronegativity and the small size of the fluoride ion account for this unusual type of complex ion bonding.

The possibility of studying complex ions polarographically was recognized by Heyrovsky and Ilkovic as early as 1935. Since 1945 the technique has been used extensively for the investigation of many complex ions. But in all of the investigations that have been reported, only one has dealt with metal-fluoride systems. This work was done by West (27). He investigated the behavior of a great many ions in a sodium fluoride medium. His purpose was simply to determine which of the ions gave polarographic waves. There was no attempt to investigate the formation of fluoride complexes.

A more thorough polarographic investigation of metal-fluoride systems seemed worthwhile both to obtain information on the existence and stability of any complexes formed and to obtain information pertinent to the analytical application of the metal-fluoride systems.

THEORETICAL CONSIDERATIONS

A. FUNDAMENTAL THEORY

Before discussing the application of the polarographic method to the investigation of complex ions, the limitations inherent in the method should be emphasized. The basic assumption used in deriving the equation of the polarographic wave requires that the rates of all possible intermediate steps at the electrode, either electrical or chemical, be so much more rapid than diffusion rates that the dropping mercury electrode is subject only to concentration polarization (16,p.3). If this basic assumption holds, the reduction of an ion at the electrode will be reversible. If it does not hold, the reduction of the ion will be irreversible and it will be impossible to use any derived polarographic equations for calculating quantitative information about the ion or the system in which it is involved. It is essential, therefore, to establish the reversibility of the electrode reaction before any quantitative conclusions may be drawn from the experimental data.

As an example, consider two complexes of cadmium. In chloride solutions, experiments indicate that chloro-cadmium complexes are formed. The reduction of these complexes at the electrode is shown to be reversible. It is possible, therefore, to determine the formation constants

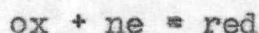
of these chloro-complexes and their formulas (6,p.1153). Comparable experiments in cyanide solutions indicate that cadmium also forms cyanide complexes, but the reduction of these complexes at the electrode is irreversible, so it is impossible to calculate their dissociation constants or formulas (21,p.1110).

The polarographic method for investigating complex metal ions is based on the fact that the formation of a complex produces a shift in the characteristic half-wave potential ($E_{1/2}$) of a simple metal ion. The magnitude of the shift of the half-wave potential varies with the concentration of the complexing agent. If the reaction at the electrode is reversible, by measuring the shift in the half-wave potential as a function of the concentration of the complexing agent, it is possible to obtain information on the formula of the complex formed and its dissociation constant.

The relationship of the half-wave potential to the formation of a complex, its dissociation constant, and its formula can best be explained by the use of a simplified mathematical derivation.¹

¹ Notations are those used in reference (9).

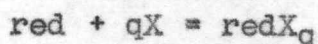
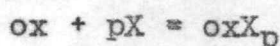
The general equation for the reduction of a metal ion is



By application of the Nernst equation, the potential for this reaction would be

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{(\text{ox})}{(\text{red})} \quad (1)$$

If a ligand is present which complexes the oxidized form of the ion or the reduced form or both, the equations for the complex formation can be written as:



where X is the ligand, p is the coordination number of the oxidized form and q is the coordination number of the reduced form.

Dissociation products for these complexes are expressed as:

$$K_{\text{ox}} = \frac{(\text{ox})(\text{X})^p}{(\text{oxX}_p)} \quad K_{\text{red}} = \frac{(\text{red})(\text{X})^q}{(\text{redX}_q)}$$

Substituting these expressions into equation 1:

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{K_{\text{ox}}(\text{ox}K_p)(\text{X})^q}{K_{\text{red}}(\text{redX}_q)(\text{X})^p} \quad (2)$$

By definition, the half-wave potential is the potential at which one half of all the oxidized form which reaches the electrode is reduced. Therefore when $E = E_{1/2}$

then

$$(\text{ox}X_p) = (\text{red}X_q)$$

and equation 2 becomes:

$$E_{1/2} = E^{\circ} + \frac{0.059}{n} \log \frac{K_{\text{ox}}}{K_{\text{red}}} (X)^{q-p} \quad (3)$$

and on rearranging:

$$E_{1/2} = E^{\circ} + \frac{0.059}{n} \log \frac{K_{\text{ox}}}{K_{\text{red}}} - \frac{0.059}{n} (p-q) \log(X) \quad (4)$$

E° is taken as equal to $E_{1/2}$ when no complexing ligand is present.

Equation 4 shows that the half-wave potential is a function of the ratio $K_{\text{ox}}/K_{\text{red}}$, the number of ligands coordinated to the oxidized and reduced forms of the ions and the concentration of the complexing substance. Therefore, to determine whether a metal forms a complex ion with a given ligand it is only necessary to determine the half-wave potentials of that metal ion in solutions of varying ligand concentration; if a complex is formed, there will be a shift in the half-wave potential with a change in the ligand concentration.

B. DETERMINATION OF DISSOCIATION PRODUCTS

1. Systems Containing One Complex Species. The fundamental principle involved in determining the dissociation product of a complex ion in a system containing a single complex species was first recognized by Heyrovsky

and Ilkovic in Czechoslovakia and developed in this country by Lingane (16).

By differentiating equation 4 with respect to $\log(X)$, the following expression is obtained:

$$\frac{d E_{1/2}}{d \log(X)} = - \frac{0.059}{n} (p-q) \quad (5)$$

From this expression it is evident that by determining the half-wave potentials at varying concentrations of ligand, X , and plotting the half-wave potentials versus $\log(X)$, $(p-q)$ can be calculated from the slope of the line thus obtained. If the number of ligands coordinated with the oxidized or reduced form of the metal ion is known, i.e., if the value of p or q is known, the number of ligands coordinated with the other form of the ion can be determined. In the special case where the metal ion in the complex is reduced to the metal and amalgamates, q is equal to zero and can be determined directly from the slope. In this special case, when two electrons are involved in the reduction, the value of the slope corresponding to a given value p is given in Table 1.

TABLE 1

<u>Slope, volts</u>	<u>p</u>
0.029	1
0.059	2
0.089	3
0.118	4

In general, knowing the values of p and q , it is possible to calculate the ratio K_{Ox}/K_{Red} from equation 4. Only the ratio can be determined in this manner. If one of the constants is known, however, the other may be calculated. In the special case where the metal amalgamates and no reduced complex is formed, equation 4 can be simplified to the following:

$$E_{1/2} = E^0 + \frac{0.059}{n} \log K_{Ox} - \frac{0.059}{n} p \log(X) \quad (6)$$

K_{Ox} can be calculated directly from this expression.

The approach just described may be used only if a single complex species exists over a wide range of ligand concentration. If several species exist within the ligand range investigated, the plot of the half-wave potentials as a function of the concentration of ligand will result in a curve rather than a straight line and no calculations based on a slope of this line are possible.

2. Systems Containing Several Complex Species.

In the last three years two polarographic methods have been developed for studying the stepwise formation of complex ions.

The first of these methods was developed by de Ford and Hume (4). This method has only limited value however, for it presupposes a reversible reaction at the electrode. Unfortunately only a few metals, e.g., Cd, Pb, Tl, Zn, have been shown to be reversibly reducible at the dropping

mercury electrode.

The second method, published last year by Ringbom and Eriksson (21) was designed, in theory, to overcome the limitations of deFord and Hume's approach. This method was used in an attempt to study the successive formation of some metal-fluoride complexes.

Ringbom and Eriksson's method is divided into two parts. By their Direct Polarographic Method it is possible to calculate the formation products of each of several complex species that exist simultaneously in a solution. By their Indirect Method it is possible, in theory, to calculate the formation products of complexes formed between a metal, M, and a ligand, which are irreversibly reduced at the electrode. This Indirect Method involves the use of an indicator ion. This indicator ion is a metal ion which also forms complexes with the ligand. However, the indicator ion complexes must be reversibly reducible at the electrode. Since both the indicator ions and the M ions are in equilibrium with the ligand, measurements on the indicator ion system can be related to the M system. In this way it is possible to calculate the formation products of the M complex ions.

In addition to being reversibly reducible, the indicator ion complexes must have a half-wave potential more positive than the half-wave potential of the M-ligand

complexes.

The Indirect Method would seem to circumvent the limitation of reversibility imposed by the deFord and Hume method for studying systems containing several complex species. The Indirect Method has been developed in theory only. There has been no report of any experimental confirmation. The Direct Method has been used by Eriksson (6) in a study of the cadmium chloride and cadmium bromide complexes.

An application of the Indirect Method requires a knowledge of the formation products of the indicator ion complexes. These products are conveniently determined by the Direct Method, so it will be discussed first. In the discussion, the following notations will be used:

	<u>Solution</u>	<u>Electrode surface</u>
Total concentration of ligand	C_x	C_x
Total concentration of metal	C_m	$\frac{i_d - i_{1/2}}{i_d} C_m = C_o m$
Concentration of free ligand	X	X_o
Concentration of free metal	M	M_o

$i_{1/2}$ = current at $E_{1/2}$	$B_1, B_2, \text{etc.}$ = formation product
	(MX_n)
i_d = diffusion current	$B_n = \frac{(MX_n)}{(M)(X)^n}$
X = ligand ion	$b_1, b_2, \text{etc.}$ = formation constant
M = metal ion	(MX_n)
g = average ligand number	$b_n = \frac{(MX_{n-1})(X)}{(MX_n)}$

subscript "o" refers to value at the electrode surface.

