Title

THE FLUORIDE COMPLEXITY OF Sc(III), Cu(II), Pb(II), Zn(II), Hg(II), Hg2(II), Sn(II), AND Ag(I) IK AQUEOUS SOLUTION

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Armine Deane Paul

April, 1955

(Thesis)

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THE FLUORIDE COMPLEXING OF Sc(III), Cu(II), Pb(II), Zn(II), Hg(II), Hg_2(II), Sn(II), AND Ag(I) IN AQUEOUS SOLUTION

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April, 1955

ABSTRACT

The fluoride complexing of Sc(III), Cu(II), Pb(II), Zn(II), Hg(II), Hg_2(II), Sn(II) and Ag(I) has been studied by EMF methods. The thermodynamic results obtained are as follows: $Sc^{+3} + HF = ScF^{+2} + H^+$, $\Delta F_{298} = -4470 \pm 50$ cal/mole, $\Delta H_{298} = -2580 \pm 1500$ cal/mole, $\Delta S_{298} = 6.3 \pm 5$ e.u.; $ScF^{+2} + HF = ScF_2{}^+$, $\Delta F_{298} = -3220 \pm 20$ cal/mole, $\Delta H_{298} = -4210 \pm 500$ cal/mole, $\Delta S_{298} = -3.3 \pm 2$ e.u.; $ScF_2{}^+ + HF = ScF_{3\,(aq)} + H^+$, $\Delta F_{298} = -1580 \pm 5$ cal/mole, $\Delta H_{298} = -4240 \pm 300$ cal/mole, $\Delta S_{298} = -8.9 \pm 1$ e.u.; $ScF_{3\,(aq)} + HF = ScF_4{}^- + H^+$, $\Delta F_{298} = 820 \pm 330$ cal/mole; $Cu^{++} + HF = CuF^+ + H^+$, $\Delta F_{298} = +3000 \pm 100$ cal/mole, $\Delta H_{298} = -2600 \pm 2700$ cal/mole, $\Delta S_{298} = -19 \pm 9$ e.u.; $Pb^{++} + HF = PbF^+ + H^+$, $\Delta F > 3700$ cal/mole; $Zn^{++} + HF = ZnF^+ + H^+$, $\Delta F_{298} = 2900 \pm 100$ cal/mole, $\Delta H_{298} = -2300 \pm 2400$ cal/mole, $\Delta S_{298} = -17 \pm 9$ e.u.; $Hg^{++} + HF = HgF^+ + H^+$, $\Delta F_{298} = +2560 \pm 50$ cal/mole, $\Delta H_{298} = -2100 \pm 1000$ cal/mole, $\Delta S_{298} = -15 \pm 4$ e.u.; $Hg_2{}^{++} + HF = Hg_2F^+ + H^+$, $\Delta F > 4000$ cal/mole; $Ag^+ + F^- = AgF_{(aq)}$, $\Delta F_{298} = 250 \pm 50$ cal/mole, $\Delta H_{298} = -2400 \pm 1000$ cal/mole, $\Delta S_{298} = -9 \pm 4$ e.u.; $Sn^{++} + HF = SnF^+ + H^+$, $\Delta F \cong -1420$ cal/mole. All values are at $\mu = 0.5$ except that for Sn^{++}, which is at $\mu = 2.0$. ΔF for Sn^{++} is only approximate, since there was difficulty in interpreting the data at high Sn^{++} concentration.

ABSTRACT

(-2-)

The fluoride complexing data can be interpreted by assuming that the bonding is primarily ionic. Good correlations can be obtained by plotting log K at $\mu = 0$ versus hydration energy, Z/d, or Z^2/r, where Z is the charge on the cation, r the ionic radius, and d the interatomic distance. No correlation is obtained with ionization potential or electronegativity. Sn(II) and Sc(III) deviate markedly from the ionic correlations. The greater stability of the Sc(III) complexes is due to a discrepancy in the heat of complexing and not in the entropy of complexing.

The correction of entropies to zero ionic strength was estimated using heat of dilution and activity coefficient data. The approximations involved in the estimation are discussed. Entropies for a variety of fluoride complexing reactions are tabulated and discussed in terms of the replacement effect and charge effect.

I. INTRODUCTION

Within the past decade a considerable amount of data has been accumulating in the literature on the stability of various complex ions. In recent years attempts have been made to correlate the stability of the complex with some property or properties of the ions involved.

The bonding in the majority of complex ions is probably a mixture of covalent, and ionic or electrostatic forces. However, it would appear that of all the possible complexing anions, the fluoride ion would tend to form the most ionic complexes, since the fluoride ion has such a low polarizability. If the fluoride complexes are assumed to be purely ionic, the theory and interpretation of the complexing becomes comparatively simple.

This work was undertaken in order to provide additional quantitative information on the stability of complex metallic fluorides and to see how these new data agreed with the ionic interpretation. The work on scandium, silver, and tin constituted a check on other data in the literature which seemed questionable. The results on copper, zinc, lead, and mercury were previously unavailable in the literature. Previously unavailable data on the heats and entropies for the fluoride complexing of all the above ions except lead and tin were also obtained.

II. EXPERIMENTAL STUDY OF FLUORIDE COMPLEXING USING THE "FERRI" METHOD

The complexing was studied potentiometrically by measuring the effect on the ferric fluoride equilibria using the ferrous-ferric electrode according to the method first described by Brosset and Orring[1] and later successfully used by Dodgen and Rollefson,[2] Connick and Tsao,[3] and Hepler, Kury, and Hugus.[4] In the presence of another cation which can also form fluoride complexes, the equilibrium of the ferric fluoride complexes will be shifted so that more ferric ion will exist in the free state. The potential of a ferrous-ferric concentration cell, one side of which contains fluoride ion, will thus be larger than the potential of a similar ferrous-ferric concentration cell, one side of which contains, in addition to fluoride ion, a cation whose complexing is to be studied. This difference in potential is a measure of the complexing of the foreign ion by fluoride ion. Since the equilibrium quotients for the formation of the ferric fluoride complexes are well known,[5] it is possible to calculate quantitatively the equilibrium quotients for the fluoride complexes of any metallic ion which may be studied.

A. Fluoride Complexing of Sc(III) at 15°, 25°* and 35°C.

This investigation was undertaken because of some unpublished work of Dodgen,[6] who found the scandium fluoride complexes to be more stable than those of other trivalent ions of similar radius. According to Pauling[7] In(III) has the same ionic radius (0.81A) as Sc(III). However, the first fluoride complex of Sc(III) is about 260 times more stable than the first fluoride complex of In(III).[4] In addition to checking the work of Dodgen, we wished to determine whether the greater stability of the scandium fluoride complexes was due to a discrepancy in the heat of complexing or in the entropy of complexing.

(*) Experiments at 25°C were performed by John W. Kury and Loren G. Hepler.

Experimental. The cells were essentially the same as those used by Dodgen and Rollefson.[2] The containers and caps with openings for stirrer, salt bridges, electrodes, and CO_2 inlet tube, were made from 5 cm ground glass joints. The insides of the containers as well as the stirrers were coated with paraffin to prevent hydrofluoric acid from attacking the glass. The ground glass joints were sealed with "Lubriseal" to prevent thermostat water from entering the cell.

Platinum electrodes of about 2 cm x 2 cm in area were used. They were stored in distilled water when not in use.

The half cells were designated as A, B, and C. Cell B-C was the reference cell and cell A-C was the cell in which the complexing of the foreign cation was studied. One-hundred-ml aliquots of stock solution containing the desired concentrations of ferrous perchlorate, ferric perchlorate, perchloric acid and sodium perchlorate were pipetted into each of the three half cells. A known volume of standard scandium perchlorate-perchloric acid solution was added to half cell A. An equal volume of sodium perchlorate-perchloric acid solution, equivalent to the scandium solution in total ionic strength and acid concentration, was added to half cells B and C. All measurements were made at an ionic strength of 0.50.

Half cells A and C, and half cells B and C were joined by 1.6M sodium perchlorate-agar-agar salt bridges in an effort to minimize the junction potentials.[2] An atmosphere of carbon dioxide or nitrogen was maintained over the solutions to prevent air oxidation of ferrous ion.

The potential of the cell was measured with a Rubicon type B, high-precision potentiometer with a DC spotlight galvanometer (sensitivity

0.009 μa/mm, period 3.2 sec. and critical damping resistance 830 ohms) for indication of the null point. The potentiometer was checked against a standard cell from time to time during an experiment.

After the small initial potential (usually less than 0.2 mv) became constant, aliquots of standard sodium fluoride solution were added to half cells A and B from calibrated "drifilmed"* micropipets and the potential measured after each addition. The potential usually attained a constant value very shortly after each addition. The additions of sodium fluoride were continued until a potential of about 150 mv was reached or until the ScF_3 precipitated. Precipitation caused the potential to drift downward rapidly. The stirrers were left on while the additions were made and while the readings were taken.

Data and Calculations. The initial conditions for each experiment are summarized in Table 1. At each temperature the acidity was varied two fold and the scandium concentration was varied at least two fold. Complete EMF data for all experiments are given in Tables 1-A through 8-A of the Appendix.

Table 1

Initial Experimental Conditions for Scandium Experiments

Expt.	Temp. °C	$Sc(ClO_4)_3$ moles/liter	$HClO_4$ moles/liter	$Fe(ClO_4)_2$ moles/liter	$Fe(ClO_4)_3$ moles/liter	$NaClO_4$ moles/liter
1	25	0.01273	0.1122	0.0003553	0.0003402	0.3087
2	25	0.001387	0.05287	0.0003869	0.0003705	0.4355
3	25	0.002741	0.05457	0.0003831	0.0003669	0.4257
1	35	0.001387	0.05277	0.0003868	0.0003704	0.4350
2	35	0.002741	0.05493	0.0003831	0.0003668	0.4252
3	35	0.006665	0.1065	0.0003721	0.0003563	0.3502
1	15	0.01387	0.05277	0.0003868	0.0003704	0.4350
3	15	0.006665	0.1065	0.0003721	0.0003563	0.3502

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*Drifilm is the trade name for dichloro dimethyl silane, a compound which prevents water from wetting glass.

The equilibria which must be considered are as follows:

$$Sc^{+3} + HF = ScF^{+2} + H^{+}, \qquad C_1 \qquad (1)$$

$$ScF^{+2} + HF = ScF_2^{+} + H^{+}, \qquad C_2 \qquad (2)$$

$$ScF_2^{+} + HF = ScF_{3\,(aq)} + H^{+}, \qquad C_3 \qquad (3)$$

$$ScF_{3\,(aq)} + HF = ScF_4^{-} + H^{+}, \qquad C_4 \qquad (4)$$

$$Fe^{+3} + HF = FeF^{+2} + H^{+}, \qquad C_5 \qquad (5)$$

$$FeF^{+2} + HF = FeF_2^{+} + H^{+}, \qquad C_6 \qquad (6)$$

$$FeF_2^{+} + HF = FeF_{3\,(aq)} + H^{+}, \qquad C_7 \qquad (7)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^{+}, \qquad C_h \qquad (8)$$

$$HF = H^{+} + F^{-}. \qquad C_{HF} \qquad (9)$$

The C's are equilibrium quotients expressed in concentrations, for example

$$C_1 = \frac{(ScF^{+2})(H^{+})}{(Sc^{+3})(HF)} ,$$

where the quantities in parenthesis represent the concentrations of the enclosed species in moles per liter. The values at $\mu = 0.5$ of C_5, C_6, C_7, and C_h used in these calculations are given in reference 4. The values of C_{HF} at $\mu = 0.5$ at 15°, 25°, and 35° are 0.00142, 0.00123, and 0.00101, respectively.[8]

The potential readings of the unknown cell (cell A-C) and the reference cell (cell B-C) were plotted versus the total fluoride ion concentration. The difference between the total fluoride ion concentration in cell A-C and that necessary to give the same potential in cell B-C was obtained from the curves. This difference $\Delta(\Sigma F^{-})$ is defined as

$$\Delta(\Sigma F^{-}) = (\Sigma F^{-})_{E_{A-C}} - (\Sigma F^{-})_{E_{B-C}} . \qquad (10)$$

The symbol Σ represents the total concentration of all forms of a given species. Because half-cells A and B have the same initial ΣFe^{+3}, ΣFe^{+2}, and ΣH^{+}, $\Delta(\Sigma F^{-})$ is a measure of the concentration of fluoride ion complexing Sc^{+3}.*

Let us represent the average number of fluoride ions held by each scandium ion by the symbol $\bar{n}$, which is defined as

$$\bar{n} = \frac{\Delta(\Sigma F^{-})}{\Sigma Sc^{+3}} . \tag{11}$$

From stoichiometry it can be seen that

$$\Delta(\Sigma F^{-}) = (ScF^{+2}) + 2(ScF_2^{+}) + 3(ScF_3)_{aq} + 4(ScF_4^{-}), \tag{12}$$

$$\Sigma Sc^{+3} = (Sc^{+3}) + (ScF^{+2}) + (ScF_2^{+}) + (ScF_3)_{aq} + (ScF_4^{-}). \tag{13}$$

Kilpatrick and Pocras[9] have found the hydrolysis constant of Sc^{+3} to be 1.17×10^{-5}. Therefore at the acidities at which these experiments were performed, the hydrolysis of Sc^{+3} was negligible.

Combining equations (12) and (13) with (1), (2), (3), and (4) yields the following expression for $\bar{n}$:

$$\bar{n} = \frac{C_1 \frac{(HF)}{(H^+)} + 2C_1C_2 \frac{(HF)^2}{(H^+)^2} + 3C_1C_2C_3 \frac{(HF)^3}{(H^+)^3} + 4C_1C_2C_3C_4 \frac{(HF)^4}{(H^+)^4}}{1 + C_1 \frac{(HF)}{(H^+)} + C_1C_2 \frac{(HF)^2}{(H^+)^2} + C_1C_2C_3 \frac{(HF)^3}{(H^+)^3} + C_1C_2C_3C_4 \frac{(HF)^4}{(H^+)^4}} . \tag{14}$$

In order to obtain values of C_1, C_2, C_3, and C_4 from equation (14) it is necessary to know the value of $\frac{(HF)}{(H^+)_A}$ for each value of $\bar{n}$, that is, as a function of E_{A-C}. Since the initial ferrous, ferric, and hydrogen ion concentrations are the same in cell A as in cell B, the quantity $\frac{(HF)}{(H^+)_A} = \frac{(HF)}{(H^+)_B}$ when $E_{A-C} = E_{B-C}$. The $\frac{(HF)}{(H^+)}$ ratio is calculated in the following manner.

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* Correction for the small volume difference between the sample and reference solutions is negligible.

From stoichiometry one obtains:

$$\Sigma(F^-)_B = (HF)_B + (F^-)_B + (FeF^{+2})_B + 2(FeF_2^{\ +})_B + 3(FeF_3)_B, \tag{15}$$

$$\Sigma(Fe^{+3})_B = (Fe^{+3})_B + (FeOH^{+2})_B + (FeF^{+2})_B + (FeF_2^{\ +})_B + (FeF_3)_B, \tag{16}$$

$$\Sigma(Fe^{+3})_C = (Fe^{+3})_C + (FeOH^{+2})_C. \tag{17}$$

Combining equations (8) and (17) gives

$$(Fe^{+3})_C = \frac{\Sigma(Fe^{+3})_C}{1 + \dfrac{C_h}{(H^+)_C}}. \tag{18}$$

The potential of the concentration cell B-C is given by

$$E = \frac{-RT}{F} \ln \frac{(Fe^{+3})_B\ (Fe^{+2})_C}{(Fe^{+2})_B\ (Fe^{+3})_C}. \tag{19}$$

If we let V_o be the initial volume in half cells B and C and let V equal the volume in half cell B after the addition of the sodium fluoride solution, we obtain from equation (19)

$$(Fe^{+3})_B = (Fe^{+3})_C\ \frac{V_o}{V}\ e^{-FE/RT}\ ; \tag{20}$$

also,

$$\Sigma(Fe^{+3})_B = \frac{V_o}{V}\ (\Sigma Fe^{+3})_C. \tag{21}$$

Combining equations (18), (20), and (21), we obtain

$$\frac{\Sigma(Fe^{+3})_B}{(Fe^{+3})_B} - 1 - \frac{C_h}{(H^+)_C} = \left(1 + \frac{C_h}{(H^+)_C}\right)\left(e^{FE/RT} - 1\right). \tag{22}$$

Combining equations (5), (6), and (7) with (16) gives

$$\frac{\Sigma(\mathrm{Fe}^{+3})_B}{(\mathrm{Fe}^{+3})_B} - 1 - \frac{C_h}{(\mathrm{H}^+)_B} = C_5 \frac{(\mathrm{HF})}{(\mathrm{H}^+)_B} + C_5C_6 \frac{(\mathrm{HF})^2}{(\mathrm{H}^+)^2_B} + C_5C_6C_7 \frac{(\mathrm{HF})^3}{(\mathrm{H}^+)^3_B}. \qquad (23)$$

Assuming that $1 + \frac{C_h}{(\mathrm{H}^+)_B} = 1 + \frac{C_h}{(\mathrm{H}^+)_C}$ we can combine equations (22) and (23) to obtain the following equation, which is used to calculate $(\mathrm{HF}/\mathrm{H}^+)$:

$$\left(1 + \frac{C_h}{(\mathrm{H}^+)_B}\right)\left(e^{FE/RT} - 1\right) = C_5 \frac{(\mathrm{HF})}{(\mathrm{H}^+)} + C_5C_6 \frac{(\mathrm{HF})^2}{(\mathrm{H}^+)^2} + C_5C_6C_7 \frac{(\mathrm{HF})^3}{(\mathrm{H}^+)^3}. \qquad (24)$$

In this derivation there are the additional assumptions that hydrolysis of ferrous ion is negligible, that there is no fluoride complexing of ferrous ion,[2] and that there is no change in the activity coefficients when scandium perchlorate is replaced by sodium perchlorate. The species (HF_2^-) was negligible in all calculations.

In order to solve equation (24) for $(\mathrm{HF}/\mathrm{H}^+)$, it is necessary to use the method of successive approximations. Using the initial hydrogen ion concentration for $(\mathrm{H}^+)_B$, and neglecting the term involving $(\mathrm{HF}/\mathrm{H}^+)^3$, equation (24) was solved for an approximate value of $(\mathrm{HF}/\mathrm{H}^+)$ using the quadratic formula. For low potential readings, this gave the correct value of $(\mathrm{HF}/\mathrm{H}^+)$. For high E readings, it was necessary to consider the term involving $(\mathrm{HF}/\mathrm{H}^+)^3$ and to use a value for $(\mathrm{H}^+)_B$ which had been corrected for the amount of $(\mathrm{HF}/\mathrm{H}^+)$ formed. This was done by successive approximations.

Knowing $\bar{n}$ and $(\mathrm{HF}/\mathrm{H}^+)$ it is possible to calculate C_1, C_2, C_3, and C_4 from equation (14). This was done by plotting $\bar{n}$ versus log $(\mathrm{HF}/\mathrm{H}^+)$ and determining the C's by a process of curve fitting. The procedure followed was to fit first the lower part of the curve using only C_1, C_2, and C_3, neglecting the terms in equation (14) involving $(\mathrm{HF}/\mathrm{H}^+)^4$. Approximate values for C_1, C_2, and C_3 were obtained by choosing three points from the lower part of the curve and solving for C_1, C_2, and C_3 from the three simultaneous equations obtained by substituting the numerical values of the three selected points into equation (14). These values of C_1, C_2, and C_3 were substituted back into equation (14) and values of $\bar{n}$ at intervals of 0.5 log (HF/H^+) calculated. Usually it was necessary to adjust slightly the values of C_1, C_2, and C_3 to get a better fit. It was found that no matter how C_1, C_2, and C_3 were adjusted, the extreme upper portion of the calculated curve always fell below the experimental curve. In order to fit this portion of the curve it was necessary to consider C_4. The value of C_4 was obtained simply by trial and error.

Values for (HF/H^+) and $\bar{n}$ are listed with the experimental data in Tables 1-A through 8-A of the Appendix. Plots of $\bar{n}$ versus log (HF/H^+) for the experiments at 15°, 25°, and 35° are shown in the Appendix in Figures 1-A, 2-A, and 3-A, respectively. The solid line represents the curve calculated using the C's listed in Table 2. It can be seen that all the experimental points fall very close to the theoretical curves.

<u>Results</u>. The values obtained in this investigation for C_1, C_2, C_3, and C_4 at 15°, 25°, and 35° at $\mu = 0.50$ are summarized in Table 2. The values which Dodgen[6] gives for C_1, C_2, C_3, and C_4 at 25°C are 1750, 242, 12.7, and 0.88 respectively.

Table 2

Summary of Equilibrium Quotients

Temp °C	C_1	C_2	C_3	C_4
15°	2180 ± 170	292 ± 8	18.4 ± 0.2	0.3 ± 0.2
25°	1880 ± 150	228 ± 7	14.4 ± 0.1	0.4 ± 0.3
35°	1630 ± 130	181 ± 5	11.4 ± 0.1	0.1 ± 0.07

In Table 3 are presented the equilibrium quotients at 25° at $\mu = 0.5$ and $\mu = 0$ for Reactions 1, 2, 3, and 4 written in terms of fluoride ion rather than HF. The values of C' were obtained by dividing the C's of Table 2 by the ionization constant of HF. The true equilibrium constants K at $\mu = 0$ were estimated by making suitable assumptions of the activity coefficients. This was done using the empirical relations given by Rabinowitch and Stockmayer,[10] and Nasanen.[11]

Table 3

Equilibrium Quotients for Reactions Written in terms of Fluoride Ion

Reaction (25°C)	C' ($\mu = 0.5$)	K ($\mu = 0$)
$Sc^{+3} + F^- = ScF^{+2}$	1.53×10^6	1.4×10^7 1.2×10^7
$ScF^{+2} + F^- = ScF_2^+$	1.86×10^5	6.3×10^5
$ScF_2^+ + F^- = ScF_{3\,(aq)}$	1.17×10^4	2.8×10^4
$ScF_{3\,(aq)} + F^- = ScF_4^-$	3×10^3	3×10^3

Table 4 summarizes the free energy, heat, and entropy changes at $\mu = 0.50$ for the complexing reactions written in terms of both (HF/H^+) and (F^-).

Table 4

Summary of Thermodynamic Functions of Scandium Fluorides

Reaction (μ=0.5)	ΔF_{298} cal/mole	ΔH_{298} cal/mole	ΔS_{298} e.u.
$Sc^{+3} + HF = ScF^{+2} + H^+$	-4470 ± 50	-2580 ± 1500	6.3 ± 5
$ScF^{+2} + HF = ScF_2^+ + H^+$	-3220 ± 20	-4210 ± 500	-3.3 ± 2
$ScF_2^+ + HF = ScF_{3\,(aq)} + H^+$	-1580 ± 5	-4240 ± 300	-8.9 ± 1
$Sc^{+3} + F^- = ScF^{+2}$	-8430 ± 50	$+400 \pm 1500$	29.4 ± 5
$ScF^{+2} + F^- = ScF_2^+$	-7190 ± 20	-1230 ± 500	19.9 ± 2
$ScF_2^+ + F^- = ScF_{3\,(aq)}$	-5550 ± 5	-1260 ± 300	14.3 ± 1

The uncertainties were calculated by refitting the $\bar{n}$ versus log (HF/H^+) curve assuming an error of 0.1 millivolt in the measured EMF's. The fact that the thermodynamic functions for reaction 1 are more uncertain than those of reactions 2 and 3 arises from the fact that C_1 is determined almost entirely by the first two or three points on the $\bar{n}$ versus log (HF/H^+) curve. These initial points have a high uncertainty because the scandium fluoride complexes are so stable that the first few additions of NaF produce relatively small EMF changes.

It is felt that C_4 represents only an order of magnitude rather than any exact value. This is because it is difficult to obtain good potential readings at high fluoride concentrations due to the tendency of ScF_3 to precipitate. Also the sensitivity of the curve fitting is very low in this region. For example, C_4 at 25° can be varied from 0.2 to 0.6 without significantly changing the curve. With C_1, C_2, and C_3, however, a change of only 2 or 3% will alter the lower portion of the curve appreciably.

B. Fluoride Complexing of Zn(II) at 15°, 25°, and 35°C.

Experimental. The apparatus and procedure were the same as described for the scandium experiments.

Data and Calculations. The initial conditions for each experiment are summarized in Table 5. At each temperature the acidity and the zinc concentration were each varied about four fold.

Table 5

Initial Experimental Conditions for Zinc Experiments

Expt.	Temp. °C	$Zn(ClO_4)_2$ moles/liter	$HClO_4$ moles/liter	$Fe(ClO_4)_2$ moles/liter	$Fe(ClO_4)_3$ moles/liter	$NaClO_4$ moles/liter
4	15	0.08676	0.005338	0.0002221	0.0006838	0.2290
5	15	0.02779	0.005699	0.0002371	0.0007299	0.4058
6	15	0.02779	0.02164	0.0002371	0.0007299	0.3899
5	25	0.08676	0.005338	0.0002221	0.0006838	0.2296
6	25	0.02779	0.005699	0.0002371	0.0007299	0.4058
7	25	0.02779	0.02164	0.0002371	0.0007299	0.3899
4	35	0.08676	0.005338	0.0002221	0.0006838	0.2296
5	35	0.02779	0.005699	0.0002371	0.0007299	0.4058
6	35	0.02779	0.02164	0.0002371	0.0007299	0.3899

The only equilibrium which must be considered is as follows:

$$Zn^{++} + HF = ZnF^{+} + H^{+} \qquad C_8 \qquad (25)$$

The equilibrium quotient for this reaction may be rewritten in the following manner:

$$\frac{1}{1 - \frac{(ZnF^{+})}{\Sigma Zn^{++}}} = 1 + C_8 \frac{(HF)}{(H^{+})} \qquad (26)$$

If the quantity on the left of equation (26) is plotted against (HF/H^{+}), a straight line is obtained whose intercept is unity and whose slope is C_8. All the data can be fit by assuming only one fluoride complex is formed.

It is obvious that the quantity $(ZnF^{+})/(\Sigma Zn^{++})$ is identical with the quantity $\bar{n}$ as defined by equation (11). The quantities $\bar{n}$ and (HF/H^{+}) were therefore calculated exactly as described for the scandium experiments.

Complete EMF data and calculated values of $\bar{n}$ and (HF/H^{+}) for each experiment are given in Tables 9-A through 17-A of the Appendix. Plots of $1/(1-\bar{n})$ versus (HF/H^{+}) for the experiments at 15°, 25°, and 35° are shown in the Appendix in Figures 4-A, 5-A, and 6-A, respectively.

Results. In Table 6 are summarized the values at 15°, 25°, and 35° of C_8 as defined by equation (25) and values of C_8', which is the equilibrium quotient for the reaction written in terms of (F^-) rather than (HF) and (H^+). An estimate at 25°C of the true equilibrium constant K at $\mu = 0$ is also given. In Table 7 are summarized the free energy, heat, and entropy changes for the reaction written in terms of both $(HF)/(H^+)$ and (F^-) at $\mu = 0.50$.

Table 6

Equilibrium Quotients for Zinc Fluoride Complex

	15°C	25°C	35°C
C_8 ($\mu = 0.5$)	$7.0 \pm 1 \times 10^{-3}$	$6.6 \pm 1 \times 10^{-3}$	$5.4 \pm 1 \times 10^{-3}$
C_8' ($\mu = 0.5$)	5.0 ± 1	5.4 ± 1	5.4 ± 1
K_8 ($\mu = 0$)		18 ± 4	

Table 7

Thermodynamic Functions of Zinc Fluoride Complex

Reaction (μ=0.5)	ΔF_{298} cal/mole	ΔH_{298} cal/mole	ΔS_{298} e.u.
$Zn^{++} + HF = ZnF^+ + H^+$	2900 ± 100	-2300 ± 2400	-17 ± 9
$Zn^{++} + F^- = ZnF^+$	-1000 ± 100	1500 ± 2400	8 ± 9

Considerable difficulty was encountered in these experiments because of impurities in the reagents. The experiments at 25° were run using zinc perchlorate prepared from three different sources of ZnO.

The values listed in Tables 6 and 7 as well as those in the Appendix were obtained using Mallinckrodt ZnO. Experiments using Merck ZnO and Baker ZnO gave values of C_8 at 25° of 5.7×10^{-3} and 1.2×10^{-2}, respectively, compared with the Mallinckrodt value of 6.6×10^{-3}. Since the uncertainty in the C's is about 1×10^{-3}, the agreement between the Merck and Mallinckrodt solutions was within the experimental error and constituted a satisfactory check on the reliability of the data. Although the Merck solution gave a slightly lower C_8, the zero readings using it were quite high, and therefore the Mallinckrodt solution was used for the experiments at 15° and 35°. The Baker solution was also run at 15° and 35°, but the results were so impossible ($\Delta S \cong - 40$ eu) that they were immediately discarded. The Baker solution was later shown by spectrochemical analyses to contain 0.2% - 0.3% of lead and titanium.

The experimental uncertainties are high because less than 1% of the total zinc was complexed. The quantity (ZnF^+) is extremely small and must be obtained from the difference of large quantities. Also, in order to get the maximum effect it is necessary to work at low acidities where the error in (HF/H^+) is larger than at high acidity. The uncertainty of 1×10^{-3} in C_8 was estimated by assuming an error of 0.1 millivolt in the measured EMF's in addition to considering the scattering of points in three experiments at a given temperature.

Since the effect is so small, it might be argued that it is being caused by specific-activity effects. Olson and Simonson[12] have shown that replacement of $Fe(ClO_4)_3$ by $NaClO_4$ to maintain constant ionic strength was responsible for a shift in the equilibrium $Fe^{+3} + H_2O = FeOH^{++} + H^+$. However, Tsao[8] has concluded from experiments on the fluoride complexing of Cr(III), similar to those carried out in this investigation, that the maximum effect due to such specific activity effects was 0.1 millivolt, which is the same order of magnitude as the experimental error. Also the fact that Ca(II),[3] Ba(II),[3] and Pb(II) have all been studied by this method and gave no measurable effect, seems to indicate that the effect, although small, is real.

C. Fluoride Complexing of Cu(II) at 15°, 25°, and 35°C.

Experimental. The apparatus and procedure were the same as described for the scandium experiments.

Data and calculations. The initial conditions for each experiment are summarized in Table 8. At each temperature the copper concentration was varied two fold or more and the acidity approximately two fold or more.

Table 8

Initial Experimental Conditions for Copper Experiments

Expt.	Temp. °C	$Cu(ClO_4)_2$ moles/liter	$HClO_4$ moles/liter	$Fe(ClO_4)_2$ moles/liter	$Fe(ClO_4)_3$ moles/liter	$NaClO_4$ moles/liter
3	15	0.08667	0.02285	0.0002221	0.0006338	0.2127
4	15	0.04543	0.01283	0.0002326	0.0007161	0.3396
5	15	0.04543	0.02260	0.0002326	0.0007161	0.3361
1	25	0.01874	0.009988	0.0003734	0.0003765	0.4305
2	25	0.04558	0.01263	0.0003628	0.0003658	0.3473
4	25	0.08703	0.02324	0.0003463	0.0003492	0.2126
4	35	0.08667	0.02285	0.0002221	0.0006338	0.2127
5	35	0.04543	0.01283	0.0002321	0.0007161	0.3396
6	35	0.04543	0.02260	0.0002326	0.0007161	0.3361

The only equilibrium which must be considered is as follows:

$$Cu^{++} + HF = CuF^{+} + H^{+}. \qquad C_9 \qquad (27)$$

As was the case for zinc, the equilibrium quotient for this reaction may be rewritten in the following manner:

$$\frac{1}{1-\frac{CuF^{+}}{\Sigma Cu^{++}}} = \frac{1}{1-\bar{n}} = 1 + C_9\,(HF)/(H^{+}). \tag{28}$$

The quantity on the left of equation (28) was plotted versus $(HF)/(H^+)$ to give a straight line whose slope was equal to C_9. The quantities $\bar{n}$ and $(HF)/(H^+)$ were calculated as described for the zinc and scandium experiments.

Complete EMF data and calculated values of $\bar{n}$ and $(HF)/(H^+)$ for each experiment are given in Tables 18-A through 26-A of the Appendix. Plots of $1/(1-\bar{n})$ versus $(HF)/(H^+)$ for the experiments at 15°, 25°, and 35° are shown in the Appendix in Figures 7-A, 8-A, and 9-A, respectively.

Results. In Table 9 are summarized the values at 15°, 25°, and 35° of C_9 as defined by equation (27) and values of C_9' which is the equilibrium quotient for the reaction written in terms of (F^-) rather than (HF) and (H^+). An estimate at 25° of the true equilibrium constant K at $\mu = 0$ is also given. In Table 10 are summarized the free energy, heat, and entropy changes for the reaction written in terms of both $(HF)/(H^+)$ and (F^-) at $\mu = 0.50$.

Table 9

Equilibrium Quotients for Cupric Fluoride Complex

	15°C	25°C	35°C
C_9 ($\mu = 0.5$)	$7.4 \pm 1 \times 10^{-3}$	$6.2 \pm 1 \times 10^{-3}$	$5.6 \pm 1 \times 10^{-3}$
C_9' ($\mu = 0.5$)	5.2 ± 1	5.0 ± 1	5.6 ± 1
K_9 ($\mu = 0$)		17 ± 4	

Table 10

Thermodynamic Functions of Cupric Fluoride Complex

Reaction (μ=0.5)	ΔF_{298} cal/mole	ΔH_{298} cal/mole	ΔS_{298} e.u.
$Cu^{++} + HF = CuF^{+} + H^{+}$	+3000 ± 100	-2600 ± 2700	-19 ± 9
$Cu^{++} + F^{-} = CuF^{+}$	-950 ± 100	900 ± 2700	6 ± 9

Difficulty was again encountered, as in the zinc experiments, because of impurities in the reagents. The experiments at 25° were performed using cupric perchlorate prepared from three different sources of CuO. The values listed in Tables 9 and 10 as well as those in the Appendix were obtained using Mallinckrodt CuO. Experiments using Baker CuO and Baker and Adamson CuO gave values of C_9 at 25° of 6×10^{-2} and 7.4×10^{-3}, respectively, compared with the Mallinckrodt value of 6.2×10^{-3}. Since the uncertainty in the C's is about 1×10^{-3}, the agreement between the Mallinckrodt and Baker and Adamson solutions was within the experimental error and constituted a satisfactory check on the reliability of the data. The Baker solution was later shown by spectrochemical analysis to contain 0.2% of iron.

Since less than 1% of the total copper was complexed, the experimental uncertainty is high, as was the case with the zinc. The "ferri" method cannot be used with any degree of accuracy to get equilibrium quotients much below 10^{-2}. In order to get better values for the complexing of copper and zinc, it would be necessary to use a different experimental method.

D. Fluoride Complexing of Pb(II) at 25°C

Experimental. The apparatus and procedure were the same as those described for the scandium experiments.

Data and Calculations. The initial conditions for the two experiments are summarized in Table 11. Complete EMF data are found in Tables 27-A and 28-A of the Appendix.

Table 11

Initial Experimental Conditions for Lead Experiments

Expt.	Temp. °C	$Pb(ClO_4)_2$ moles/liter	$HClO_4$ moles/liter	$Fe(ClO_4)_2$ moles/liter	$Fe(ClO_4)_3$ moles/liter	$NaClO_4$ moles/liter
1	25	0.04562	0.01089	0.0003628	0.0003658	0.3490
2	25	0.01876	0.003471	0.0003734	0.0003765	0.4366

The equilibrium which must be considered is as follows:

$$Pb^{++} + HF = PbF^{+} + H^{+} \qquad C_{10} . \qquad (29)$$

Calculations were carried out in the same manner as described for the zinc experiments.

Results. It can be seen from Table 27-A and 28-A that in Experiment 1 the potentials of cells A-C and B-C were essentially the same up to a total EMF of 143 mv and a total fluoride ion concentration of 0.00322M. In Experiment 2, where the acidity was decreased by a factor of 3, the potentials of the two cells were still the same up to a potential of 122 mv, and it was only when the fluoride ion concentration was increased to 0.0037M that a significant difference of 0.25 mv was obtained at a total potential reading of 182 mv. The fluoride concentration could not be increased further because of the precipitation of PbF_2.

If one assumes that the maximum voltage difference between the two cells is 0.5 mv, then at $\mu = 0.50$, an upper limit of 2×10^{-3} is obtained for C_{10} as defined by equation (29). For the reaction written in terms of (F^-), an upper limit of 2 is obtained for C'_{10}. The true equilibrium constant K_{10} at $\mu = 0$ is estimated to be less than 6.

III. FLUORIDE COMPLEXING OF Hg_2(II) AND Hg(II) AT 15°, 25°, AND 35°

The complexing of Hg_2(II) was studied using a Hg-Hg_2^{++} concentration cell. The complexing of Hg(II) was measured using a cell, one half of which contained a Hg-Hg_2^{++} couple and the other half a Hg_2^{++}-Hg^{++} couple. Since the Hg_2^{++} concentration was the same in each half, the EMF was determined by the Hg^{++} concentration, and therefore by measuring the EMF of the cell as a function of the Hg^{++} and HF concentrations, the stability of the complex could be determined.

Experimental. Three half cells were used which will be designated A, B, and C. Half cells A-B and B-C were connected by means of sodium perchlorate-agar agar salt bridges. Cell B-C was the Hg-Hg_2^{++} concentration cell used to study the complexing of Hg_2^{++} and cell A-B was the cell used to study the complexing of Hg^{++}. Half cells B and C initially contained a mercury electrode and solutions of mercurous perchlorate, sodium perchlorate, and perchloric acid. Half cell A initially contained a platinum electrode and solutions of mercurous perchlorate, mercuric perchlorate, sodium perchlorate, and perchloric acid.

The cells, measuring apparatus, and platinum electrodes were the same as described for the scandium experiments. The mercury electrodes were J - shaped pieces of glass tubing, the short arm consisting of a small cup with a sealed-in platinum wire connecting to a short column of mercury for electrical contact in the long arm. The cup-like portion was filled with triple-distilled mercury.

One-hundred-and-twenty-five-ml aliquots of stock solution containing the desired concentrations of mercurous perchlorate, sodium perchlorate, and perchloric acid were pipetted into each of the three half cells.

A known volume of standard mercuric perchlorate-perchloric acid solution was added to half cell A. An equal volume of sodium perchlorate-perchloric acid solution, equivalent to the mercuric perchlorate solution in acidity and total ionic strength, was added to half cells B and C. All measurements were made at an ionic strength of 0.50. The solutions were continuously stirred and an atmosphere of nitrogen was maintained over each to prevent oxidation of the mercurous ion.

Although reproducible and reversible, the response of the Hg_2^{++}-Hg^{++} couple was not so rapid as could be desired. Cell A-B usually required from one to two hours to reach initial equilibrium, whereas cell B-C required a half hour at most. Likewise, cell A-B required ten minutes to reach equilibrium after each fluoride addition, while the response of cell B-C was practically instantaneous.