The formation products are calculated as follows:

From polarograms taken at various ligand concentrations, values of $\Delta E_{1/2}$, the difference between the half-wave potentials of a metal ion in a solution containing a complexing ligand and a solution without any ligand, are determined.

The average ligand number, g , of the system defined as

$$g = \frac{\text{number of bound ligands}}{\text{total number of metal atoms}} \quad (6)$$

is computed from the expression:

$$g = \frac{-d\Delta E_{1/2}}{d \ln X} \cdot \frac{nF}{RT} \quad (7)$$

With a divalent ion at 25°C this expression becomes:²

$$g_0 = \frac{-d\Delta E_{1/2}}{d \log X_0} (0.03381) \quad (8)$$

g_0 can be determined from this expression by using differences instead of differentials. X_0 is not known, so the value of C_x is used as a first approximation.

X_0 is the total concentration of the ligand at the electrode surface. It is equal to the total concentration of ligand in the solution corrected for the amount of ligand coordinated with the metal ion. X_0 is computed from the expression:

² Note the similarity between equation 8 and equation 5. The only difference is that equation 8 is based on concentrations at the electrode surface and equation 5 assumes that concentrations at the electrode surface are the same as those in the body of the solution.

$$X_0 = C_x - g_0 \frac{i_d - i_{1/2}}{i_d} C_m \quad (9)$$

using values of g_0 obtained from equation 8.

Employing these approximate X_0 values, new g_0 values are computed using equation 8 and then more accurate X_0 values from equation 9. This procedure is continued until two successive g_0 and X_0 values agree.

The concentration of the metal at the electrode surface, M_0 , can be calculated from the equation:

$$\Delta E_{1/2} = -29.58 \log \frac{C_0 m}{M_0} \quad (10)$$

The best way to calculate the formation products is a partly graphical method. It involves the use of functions, f_n , defined as follows:

$$f_1 = B_1 + B_2 X_0 + B_3 X_0^2 + \dots$$

$$f_2 = \frac{F_1}{X_0} = \frac{B_1}{X_0} + B_2 + B_3 X_0 + \dots$$

or generally

$$f_n = \frac{F_1}{X_0^{(n-1)}} \quad (11)$$

In terms of the quantities calculated above:

$$f_n = \frac{C_0 m - M_0}{M_0 X_0^n} = \frac{\frac{C_0 m}{M_0} - 1}{X_0^n} \quad (12)$$

All of the quantities on the right side of equation 12 are known, so f_n , corresponding to various values of X_0 can be determined.

f_1 is then plotted as a function of X_0 . The point of intersection of the extrapolated curve with the f_1 axis gives B_1 and the slope of the curve at the point, B_2 .

B_4 and B_3 can be determined in a comparable way by plotting f_4 as a function $1/X_0$.

After determining the formation products for a reversible metal-ligand system, the metal may be used as an indicator ion in the investigation of other metals that form complexes with the same ligand.

In essence, the indicator ion serves as a means of measuring the ligand concentration. Indicator ions are added to a solution containing M ions and ligand. The half-wave potential of the indicator ion is measured. From a graph showing the relationship between the half-wave potential and the ligand concentration, the concentration of ligand in the solution being investigated can be determined.

The Indirect Method relates the shift in the half-wave potential of the indicator ion to the formation products of the M -ligand complex in the following manner:

$$E_{0\ m} = \frac{\text{number of bound ligands}}{\text{total number of metal atoms}}$$

For the M -ligand species, the number of bound ligands would be the total ligand concentration corrected for the free ligands and the ligands associated with the indicator

ions. The average ligand number for M can be determined from:

$$\xi_{0\ m} = \frac{C_x - X_0 - \xi_{0\ \text{indicator}} C_{0\ \text{indicator}}}{C_m} \quad (13)$$

The X_0 can be determined by measuring the half-wave potential of the indicator ion and determining the X_0 from a graph of half-wave potential versus X_0 . The $\xi_{0\ \text{indicator}}$ can likewise be determined from a graph of X_0 versus $\xi_{0\ \text{indicator}}$. C_x and C_m are known from the composition of the solution, so it is possible to calculate $\xi_{0\ m}$.

$\xi_{0\ m}$ can be defined in terms of the formation products:

$$\xi_{0\ m} = \frac{B_1 X_0 + 2B_2 X_0^2 + \dots + nB_n X_0^n}{1 + B_1 X_0 + B_2 X_0^2 + \dots + B_n X_0^n} \quad (14)$$

which on rearrangement gives:

$$\xi_{0\ m} + (\xi_{0\ m} - 1)X_0 B_1 + (\xi_{0\ m} - 2)X_0^2 B_2 + \dots + (\xi_{0\ m} - n)X_0^n B_n = 0 \quad (15)$$

From a plot of $\xi_{0\ m}$ versus X_0 , various values of $\xi_{0\ m}$ and their corresponding X_0 values can be obtained. These are substituted into equation 15 and the formation products calculated.

EXPERIMENTAL PROCEDURE

A. THE EQUIPMENT AND MATERIALS

The recording polarograph was constructed by several graduate students in the summer of 1953. It was patterned after the Sargent Model XXI Polarograph. The recorder was a Brown Potentiometer, Model Y153X12V-X-30K(V), manufactured by Brown Instrument Division, Minneapolis-Honeywell Regulator Co.

The polarographic cells were cylindrical in form. They were water jacketed with an inside diameter of 31 mm. and an outside diameter of 41 mm. The depth of the inner section of the cells was 95 mm. They had a volume of approximately 50 ml.

Water was circulated through the cells from a constant temperature bath maintained at $25.0 \pm 0.2^{\circ}\text{C}$.

All solutions were deaerated by bubbling nitrogen through them. The nitrogen was Matheson Company's Pre-purified Grade containing less than 0.001% oxygen. It was used without further treatment.

Mercury for the dropping mercury electrode was cleaned by spraying it through a tower 40 inches high and one inch in diameter. The cleaning process consisted of washing the mercury consecutively with 10% potassium hydroxide, 10% nitric acid and finally distilled water.

Potentials across the polarographic cell were measured with a Leeds and Northrup Type K Potentiometer. These potentials were measured versus a saturated calomel electrode. A pencil-type electrode was used (2). It was connected by a saturated sodium chloride salt bridge to the solution being polarographed. The potential of this electrode was checked against that of a new Beckman calomel, both dipping in a saturated potassium chloride solution, and found to agree within 1 millivolt.

The pencil electrode, including the salt bridge, had a resistance of approximately 120 ohms (measured at 2000 cycles on an alternating current bridge). The resistance of the system - dropping mercury electrode, solution 1M in sodium perchlorate and 30 mM in sodium fluoride, calomel electrode - was approximately 350 ohms, measured in the same manner as above.

B. THE SOLUTIONS

In all solution polarographed, the ionic strength was maintained at one using sodium perchlorate.

Stock solutions of sodium fluoride were prepared from C.P. sodium fluoride.

Stock tin(II) solutions were prepared by dissolving fresh C.P. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in water that had been previously deaerated. In most cases, sodium fluoride was added to the solution to prevent hydrolysis. If experimental

conditions required the absence of fluoride, the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in water and the solution was used as soon as possible. Hydrolysis of the tin(II) was very rapid, especially if fluoride was absent. Therefore an aliquot of the solution was analyzed iodimetrically (13, p.604) for the free tin(II) concentration at the same time another aliquot was being polarographed.

Titanium(IV) solutions were prepared by dissolving C.P. titanous sulfate in hot, 4M sulfuric acid. The titanium(III) was oxidized to titanium(IV) by bubbling oxygen through the hot acid solution. As the titanium (III) was oxidized, the color of the solution changed from deep purple to colorless. After completing the oxidation, the solution was filtered to remove the small amount of solid material that remained. The titanium(IV) concentration was determined by precipitating hydrous titanium oxide with ammonium hydroxide, igniting and weighing as the oxide.

A stock titanium(IV) solution was prepared for polarographic runs by adding an aliquot of the acid solution to a 700 mM sodium fluoride solution and neutralizing with sodium hydroxide. The volume of this solution was adjusted and aliquots used for polarograms.

C. POLAROGRAPHIC MEASUREMENTS

Before being polarographed, all solutions were de-aerated for at least 15 minutes. If the metal ion under investigation was sensitive to air oxidation, it was not added until after the deaeration.

The initial and final potentials on the polarogram were measured to 0.1 mv with the potentiometer. The voltage divider in the polarograph was shown to be linear, so intermediate points on the polarogram were determined by extrapolation.