Two sets of experiments were performed. In the first set, known quantities of sodium fluoride were added to half cells A and B, and the same quantity of sodium perchlorate added to half cell C. The difference in potential from the initial zero reading was then measured. These experiments provoked several criticisms. First of all, the acidity was considerably lowered after each addition of sodium fluoride owing to the formation of HF in the solution. The final free acid concentration at the end of an experiment was about ten times less than the total initial acidity. This could have been taken into account in the calculations at 25°, but not at 15° or 35°, since the hydrolysis constant of Hg^{++} is known at 25°, but not at 15° or 35°. Secondly, because the acidity was constantly changing, the ionic strength was no longer constant. Thirdly, the zero readings of the four experiments did not agree.

Therefore, a second set of experiments was performed in which both perchloric acid (about 1M) and sodium fluoride were added to half cells A and B and nothing added to half cell C. The quantity of perchloric acid added was such as to compensate exactly for the amount of acid used in forming the HF. The acidity was thus kept constant within 10% and therefore no correction was made for changes in hydrolysis throughout the course of an experiment. The ionic strength was also much more constant than in the first set of experiments. The data and results of all mercury experiments reported in this paper were obtained using this second technique. In these experiments, greater care was taken to reach the true initial equilibrium. This usually necessitated waiting considerably longer for cell A-B to reach equilibrium than was done in the first set of experiments, but as a result the zero potentials for a group of experiments at a given temperature agreed to within 0.5 mv or better and their values were within 2 millivolts or better of the potential predicted for the reaction, $Hg + Hg^{++} = Hg_2^{++}$. The ionic strength correction of this potential is negligible.

Data and Calculations. The initial conditions for each experiment are summarized in Table 12. At each temperature the acidity was varied three fold and the mercuric concentration varied four fold. Complete EMF data for all experiments are given in Tables 29-A through 40-A of the Appendix.

Table 12

Initial Experimental Conditions for Mercury Experiments

Expt.	Temp. °C	$Hg(ClO_4)_2$ moles/liter	$Hg_2(ClO_4)_2$ moles/liter	$HClO_4$ moles/liter	$NaClO_4$ moles/liter
1	15	0.06980	0.008654	0.01732	0.2648
2	15	0.1302	0.01610	0.01833	0.0428
3	15	0.03627	0.01795	0.006734	0.3305
4	15	0.03627	0.01795	0.01658	0.3208
9	25	0.06980	0.008654	0.01732	0.2648
10	25	0.1302	0.01610	0.01833	0.0428
11	25	0.03627	0.01795	0.006734	0.3305
12	25	0.03627	0.01795	0.01658	0.3208
1	35	0.06980	0.008654	0.01732	0.2648
2	35	0.1302	0.01610	0.01833	0.0428
3	35	0.03627	0.01795	0.006734	0.3305
4	35	0.03627	0.01795	0.01658	0.3208

The equilibria which must be considered are as follows:

$$Hg^{++} + HF = HgF^{+} + H^{+}, \qquad C_{11} \qquad (30)$$

$$Hg_2^{++} + HF = Hg_2F^{+} + H^{+}, \qquad C_{12} \qquad (31)$$

$$Hg^{++} + H_2O = HgOH^{+} + H^{+}, \qquad C_h \qquad (32)$$

$$HF = H^{+} + F^{-}. \qquad C_{HF} \qquad (9)$$

Hietanen and Sillen's[13] value for C_h at 25° and $\mu = 0.5$ of 2×10^{-4} was used in calculating all experiments, since there were no available data at 15° and 35°. Since the acidity was essentially constant throughout the course of an experiment, this did not cause any serious error, because the only time it was necessary to use C_h was to calculate the mercuric ion concentration initially present in the solution.

The entire purpose of cell B-C was to determine whether there was complexing of mercurous ion by fluoride ion. If no complexing occurs, the EMF of the cell after each fluoride addition should be described by the relation

$$E = E_o - \frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C} = E_o - \frac{RT}{2F} \ln \frac{V_C}{V_B}, \qquad (33)$$

where V_C is the constant volume of solution in cell C, V_B is the total volume in cell B, and R, T, and F have their usual significance. As can be seen from columns 6 and 7 of the Tables in the Appendix, the measured EMF's of cell B-C agreed with those predicted by equation (34) within several hundredths of a millivolt, and therefore the complexing of mercurous ion was negligible in calculating the complexing of mercuric ion.

The behavior of cell A-B is determined by the equations

$$E_i = E_o - \frac{RT}{F} \ln \frac{(Hg_2^{++})_i}{(Hg^{++})_i}, \qquad (34)$$

$$E_f = E_o - \frac{RT}{F} \ln \frac{(Hg_2^{++})_f}{(Hg^{++})_f}, \qquad (35)$$

where the subscript i represents the initial conditions when no NaF has been added and the subscript f represents the conditions after a given amount of NaF has been added.

Subtracting (34) from (35) gives

$$-\Delta E = E_f - E_i = \frac{RT}{F} \ln \frac{(Hg_2^{++})_i \quad (Hg^{++})_f}{(Hg_2^{++})_f \quad (Hg^{++})_i}. \qquad (36)$$

Written exponentially, this becomes

$$(Hg^{++})_f = \frac{(Hg_2^{++})_f}{(Hg_2^{++})_i} (Hg^{++})_i \; e^{-F\Delta E/RT} = \frac{V_i}{V_f} (Hg^{++})_i \; e^{-F\Delta E/RT}, \qquad (37)$$

where V_i and V_f are the initial and final volumes, respectively. $(Hg^{++})_i$ is calculated from the initial conditions, taking the hydrolysis constant of Hg^{++} into account. Knowing the (Hg^{++}) concentration from equation (37), the concentration of (HgF^{+}) is obtained by difference, assuming the $(HgOH^{+})$ concentration is constant during the course of an experiment.

The (HF) concentration was calculated using equation (9) and the quadratic formula. Substitution in equation (9) gives

$$C_{HF} = \frac{(H^{+})(F^{-})}{(HF)} = \frac{(\Sigma H_{o}^{+} - HF)(\Sigma F^{-} - HgF^{+} - HF)}{(HF)} . \qquad (38)$$

Cross-multiplication and application of the quadratic formula yields equation (39), from which the HF concentration can be directly calculated:

$$(HF) = \frac{(C_{HF} + \Sigma H_{o}^{+} + \Sigma F^{-} - HgF^{+}) \pm \sqrt{(C_{HF} + \Sigma H_{o}^{+} + \Sigma F^{-} - HgF^{+})^{2} - 4\Sigma H_{o}^{+} (\Sigma F^{-} - HgF^{+})}}{2} , \qquad (39)$$

The free (H^{+}) is then obtained by subtracting (HF) from ΣH_{o}^{+}. Values of $(HgF^{+})/(Hg^{++})$ and $(HF)/(H^{+})$ for each experiment are in the Appendix. Plots of these quantities for the experiments at 15°, 25°, and 35° are also given in the Appendix in Figures 10-A, 11-A, and 12-A, respectively.

Results. In Table 13 are summarized the values at 15°, 25°, and 35° of C_{11} as defined by equation (30) and values of C'_{11}, which is the equilibrium quotient for the reaction written in terms of (F^{-}) instead of (HF) and (H^{+}). An estimate at 25°C of the true equilibrium constant K at $\mu = 0$ is also given. In Table 14 are summarized the free energy, heat, and entropy changes for the reaction written in terms of both $(HF)/(H^{+})$ and (F^{-}) at $\mu = 0.50$.

Table 13

Equilibrium Quotients for Mercuric Fluoride Complex

	$15^\circ C$	$25^\circ C$	$35^\circ C$
C_{11} ($\mu = 0.5$)	0.0146 ± 0.001	0.0132 ± 0.001	0.0114 ± 0.001
C'_{11} ($\mu = 0.5$)	10.3 ± 1	10.7 ± 1	11.3 ± 1
K_{11} ($\mu = 0$)		36 ± 4	

Table 14

Thermodynamic Functions of Mercuric Fluoride Complex

Reaction (μ=0.5)	ΔF_{298}	ΔH_{298}	ΔS_{298}
$Hg^{++} + HF = HgF^+ + H^+$	$+2560 \pm 50$	-2100 ± 1000	-15 ± 4
$Hg^{++} + F^- = HgF^+$	-1400 ± 50	$+ 850 \pm 1000$	8 ± 4

An upper limit of the fluoride complexing of Hg_2^{++} at 25° was estimated by assuming a maximum observable potential difference of 0.25 mv. The difference actually observed was about 0.05 mv. Assuming 0.25 mv difference, the value of C_{12} as defined by equation (31) was estimated to be less than 1.2×10^{-3} at μ=0.5. C'_{12} at $\mu = 0.5$ is therefore less than 1, and K_{12} at $\mu = 0$ estimated to be less than 3.4.

The uncertainty is high, because the measured EMF differences are small. The maximum observable difference was only about 2 millivolts. However, this corresponds to complexing about 8% of the total Hg^{++}, so that the results are more reliable than for the copper and zinc experiments, and the error due to impurities is considerably diminished.

The uncertainties tabulated above were calculated assuming an error of 0.1 mv in the measured E readings. It should be pointed out that the variation of C_{11} with temperature arose not because of any significant variation with temperature of the EMF readings, but because the factors C_{HF} and $e^{FE/RT}$ used in the calculations are temperature-dependent.

Theoretically, it would be possible to go to higher fluoride concentrations than were reached in these experiments. This was not done because of the slow response of the Hg_2^{++} - Hg^{++} electrode. The experiments were usually continued for about 4 hours and then stopped, because it was felt that during this period of time the initial zero reading might have changed by more than 0.1 mv.

IV. FLUORIDE COMPLEXING OF Ag AT 15°, 25°, AND 35°C

Leden and Marthen[14] have studied the formation of the silver fluoride complex using a silver-silver chloride electrode coupled with a mercury-mercurous sulfate reference electrode, and have obtained a value at 25°C and $\mu = 1$ of 0.48 for the formation of the first fluoride complex. The present investigation was carried out in order to check the value of Leden and Marthen and to provide additional information on the heat and entropy of the complexing. The complexing was studied using a concentration cell, each half of which contained a silver-silver ion electrode.

Experimental. Two half cells were used, which will be designated A and B. The half cells were connected by means of a sodium perchlorate-agar agar salt bridge and an atmosphere of nitrogen was maintained over each. Each half cell initially contained solutions of silver perchlorate, sodium perchlorate, and perchloric acid. The solutions were continuously stirred.

The cells and measuring apparatus were the same as described for the scandium experiments. The cells and caps were painted black to prevent action of light on the silver.

The silver-silver ion electrodes were prepared by rapidly electrolyzing a silver nitrate solution onto platinum. An 0.1N silver nitrate solution, which had been slightly acidified with nitric acid, was used. The more rapid the electrolysis, the more rapid, reversible, and reproducible were the electrodes. However, under these conditions the silver deposit was so spongy that it would not adhere well to the platinum. In practice, the electrodes were usually electrolyzed at a current of about 30 milliamps for 5 or 10 minutes or until the surface of the platinum was entirely covered with silver. Before the plating, the electrodes were cleaned by dipping for a second in warm aqua regia. Electrodes prepared under these conditions usually agreed within 0.2-0.3 mv and came to equilibrium within 5 minutes.

One-hundred-ml aliquots of stock solution containing the desired concentrations of silver pechlorate, perchloric acid, and sodium perchlorate were pipetted into each half cell. The concentrations were adjusted so that the initial ionic strength was 0.50. After the initial zero potential had become constant, known quantities of sodium fluoride were added to half cell A and the same quantity of sodium perchlorate added to half cell B and the difference in potential from the initial zero potential measured after each addition. Since AgF is quite soluble, there was no limit on the amount of sodium fluoride which could be added.

The ionic strength was not kept constant during the course of an experiment, but decreased from 0.5 initially to about 0.495 at the end. Since the activity coefficient of $AgNO_3$[48] varies only from 0.534 to 0.535 in going from $\mu = 0.5$ to $\mu = 0.495$ this would not cause any significant error in the equilibrium quotient.

Data and Calculations. The initial conditions for each experiment are summarized in Table 15. At each temperature the acidity was varied at least twenty fold and the silver ion concentration was varied five fold. Complete EMF data for all experiments are given in Tables 41-A through 49-A of the Appendix.

Table 15

Initial Experimental Conditions for Silver Experiments

Expt.	Temp. $^\circ C$	$HClO_4$ moles/liter	$AgClO_4$ moles/liter	$NaClO_4$ moles/liter
1	15	0.02145	0.04190	0.4368
2	15	0.004849	0.2100	0.2851
3	15	0.0009675	0.04190	0.4571
1	25	0.04126	0.1053	0.3534
2	25	0.004862	0.2106	0.2846
3	25	0.0009704	0.04203	0.04571
1	35	0.02145	0.04190	0.4368
2	35	0.004849	0.2100	0.2851
3	35	0.0009675	0.04190	0.4575

The equilibria which must be considered are as follows:

$$Ag^+ + F^- = (AgF)_{aq}, \qquad C'_{13} \qquad (40)$$

$$HF = H^+ + F^-. \qquad C_{HF} \qquad (9)$$

The behavior of the cell can be described by the following equations:

$$E_i = \frac{-RT}{nF} \ln \frac{(Ag_A^+)_i}{(Ag_B^+)_i}, \qquad (41)$$

$$E_f = \frac{-RT}{nF} \ln \frac{(Ag_A^+)_f}{(Ag_B^+)_f}, \qquad (42)$$

where the subscript i represents the initial conditions when no NaF has been added and the subscript f represents the conditions after a given amount of NaF has been added.

Subtracting (41) from (42) gives

$$-\Delta E = E_f - E_i = \frac{-RT}{F} \ln \frac{(Ag_A^+)_f}{(Ag_B^+)_f} \frac{(Ag_B^+)_i}{(Ag_A^+)_i}. \qquad (43)$$

Written exponentially, this becomes

$$(Ag_A^+)_f = (Ag_A^+)_i \frac{(Ag_B^+)_f}{(Ag_B^+)_i} e^{-F\Delta E/RT} = (Ag_A^+)_i \frac{V_i}{V_f} e^{-F\Delta E/RT}, \qquad (44)$$

where V_i and V_f are the initial and final volumes, respectively. Knowing the concentration of free (Ag^+) from equation (44), the $(AgF)_{aq}$ concentration is obtained by difference.

The (HF) concentration was calculated in the same manner as described for the mercury experiments, using equation (39). The (HF) concentration and the (AgF) concentration were then subtracted from the total fluoride ion concentration to obtain the free fluoride ion concentration. The species (HF_2^-) was negligible in all calculations.

Plots of $(AgF)/(Ag^+)$ vs. (F^-) for the experiments at 15°, 25°, and 35° are given in Figures 13-A, 14-A, and 15-A of the Appendix.

Results. In Table 16 are summarized the values at 15°, 25°, and 35° of C'_{13} as defined by equation (40). An estimate at 25°C of the true equilibrium constant K_{13} is also given. In Table 17 are summarized the free energy, heat, and entropy changes for the reaction at $\mu = 0.50$.

Table 16

Equilibrium Quotients for Silver Fluoride Complex

	15°C	25°C	35°C
C'_{13} $(\mu = 0.5)$	0.75 ± 0.05	0.65 ± 0.05	0.55 ± 0.05
K_{13} $(\mu = 0)$		2.3 ± 0.2	

Table 17

Thermodynamic Functions of Silver Fluoride Complex

Reaction (μ = 0.5)	ΔF_{298}	ΔH_{298}	ΔS_{298}
$Ag^+ + F^- = (AgF)_{aq}$	250 ± 50	-2400 ± 1000	-9 ± 4

Leden and Marthen's value of C'_{13} was corrected to μ = 0.5 using the activity coefficients of $AgNO_3$.[48] The value obtained was 0.74, which is in fair agreement with the present value of 0.65.

The uncertainties tabulated above were calculated assuming an error of 0.1 millivolt in the measured E readings. Although the complexing is much weaker than for the other ions which were studied, the absolute accuracy is quite good, both because it was convenient to go to high fluoride concentrations and because the acidity was low, enabling the complexing to be studied directly in terms of F^- instead of HF. The maximum observable EMF difference was about 2.5 millivolts, which corresponds to complexing about 10% of the total silver.

V. FLUORIDE COMPLEXING OF Sn(II) AT 25°C

This work was undertaken because of the polarographic work of Schaap, Davis, and Nebergall,[15] who found the stannous fluoride complexes to be exceedingly stable. Over a pH range of 5.6 to 7.1 and a stannous ion concentration of 10^{-3} to 10^{-4} M these authors found the principal species to be SnF_3^-, for which at $\mu = 0.8$ they quote an equilibrium quotient of 1.2×10^{-10} for the reaction $SnF_3^- = Sn^{+2} + 3F^-$.

A. EMF Studies

The present experiments were performed using a concentration cell, each half of which contained a tin amalgam-stannous ion electrode. The general procedure of Vanderzee and Rhodes[16] in their study of the stannous chloride complexes was followed.

Experimental. Two half cells were used, which will be designated A and B. Each half cell initially contained solutions of stannous perchlorate, perchloric acid, and sodium perchlorate. At low acidities, the cells were connected by means of the usual sodium perchlorate-agar agar salt bridge. However, the agar agar is not stable in perchloric acid solutions whose concentration is greater than 1M, so that for such solutions it was necessary to use a bridge containing tiny glass stoppers at each end and filled with a perchloric acid-sodium perchlorate solution whose concentration was equal to that in the cells.

The cells and measuring apparatus were the same as described for the scandium experiments. The electrodes were the same as used for the mercury experiments except that they were filled with tin amalgam instead of mercury. A saturated[17] tin amalgam was used for most of the experiments. This was prepared by warming about 1.2g of metallic tin in 10 cc of triply distilled mercury. The electrodes responded rapidly, were reversible and reproducible, and came to equilibrium almost instantaneously.

The cells were flushed out with nitrogen for 15 minutes before use. Known volumes of sodium perchlorate, perchloric acid, boiled conductivity water, and freshly prepared stannous perchlorate were then added to each half cell. The stannous perchlorate was prepared not more than an hour before use. The initial ionic strength was either 0.50 or 2.00. The cells were stirred constantly and an atmosphere of nitrogen was maintained over each. The nitrogen was purified by passing it through solutions of vanadyl sulfate according to the method of Meites and Meites.[18] Under these conditions not more than 1% of the total tin was oxidized to stannic at the end of an experiment as shown by an iodine titration. It was also shown that the presence of this quantity of stannic ion would not affect the behavior of the tin amalgam-stannous ion electrode.

After the initial zero potential had become constant, known quantities of sodium fluoride were added to half cell A and the same quantity of sodium perchlorate added to half cell B and the difference in potential from the initial zero potential measured after each addition. Since SnF_2 is quite soluble, there was no limit on the amount of sodium fluoride which could be added.

Data and Calculations. The initial conditions for each experiment are summarized in Table 18. All experiments were performed at 25°C. Complete EMF data for all experiments are given in Tables 50-A through 57-A of the Appendix.

Table 18

Initial Conditions for Tin Experiments

Expt.	$HClO_4$ moles/liter	$Sn(ClO_4)_2$ moles/liter	$NaClO_4$ moles/liter	μ	C_{14}
4	0.1605	0.03947	0.2214	0.50	18.8
5	0.1633	0.09541	0.0506	0.50	13.8
7	0.08965	0.06849	0.2047	0.50	8.8
8	0.4225	0.01580	0.00	0.50	25.0
9	0.3998	0.03359	0.00	0.50	18.2
11	1.6936	0.01603	0.2584	2.00	10.6
12	1.6723	0.1044	0.0210	2.00	8.0
14	1.7085	0.003995	0.2794	2.00	11.2

The behavior of the cell can be described by the equation

$$(Sn_A^{++})_f = (Sn_A^{++})_i \frac{(Sn_B^{++})_f}{(Sn_B^{++})_i} e^{-F\Delta E/nRT} = (Sn_A^{++})_i \frac{V_i}{V_f} e^{-F\Delta E/2RT}. \qquad (45)$$

The derivation of this equation is the same as that for the behavior of the silver electrode and the symbols and subscripts have the same significance as in the silver section.

Discussion. Several factors made it impossible to fully interpret the EMF data. First of all, there are considerable discrepancies in the literature regarding the hydrolysis of stannous ion, which make it impossible to know the quantity $(Sn_A^{++})_i$ with any degree of accuracy at low acidities. Vanderzee,[16] using the hydrolysis constant as an empirical constant in fitting his chloride complexing data, reports $K_h = 0.02$ at $\mu = 3$. Gorman,[19] from hydrogen electrode measurements, reports a K_h of 0.02 at $\mu = 0$ and Garrett and Heiks[20] from solubility measurements of SnO in HCl report a K_h of 0.0085 at $\mu = 0$. All these workers assume that the principal reaction is $Sn^{++} + H_2O = SnOH^+ + H^+$. Prytz,[21] however, has studied the hydrolysis of stannous ion using both the hydrogen and tin electrodes and has not been able to interpret her data using the above equation. She reports a K of 0.0018 for the reaction $2Sn^{++} + H_2O = Sn_2O^{++} + 2H^+$.

The above-mentioned solubility measurements of SnO in HCl of Garrett and Heiks[20] conflict with the solubility measurements in $HClO_4$ of Gorman and Leighton.[22] Within experimental error the solubility of SnO in both solvents is the same, which is anomalous with the work of Vanderzee[16] and other workers,[23-27] who report the existence of moderately stable stannous chloride complexes.

A side experiment was performed in which the stannous ion activity was measured using the tin amalgam electrode coupled with a hydrogen reference electrode. The acidity was kept constant while the stannous concentration was varied. Two sets of experiments were performed, one set at 0.1M total acid, and the other at 1M total acid. In both cases, a plot of EMF versus log (Sn^{++}) revealed a straight line with the theoretical slope from 0.1 to 0.001M Sn^{++}. There was no evidence of the presence of any polymeric tin species, although the acidity was higher than Prytz used. The experiments also indicated that the hydrolysis was less than the values[16,19,20] in the literature, although the acidity was so high that no accurate calculations could be made. Deviations from the straight line occurred below 0.001M Sn^{++}, which could be explained by oxidation of some of the tin to Sn^{+4}.

A second difficulty in interpreting the data was a lack of knowledge concerning the principal species present in the fluoride solutions. The data for experiments 5 and 7 at low fluoride concentrations definitely showed that more than one stannous ion was used per fluoride ion, suggesting the possibility of polymers such as

Sn_2F^{+3}, etc. Also Vanderzee,[16] in his study of the stannous chloride complexes, showed that mixed complexes of the form SnOHCl were important. The only quantity directly calculable from the experimental data is the uncomplexed stannous ion. If the principal fluoride species is known, the quantity $(HF)/(H^+)$ can be deduced indirectly. However, knowing neither $(HF)/(H^+)$ nor the composition of the principal species, complete interpretation of the data is difficult if not impossible, since it is quite possible that there are several equilibria which must be considered, even at low fluoride concentrations. This difficulty is further enhanced by the fact that neither the acidity nor the total stannous ion concentration was constant during the course of an experiment.

An attempt was made to interpret the data by plotting the quantity (complexed stannous ion)/(uncomplexed stannous ion) versus (HF/H^+), assuming the principal reaction to be

$$Sn^{++} + HF = SnF^+ + H^+. \qquad C_{14} \qquad (46)$$

The slope of such a plot should be equal to C_{14}. Plots for experiments 11, 12, and 14 are shown in Figures 16-A, 17-A, and 18-A of the Appendix. Only the initial portion of each curve was a straight line. At high (HF/H^+) the curves bent upward, indicating the presence of higher complexes. The slope of the initial portion of the curve for each experiment is given in the last column of Table 18. The values of C_{14} at $\mu = 2.00$ can be converted to $\mu = 0.50$ by multiplying the former by a factor of two. This conversion factor was obtained by making suitable assumptions of the activity coefficients.

It is obvious from Table 18 that C_{14} is not constant. Several interesting features can be noted from the variation of C_{14} with acidity and stannous concentration. For a given μ, the highest values of C_{14} are obtained when the acidity is high and the total stannous concentration low (Experiments 8 and 14). For a given total stannous ion concentration, C_{14} does not vary much with acidity (Experiments 4 and 9, 5 and 12, 8 and 11). At constant acidity and varying stannous concentration, C_{14} varies widely (Experiments 4 and 5, 11 and 12, 8 and 9). The only exception to this last statement is given by Experiments 11 and 14. Here the acidity is constant and the stannous concentration varied four fold, yet C_{14} varies only 6%. However, it must be noted that when the stannous ion concentration is further increased 6.5 fold from Experiment 11 to 12, then C_{14} again decreases by 20%. The most consistent results seem to be obtained at the higher acidities.

The cause of these discrepancies is not apparent. If one attempts to interpret the data assuming the principal reaction to be $2Sn^{++} + HF = Sn_2F^{+3} + H^+$, the discrepancies are even worse, since one essentially divides the C's in Table 18 by (Sn^{++}). Interpretation assuming the reaction to be $SnOH^+ + HF = SnF^+ + H_2O$ likewise proved futile. More than one equilibrium should probably be considered at the low acidities, but such calculations are extremely difficult. At high acid, however, it seems that no combination of equilibria would account for the discrepancies.

The reproducibility of the experiments was shown by repeating #4 and #12 under identical conditions. Each EMF reading of the repeat experiments agreed with the original results to within 0.05 mv. A third experiment was repeated using dilute tin amalgam instead of saturated amalgam in the electrode, and again the two sets of results checked to within 0.05 mv.

The chloride complexing of stannous ion has been studied by Vanderzee,[16] Prytz,[23] and Duke and Courtney,[24] all of whom used tin or tin amalgam electrodes. All of these investigators worked at stannous ion concentrations less than 0.01<u>M</u>, and all except Prytz[23] worked at acidities of 2 or 3<u>M</u>. The fact that the equilibrium constants of all these workers are self-consistent, and the fact that the constants are of the same order of magnitude as those obtained by conductivity,[27] light absorption,[26] and kinetics,[25] seems to indicate that the electrode is behaving properly, at least in solutions whose stannous ion concentration is less than 0.01<u>M</u>.

Possible explanations of the discrepancies of Table 18 are that the electrode is not responding properly in solutions of high stannous ion concentration or that there is something peculiar about the solutions themselves. The following experiments were performed in an attempt to shed light on the above discrepancies.

B. Miscellaneous Experiments

It was suggested that perhaps the stannic fluoride complexes were stable enough to cause the disproportionation reaction $2Sn^{++} + F^{-} = SnF^{+3} + Sn$ to occur. This postulate was tested by titrating solutions of Sn^{++}, H^{+}, F^{-}, and ClO_4^{-} with triiodide solution. The stannous concentrations were 0.01 or 0.1<u>M</u>, and the fluoride concentration in each case varied from 0 to about 0.1<u>M</u>. Within experimental error, the amount of triiodide required for the titrations was the same as that required for a solution with no added fluoride. Also no precipitate of metallic tin was visible in any of the solutions.

In order to check on the behavior of the electrodes, the complexing was further studied by measuring the (HF/H^{+}) concentration.

This was done spectrophotometrically by studying the competition between uranyl ion and stannous ion for fluoride ion. The measurements were made with a Beckman Model DU spectrophotometer at 4750A. At this wave length the percentage difference in optical density between uranyl perchlorate solutions and uranyl perchlorate solutions containing sodium fluoride was greatest. There was the disadvantage, however, that the extinction coefficient of uranyl ion in this region is so low ($\epsilon = 0.27$) that it was necessary to work at rather high (0.04M) uranyl concentrations. This made the calculations difficult, since one did not know the (HF/H^+) ratio with any certainty. It was not possible to work in the ultraviolet region where uranyl ion has a high extinction coefficient, because of the intense absorption of stannous ion in this region.

A series (#1) of solutions was prepared with $\Sigma UO_2^{++} = 0.0387\underline{M}$, $(H^+) = 0.5\underline{M}$, and $\Sigma F^- = 0 - 0.2\underline{M}$. A second series (#2) was prepared with the same uranyl and fluoride concentrations, but with $(H^+) = 0.09\underline{M}$. From these data an equilibrium quotient C_{15} for the reaction

$$UO_2^{++} + HF = UO_2F^+ + H^+ \qquad C_{15} \qquad (47)$$

was calculated. The calculations were performed by first assuming a value of C_{15} from which (HF/H^+) was calculated. Knowing (HF/H^+) the extinction coefficient of (UO_2F^+) could be determined. This quantity was calculated for various values of C_{15}, and the value of C_{15} which gave the most constant $\epsilon_{UO_2F^+}$ was taken to be the true value. The value of C_{15} was found to be 15, which agrees reasonably well with the value at 25° and $\mu = 0.5$ of 25 reported by Day and Powers[28] from extraction studies with TTA. The value of $\epsilon_{UO_2F^+}$ was found to be 1.43. At total fluoride ion concentrations greater than 0.01M, the species UO_2F_2 begins to become important. No calculations were made of equilibria involving this species.

Series 1 and 2 described in the preceding paragraph were again prepared, this time containing 0.01669<u>M</u> Sn^{++} and 0.06674<u>M</u> Sn^{++} respectively. These conditions were such as to resemble very closely the conditions for EMF experiments 8 and 7. Titration with triiodide after the optical density measurements were made indicated that less than 1% of the total tin was oxidized to Sn^{+4}.

The optical density D of uranyl fluoride solutions under conditions where the principal species is UO_2F^+ is given by the equation

$$\frac{D}{(\Sigma UO_2^{++})(L)} = \frac{\epsilon_o + C_{15}\, \epsilon_1 (\frac{HF}{H^+})}{1 + C_{15}(\frac{HF}{H^+})}, \tag{48}$$

where L is the cell length in cm, ϵ_o the extinction coefficient of UO_2^{++}, and ϵ_1 the extinction coefficient of UO_2F^+. The $(HF)/(H^+)$ ratio for uranyl solutions containing stannous ion can be calculated from this equation. Knowing $(HF)/(H^+)$, the SnF^+ concentration can be calculated from the equations

$$\Sigma UO_2^{++} = UO_2^{++} + UO_2F^+, \tag{49}$$

$$\Sigma F^- = HF + F^- + UO_2F^+ + SnF^+. \tag{50}$$

Values of C_{14} were calculated for series 1 and 2. In the case of series 1, C_{14} was found to be a constant with a value of 23.5, which agrees exceptionally well with the value obtained in experiment 8 of the EMF measurements. For series 2, C_{14} was found to vary from 5 to 12, increasing regularly with increasing fluoride concentration. It should be noted, however, that this is of the same order of magnitude as was found in experiment 7 of the EMF measurements.

Although the spectrophotometric method is not nearly so accurate as the EMF method, yet it does confirm the EMF measurements and shows that the tin amalgam-stannous ion electrode was functioning properly. One seems therefore to be forced to the conclusion that something peculiar is occurring at high tin concentrations which cannot be interpreted by a simple equilibrium such as that of equation (46).

Results. Due to the variation of C_{14} with stannous concentration, it is impossible to quote a precise value for C_{14}. However, from EMF experiments 11 and 14, it would seem that the best value of C_{14} at $\mu = 2.00$ is about 11. It should be noted that this value does not appear to hold for stannous ion concentrations greater than 0.01M. For reaction (46) written in terms of F^- instead of (HF/H^+), C'_{14} is about 10^4 at $\mu = 2.00$ and about 7×10^4 at $\mu = 0$. These results are in qualitative agreement with the polarographic work of Schaap,[19] if one assumes that the stability of the successive fluoride complexes differs by a factor of 10.

VI. DISCUSSION

A. Stability Considerations

The general reaction for the formation of a fluoride complex can be written as

$$M(H_2O)_x^{+m} + F^- = MF(H_2O)_{x-1}^{+m-1} + H_2O. \qquad K \qquad (51)$$

In the normal complex it is assumed that one water molecule in the first coordination sphere of the metallic ion is replaced by a fluoride ion.

Since the fluoride ion has such a low polarizability, one would expect the bond between metallic and fluoride ions to be essentially ionic. If only electrostatic forces are holding the two ions together, the stability of the fluoride complex should depend only on the charge and radius of the metallic cation. Specifically, one would expect the stability of a fluoride complex to be greater the higher the charge and the smaller the radius of the complexing cation.

Connick[29] has shown that a reasonably good correlation of the stability of complex fluorides with charge and radius may be obtained by plotting log K versus Z/d where K is the equilibrium constant for the formation of the first fluoride complex at $\mu = 0$, Z is the charge on the metallic ion, and d is the interatomic distance in angstroms, equal to the radius of the cation plus the radius of the fluoride ion. Such a plot of the existing data, including those obtained in this investigation, is presented in Figure 1. The data used in Figure 1 and the sources of data are given in Table 19.

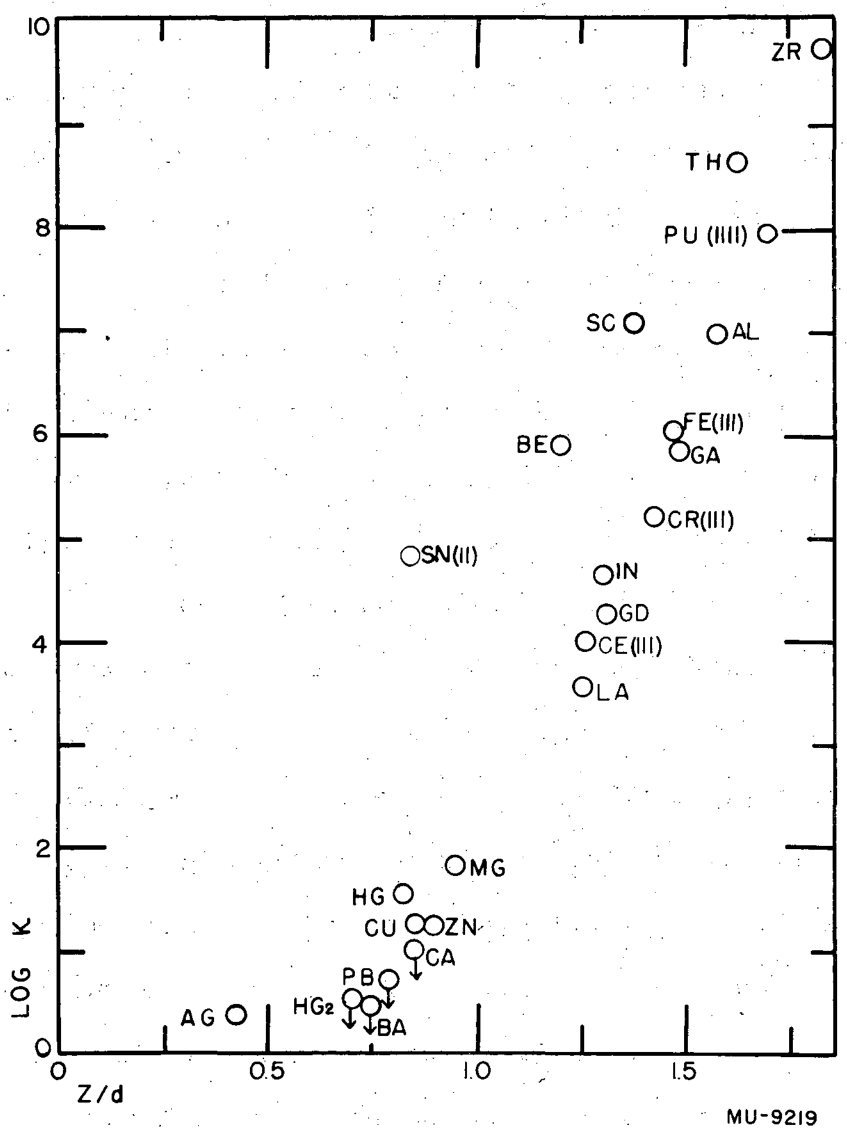

Fig. 1 Correlation of Stability of First Flouride Complex with Function Z/d

Table 19

Data and Sources of Data for Figures 1-4

Cation	Ionic Radius (A)	$K_{\mu = 0}$	Reference
Ag^{+}	0.97	2.3	This work
Mg^{++}	0.75	66	(3)
Ca^{++}	1.00	<11	(3)
Ba^{++}	1.32	< 2.8	(3)
Cu^{++}	0.98	17	This work
Zn^{++}	0.83	18	This work
Hg^{++}	1.04	36	This work
Hg_2^{++}	1.44	< 3.4	This work
Pb^{++}	1.21	< 5.4	This work
Sn^{++}	1.02	7×10^4	This work
Be^{++}	0.30	7.7×10^5	(30), (6)
Al^{+3}	0.55	1.0×10^7	(1)
Fe^{+3}	0.67	1.1×10^6	(5)
Ga^{+3}	0.65	7.3×10^5	(32), (6)
Cr^{+3}	0.70	1.6×10^5	(32)
In^{+3}	0.95	4.3×10^4	(4)
Sc^{+3}	0.83	1.2×10^7	This work
Gd^{+3}	0.94	1.8×10^4	(33)
Ce^{+3}	1.03	9.8×10^3	(33)
La^{+3}	1.06	3.6×10^3	(33)
Zr^{+4}	0.80	6.3×10^9	(34)
Th^{+4}	1.10	4.5×10^8	(2)
Pu^{+4}	~ 1	8.7×10^7	(35)

Most of the crystal radii are those of Wyckoff,[36] who gives a more complete tabulation than Pauling.[7] Radii of Cu^{++}, Hg^{++}, Pb^{++}, Ca^{++}, and Ba^{++} were calculated directly from Wyckoff's crystallographic data for the crystalline fluorides. Radii of Ce^{+3}, Gd^{+3}, and La^{+3} were taken from the work of Templeton and Dauben.[37] The radius of the fluoride ion was taken to be 1.36A. Although it is doubtful that the crystal radius of an ion is exactly equal to its radius in solution, it is probable that the radius in solution is proportional to the crystal radius.

Other types of ionic correlations are presented in Figures 2, 3, and 4. In Figure 2, log K is plotted versus Z/r, where r is the ionic radius. In Figures 3 and 4, log K is plotted versus Z^2/d and Z^2/r, respectively. The Z/d and Z^2/r correlations seem to be the most consistent, and it is interesting to note that they both have some theoretical significance.

The correlation with Z/d can be interpreted in terms of a simple coulombic picture. The electrostatic free energy of bringing the ions together is given by the equation

$$\Delta F = \frac{-Ze^2}{D\ d}\ , \tag{52}$$

where D is the effective dielectric constant. From the slope of the data in Figure 1, D has an effective value of about 25. Presumably the value is less than that of pure water because of dielectric saturation in the neighborhood of the cations.

There is an additional free-energy term, apart from the electrostatic term, which arises from the entropy of combining two freely moving species into one. This should amount to approximately -4 e.u.[3] for a six-coordinated cation. Because of this term the log K versus Z/d curve should theoretically intersect the ordinate axis at about -0.9.