No maximum suppressor was required for the fluoride systems studied.

The half-wave potentials were determined either from a plot of the $\log i/(i_d - i)$ against applied potential or by Sargent's method (22, pp.19-21).

The capillary tube in the dropping mercury electrode was cleaned periodically by immersion in concentrated nitric acid while the mercury was flowing. This treatment was sometimes inadequate and it was then necessary to break off the tip of the capillary.

RESULTS AND DISCUSSION

Several metals were investigated for the formation of fluoride complexes in a neutral sodium fluoride medium.

The complexes formed that were reversibly reduced were investigated by the method developed by Heyrovsky, Ilkovic and Lingane (9) or the Direct Method of Ringbom and Eriksson (21).

The Indirect Method of Ringbom and Eriksson (21) was used in an attempt to investigate the complexes that were irreversibly reduced.

A. METAL-FLUORIDE SYSTEMS

The formation of a complex is indicated by a shift in the half-wave potential of the metal with a change in the ligand concentration. When metals were being investigated to determine if fluoride complexes were formed, two polarograms were made initially, one at a low fluoride concentration and the other at a high fluoride concentration. If there was no shift in the half-wave potential between these two fluoride concentrations or if there was only a small shift (20 millivolts or less), no further investigation was warranted for any complex formed would be very weak.

If the shift in the half-wave potential was large enough to indicate the formation of a reasonably stable complex it was next necessary to determine whether the

reduction of the metal at the electrode was reversible. There are several methods for determining reversibility (18,p.562) but only two were used in these investigations.

The first of these was a method developed by Tomes (14,p.228). The equation of a polarographic wave of a reversible reaction is

$$E_{dme} = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i} \quad (16)$$

If the potential of the dropping mercury electrode (E_{dme}) is determined at two positions on the rising portion of the wave - usually the positions chosen are those where the current is equal to 1/4 and 3/4 of the diffusion current - the difference between these two potentials will be

$$E_{3/4} - E_{1/4} = -\frac{0.059}{n} \log 9 = -\frac{0.056}{n} \quad (17)$$

To determine if the reduction is reversible it is only necessary to measure $E_{3/4}$ and $E_{1/4}$ and determine if the difference between them is equal to $0.056/n$. If it is, the electrode reaction is reversible.

The other method for determining reversibility is based also on equation 16. A plot is prepared of E_{dme} versus $\log i/i_d - i$. If the plot is straight and has a slope of $0.059/n$, the reaction is reversible (14,p.194).

In all of the solutions polarographed, the ionic strength was adjusted to one using sodium perchlorate.

The perchlorate ion was used because of its non complexing character.

Sodium fluoride was used as a source of fluoride ion. Because of the limited solubility of this salt, the maximum fluoride concentration that could be obtained was 0.8 M. The more soluble potassium fluoride could not be used as a source of fluoride because of the formation of insoluble potassium perchlorate.

1. Zinc-Fluoride System. The shift in the half-wave potential was too small to indicate the formation of a stable complex. Also, a precipitate formed in the solutions shortly after they were prepared. It was probably zinc hydroxide.

TABLE 2

ZINC-FLUORIDE SYSTEM

<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>
200	991
400	1001
600	1002

2. Thallium-Fluoride System. No complex was formed.

TABLE 3

THALLIUM-FLUORIDE SYSTEM

<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>
5	471
50	472
500	470

3. Cadmium-Fluoride System. Again the shift in half-wave potential was too small to indicate the formation of a very strong complex. In the 700 mM sodium fluoride solution, a fine white precipitate formed about half an hour after preparation of the solution. It was probably cadmium fluoride.

TABLE 4

CADMIUM-FLUORIDE SYSTEM

<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>
50	577
700	595

4. Nickel-Fluoride System. Nickel, in this neutral sodium fluoride medium, gave polarographic waves that failed to level off to form diffusion current plateaus.

5. Manganese(II)-Fluoride System. A fluoride complex is formed. For a reversible 2-electron reduction, however, $E_{3/4}-E_{1/4}$ should have a value of -29 millivolts.

TABLE 5

MANGANESE(II)-FLUORIDE SYSTEM

<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>	<u>E_{3/4}-E_{1/4}, mV</u>
95	1.476	-26
284	1.497	-22
473	1.507	-32
663	1.513	-30

6. Copper(II)-Fluoride System. Calculations based on the data in Table 6 indicated that two complexes were formed.

TABLE 6

COPPER(II)-FLUORIDE SYSTEM			
<u>NaF, mM</u>	<u>E_{1/2}, mV</u>	<u>NaF, mM</u>	<u>E_{1/2}, mV</u>
85	+17.5	284	+ 5.7
95	+17.4	331	+ 5.1
104	+14.8	378	+ 2.9
132	+13.1	473	- 2.3
142	+12.6	567	- 6.3
189	+10.8	662	- 9.1
236	+ 8.5		

The average value for $E_{3/4}-E_{1/4}$ was -31 millivolts. This is in good agreement with the theoretical value of -29 millivolts for a reversible reduction.

The half-wave potentials reported in this table are an average of 3 to 5 individual determinations. In most cases, the half-wave potentials were reproducible to only ± 2 millivolts.

Figure 1 was prepared using data from Table 6. The two straight lines on the graph indicate the existence of two copper-fluoride complexes. The slope of the left line is 0.021 volt and for the right line 0.058 volt. Comparing the values with the theoretical values in Table 1, the 0.058 volt is in good agreement with the theoretical value of 0.059 volt for a complex with two coordinating ligand

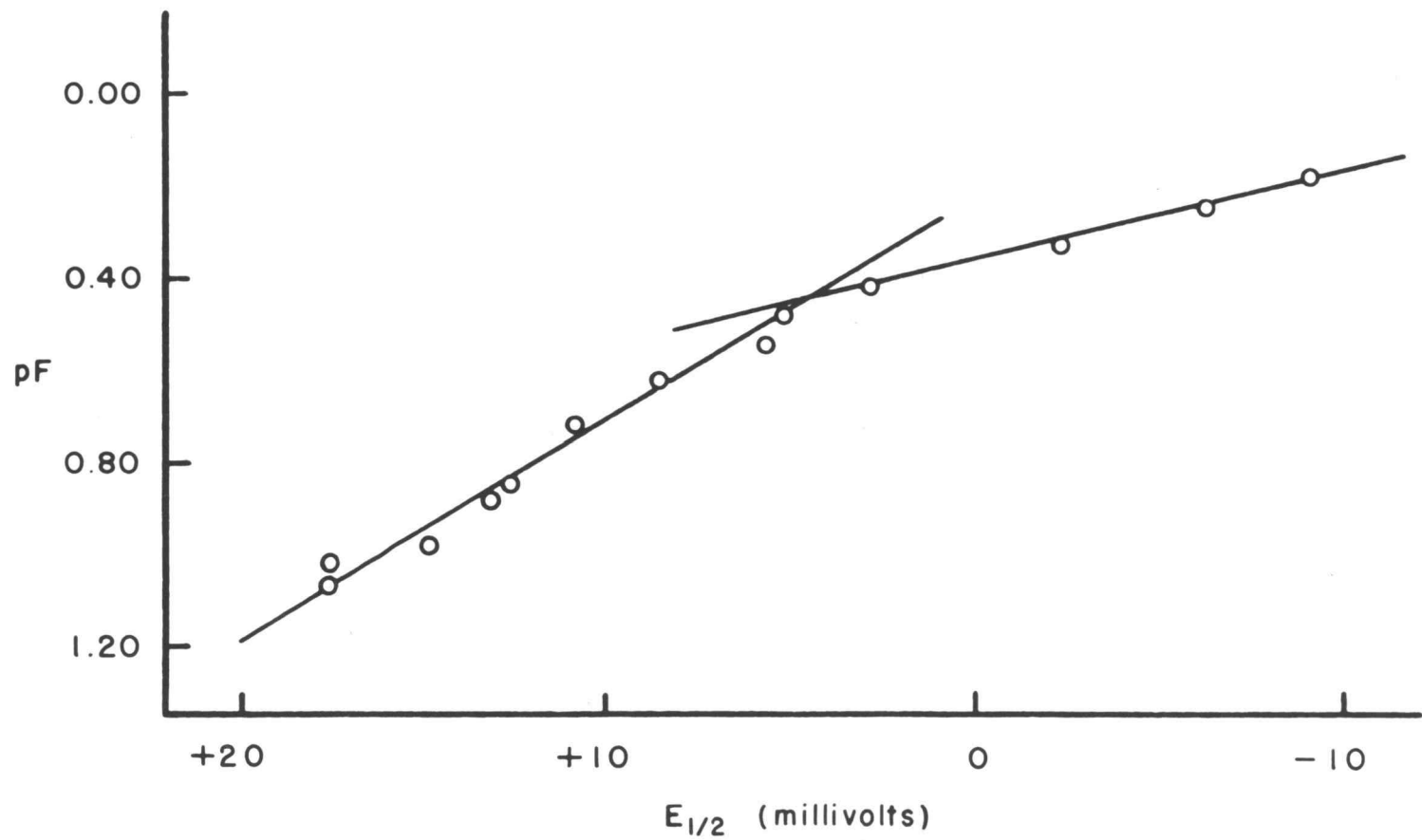


Figure 1. Variation of pF with $E_{1/2}$ in Copper(II)-fluoride System

atoms. The slope of 0.021 volt for the left line does not agree as well with the theoretical value of 0.029 volt for a complex containing one ligand, but this can be attributed in part to the scattering of points at low fluoride concentrations.

The dissociation products of these two complexes were calculated using equation 6. The results are given in Table 7. Also included in Table 7 are the formation products for the two complexes.

TABLE 7
DISSOCIATION AND FORMATION PRODUCTS
FOR COPPER(II)-FLUORIDE COMPLEXES

<u>Complex</u>	<u>Dissociation Product</u>	<u>Formation Product</u>
CuF ⁺	2.7 ± 0.4	0.37 ± 0.05
CuF ₂	1.0 ± 0.2	1.0 ± 0.2

The deviation in the products was calculated on the basis of a ± 2 millivolt deviation in the half-wave potentials.

7. Tin-Fluoride System. The large shift in the half-wave potentials indicated the formation of a strong complex.

The average $E_{3/4} - E_{1/4}$ value was -0.032 volt which is in good agreement with the theoretical value of -0.029 volt for a reversible reaction.

TABLE 8
TIN(II)-FLUORIDE SYSTEM

<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>	<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>
0	421.0	128	628.6
10	528.8	162	639.0
13	540.7	197	646.6
17	551.3	232	654.0
20	557.9	267	660.1
27	568.6	303	665.6
35	577.6	388	677
41	585.4	483	685
59	598.9	578	690
76	609.1	672	694

At sodium fluoride concentrations lower than 10 mM, the tin hydrolyzed quite rapidly. Polarograms in these solutions were irreversible.

Below 60 mM sodium fluoride, the half-wave potentials were reproducible to ± 2 millivolts. Above 60 mM sodium fluoride, they were reproducible to ± 1 millivolt.

The half-wave potentials for the tin-fluoride system were plotted as a function of pF in Figure 2. All of the points lay on a straight line. The slope of this line is 0.0875 volt, in excellent agreement with the theoretical value of 0.0886 volt for a complex with three ligands - SnF_3^- .

The dissociation and formation products for SnF_3^- were calculated in the same manner as in the copper-fluoride system. The value for the dissociation product is $2.2 \pm 0.2 \times 10^{-10}$; the stability product $4.6 \pm 0.4 \times 10^9$.

The deviations in the constants were calculated on the basis of a ± 1 millivolt deviation in half-wave potentials.

Polarograms were made on the tin-fluoride system in acid solutions. The results are given in Table 9.

TABLE 9

EFFECT OF ACID CONCENTRATION ON THE
HALF-WAVE POTENTIAL AND REVERSIBILITY
OF THE TIN-FLUORIDE COMPLEX

Ionic strength = 1		Tin(II) = 3 mM	
<u>HClO₄, M</u>	<u>NaF, mM</u>	<u>-E_{1/2}, mV</u>	<u>E_{3/4}-E_{1/4}, mV</u>
0.01	0	443	-46
0.01	5	460	-65
0.1	0	443	-63
0.1	5	465	-63
0.1	50	477	-58
1.0	0	461	--
1.0	10	457	-76
1.0	100	446	-61

The shift in half-wave potentials indicates that fluoride complexes were formed. But in all cases, the electrode reaction was irreversible.

The irreversibility obviates the use of tin as an indicator ion in acid fluoride solutions. In neutral fluoride solutions, however, tin meets with the requirements for an indicator ion.

In order to use tin as an indicator ion it was necessary to make the following graphs and calculations:

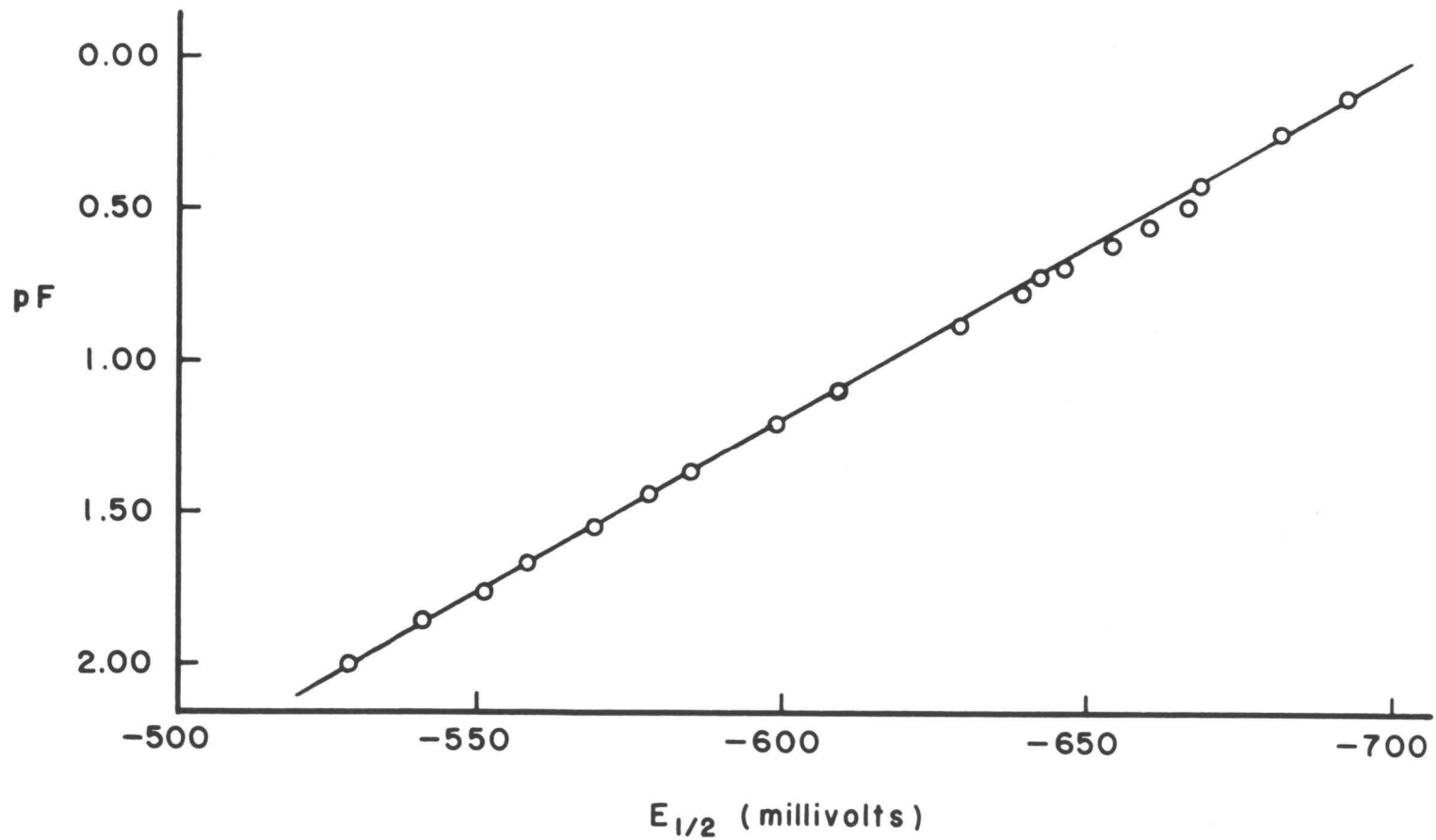


Figure 2. Variation of pF with $E_{1/2}$ in Tin(II) - fluoride System

1. Graph of the relationship between the half-wave potential and the fluoride concentration;
2. Calculation of the average ligand number for the tin at various fluoride concentrations;
3. Calculation of the formation product constants.

The relation between the half-wave potentials and the fluoride concentration is shown in Figure 3. The concentration of fluoride in a solution containing tin as an indicator ion can be determined by measuring the half-wave potential of the tin wave and from this graph determine the corresponding fluoride concentration.

The average ligand numbers for tin were calculated and the results are given in Table 10. The numbers above the columns in the table refer to the equations used to calculate the values given in the columns.

Figure 4 shows the relationship between these average ligand numbers and the concentration of ligand.

It is interesting to compare Figure 4 with Figure 2. The same experimental data were used to prepare both graphs. In Figure 2 the slope of the line does not deviate from a value indicating a complex containing three ligands. In Figure 4, however, the average ligand numbers become quite scattered and appear to decrease at high fluoride concentrations.