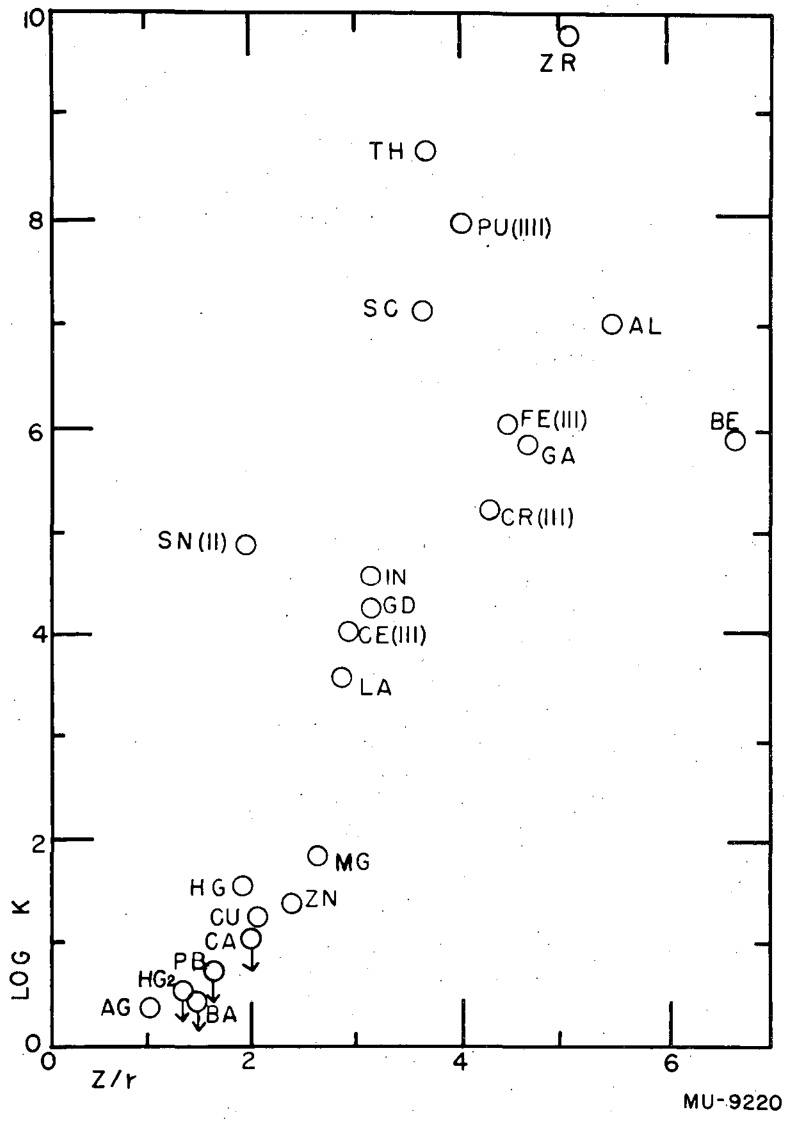

Fig. 2 Correlation of Stability of First Fluoride Complex with Function Z/r

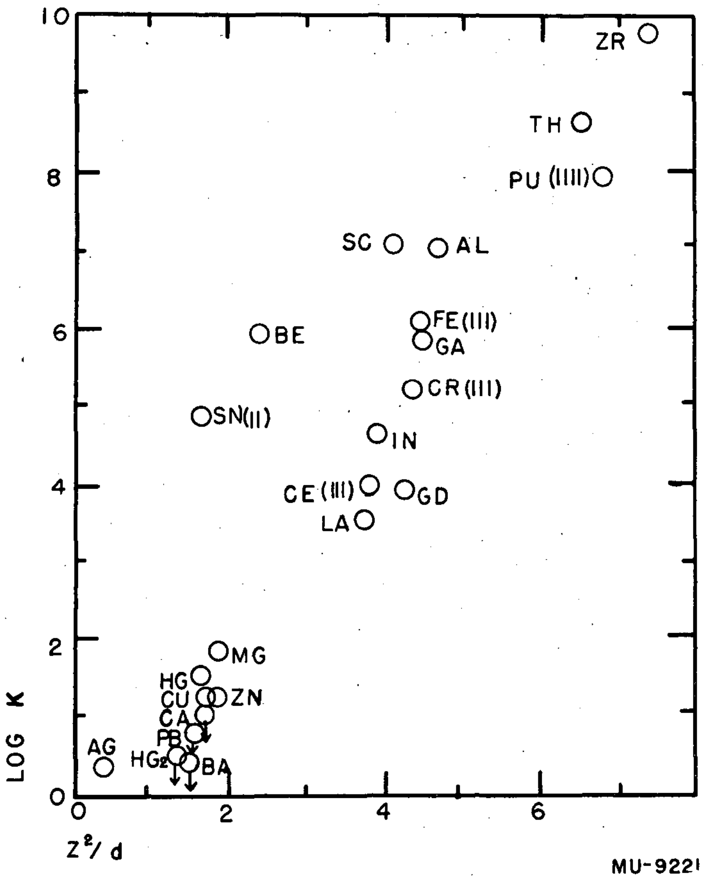

Fig. 3 Correlation of Stability of First Fluoride Complex with Function Z^2/d

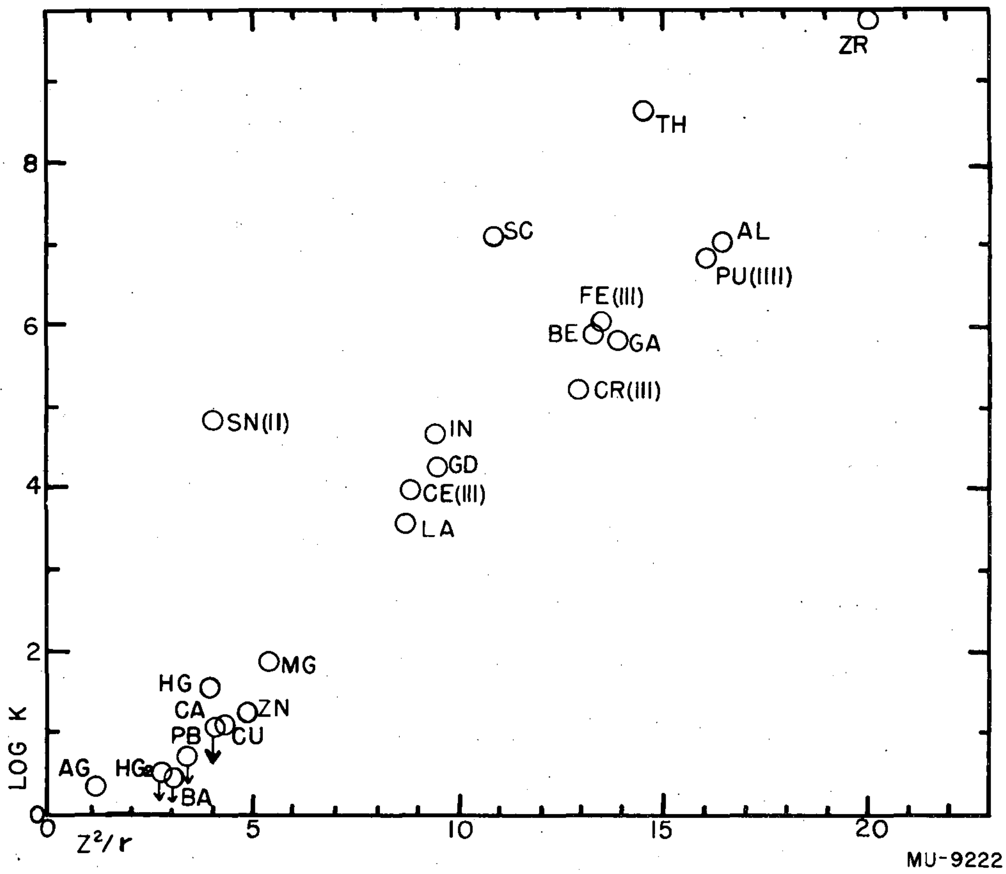

Fig. 4 Correlation of Stability of First Fluoride Complex with Function Z^2/r

The Z^2/r correlation can also be given some theoretical significance from the Born equation. Born[38] has shown that for spherical ions the energy of solution of gaseous ions is expressed by the equation

$$\Delta E = \frac{Z^2}{2r} \left(1 - \frac{1}{D}\right), \tag{53}$$

where D is the dielectric constant of the solvent. Since E is a measure of the binding energy of the coordinated water molecules about an ion, log K is related to E, and therefore it is not surprising that one obtains a good correlation with Z^2/r.

The success of the Z^2/r plot suggested plotting log K versus the experimental heat of hydration instead of the theoretical quantity predicted by the Born equation. Such a plot is shown in Figure 5, and the correlation is again good. The experimental heats of hydration are those of Brewer.[39]

Much work has been done recently on the correlation of stability of metal chelates. Calvin[40] has found that the stability of a variety of metal chelates can be correlated with the ionization potential of the last electron. Fernelius[41] and co-workers have been successful in correlating the stability with electronegativity. Plots of the complex fluoride stabilities versus last ionization potential and electronegativity are shown in Figures 6 and 7, respectively. The ionization potentials were taken from Latimer.[42] Electronegativities are those of Haissinsky,[43] who gives a more complete tabulation than does Pauling.[7]

It is not surprising that correlations of the stability of the complex fluorides with ionization potential and electronegativity should fail. Both ionization potentials and electronegativities are related to the tendency of an atom to form covalent bonds. It was mentioned earlier that the fluoride complexes would be expected to be essentially ionic.

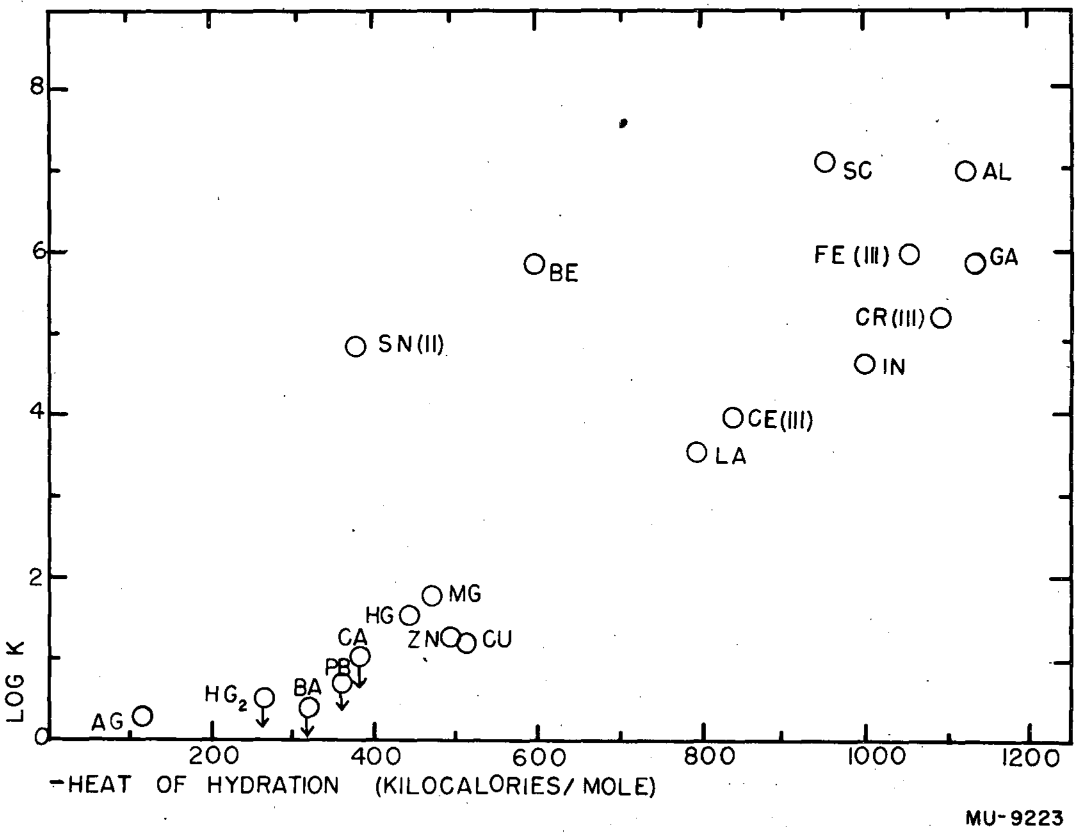

Fig. 5 Correlation of Stability of First Fluoride Complex with Hydration Energy

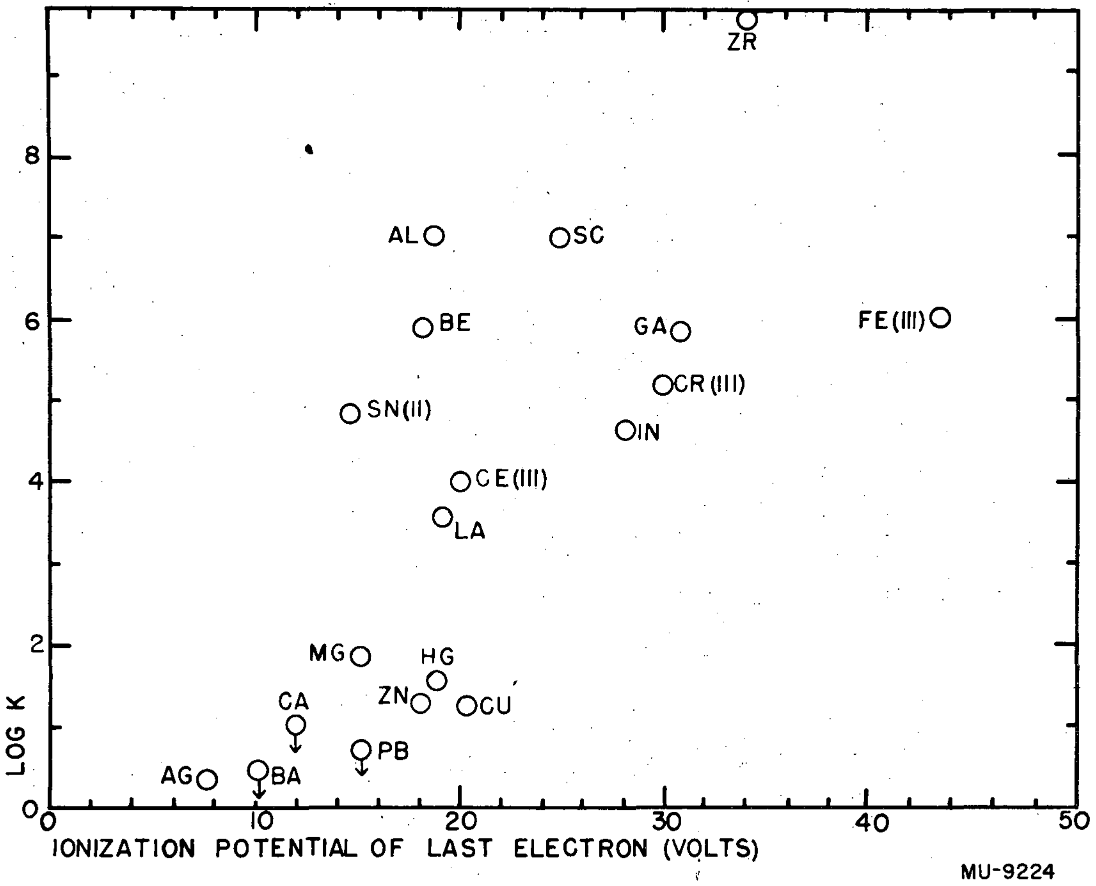

Fig. 6 Correlation of Stability of First Fluoride Complex with Last Ionization Potential

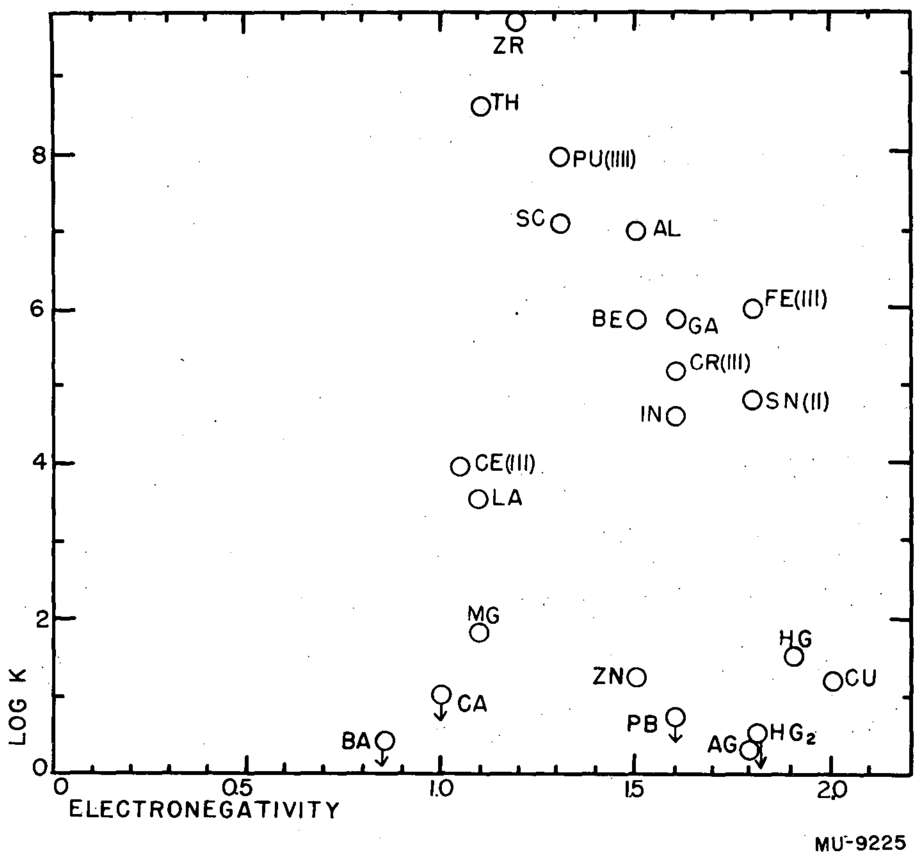

Fig. 7 Correlation of Stability of First Fluoride Complex with Electronegativity

In all the ionic correlations attempted, Sc(III) and Sn(II) deviate considerably. On some of the plots (See Figures 1-4), Be(II) and Th(IV) also deviate. The deviation of Be(II) may perhaps be overlooked. Since it was the smallest ion investigated, its correlation might be expected to be poorest. The deviation of Th(IV) is apparent only in the Z^2/r plot. The deviations of Sc(III) and Sn(II) are indeed considerable, and at present there is no satisfactory explanation which would account for the abnormal behavior of either of these ions.

It was mentioned earlier that according to Pauling,[7] the crystal radii of Sc(III) and In(III) were equal and that the stability of the Sc(III) and In(III) fluoride complexes should be roughly equal. However, a survey of crystal parameters confirms Wyckoff's[36] data that the crystal radius of Sc(III) is indeed smaller than that of In(III), which would account for the Sc(III) complexes' being more stable than the In(III) complexes, but not by so large an amount.

To get an insight into the cause of this abnormal behavior of Sc(III) let us compare the thermodynamic functions for the fluoride complexing of Al(III)[31] and Fe(III)[5] with those of Sc(III). The data given in Table 20 are at an ionic strength of 0.5.*

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*ΔH's for Al reactions were measured at $\mu = 0.06$ to $\mu = 0.2$.

Table 20

Thermodynamic Functions of Sc(III), Fe(III), and Al(III) Fluoride Complexes

Reaction	ΔF_{298}	ΔH_{298}	ΔS_{298}
$Sc^{+3} + F^- = ScF^{+2}$	-8440	+400	+29
$ScF^{+2} + F^- = ScF_2^+$	-7190	-1230	+20
$ScF_2^+ + F^- = ScF_{3(aq)}$	-5550	-1260	+14
$ScF_{3(aq)} + F^- = ScF_4^-$	-4740	-	-
$Fe^{+3} + F^- = FeF^{+2}$	-6060	+2330	+31
$FeF^{+2} + F^- = FeF_2^+$	-4360	+1770	+24
$FeF_2^+ + F^- = FeF_{3(aq)}$	-2970	+2980	+23
$Al^{+3} + F^- = AlF^{+2}$	-8370	+1150	+32
$AlF^{+2} + F^- = AlF_2^+$	-6850	+ 780	+26
$AlF_2^+ + F^- = AlF_{3(aq)}$	-5250	+ 190	+18
$AlF_{3(aq)} + F^- = AlF_4^-$	-3740	+ 280	+13

It is apparent from Table 20 that the greater stability of the scandium fluoride complexes is due to a discrepancy in the heat of complexing. The entropies for the scandium reactions are in excellent agreement with those for the corresponding iron and aluminum reactions. One would not expect the entropies of these reactions to vary appreciably. The heat term for the scandium complexes, however, is considerably more negative than that for the aluminum and ferric complexes.

It is difficult to find an explanation for the abnormal stability and heat of formation of the scandium fluoride complexes. It seems doubtful that Sc(III) could be using its d orbitals, since Fe(III) and some of the other ions plotted also have vacant d orbitals which could be used for this purpose. These ions, however, seem to be in agreement with the ionic interpretation. Another objection to the covalent interpretation is that if covalent orbitals were used, one would expect the water molecules in the first coordination sphere to be bound more tightly, since the polarizability of a water molecule is greater than for a fluoride ion. This would make replacement by a fluoride ion more difficult and the complex less stable.

It also seems improbable that the greater stability of the scandium fluorides is due to a change in coordination number of the scandium ion. If this were the case there would be a noticeable discrepancy in the entropy of complexing, which was not observed.

The only other complex of Sc(III) which has been quantitatively studied is the hydroxide. Kilpatrick and Pocras[9] report a K_h at $\mu = 1.0$ of 1.17×10^{-5}, which when converted to $\mu = 0$ becomes 5.57×10^{-5}. The corresponding values at $\mu = 0$ for Al(III)[44] and Fe(III)[10] are 5.07×10^{-6} and 4×10^{-3}, respectively. Scandium seems to form a more stable hydroxide complex than does aluminum, which is the same trend as was found with fluoride ion.

It is also difficult to explain why the stannous fluoride complex is so stable. Stannous ion, with the same ionic radius as mercuric ion, forms a fluoride complex several thousand times more stable than the corresponding mercuric fluoride complex. Yet Pb(II) with the same electronic structure as Sn(II) forms an exceptionally weak fluoride complex. There are no available data on the crystal structure of SnF_2. The structure of SnO, however, is somewhat peculiar, although it is the same as the structure of red PbO.

It is interesting to compare the complexing of F^-, Cl^-, Br^-, and OH^- with Hg^{++} and Sn^{++}. The data are presented in Table 21. The K's are at $\mu = 0$. The source of the data is given in parenthesis after each value.

Table 21

Comparison of Stability of Various Stannous and Mercuric Complexes

Reaction	$K_{Sn^{++}}$	$K_{Hg^{++}}$
$M^{++} + F^- = MF^+$	7×10^4	3.6×10^1
$M^{++} + Cl^- = MCl^+$	4.4×10^1 (16)	1.87×10^7 (46)
$M^{++} + Br^- = MBr^+$	1.7×10^1 (45)	3.81×10^9 (46)
$M^{++} + OH^- = MOH^+$	8.5×10^{11}(20)	3×10^{10}(13)

It is apparent that for Sn^{++}, the fluoride complex is the most stable of the halide series, while for Hg^{++} the reverse is true. There is considerable evidence[46] that the molecules $HgCl_2$ and $HgBr_2$ are nearly linear, and therefore s-p bonding is probably used. Since the polarizability of $F^- < Cl^- < Br^-$, the above order for the mercuric fluoride complexes would be expected if covalent effects were predominant. Likewise, the order obtained for the stannous complexes is that which one would expect if the ionic effect were the most important. It seems that there is something peculiar about stannous ion which lends itself particularly well to the formation of ionic complexes. The hydroxide complex of stannous is also more stable than that of mercuric ion. However, as was mentioned earlier, there is considerable uncertainty in the order of magnitude of the hydrolysis of stannous ion.

B. Correction of Entropies to Zero Ionic Strength.

There has been considerable interest in recent years in the prediction and correlation of entropies of complex ions. Unfortunately the experimental determination of entropies is made at a finite ionic strength, and the correction to zero ionic strength is usually neglected.

Adequate data are not available for an accurate estimate of this correction. There are no equilibrium data for the formation of a complex ion as a function of temperature and ionic strength, nor are there both heat of dilution and activity data for stable complex ions, such as uranyl ion, cobalt amines, or normal chromic complexes. One is therefore forced to use heats of dilution and activity coefficients of individual salts, usually nitrates, chlorides, and bromides. Although most complexing reactions are studied in perchlorate solution, there are not enough heat-of-dilution data for perchlorates to enable one to make the correction using perchlorates. This is unfortunate since, as will be shown later, the correction varies appreciably depending on whether one uses the data for nitrates or chlorides. A final difficulty in making such a correction arises from the fact that there are only fragmentary data on the heat of dilution of one salt in the presence of another. For 1-1 electrolytes this effect is of the order of 20 cal[47] at $\mu=1$ and is probably negligible, but for higher valence types it may be of the order of several kilocalories.[47]

Using the activity coefficients of Harned and Owen[48] and the heats of dilution given by the Bureau of Standards[49] for all salts except the rare earth chlorides, where the heats of dilution of Spedding[50,51] were used, the partial molal entropies of dilution were calculated for the individual salts. The data presented in Table 22 are for dilution from $\mu = 0.5$ to $\mu = 0$.

Table 22

Partial Molal Free Energies, Heats, and Entropies of Dilution of Electrolytes from $\mu = 0.5$ to $\mu = 0$

Electrolyte	$\overline{F}_2^o - \overline{F}_2$ (cal/mole)	$\overline{L}_2^o - \overline{L}_2$ (cal/mole)	$\overline{S}_2^o - \overline{S}_2$ (e.u.)	$\overline{S}_2^o - \overline{S}_2$ (e.u.) (from Eq. 56)
$HClO_4$	+340	+100	-0.8	-1.7
HCl	+330	-450	-2.6	-1.7
HBr	+280	-350	-2.1	-1.5
HI	+210	-250	-1.5	-1.1
HNO_3	+400	-160	-1.9	-2.1
LiCl	+350	-365	-2.4	-1.8
NaCl	+450	+ 20	-1.4	-2.3
NH_4Cl	+570	-160	-2.4	-3.0
KCl	+510	+ 30	-1.6	-2.7
RbCl	+540	+105	-1.5	-2.8
CsCl	+600	+420	-0.6	-3.1
LiBr	+330	-315	-2.0	-1.7
NaBr	+430	+ 25	-1.3	-2.2
KBr	+500	+110	-1.3	-2.6
LiI	+240	-205	-1.5	-1.2
NaI	+380	+ 20	-1.2	-2.0
KI	+470	+185	-1.0	-2.4
$NaNO_3$	+580	+390	-0.6	-3.0
KNO_3	+730	+125	-2.0	-3.8
NH_4NO_3	+690	+365	-1.1	-3.6
$RbNO_3$	+740	+520	-0.7	-3.8
$CsNO_3$	+740	+520	-0.7	-3.8
NaAc	+360	-350	-2.4	-1.9
KAc	+340	-490	-2.8	-1.8
NaSCN	+400	+195	-0.7	-2.1
KSCN	+520	+250	-0.9	-2.7
NaF	+550	-255	-2.7	-2.9
KF	+470	-185	-2.2	-2.4
$NaClO_3$	+520	+110	-1.4	-2.7

(continued)

Table 22
(-2-)

Electrolyte	$\overline{F}_2^\circ - \overline{F}_2$ (cal/mole)	$\overline{L}_2^\circ - \overline{L}_2$ (cal/mole)	$\overline{S}_2^\circ - \overline{S}_2$ (e.u.)	$\overline{S}_2^\circ - \overline{S}_2$ (e.u.) (from Eq. 56)
$KClO_3$	+670	+450	-0.7	-3.5
LiOH	+570	-395	-3.2	-3.0
KOH	+380	-240	-2.1	-2.0
NaOH	+430	-100	-1.8	-2.2
K_2CrO_4	+1620	+810	-2.7	-8.4
Na_2SO_4	+1670	- 25	-5.7	-8.7
K_2SO_4	+1700	-180	-6.3	-8.8
$(NH_4)_2SO_4$	+2170	-215	-8.0	-11.3
Li_2SO_4	+1550	-155	-5.7	-8.1
$NiSO_4$	+2340	-2050	-14.6	-7.0
$CuSO_4$	+2340	-1345	-12.3	-7.0
$CdSO_4$	+2340	-1665	-13.4	-7.0
$MnSO_4$	+2340	-1445	-12.6	-7.0
$MgSO_4$	+2340	-1095	-11.5	-7.0
$ZnSO_4$	+2340	-1180	-11.7	-7.0
$CeCl_3$	+2490	-1800	-14.3	-12.9
$ErCl_3$	+2490	-1800	-14.3	-12.9
$LaCl_3$	+2460	-2370	-16.1	-12.8
YCl_3	+2460	-2550	-16.7	-12.8
$YbCl_3$	+2460	-2550	-16.7	-12.8
$SmCl_3$	+2500	-1680	-13.9	-13.0
$NdCl_3$	+2500	-1680	-13.9	-13.0
$BaBr_2$	+1320	-520	-6.1	-6.8
$Ba(NO_3)_2$	+1260	+180	-3.6	-6.6
$BaCl_2$	+1410	-620	-6.7	-7.3
$CuCl_2$	+1380	-1405	-9.3	-7.2
$Cu(NO_3)_2$	+1320	+ 30	-4.3	-6.9

(continued)

Table 22

(-3-)

Electrolyte	$\bar{F}_2^o - \bar{F}_2$ (cal/mole)	$\bar{L}_2^o - \bar{L}_2$ (cal/mole)	$\bar{S}_2^o - \bar{S}_2$ (e.u.)	$\bar{S}_2^o - \bar{S}_2$ (e.u.) (from Eq. 56)
$MgBr_2$	+1050	-820	-6.2	-5.5
$Mg(NO_3)_2$	+1260	-435	-5.7	-6.5
$MgCl_2$	+1110	-860	-6.6	-5.8
$ZnCl_2$	+1380	-1570	-9.8	-7.2
$CdCl_2$	+3000	-1210	-14.0	-15.6
$CdBr_2$	+3390	+25	-11.2	-17.6
$NiCl_2$	+1260	-920	-7.3	-6.6
$CaCl_2$	+1230	-685	-6.4	-6.4
$CaBr_2$	+1320	-775	-7.0	-6.9
$Ca(NO_3)_2$	+1260	+130	-3.8	-6.5
$SrCl_2$	+1320	-665	-6.6	-6.9
$SrBr_2$	+1320	-620	-6.5	-6.9
$Sr(NO_3)_2$	+1260	+220	-3.5	-6.5

It will be noted from Table 22 that the partial molal entropies of dilution of salts of a given valence type are very nearly the same, with the exception of the nitrates, chlorates, and other salts with large anions, whose entropies of dilution appear to be significantly less negative.

It is interesting to compare the experimental entropies of dilution with those predicted by the Debye-Huckel limiting law. The Debye-Huckel limiting law is given by

$$\ln \gamma_{\pm} = -\frac{1}{\nu} Z_A \, Z_B (\mu)^{1/2} \left[\frac{\pi \, N \, \epsilon^6}{1000(kDT)^3} \right]^{1/2} , \qquad (52)$$

where $\gamma_{\pm}$ is the mean activity coefficient, μ the ionic strength, Z_A the charge of the cation, Z_B the charge of the anion, N Avogadro's number, k the Boltzmann constant, D the dielectric constant, T the absolute temperature, ϵ the electronic charge, and ν the number of ions produced by the dissociation of one mole of electrolyte. Combining equation (52) with the free energy equation gives

$$\Delta F = - \nu RT \ln \gamma_{\pm} = 2.303\ RT\ Z_A\ Z_B\ (\mu)^{1/2} \left[\frac{\pi\ N\ \epsilon^6}{1000\ (k\ DT)^3}\right]^{1/2} . \qquad (53)$$

Differentiating equation (53) with respect to temperature, one obtains

$$\frac{d\ \Delta\ F}{d\ T} = -\Delta S = 2.303\ R\ Z_A\ Z_B (\mu)^{1/2} \left[\frac{\pi\ N\ \epsilon^6}{1000\ k^3}\right] \left[-\frac{1}{2} + \frac{3}{2}\ \frac{T}{D}\ \frac{(dD)}{(dT)}\right] . \qquad (54)$$

Evaluation of the numerical constants using D and dD/dT for pure water gives

$$-\Delta S = 2.303 R\ Z_A\ \ Z_B\ (\mu)^{1/2}\ \ (0.505)(1.56) . \qquad (55)$$

Since the quantity $\left[2.303\ RT\ Z_A\ Z_B\ (\mu)^{1/2}\ (0.505)\right]$ is equal to ΔF, it is obvious that

$$T\ \Delta\ S = -1.56\ \Delta F . \qquad (56)$$

The last column of Table 22 lists the partial molal entropies of dilution predicted by equation (56) and the free energies of dilution listed in column 1. With the exception of the 2-2 electrolytes and the cadmium salts which are known to be peculiar, the predicted entropies agree with the experimental values within about 3 entropy units. The agreement is much better if only the halide salts are considered. In general, the predicted partial molal entropies for salts with large anions such as NO_3^-, ClO_3^-, SCN^-, etc., are generally several entropy units too negative.

Using the values in Table 22, it is possible to correct the entropies for complexing reactions to zero ionic strength, keeping in mind, of course, the assumptions and approximations mentioned earlier. For example, for a reaction of the type $M^{+3} + X^- = MX^{+2}$, the change in entropy upon dilution from $\mu = 0.5$ to $\mu = 0$ is obtained by subtracting the partial molal entropy of dilution of a 3-1 salt from that of a 2-1 salt. Table 23 shows the value of the correction $\Delta(\Delta S)$ obtained for several types of reactions using various combinations of salts.

Table 23

Entropy Corrections from $\mu = 0.5$ to $\mu = 0$ for Equilibrium Reactions

Reaction	$\Delta(\Delta S)$ (e.u.)
$M^{+3} + X^- = MX^{+2}$	
using $LaCl_3$ and $BaCl_2$	9.4
using $CeCl_3$ and $BaCl_2$	7.6
$M^{++} + X^- = MX^+$	
using $BaCl_2$ and KCl	5.1
using $Ba(NO_3)_2$ and KNO_3	1.6
using $Mg(NO_3)_2$ and KNO_3	3.7
using $CaBr_2$ and KBr	5.7
$M^+ + X^- = MX_{(aq)}$	
using LiI	1.5
using $RbNO_3$	0.7
using NaF	2.4
$MX_4^- + X^- = MX_5^{-2}$	
using KCl and K_2SO_4	-3.1
using $NaNO_3$ and Na_2SO_4	-4.5
$MX_5^{-2} + X^- = MX_6^{-3}$	
using $LaCl_3$, $BaCl_2$, KCl	-6.0

It is obvious from Table 23 that there is a considerable variation in the correction depending on whether one uses the data for nitrates or chlorides. It is unfortunate that there are no heat-of-dilution data for perchlorates. For consistency, the corrections in this paper were all made using chloride data except for reactions involving ions with a charge of -2, where data for sulfates were used. The difficulties which were outlined in the opening paragraphs of this section should be kept in mind when using Table 23 to make such corrections.

C. Entropies of Complex Fluorides

The two factors which determine the entropy change in complex ion formation are (1) the entropy change due to the replacement of a water molecule in the first coordination sphere by the complexing anion (replacement entropy), and (2) the effect on the surrounding water molecules due to changing the charge on the central ion (charge effect).[31]

For fluoride complexing, the replacement entropy can be calculated from the relation

$$H_2O\ (\text{bound}) + F^-\ (\text{aq}) = H_2O\ (l) + F^-\ (\text{bound}). \qquad (57)$$

Using the entropies given by Latimer[42] for each species, the replacement entropy is about 14 e.u. It varies slightly depending on the charge of the cation to which the fluoride ion is bound.

Subtraction of the replacement entropy from the total experimental entropy gives the charge effect. There is no theoretical way of evaluating the charge effect. However, Tsao[8] has derived an empirical rule for calculating the charge effect which is of the form

$$\text{Charge effect} = -3(Z^2_{\text{complex ion}} - Z^2_{\text{uncomplexed ion}}). \qquad (58)$$

For example, for a reaction of the type $M^{+3} + X^- = MX^{+2}$, the charge effect would be $-3(2^2 - 3^2) = 15$ e.u. By differentiation of the Born[38] equation with respect to temperature, Tsao[8] has further shown that equation (58) has some theoretical significance and was able to derive the constant -3 assuming the radius of the ion to be 0.5Å plus the diameter of a water molecule.

Tsao[8] was quite successful in using equation (58) to predict the charge-effect entropies for a variety of fluoride complexing reactions. The predicted charge effect was always of the correct sign and did not deviate more than 5 e.u. from the experimental value. The experimental values used for comparison were all at $\mu = 0.50$.

In Table 24 are presented all the known entropy data for fluoride complexing reactions. The source of the data may be obtained from Table 19. In the first column are listed the experimental entropies at $\mu = 0.5$. Column 2 gives the entropies corrected to $\mu = 0$, using the method of correction described in the preceding section. Column 3 lists the replacement entropy calculated according to equation (57). In column 4 the replacement entropies are corrected, assuming the absolute entropy of H^+ to be -2.1 e.u.[52] The last two columns list the experimental charge effects and the charge effects predicted using Tsao's rule.

Table 24

Entropies of Fluoride Complexing Reactions

Reaction	ΔS exptl (μ=0.5)	ΔS (μ=0)	ΔS replacement	ΔS replacement (absolute)	ΔS charge effect	ΔS charge effect from Tsao's rule
$Mg^{++} + F^- = MgF^+$	19	24	14.3	12	12	9
$Cu^{++} + F^- = CuF^+$	6	11	14.3	12	-1	9
$Zn^{++} + F^- = ZnF^+$	8	13	14.3	12	1	9
$Hg^{++} + F^- = HgF^+$	8	13	14.3	12	1	9
$Ag^+ + F^- = AgF_{(aq)}$	-9	-7	15.1	13	-20	3
$Sc^{+3} + F^- = ScF^{+2}$	29	37	13.6	11	26	15
$ScF^{+2} + F^- = ScF_2^+$	20	25	14.3	12	13	9
$ScF_2^+ + F^- = ScF_3$ (aq)	14	16	15.1	13	3	3
$Fe^{+3} + F^- = FeF^{+2}$	31	39	13.6	11	28	15
$FeF^{+2} + F^- = FeF_2^+$	24	29	14.3	12	17	9
$FeF_2^+ + F^- = FeF_{3(aq)}$	23	25	15.1	13	12	3
$Al^{+3} + F^- = AlF^{+2}$	32	39	13.6	11	28	15
$AlF^{+2} + F^- = AlF_2^+$	26	31	14.3	12	19	9
$AlF_2^+ + F^- = AlF_{3(aq)}$	18	20	15.1	13	7	3
$AlF_{3(aq)} + F^- = AlF_4^-$	13	13	16	14	-1	-3
$AlF_4^- + F^- = AlF_5^{-2}$	5	-2	16	14	-16	-9
$AlF_5^{-2} + F^- = AlF_6^{-3}$	-3	-6	16	14	-20	-15
$In^{+3} + F^- = InF^{+2}$	25	33	13.6	11	22	15
$InF^{+2} + F^- = InF_2^+$	25	33	14.3	12	21	9

It can be seen from Table 24 that there is a considerable difference between the experimental and predicted charge effects. With the exception of Ag(I), the largest deviations seem to be obtained for the highly charged ions Fe(III), Al(III), and Sc(III). It is surprising that Tsao's[8] empirical rule works so much better at $\mu = 0.5$ than at $\mu = 0$. It is possible, of course, that the corrections from $\mu = 0.5$ to $\mu = 0$ are not even of the correct order of magnitude due to the many assumptions and approximations involved in making the correction.