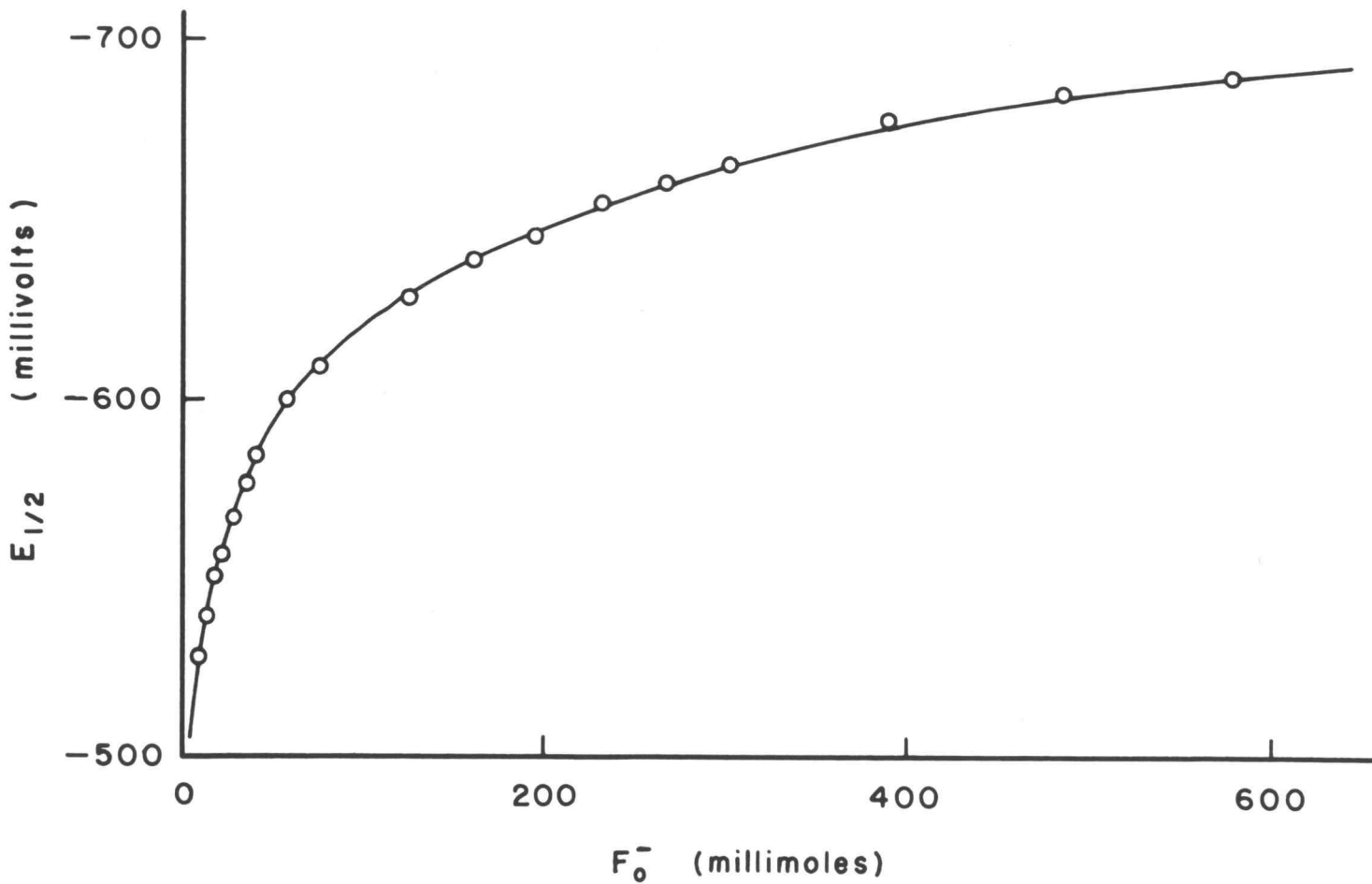


Figure 3. Variation of $E_{1/2}$ with F_0^- in Tin(II)-fluoride System

TABLE 10

AVERAGE LIGAND NUMBERS AND f-VALUES
FOR THE TIN(II)-FLUORIDE SYSTEM

Ionic strength = 1 Tin(II) = 1 mM
E_{1/2} with no fluoride = -421.1 mM

No	C _{F⁻} mM	- E _{1/2} mV	(9) F ₀ ⁻	(8) ε ₀	(10) C ₀ Sn ⁺² x 10 ⁻⁵	(12) f ₁ x 10 ⁻⁷	(12) f ₄ x 10 ⁻⁹	1/F ₀ ⁻ M ⁻¹
1	10	107.7	9		0.044	0.051	800	120
2	13	119.6	12	2.8	0.11	0.093	550	84
3	17	130.2	16	3.0	0.25	0.16	430	64
4	20	136.8	19	2.5	0.42	0.22	310	52
5	27	147.5	26	2.7	0.97	0.37	210	38
6	35	156.5	33	3.0	2.0	0.59	160	30
7	41	164.3	40	3.3	3.6	0.90	140	25
8	59	177.8	57	2.9	10	1.8	95	17
9	76	188.0	75	3.0	23	3.0	72	13
10	127	207.5	125	3.0	100	8.3	43	8.0
11	162	217.9	160	3.3	230	15	36	6.2
12	197	225.5	195	3.0	420	22	29	5.1
13	232	232.9	230	3.5	750	33	27	4.3
14	267	239.0	265	3.3	1200	45	24	3.8
15	303	244.5	301	3.4	1800	61	22	3.3
16	388	253.9	387	2.9	3800	99	17	2.6
17	483	261.6	482	2.7	7000	140	13	2.0
18	578	266.1	577	2.0	10000	170	8.9	1.7
19	672	270.1	671	2.1	13000	200	6.7	1.5

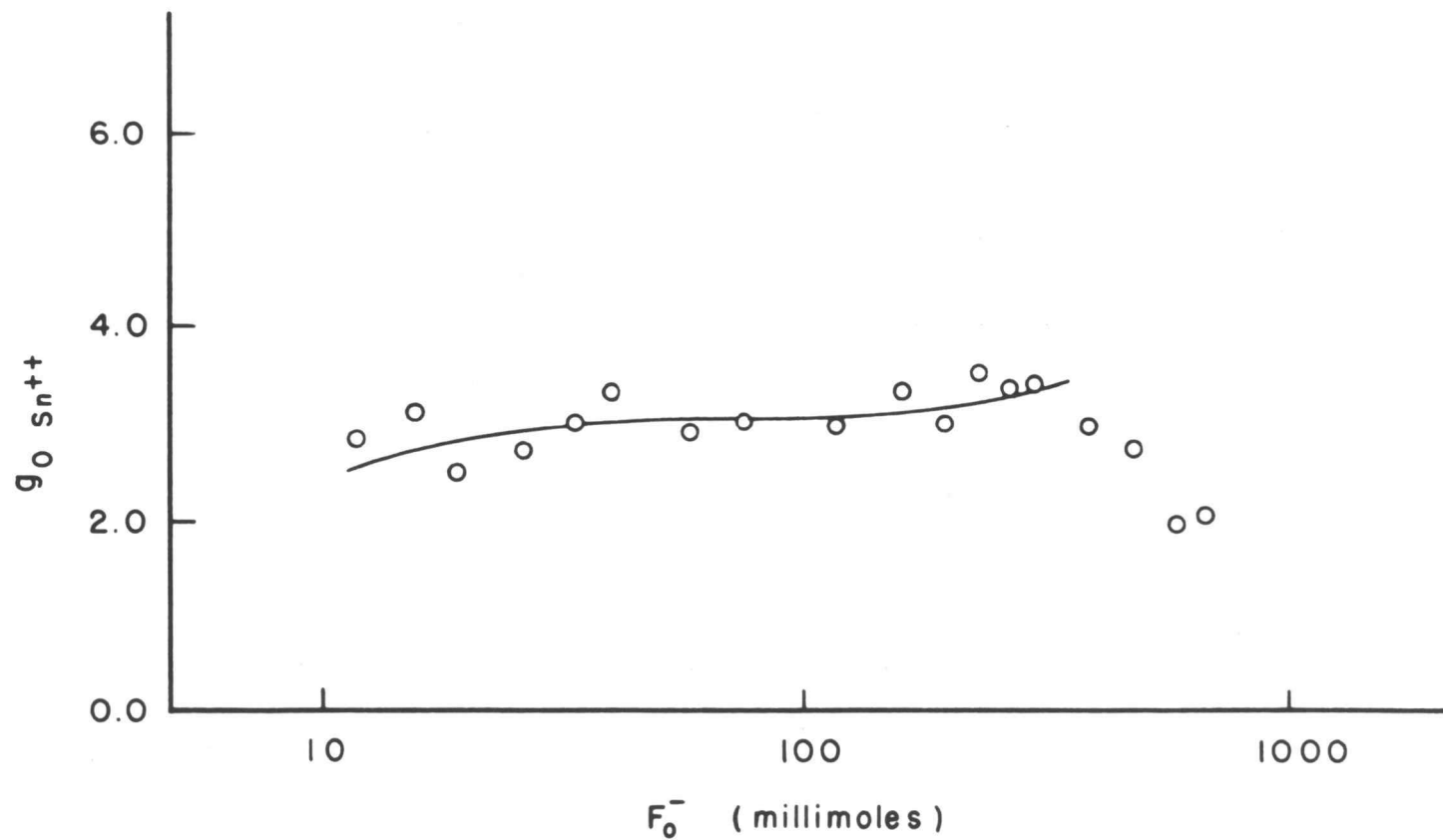


Figure 4. Variation in Average Ligand Number of Tin(II) with F_0^-

This same scattering of points at high ligand concentration was observed by Eriksson in his study of the chloro- and bromo-cadmium complexes (6, pp. 1151 and 1153). He attributed this to an effect of high ligand concentration on the activities of the complex species.