Quite large deviations are obtained for the ions Cu(II), Zn(II), Hg(II), and Ag(I). The entropies of the Cu(II), Zn(II), and Hg(II) fluoride complexing reactions seem to be considerably less positive than for the Mg(II) reaction. It should be noted, however, that the uncertainty in the entropies of the Cu(II), Zn(II), and Hg(II) reactions as well as for the Mg(II) reaction is 5 - 10 e.u., and it is therefore difficult to say whether the discrepancies between Mg(II) and Cu(II), Zn(II) and Hg(II) have any significance.

The discrepancy between the predicted and experimental charge effects for these ions can be reduced about 2 e.u., by assuming the radius to be 1A plus the diameter of a water molecule, instead of 0.5A plus the diameter of a water molecule. The resulting constant in Tsao's rule then becomes -2.4 instead of -3.

It is possible that Ag(I), Cu(II), Zn(II), and Hg(II) have coordination numbers less than six. If this were the case, it might be possible for a fluoride ion to fit into the coordination sphere without replacing a fully coordinated water molecule. This would cause the replacement entropy to be less positive and would bring the experimental charge effect into closer agreement with the predicted value. Further data on the entropies of fluoride complexing reactions for divalent ions whose coordination number is known to be six are needed in order to test the above hypothesis.

In Table 25 are summarized the relative and absolute partial molal entropies at $\mu = 0$ of all the fluoride complex ions for which data are available. The entropies of the uncomplexed ions were taken from Latimer,[42] and the correction to the absolute scale made by assuming the absolute entropy of H^+ to be -2.1 e.u.[52]

Table 25

Relative and Absolute Partial Molal Entropies of Complex Fluorides

Ion	$\overline{S}^\circ$(e.u.) (relative)	$\overline{S}^\circ$(e.u.) (absolute)	$\overline{S}^\circ$(e.u.) (from Eq. 59 and 60)
MgF^+	-6.5	-2.3	18.8
CuF^+	-14.9	-10.7	23.4
ZnF^+	-14.8	-10.6	20.5
HgF^+	+5.3	+9.5	24.1
$AgF_{(aq)}$	+8.4	+12.6	-3.3
ScF^{+2}	-21.3	-17.1	-24.7
ScF_2^+	+1.4	+7.7	37.2
ScF_3 (aq)	+15.1	+23.5	20.5
FeF^{+2}	-33.4	-29.2	-31.8
FeF_2^+	-6.7	-0.4	+33.6
FeF_3 (aq)	+16.0	+24.4	+7.7
AlF^{+2}	-38.2	-34.0	-37.3
AlF_2^+	-9.5	-3.2	+30.6
AlF_3 (aq)	+8.2	+16.6	-3.2
AlF_4^-	+18.9	+29.4	+64
AlF_5^{-2}	+14.6	+27.2	+29.5
AlF_6^{-3}	+6.3	+21.0	-6.4
InF^{+2}	-31.3	-29.1	-20.0
InF_2^+	-0.6	+5.7	+39.4

Cobble[53] has recently shown that the entropies of complex ions can be successfully predicted by the equations

$$\bar{S}^{\circ} = n\,S^{\circ}_{(H_2O)} + 49 - 99\,Z/r_{12} \quad \text{for charged complexes,} \qquad (59)$$

$$\bar{S}^{\circ} = n\,S^{\circ}_{(H_2O)} + 132 - 354/r_{12} \quad \text{for uncharged complexes,} \qquad (60)$$

where n is the number of water molecules replaced, $S^{\circ}_{(H_2O)}$ is the entropy of pure water, Z is the charge on the complex, and r_{12} is the radius in angstroms of the cation plus the radius of the complexing anion. The last column of Table 25 lists the entropies predicted by equations (59) and (60). The agreement in general is poor, probably because the constants in equations (59) and (60) were evaluated from data which had not been corrected to zero ionic strength.

VII. PREPARATION AND ANALYSIS OF REAGENTS

H_2O. - Conductivity water was used for all solutions.

$Fe(ClO_4)_2$ - $Fe(ClO_4)_3$ - $HClO_4$. - A stock solution of ferrous perchlorate, ferric perchlorate, and perchloric acid was prepared by dissolving electrolytic iron with excess perchloric acid and then oxidizing a portion of the ferrous perchlorate to ferric perchlorate with hydrogen peroxide. The ferrous ion concentration was determined by titration with standard ceric sulfate. Since the ferrous perchlorate, total iron, and initial perchloric acid concentrations were known, the final ferric perchlorate and perchloric acid concentrations could be calculated by difference. These agreed with those experimentally determined using the method of Schumb, Sherrill, and Sweetser.[54]

NaF. - Baker CP sodium fluoride was dried at 150° and dissolved in conductivity water. The concentration was calculated from the weight of the salt used.

$HClO_4$. - Double vacuum-distilled 62% perchloric acid was diluted with conductivity water and standardized against mercuric oxide using methyl red indicator.

$NaClO_4$. - Analytical grade sodium carbonate was treated with an excess of double vacuum-distilled perchloric acid. The solution was boiled to expel carbon dioxide and the acidity then adjusted to a pH of 5 or 6 on a pH meter by addition of carbonate-free sodium hydroxide. The resulting $NaClO_4$ solution was standardized by evaporating aliquots to dryness and weighing as $NaClO_4$ after drying at 150° for two hours.

Salt Bridges. - One gram of agar agar was added to 15 ml of 1.6N $NaClO_4$ which had been heated to boiling. The resulting gel was drawn into the glass tubing by vacuum and then allowed to set in ice water over night.

$Sc(ClO_4)_3 - HClO_4$. - Sc_2O_3 was dissolved in perchloric acid. Spectrochemical analysis of the resulting scandium perchlorate solution showed only extremely small traces of Al, Fe, Mg, Zr, and Ca. The acidity was determined by precipitating the scandium as ScF_3 and subsequent titration with NaOH. The scandium concentration was determined by precipitating the scandium as the hydroxide and weighing as Sc_2O_3.

$Zn(ClO_4)_2$. - Mallinckrodt Analytical Grade ZnO was added in excess to perchloric acid and the unreacted ZnO filtered off. The resulting solution had a pH of about 6 on the Beckmann pH meter. The zinc concentration was determined volumetrically by titration with standard potassium ferrocyanide using diphenylamine indicator.

$Pb(ClO_4)_2$. - Mallinckrodt Analytical Grade PbO was added in excess to perchloric acid and the unreacted PbO filtered off. The resulting solution had a pH of 6 on the pH meter. The lead concentration was determined gravimetrically as $PbSO_4$.

$Cu(ClO_4)_2 - HClO_4$. - Mallinckrodt Analytical Grade CuO was dissolved in perchloric acid. The copper concentration was determined volumetrically by precipitating the copper as CuI and titrating the liberated iodine with standard sodium thiosulfate. The acidity was determined by precipitating the copper as CuS and titrating the free acid with standard sodium hydroxide.

$AgClO_4 - HClO_4$. - Mallinckrodt Analytical Grade Ag_2O was dissolved in perchloric acid. The silver concentration was determined by titration with standard sodium chloride according to Mohr's method. The acidity was determined by precipitating the silver as AgCl and titrating with standard sodium hydroxide to the phenolphthalein end point.

$Hg(ClO_4)_2$ - $HClO_4$. - Mallinckrodt Analytical Grade HgO was dissolved in perchloric acid. The mercuric ion concentration was determined by titration with standard ammonium thiocyanate. The acidity was determined by complexing the mercuric ion with chloride ion and subsequent titration with standard sodium hydroxide to the phenolphthalein end point.

$Hg_2(ClO_4)_2$ - $HClO_4$. - A portion of the $Hg(ClO_4)_2$ - $HClO_4$ solution previously described was shaken at 50°C for several hours with excess metallic mercury. The excess mercury was left in the solution to prevent oxidation to Hg(II). The mercurous ion concentration was determined by titration with standard sodium chloride using bromphenol blue as adsorption indicator according to the method of Kolthoff and Larson.[55] The acidity was determined by precipitating the mercurous ion with sodium chloride and subsequent titration with standard sodium hydroxide to the phenolphthalein end point.

$Sn(ClO_4)_2$ - $HClO_4$. - Solutions of $Sn(ClO_4)_2$ - $HClO_4$ were prepared by passing a solution of cupric perchlorate through a column containing metallic tin according to the method of Noyes and Toabe.[56] The column and flask in which the stannous perchlorate was collected were filled with nitrogen at all times to prevent oxidation. Stannous ion was determined by titration with standard iodine under an atmosphere of nitrogen, and the acidity determined by titration with standard sodium hydroxide. The stannous ion concentration and acidity determined by this method agreed sufficiently well with the copper concentration and acidity of the initial cupric perchlorate solution so that in later experiments the iodine titration was eliminated and the stannous ion concentration taken to be equal to the copper concentration and the acidity taken to be equal to the acidity of the cupric perchlorate solution.

$UO_2(ClO_4)_2 - HClO_4$. - UO_3 was dissolved in excess perchloric acid. The concentration of uranyl ion was determined by evaporating to dryness and igniting at 900°C to U_3O_8. The acidity was determined by precipitating the uranium as $UO_4 \cdot x H_2O$ with hydrogen peroxide and titrating with standard NaOH to the phenolphthalein end point.

VIII. APPENDIX

Table 1 - A

Fluoride Complexing of Scandium, Experiment 1 at 15°C

Initial Concentrations

$HClO_4$ = 0.05277M

$Sc(ClO_4)_3$ = 0.001387M

$Fe(ClO_4)_2$ = 0.0003868M

$Fe(ClO_4)_3$ = 0.0003704M

$NaClO_4$ = 0.4350M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 100.95 ml

NaF = 0.5038M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0792	14.59	0.4984	14.31	1.516	0.00395
0.1584	27.30	0.6976	29.02	1.893	0.01047
0.2376	37.53	0.8968	44.31	2.135	0.02102
0.3168	45.93	1.0960	57.32	2.296	0.03409
0.5160	61.73	1.2952	68.17	2.421	0.04855
0.7152	73.78	1.4944	77.75	2.508	0.06456
1.2136	97.02	1.6936	86.44	2.576	0.08214
1.7120	114.64	1.8928	94.29	2.667	0.1009
2.2104	129.32	2.0920	101.51	2.729	0.1208
2.7088	142.18	2.5904	117.25	2.799	0.1746
		3.0888	130.92	2.880	0.2351
		3.5872	143.23	2.932	0.3030

Table 2 - A

Fluoride Complexing of Scandium, Experiment 3 at 15°C

Initial Concentrations

$HClO_4$ = 0.1065M

$Sc(ClO_4)_3$ = 0.006665M

$Fe(ClO_4)_2$ = 0.0003721M

$Fe(ClO_4)_3$ = 0.0003663M

$NaClO_4$ = 0.3502M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 104.94 ml

NaF = 0.5038M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0792	9.59	0.4984	1.00	0.352	0.000215
0.1584	18.00	0.9968	2.75	0.703	0.00061
0.3576	33.94	1.4952	5.77	1.044	0.00135
0.5568	45.27	1.9936	10.87	1.369	0.00279
1.0552	64.91	2.4920	19.17	1.700	0.00573
1.5536	79.52	2.9904	30.58	1.926	0.01125
2.0520	91.17	3.4888	43.23	2.130	0.01994
3.0488	109.79	3.9872	55.21	2.286	0.03138
4.0456	124.63	4.4856	66.30	2.417	0.04540
5.0424	137.49	4.9840	76.46	2.520	0.06171
		5.9808	94.01	2.678	0.09941

Table 3 - A

Fluoride Complexing of Scandium, Experiment 1 at 25°C

Initial Concentrations

$HClO_4$ = 0.1122M

$Sc(ClO_4)_3$ = 0.01273M

$Fe(ClO_4)_2$ = 0.0003553M

$Fe(ClO_4)_3$ = 0.0003402M

$NaClO_4$ = 0.3087M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 109.93 ml

NaF = 0.4702M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	(HF)/(H^+)
0.0747	7.95	0.0747	0.00	-	-
0.1494	14.99	0.1494	0.00	-	-
0.2241	21.08	0.2241	0.00	-	-
0.2988	26.32	0.7241	0.60	0.243	0.0001293
0.3735	30.92	1.7225	2.13	0.576	0.0004749
0.4482	34.96	2.7209	4.82	0.905	0.001127
0.9482	54.00	3.7193	9.43	1.23	0.00239
1.4482	70.30	4.7177	17.02	1.53	0.00494
		5.7161	28.55	1.81	0.01020
		6.7145	43.20	2.04	0.02004
		7.7129	58.31	2.21	0.03520

Table 4 - A

Fluoride Complexing of Scandium, Experiment 2 at 25°C

Initial Concentrations

$HClO_4$ = 0.05287$\underline{M}$

$Sc(ClO_4)_3$ = 0.001387$\underline{M}$

$Fe(ClO_4)_2$ = 0.0003869$\underline{M}$

$Fe(ClO_4)_3$ = 0.0003705$\underline{M}$

$NaClO_4$ = 0.4355$\underline{M}$

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 100.95 ml

NaF = 0.4702$\underline{M}$

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0747	13.25	0.0747	0.72	0.240	0.000153
0.1494	24.98	0.1494	1.74	0.474	0.000393
0.2241	34.71	0.2241	3.16	0.698	0.000734
0.2988	42.84	0.2988	5.12	0.913	0.001224
0.3735	49.75	0.3735	7.76	1.12	0.001947
0.4482	55.84	0.4482	11.15	1.30	0.002897
0.5229	61.24	0.5229	15.33	1.47	0.004396
0.5976	66.11	0.5976	20.18	1.61	0.006309
0.6723	70.53	0.7470	31.05	1.85	0.01179
1.1707	93.67	0.8964	41.90	2.03	0.01928
1.6691	110.77	1.0458	51.80	2.16	0.02822
2.1675	124.57	1.1952	60.60	2.27	0.0383
2.6659	136.10	1.3446	68.44	2.37	0.04916
3.1643	146.80	1.5687	78.68	2.49	0.06647
		2.1418	99.97	2.66	0.1161
		2.6402	114.89	2.77	0.1647
		3.1386	127.61	2.80	0.2172
		3.6370	139.0	2.73	0.2747

Table 5 - A

Fluoride Complexing of Scandium, Experiment 3 at 25°C

Initial Concentrations

$HClO_4$ = 0.05457M

$Sc(ClO_4)_3$ = 0.002741M

$Fe(ClO_4)_2$ = 0.0003831M

$Fe(ClO_4)_3$ = 0.0003669M

$NaClO_4$ = 0.4257M

Ionic strength = 0.5000M

T = 25.00 ± 0.01°C

V_o = 101.94 ml

NaF = 0.4702M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0747	12.97	0.4984	3.93	0.80	0.000807
0.1494	24.36	0.9968	16.55	1.52	0.004844
0.2241	33.89	1.0715	19.62	1.61	0.006068
0.2988	41.86	1.1462	23.03	1.69	0.00757
0.3735	48.69	1.2956	30.53	1.85	0.01148
0.4482	54.66	1.4450	38.48	1.98	0.01621
0.9466	82.63	1.5944	46.33	2.09	0.02298
1.4450	102.01	1.6691	50.12	2.14	0.02653
1.9434	117.45	2.1675	72.31	2.40	0.05523
2.4418	130.70	2.6659	90.07	2.57	0.09042
		3.1643	105.18	2.68	0.1316
		3.6627	118.30	2.81	0.1775
		4.1611	130.20	2.87	0.2292

Table 6 - A

Fluoride Complexing of Scandium, Experiment 1 at 35°C

Initial Concentrations

$HClO_4$ = 0.05277M

$Sc(ClO_4)_3$ = 0.001387M

$Fe(ClO_4)_2$ = 0.0003868M

$Fe(ClO_4)_3$ = 0.0003704M

$NaClO_4$ = 0.4350M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 100.95 ml

NaF = 0.5038M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0793	14.56	0.1996	3.23	0.660	0.00076
0.1586	27.27	0.3992	11.41	1.215	0.00309
0.2379	37.69	0.5988	25.38	1.633	0.00846
0.3172	46.26	0.7984	41.06	1.906	0.01857
0.3965	53.58	0.9980	54.36	2.128	0.03062
0.4758	59.99	1.198	67.24	2.222	0.0466
0.5551	65.68	1.397	77.20	2.340	0.0623
0.6344	70.81	1.597	86.12	2.419	0.0794
0.8340	81.87	1.796	94.00	2.456	0.0971
1.034	91.15	1.996	101.24	2.528	0.1174
1.233	99.28	2.494	117.46	2.619	0.1687
1.433	106.68	2.993	131.95	2.633	0.2275
1.931	122.94				
2.429	136.92				
2.928	149.39				

Table 7 - A

Fluoride Complexing of Scandium, Experiment 2 at 35°C

Initial Concentrations

$HClO_4$ = 0.05493M

$Sc(ClO_4)_3$ = 0.002741M

$Fe(ClO_4)_2$ = 0.0003831M

$Fe(ClO_4)_3$ = 0.0003668M

$NaClO_4$ = 0.4252M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 101.94 ml

NaF = 0.5038M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0795	14.43	0.4980	5.07	0.849	0.00124
0.1590	26.90	0.6974	9.79	1.163	0.00258
0.2385	37.02	0.8968	16.97	1.444	0.00506
0.3180	45.48	1.0962	26.67	1.690	0.00940
0.3975	52.69	1.2956	37.88	1.886	0.01617
0.5969	67.19	1.4950	49.10	2.048	0.02530
0.7963	78.56	1.6944	59.53	2.173	0.03637
0.9957	88.03	1.8938	68.98	2.271	0.04896
1.4937	107.23	2.0932	77.54	2.359	0.06276
1.9917	122.92	2.2926	85.32	2.425	0.07756
2.4897	136.47	2.4920	92.46	2.478	0.09326
2.9877	148.61	2.990	108.38	2.603	0.1380
		3.488	122.34	2.697	0.1859
		3.986	134.76	2.742	0.2405
		4.484	146.24	2.798	0.3014

Table 8 - A

Fluoride Complexing of Scandium, Experiment 3 at 35°C

Initial Concentrations

$HClO_4$ = 0.1065M

$Sc(ClO_4)_3$ = 0.006665M

$Fe(ClO_4)_2$ = 0.0003721M

$Fe(ClO_4)_3$ = 0.0003563M

$NaClO_4$ = 0.3502M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 104.94 ml