It was also necessary to determine the formation products, B_n , for the tin-fluoride complex. This was done in a graphical manner using functions defined in equation 12. The values for the functions f_1 and f_4 were calculated and the results recorded in Table 10.

f_1 was plotted versus F_0^- . The point of intersection of the extrapolated curve with the f_1 axis should give B_1 and the slope of the curve at that intersection, B_2 . However, the values obtained by this extrapolation were meaningless. The extrapolated value for B_1 was someplace near zero, but the units on the f_1 axis were so large that the error in this value could be several orders of magnitude. It was impossible to obtain values of f_1 at low fluoride concentrations so that the extrapolation could be more carefully done because of hydrolysis of the tin.

f_4 was plotted versus $1/F_0^-$ in Figure 5. The point of intersection of the extrapolated curve with the f_4 axis gave B_4 and the slope of the curve at this intersection, B_3 . The formation products determined from this graph are:

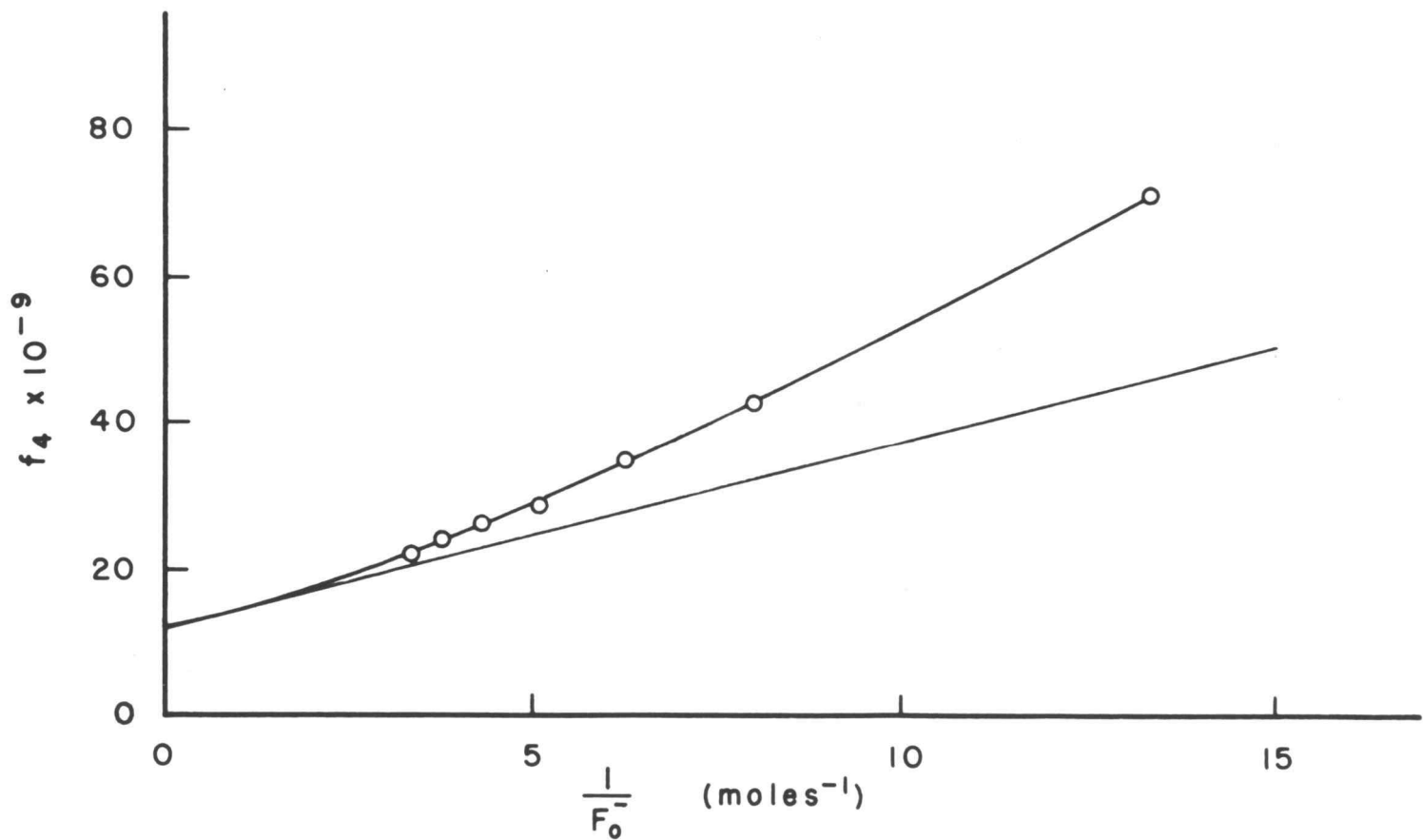


Figure 5. Variation of f_4 with $\frac{1}{F_0}$ in Tin (II) - fluoride System

$B_3 = 2.5 \times 10^9$ and $B_4 = 1.2 \times 10^8$.

It is gratifying to note that the formation product, B_3 , for SnF_3^- , agrees well with the value of 4.6×10^9 obtained previously by the method of Heyrovsky, Ilkovic and Lingane.

The physical significance of B_4 is doubtful because the existence of the complex it represents is uncertain. At high fluoride concentration, where SnF_4^{-2} would be expected to exist, there is an increase in the ligand number. However, as the fluoride concentration is increased, the average ligand number falls off sharply.

8. Titanium-Fluoride System. It was difficult to prevent titanium from hydrolyzing in a neutral fluoride medium. In sodium fluoride concentrations less than 100 mM, solutions containing 5 to 10 mM of titanium hydrolyzed almost immediately. In sodium fluoride concentrations higher than 100 mM, however, the hydrolysis was less rapid, but even in 700 mM sodium fluoride, a visible precipitate of titanium hydroxide was observed within an hour after preparing the solution.

Hydrolysis of titanium can usually be prevented by working in acid solutions. If polarographic waves can be obtained for titanium in acid solutions, the formation of fluoride complexes in these solutions could be investigated.

Zeltzer reported in 1932 that he obtained good waves for the reduction of titanium (IV) in 0.1 N hydrochloric, sulfuric and nitric acids (14,p.442). In a repetition on his work, however, we found that a well developed wave was obtained in the hydrochloric acid solution only. In the other acids, the titanium wave began at a potential only slightly more positive than that of the hydrogen wave and it ran into the hydrogen wave without the formation of a diffusion current plateau.

The effect of fluoride on the reversibility and half-wave potential of titanium in the hydrochloric acid was investigated. The results are given in Table 11.

TABLE 11

EFFECT OF FLUORIDE CONCENTRATION ON THE HALF-WAVE POTENTIAL AND REVERSIBILITY OF THE TITANIUM-FLUORIDE COMPLEX IN 0.1 M HCl

Titanium = 1 mM

<u>NaF, mM</u>	<u>$-E_{1/2}$, mV</u>	<u>$E_{3/4}-E_{1/4}$, mV</u>
0	768	-108
10	521	-186
100	392	- 30

The values for $E_{3/4}-E_{1/4}$ indicate that the reduction is irreversible. For a reversible reduction involving one electron, i.e. Ti(IV) \rightarrow Ti(III), $E_{3/4}-E_{1/4}$ should have a value of -56 millivolts.

It is interesting to observe that an increase in sodium fluoride concentration shifts the half-wave potential in the positive direction. In most cases of complex formation the shift is in the negative direction. This positive shift is not unique for titanium however (14, p.481). It has been observed with other metals, and the explanation given is that the reduction of the complex formed is more reversible than the reduction of the initial complex. Note Table 9. The tin-fluoride complex undergoes this same positive shift in 1 N perchloric acid.

The irreversible character of the titanium in the hydrochloric acid solution does not permit the use of this solution in investigating the fluoride complexes of titanium.

A possibility existed for studying the fluoride complexes of titanium in solution containing Versene (the disodium salt of ethylenediaminetetraacetic acid, dihydrate). The complexes formed between titanium and Versene are very stable. They prevent the hydrolysis of titanium even in neutral solution (20).

It was necessary to determine if fluoride complexes are formed in titanium Versene solutions. This was done by making a series of polarograms in solutions containing 0.7 mM titanium, 5 mM Versene, 0.1 M acetate buffer, and increasing amounts of sodium fluoride. With no sodium

fluoride present, there was only one wave at -378 millivolts due to the titanium-Versene complex. At 20 mM sodium fluoride a wave began to form at -1.2 volts. The height of this wave increased with increasing concentration of sodium fluoride while the height of the titanium-Versene wave decreased. By the time the sodium fluoride concentration had reached 100 mM, the titanium-Versene wave had completely disappeared.

The wave at -1.2 volts was due, no doubt, to the reduction of a titanium fluoride complex. Further proof of this was obtained, however, by polarographing a solution containing 1 mM titanium, 100 mM sodium fluoride and 0.1 M acetate buffer. Only one wave was obtained and it was at -1.2 volts. Incidentally, the value of $E_{3/4} - E_{1/4}$ for this wave was -108 millivolts indicating an irreversible reduction of the titanium-fluoride complex in an acetate buffer solution.

Titanium in an acetate buffer without fluoride hydrolyzed immediately.

The reversibility of the titanium fluoride complex in solutions containing Versene was investigated. The results are given in Table 12. The half-wave potentials for the waves are also included in this table.

The values for $E_{3/4} - E_{1/4}$ indicate that the reduction of the fluoride complex is irreversible.

TABLE 12

EFFECT OF FLUORIDE CONCENTRATION ON THE
 HALF-WAVE POTENTIAL AND REVERSIBILITY OF
 THE TITANIUM-FLUORIDE COMPLEX IN VERSENE SOLUTIONS

Versene = 5 mM Titanium = 1 mM Acetate buffer = 0.1M

<u>NaF, mM</u>	<u>$E_{3/4}-E_{1/4}$, V</u>	<u>$-E_{1/2}$, mV</u>
20	-1.260	147
100	-1.256	82

Note that the half-wave potentials are about the same at both fluoride concentrations. There is apparently no change in the species of the complex ions within the range of fluoride concentrations investigated.

The irreversible character of the titanium fluoride complex in the Versene solutions does not permit the use of these solutions for investigating the fluoride complexes of titanium.

Of all of the metal-fluoride systems investigated, only the tin and the copper contained complexes that were reversibly reducible at the dropping mercury electrode. This reversibility permitted the use of direct methods for the calculation of formulas and dissociation products for these complexes.

As has been indicated previously in the discussion of polarographic theory, the irreversible reduction of complex ions precludes the use of the usual direct methods

for calculating quantitative information about the ions. By the use of Ringbom and Eriksson's Indirect Method (21) it is theoretically possible, however, to investigate quantitatively a metal-ligand complex even though it is irreversibly reduced. This Indirect Method requires the use of an indicator ion, the function and requirements of which have been described previously. Experimental results indicate that in a neutral fluoride medium tin(II) satisfies the requirements for such an indicator ion.

The investigation of irreversible metal-fluoride complexes, using tin(II) as an indicator ion, is discussed in the following section.

APPLICATION OF TIN(II) AS AN INDICATOR ION
IN THE INVESTIGATION OF FLUORIDE COMPLEXES

Tin(II) was used as an indicator ion in an attempt to investigate the fluoride complexes of titanium(IV).

Stock solutions of titanium were prepared as described in the experimental section. Since these solutions hydrolyzed in about an hour, a new stock solution was prepared every 35 to 45 minutes throughout the series of runs.

The average ligand numbers for the titanium, i.e. the average number of fluoride ions coordinated with one titanium ion, were calculated using Ringbom and Eriksson's Indirect Method. The results are given in Table 13.

The average ligand number varied from 7.6 to 10.5. These are unreasonably large values. An attempt was made to find an explanation for them.

Ringbom and Eriksson indicated at the beginning of their article (21,p.1105) that the advantage of their Indirect Method was that it could be used in the investigation of metal complexes that were not reversibly reducible at the electrode. But at the end of the discussion of the method they indicated it had a weak point:

"If the metal M is not reversibly reducible, the reaction between M and the ligand does not occur instantaneously. Consequently,

TABLE 13

AVERAGE LIGAND NUMBERS FOR
TITANIUM-FLUORIDE SYSTEM

Ionic strength = 1.7
 Tin(II) = 1 mM
 Titanium(IV) = 8 mM

No	C_{F^-} mM	$-E_{1/2}$ mV	F_o^- mM	$C_{F^- - F_o^-}$ mM	$C_{F^- - F_o^- - 1.5}$	$\epsilon_o T_1$
1	106	585.4	40	66	64.5	7.7
2	109	587.0	42	67	65.5	7.8
3	116	592.1	48	68	66.5	7.9
4	129	601.0	59	70	78.5	9.3
5	160	609.8	75	85	83.5	9.9
6	206	633.7	141	65	63.5	7.6
7	269	647.5	198	71	69.5	8.3
8	301	652.0	220	81	79.4	9.5
9	364	661.4	274	90	88.4	10.5

even if it is possible to calculate all the concentrations at the electrode surface, it is not certain that the M ions are in equilibrium with the ligands liberated at the surface." (21,p.1110)

It seemed desirable to determine just what effect an irreversible system had on the indirect method.

In a review on polarography, Tanford stated that one of the causes of irreversible polarographic reactions is a slow chemical process at the electrode (24,p.248). Non-instantaneous attainment of equilibrium could be classified as a slow chemical process and therefore could be expected to cause irreversible electrode behavior.

The theory of the use of an indicator ion demands that equilibrium between the metal being studied and the ligand be established instantaneously. The concentration of ligand involved in this equilibrium is measured by the indicator ion. This measured ligand concentration is then used to calculate the average ligand number of the metal complex. If the equilibrium between the ligand and the metal has not been attained, the whole method fails and the calculated average ligand number has no physical significance.

It is possible to investigate the effect of non-attainment of equilibrium on the average ligand number of a metal by investigating a metal-fluoride system that is known to be irreversible. Polarograms could be obtained from a series of solutions in which the concentration of the irreversible metal was varied while the concentrations of ligand and indicator ions remain constant. Under such conditions, if equilibrium is not attained at the electrode between the metal and the ligand, the average ligand

number of the metal would be expected to decrease with increasing concentration of the metal. This would be the case, because in a given time (less than the drop time of the electrode) only a certain fraction of the ligand would complex with the metal. But as the concentration of the metal was increased while the ligand concentration remained constant more metal would be available within this given time to complex with the ligand. And so, the ligand concentration would decrease. This situation would be indicated by a decrease in the average ligand number of the metal.

If a reversible metal system were used instead of an irreversible system, the average ligand number would remain constant throughout the whole range of metal concentrations.

Experiments were conducted using nickel(II) and manganese(II), both of which were known to be irreversibly reducible in a fluoride medium. The concentration of the nickel or manganese was varied while the concentration of the tin(II) - the indicator ion - and sodium fluoride were maintained constant. The average ligand numbers were calculated from the data obtained. Results are given in Tables 14 and 15.

Note that the average ligand number of both metals decreased as the concentration of the metals increased.

This was the expected behavior.

TABLE 14

EFFECT OF CONCENTRATION OF NICKEL
ON ITS AVERAGE LIGAND NUMBER

NaF = 279 mM

Tin(II) = 1 mM

<u>Ni, mM</u>	<u>ϵ_0</u>
1	18.5
5	9.2
10	1.1
20	1.6
30	1.6

TABLE 15

EFFECT OF CONCENTRATION OF MANGANESE
ON ITS AVERAGE LIGAND NUMBER

NaF = 279 mM

Tin(II) = 1 mM

<u>Mn, mM</u>	<u>ϵ_0</u>
1	16.5
5	2.3
10	2.6
20	1.4

The results from these experiments would indicate that the Indirect Method could not be used for investigating irreversibly reducible metal systems.

However, these experiments involved only one ligand. Before any final conclusions can be drawn, it would be highly desirable to investigate metal complexes involving other ligands. If this could be done in systems amenable to investigation by other polarographic methods for studying complex formation, a better understanding of the applicability and limitations of the Indirect Method could be obtained.

ANALYTICAL APPLICATION OF
TIN(II)-FLUORIDE SYSTEM

The possibility of using the tin(II)-fluoride system for the quantitative determination of tin is inviting, especially in the analysis of those metals which are soluble only in hydrofluoric acid, i.e., zirconium, niobium, tantalum and their alloys. Such a procedure offers the possibility of determining tin simply by dissolving the sample, adjusting the pH and volume, polarographing a suitable aliquot and measuring the diffusion current.

The relationship between the diffusion current and the concentration of tin is expressed by the Ilkovic equation

$$i_d = k C_{Sn} \quad (18)$$

where i_d is the diffusion current, C_{Sn} is the concentration of tin and k is a constant (25,p.63). If it can be shown that k has a constant value over a given range of tin concentrations, the concentration of tin in a sampling falling within this range can be determined by substituting the diffusion current and k into equation 18 and calculating C_{Sn} .

If k is not constant, the diffusion currents can be determined for known concentrations of tin and a graph made of these diffusion currents versus the tin

concentrations. This plot can then serve as a standard curve for the evaluation of tin concentrations from measured diffusion coefficients.

The relationship between the concentration of tin and the diffusion current was studied first in fluoride solutions containing tin only and then in synthetic mixtures of zirconium and tin.

A. EXPERIMENTAL PROCEDURE

1. Reagents. C.P. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as a source of tin(II).

Metallic zirconium in the form of turnings was obtained from the Bureau of Mines, Albany, Oregon. It was designated "Special Ingot".

The hydrofluoric acid used to dissolve the zirconium was Baker and Adamson's Reagent Grade, 48%.

2. Procedure. The polarographic procedure was the same as that used previously in this thesis.

The metallic zirconium was dissolved by carefully adding hydrofluoric acid to the turnings covered with 15 to 20 milliliters of water in a plastic beaker immersed in an ice bath. The proper amount of hydrochloric acid was added and the solution was diluted to volume in a plastic bottle.

Tin(II) master solutions were prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.8 M sodium fluoride for the investigation of the diffusion current of tin in neutral sodium fluoride solutions and in solutions 0.8 M in hydrofluoric acid and 0.06 M in hydrochloric acid for investigations in acid solution.

The ionic strength was not maintained constant.

B. RESULTS AND DISCUSSION

Increasing concentrations of tin were polarographed in 0.8 M sodium fluoride. The diffusion currents were measured and the constant, k , was calculated. The results are given in Table 16.

TABLE 16

RELATIONSHIP BETWEEN DIFFUSION CURRENT AND
THE CONCENTRATION OF TIN(II) IN 0.8 M NaF

Tin(II) = 1 mM

NaF = 0.8 M

<u>Sn⁺², mM</u>	<u>i_d, amp</u>	<u>k</u>
0.97	8.2	8.5
1.87	17.2	9.2
4.28	39.9	9.3
7.50	71.8	9.6

These results indicate that for very accurate results it would be necessary to construct a standard curve.

Before preparing synthetic mixtures of tin and zirconium, a polarogram was run on the zirconium in a solution 0.8 M in hydrofluoric acid and 0.06 M in hydrochloric acid. No wave was observed before the hydrogen wave at -1.3 volts.

Synthetic mixture of zirconium and tin were prepared and polarographed. The results are given in Table 17.

TABLE 17
SYNTHETIC MIXTURES OF ZIRCONIUM AND TIN(II)

<u>Sn⁺², %</u>	<u>i_d, amp</u>	<u>k</u>
1	6.7	6.7
2	14.3	7.1
5	33.9	6.8

These results indicate that the Ilkovic equation may be used to calculate the concentration of tin.

This exploratory work indicates that it would be possible to develop a polarographic method for the determination of tin in zirconium using a fluoride medium. Further work must be done, however, to determine the optimum pH and fluoride concentration and to investigate interferences.

SUMMARY AND CONCLUSIONS

1. Several metal fluoride systems were investigated to determine if metal-fluoride complexes were formed in a neutral fluoride medium. Of those investigated, zinc, cadmium, and thalium did not form complexes. Manganese(II), copper(II), tin(II), titanium(IV) did.

2. Of those metals that formed fluoride complexes, only the tin(II) and copper(II) systems were reversibly reducible at the dropping mercury electrode.

3. The formulas of the tin(II) and copper(II) complex ions were determined using the method developed by Heyrovsky, Ilkovic and Lingane.

4. The dissociation products for the tin(II) and copper(II) complexes were determined using the method of Heyrovsky, Ilkovic and Lingane. The formation product for the tin(II)-fluoride complex was determined using the Direct Method of Ringbom and Eriksson.

5. An attempt was made to study the irreversibly reducible titanium-fluoride complex using the Indirect Method of Ringbom and Eriksson. Unreasonably high results were obtained for the average ligand number of the titanium-fluoride complex. A weakness in the theory of the Indirect Method was postulated as being the cause of these high results.

6. The failure of the Indirect Method leaves no other polarographic method available for the investigation of the irreversibly reducible fluoride complexes.

7. A preliminary investigation of the application of the tin-fluoride system for the quantitative determination of tin was made.

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APPENDICES

APPENDIX A

The data on fluoride complexes available in the literature is given in Table 18.

TABLE 18
DATA ON FLUORIDE COMPLEXES
AVAILABLE IN THE LITERATURE

Element	Equilibrium	Formation Constant	Reference
Al	$\text{Al}^{+3} + \text{F}^- = \text{AlF}^{+2}$	1.4×10^6	6, p. 238
	$\text{Al}^{+3} + 2\text{F}^- = \text{AlF}_2^+$	1.4×10^{11}	
	$\text{Al}^{+3} + 3\text{F}^- = \text{AlF}_3$	1×10^{15}	
	$\text{Al}^{+3} + 4\text{F}^- = \text{AlF}_4^-$	5.6×10^{17}	
	$\text{Al}^{+3} + 5\text{F}^- = \text{AlF}_5^{2-}$	2.3×10^{19}	
	$\text{Al}^{+3} + 6\text{F}^- = \text{AlF}_6^{3-}$	6.9×10^{19}	
Zr	$\text{Zr}^{+4} + \text{HF} = \text{ZrF}^{+3} + \text{H}^+$	6.3×10^5	7, p. 3189
	$\text{ZrF}^{+3} + \text{HF} = \text{ZrF}_2^{+2} + \text{H}^+$	2.10×10^4	
	$\text{ZrF}_2^{+2} + \text{HF} = \text{ZrF}_3^+ + \text{H}^+$	6.7×10^2	
Fe	$\text{Fe}^{+3} + \text{HF} = \text{FeF}^{+2} + \text{H}^+$	189	8, p. 2604
	$\text{FeF}^{+2} + \text{HF} = \text{FeF}_2^+ + \text{H}^+$	10.4	
	$\text{FeF}_2^+ + \text{HF} = \text{FeF}_3 + \text{H}^+$	0.58	
Th	$\text{Th}^{+4} + \text{HF} = \text{ThF}^{+3} + \text{H}^+$	$4.5 \pm 0.5 \times 10^4$	8, p. 2606
	$\text{ThF}^{+3} + \text{HF} = \text{ThF}_2^{+2} + \text{H}^+$	650 ± 15	
	$\text{ThF}_2^{+2} + \text{HF} = \text{ThF}_3^+ + \text{H}^+$	32 ± 2	
Cr	$\text{Cr}^{+3} + \text{HF} = \text{CrF}^{+2} + \text{H}^+$	26.0	9, p. 3511
	$\text{CrF}^{+2} + \text{HF} = \text{CrF}_2^+ + \text{H}^+$	2.45	
	$\text{CrF}_2^+ + \text{HF} = \text{CrF}_3 + \text{H}^+$	0.35	
Ga	$\text{Ga}^{+3} + \text{HF} = \text{GaF}^{+2} + \text{H}^+$	$1.2 \pm 0.2 \times 10^2$	9, p. 3512
Mn	$\text{Mn}^{+3} + \text{HF} = \text{MnF}^{+2} + \text{H}^+$	2.7×10^2	10, p. 3932
Si	$\text{SiO}_2 + 4\text{H}^+ + 6\text{F}^- = \text{SiF}_6^{2-} + 2\text{H}_2\text{O}$	5×10^{26}	6, p. 145

TABLE 18 (Cont'd.)

<u>Element</u>	<u>Equilibrium</u>	<u>Formation Constant</u>	<u>Reference</u>
Sn	$\text{Sn}^{+4} + 6\text{F}^- = \text{SnF}_6^{-2}$	1×10^{18}	6, p.150
Tl	$\text{TlO}^{++} + \text{F}^- = \text{TlOF}^+$	3.8×10^6	11
In	$\text{In}^{+3} + \text{HF} = \text{InF}^{+2} + \text{H}^+$ $\text{InF}^{+2} + \text{HF} = \text{InF}_2^+ + \text{H}^+$	6.9 0.5	12, p.28
Sc	$\text{Sc}^{+3} + 6\text{F}^- = \text{ScF}_6^-$	2×10^{17}	6, p.284
Pu	$\text{Pu}^{+4} + \text{F}^- = \text{PuF}^{+3}$	6.2×10^6	6, p.309

ADVANCE BOND

C. H. BROWN & SONS

APPENDIX B

The following polarogram is included to illustrate the Sargent method for determining the half-wave potential and the method for measuring the diffusion current.

ANCE BOND

BROWN

Final
Span -0.90940 V Sens. 0.060 ua/mm

Initial -0.51223 Damping off

% Span — Chart speed L
in per min.

Sample 1 mM Sn²⁺
369 mM NaF
0.6 M NaClO₄

Operator JAM

Date 6/13

90940
-51223
39717

$$E_{\text{Total}} = 4275$$

$$\rightarrow E_{1/2} = 1780$$

$$E_{1/2} = -\frac{1780}{4275}(397.2) - 512.2$$

$$= -165.3 - 512.2$$

$$= -677.5 \text{ mV}$$

$$i_d = 1780 \text{ nA}$$

$$= 11.9 \mu\text{amp}$$