NaF = 0.5038M

NaF added to Cell B (ml)	E_{B-C} (mv)	NaF added to Cell A (ml)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0795	9.58	0.4980	1.32	0.353	0.000292
0.1590	17.91	0.9960	3.65	0.696	0.000846
0.2385	25.00	1.494	7.57	1.031	0.00187
0.4379	38.90	1.992	14.03	1.346	0.00409
0.6373	49.39	2.490	23.63	1.630	0.00799
0.8367	57.90	2.988	35.88	1.866	0.01444
1.0361	65.06	3.486	48.81	2.049	0.02446
1.5364	79.59	3.984	60.97	2.189	0.03731
2.0321	91.34	4.482	71.86	2.299	0.05225
2.5301	101.30	4.980	81.73	2.390	0.06906
3.0281	110.16	5.478	90.69	2.456	0.08747
		5.976	98.78	2.520	0.1070
		6.474	106.41	2.570	0.1283
		6.972	113.19	2.641	0.1496

Table 9 - A

Fluoride Complexing of Zinc, Experiment 4 at 15°C

Initial Concentrations

$HClO_4$ = 0.005338$\underline{M}$

$Zn(ClO_4)_2$ = 0.0002221$\underline{M}$

$Fe(ClO_4)_2$ = 0.0006838$\underline{M}$

$Fe(ClO_4)_3$ = 0.08676$\underline{M}$

$NaClO_4$ = 0.2296$\underline{M}$

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 110.06 ml

NaF = 0.5000$\underline{M}$

NaF added to Cells A and B (ml)	E_{B-C}(mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0495	8.15	8.14	-	-
0.0990	18.97	18.67	0.0000496	0.006644
0.1485	31.83	31.27	0.0000888	0.01380
0.1980	45.68	45.02	0.000104	0.02522
0.2475	59.03	58.27	0.000138	0.04057
0.2970	71.44	69.81	0.000346	0.05832
0.3465	82.76	80.87	0.000474	0.07995
0.3960	93.18	90.95	0.000613	0.1044
0.4455	102.50	99.79	0.000786	0.1298
0.5196	114.51	111.54	0.001042	0.1706
0.5937	125.12	121.08	0.001506	0.2110
0.6678	134.80	130.01	0.001866	0.2549
0.7419	144.00	138.76	0.002216	0.3048
0.8160	153.04	146.83	0.002624	0.3575
0.8901	161.35	154.74	0.003021	0.4162

Table 10 - A

Fluoride Complexing of Zinc, Experiment 5 at 15°C

Initial Concentrations

$HClO_4$ = 0.005699M

$Zn(ClO_4)_2$ = 0.02779M

$Fe(ClO_4)_2$ = 0.0002371M

$Fe(ClO_4)_3$ = 0.0007299M

$NaClO_4$ = 0.4058M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 103.10 ml

NaF = 0.5000

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0495	8.27	8.25	0.000032	0.002418
0.0990	18.86	18.80	0.000057	0.006630
0.1485	31.70	31.45	0.000111	0.01382
0.1980	45.56	45.21	0.000155	0.02515
0.2475	59.15	58.68	0.000216	0.04075
0.2970	71.74	71.24	0.000360	0.06030
0.3465	83.22	82.28	0.000613	0.08244
0.3960	93.64	92.75	0.000830	0.1084
0.4701	107.12	106.17	0.000938	0.1500
0.5196	115.00	113.86	0.001121	0.1788
0.5937	125.56	124.36	0.001483	0.2249
0.6678	135.36	132.77	0.001955	0.2682
0.7419	145.00	143.32	0.002138	0.3320
0.8160	154.41	152.32	0.002792	0.3953
0.8901	163.46	161.27	0.003207	0.4680

Table 11 - A

Fluoride Complexing of Zinc, Experiment 6 at 15°C

Initial Concentrations

$HClO_4$ = 0.02164M

$Zn(ClO_4)_2$ = 0.02779M

$Fe(ClO_4)_2$ = 0.0002371M

$Fe(ClO_4)_3$ = 0.0007299M

$NaClO_4$ = 0.3899M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 103.10 ml

NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0495	7.17	7.27	-	-
0.0990	15.47	15.56	-	-
0.1485	24.72	24.71	-	-
0.1980	33.80	33.76	0.000047	0.01370
0.2721	46.40	46.32	0.000108	0.02350
0.3462	56.72	56.60	0.000180	0.03413
0.4203	66.59	66.40	0.000252	0.04727
0.4944	74.65	74.41	0.000325	0.06027
0.5685	81.68	81.39	0.000543	0.07352
0.7679	98.69	98.28	0.000688	0.1144
0.9673	113.14	112.54	0.001053	0.1607
1.1667	126.00	125.46	0.001564	0.2141
1.3661	135.23	134.74	0.001895	0.2605
1.5655	144.71	144.18	0.002192	0.3156

Table 12 - A

Fluoride Complexing of Zinc, Experiment 5 at 25°C

Initial Concentrations

$HClO_4$ = 0.005338M

$Zn(ClO_4)_2$ = 0.08676M

$Fe(ClO_4)_2$ = 0.0002221M

$Fe(ClO_4)_3$ = 0.0006838M

$NaClO_4$ = 0.2296M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 110.06 ml

NaF = 0.5000M

NaF added to Cells B and C (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0489	8.65	8.26	0.000115	0.002717
0.0978	19.51	18.91	0.000136	0.008878
0.1467	32.43	31.57	0.000167	0.01532
0.1956	46.32	45.15	0.000207	0.02740
0.2445	59.07	58.02	0.000219	0.04312
0.2934	71.97	70.23	0.000300	0.06281
0.3423	83.42	81.05	0.000555	0.08492
0.3912	93.98	90.70	0.000821	0.1088
0.4648	108.12	105.41	0.001088	0.1545
0.5384	120.84	116.46	0.001181	0.1974
0.6120	132.14	127.71	0.001541	0.2500
0.6856	142.13	136.12	0.002505	0.2961
0.7592	151.28	142.19	0.003702	0.3333

Table 13 - A

Fluoride Complexing of Zinc, Experiment 6 at 25°C

Initial Concentrations

$HClO_4$ = 0.005699M	Ionic strength = 0.5000
$Zn(ClO_4)_2$ = 0.02779M	T = 25.00 ± 0.01°C
$Fe(ClO_4)_2$ = 0.0002371M	V_o = 103.10 ml
$Fe(ClO_4)_3$ = 0.0007299M	NaF = 0.5000M
$NaClO_4$ = 0.4058M	

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0489	8.68	8.67	-	-
0.0978	19.70	19.67	-	-
0.1467	32.75	32.78	-	-
0.1956	46.76	46.73	0.0000025	0.02870
0.2445	60.28	60.03	0.000180	0.04545
0.2934	73.01	72.52	0.000216	0.06632
0.3423	84.56	83.91	0.000505	0.09056
0.3912	95.26	94.03	0.000902	0.1170
0.4648	109.46	108.14	0.001156	0.1629
0.5384	122.03	120.49	0.001627	0.2132
0.6120	133.00	131.37	0.002062	0.2670
0.6856	142.62	141.00	0.002209	0.3230
0.7592	151.83	149.82	0.002500	0.3822

Table 14 - A

Fluoride Complexing of Zinc, Experiment 7 at 25°C

Initial Concentrations

$HClO_4$ = 0.02164M

$Zn(ClO_4)_2$ = 0.02779M

$Fe(ClO_4)_2$ = 0.0002371M

$Fe(ClO_4)_3$ = 0.0007299M

$NaClO_4$ = 0.3899M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 103.10

NaF = 0.5000

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0489	7.45	7.54	-	-
0.0978	16.44	16.49	-	-
0.1467	25.88	25.90	-	-
0.1956	35.31	35.32	-	-
0.2445	42.63	42.63	-	-
0.3181	56.05	55.95	0.000288	0.03398
0.3917	66.15	65.99	0.000397	0.04720
0.4653	75.00	74.71	0.000506	0.06130
0.5389	82.85	82.57	0.000578	0.07640
0.6125	89.98	89.63	0.000687	0.09212
0.8112	104.77	104.38	0.000979	0.1326
1.0099	118.63	118.15	0.001271	0.1814
1.2086	131.59	131.02	0.001528	0.2384
1.4073	142.42	141.75	0.002115	0.2960
1.6060	152.42	151.78	0.002500	0.3711

Table 15 - A

Fluoride Complexing of Zinc, Experiment 4 at 35°C

Initial Concentrations

$HClO_4$ = 0.005338M	Ionic strength = 0.5000
$Zn(ClO_4)_2$ = 0.08676M	T = 35.00 ± 0.01°C
$Fe(ClO_4)_2$ = 0.0002221M	V_o = 110.06 ml
$Fe(ClO_4)_3$ = 0.0006838M	NaF = 0.5000M
$NaClO_4$ = 0.2296M	

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	8.69	8.81	-	-
0.0988	19.47	19.59	-	-
0.1482	32.02	32.01	-	-
0.1976	45.59	45.33	0.000069	0.03107
0.2470	58.82	58.26	0.000103	0.04772
0.2964	71.29	69.48	0.000404	0.06662
0.3458	82.87	80.33	0.000601	0.08925
0.3952	93.50	90.81	0.000705	0.1159
0.4446	103.39	100.31	0.000786	0.1446
0.5185	116.80	114.10	0.000822	0.1952
0.5924	128.76	124.58	0.001506	0.2421
0.6663	139.86	134.72	0.001785	0.2953
0.7402	150.12	145.03	0.001949	0.3586
0.8141	159.69	154.04	0.002322	0.4224

Table 16 - A

Fluoride Complexing of Zinc, Experiment 5 at 35°C

Initial Concentrations

$HClO_4$ = 0.005699M

$Zn(ClO_4)_2$ = 0.02779M

$Fe(ClO_4)_2$ = 0.0002371M

$Fe(ClO_4)_3$ = 0.0007299M

$NaClO_4$ = 0.4058M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 103.10 ml

NaF = 0.5000

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	8.57	8.58	-	-
0.0988	19.04	19.03	-	-
0.1482	31.38	31.37	-	-
0.1976	44.98	44.91	0.000086	0.02977
0.2470	58.37	58.20	0.000180	0.04678
0.2964	71.07	70.69	0.000324	0.06779
0.3458	82.68	81.98	0.000469	0.09168
0.3952	93.33	92.67	0.000686	0.1195
0.4446	103.07	102.14	0.001011	0.1485
0.5185	116.57	115.58	0.001084	0.1989
0.5924	128.67	127.58	0.001302	0.2538
0.6663	140.03	138.98	0.001448	0.3165
0.7402	150.29	148.70	0.002029	0.3792
0.8141	160.05	158.24	0.002523	0.4500

Table 17 - A

Fluoride Complexing of Zinc, Experiment 6 at 35°C

Initial Concentrations

$HClO_4$ = 0.02164M

$Zn(ClO_4)_2$ = 0.02779M

$Fe(ClO_4)_2$ = 0.0002371M

$Fe(ClO_4)_3$ = 0.0007299M

$NaClO_4$ = 0.3899M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 103.10 ml

NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	7.68	7.66	0.000014	0.00211
0.0988	16.49	16.41	0.000022	0.00524
0.1482	25.73	25.59	0.000035	0.00954
0.1976	34.99	34.79	0.000159	0.01510
0.2715	47.69	47.41	0.000217	0.02537
0.3454	58.77	58.49	0.000325	0.03740
0.4193	68.42	68.17	0.000361	0.05062
0.4932	77.04	76.69	0.000433	0.06472
0.5671	84.75	84.48	0.000471	0.07987
0.7662	102.13	101.76	0.000652	0.1226
0.9653	116.77	116.36	0.000835	0.1702
1.1644	129.05	128.58	0.001018	0.2200
1.3635	140.64	139.94	0.001676	0.2758
1.5626	151.12	150.40	0.001899	0.3366

Table 18 - A

Fluoride Complexing of Copper, Experiment 3 at 15°C

Initial Concentrations

$HClO_4$ = 0.02285M

$Cu(ClO_4)_2$ = 0.08667M

$Fe(ClO_4)_2$ = 0.0002221M

$Fe(ClO_4)_3$ = 0.0006338M

$NaClO_4$ = 0.2127M

Ionic Strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 110.06 ml

NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0495	6.85	6.79	0.000019	0.00201
0.0990	14.47	14.35	0.000038	0.00409
0.1485	22.82	22.67	0.000054	0.00752
0.1980	31.53	31.26	0.000079	0.01212
0.2475	39.49	39.02	0.000115	0.01737
0.3217	49.79	49.48	0.000173	0.02646
0.3959	59.33	58.75	0.000231	0.03680
0.4701	68.71	67.86	0.000359	0.04939
0.5443	76.12	75.37	0.000511	0.06184
0.7434	91.91	90.81	0.000731	0.09451
0.9425	107.24	106.08	0.001023	0.1381
1.1416	119.71	118.13	0.001410	0.1821
1.3407	130.66	129.23	0.001541	0.2318
1.5398	139.48	137.74	0.002070	0.2767
1.7389	147.28	145.71	0.002191	0.3249

Table 19 - A

Fluoride Complexing of Copper, Experiment 4 at 15°C

Initial Concentrations

$HClO_4$ = 0.01283$\underline{M}$

$Cu(ClO_4)_2$ = 0.04543 $\underline{M}$

$Fe(ClO_4)_2$ = 0.0002326$\underline{M}$

$Fe(ClO_4)_3$ = 0.0007161$\underline{M}$

$NaClO_4$ = 0.3396$\underline{M}$

Ionic strength = 0.5000

$T = 15.00 \pm 0.01^{\circ}C$

V_o = 105.09 ml

NaF = 0.5000$\underline{M}$

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0495	8.18	8.15	0.000030	0.00216
0.0990	17.41	17.36	0.000055	0.00542
0.1485	28.01	26.90	0.000121	0.00998
0.1980	38.65	38.51	0.000158	0.01758
0.2475	48.38	48.11	0.000220	0.02593
0.2970	56.74	56.28	0.000286	0.03481
0.3465	64.78	64.23	0.000354	0.04530
0.4207	76.23	75.70	0.000419	0.06409
0.4949	82.97	82.47	0.000531	0.07753
0.5691	89.26	88.55	0.000752	0.09130
0.7682	105.07	104.27	0.001064	0.1348
0.9673	120.87	119.77	0.001510	0.1926
1.1664	134.73	133.69	0.001914	0.2595
1.3655	148.27	147.01	0.002497	0.3395

Table 20 - A

Fluoride Complexing of Copper, Experiment 5 at 15°C

Initial Concentrations

$HClO_4$ = 0.02260M

$Cu(ClO_4)_2$ = 0.04543M

$Fe(ClO_4)_2$ = 0.0002326M

$Fe(ClO_4)_3$ = 0.0007161M

$NaClO_4$ = 0.3361M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 105.09 ml

NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	(HF)/(H^+)
0.0495	7.01	7.01	-	-
0.0990	15.33	15.30	0.000033	0.004445
0.1485	24.64	24.59	0.000055	0.008450
0.1980	33.33	33.22	0.000114	0.01335
0.2475	41.76	41.62	0.000154	0.01941
0.3217	52.99	52.83	0.000220	0.02995
0.3959	62.74	63.59	0.000265	0.04318
0.4701	71.19	70.82	0.000331	0.05409
0.5443	78.58	78.22	0.000464	0.06715
0.7434	96.09	95.52	0.000753	0.1065
0.9425	109.71	109.01	0.001043	0.1478
1.1416	122.49	121.58	0.001424	0.1965
1.3407	133.71	132.65	0.001939	0.2491
1.5398	142.85	141.83	0.002300	0.3007

Table 21 - A

Fluoride Complexing of Copper, Experiment 1 at 25°C

Initial Concentrations

$HClO_4$ = 0.009988M

$Cu(ClO_4)_2$ = 0.01874M

$Fe(ClO_4)_2$ = 0.0003734M

$Fe(ClO_4)_3$ = 0.0003765M

$NaClO_4$ = 0.4305M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 101.94 ml

NaF = 0.5038M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	16.41	16.50	0.00	0.005515
0.0988	30.69	30.73	0.00	0.01310
0.1482	43.09	43.04	0.000107	0.02260
0.1976	55.02	54.90	0.000160	0.03515
0.2470	65.95	65.81	0.000268	0.05012
0.2964	76.27	76.09	0.000375	0.06810
0.3458	85.32	85.03	0.000429	0.08661
0.3952	93.57	92.87	0.000643	0.1058
0.4745	104.68	104.15	0.000858	0.1391
0.5538	114.09	113.45	0.001127	0.1720
0.6331	122.63	122.15	0.001289	0.2078
0.7124	130.76	130.21	0.001451	0.2458
0.9117	149.23	148.52	0.002100	0.3530

Table 22 - A

Fluoride Complexing of Copper, Experiment 2 at 25°C

Initial Concentrations

$HClO_4$ = 0.01263M

$Cu(ClO_4)_2$ = 0.04558M

$Fe(ClO_4)_2$ = 0.0003628M

$Fe(ClO_4)_3$ = 0.0003658M

$NaClO_4$ = 0.3473M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 104.94 ml

NaF = 0.5038M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	16.25	16.30	-	-
0.0988	30.54	30.60	-	-
0.1482	43.01	42.90	0.000044	0.02192
0.1976	54.80	54.52	0.000110	0.03379
0.2470	65.70	65.36	0.000198	0.04850
0.2964	75.95	74.79	0.000418	0.06390
0.3458	85.88	84.98	0.000506	0.08460
0.3952	93.76	92.76	0.000617	0.1033
0.4745	104.89	103.87	0.000749	0.1354
0.5538	113.42	112.22	0.000993	0.1640
0.6331	121.53	120.40	0.001126	0.1965
0.7124	129.40	128.08	0.001392	0.2310
0.9117	147.44	145.71	0.001969	0.3289

Table 23 - A

Fluoride Complexing of Copper, Experiment 4 at 25°C

Initial Concentrations

$HClO_4$ = 0.02324M	Ionic strength = 0.5000
$Cu(ClO_4)_2$ = 0.08703M	T = 25.00 ± 0.01°C
$Fe(ClO_4)_2$ = 0.0003463M	V_o = 109.93 ml
$Fe(ClO_4)_3$ = 0.0003492M	NaF = 0.5038M
$NaClO_4$ = 0.2126M	

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0494	14.05	14.10	0.00	0.004116
0.0988	24.09	24.10	0.00	0.006894
0.1482	36.37	36.33	0.0000138	0.01569
0.1976	46.13	46.04	0.0000334	0.02353
0.2470	54.33	54.12	0.0000461	0.03172
0.2964	61.72	61.45	0.0000576	0.04064
0.3761	71.86	71.52	0.000127	0.05563
0.4558	80.52	79.92	0.000300	0.07078
0.5355	88.05	87.46	0.000346	0.08677
0.6152	94.76	93.60	0.000497	0.1017
0.6949	100.86	99.95	0.000601	0.1189
0.7746	106.61	105.69	0.000648	0.1363
0.8543	112.00	110.88	0.000869	0.1536
1.0537	124.47	123.17	0.001172	0.2015
1.2531	135.74	134.00	0.001557	0.2527
1.4525	145.80	144.27	0.001921	0.3102

Table 24 - A

Fluoride Complexing of Copper, Experiment 4 at 35°C

Initial Concentrations

$HClO_4 = 0.02285\underline{M}$

$Cu(ClO_4)_2 = 0.08667\underline{M}$

$Fe(ClO_4)_2 = 0.0002221\underline{M}$

$Fe(ClO_4)_3 = 0.0006338\underline{M}$

$NaClO_4 = 0.2127\underline{M}$

Ionic strength = 0.5000

$T = 35.00 \pm 0.01^{\circ}C$

$V_o = 110.06$ ml

$NaF = 0.5000\underline{M}$

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0248	3.68	3.61	0.000018	0.00092
0.0745	11.86	11.64	0.000036	0.00341
0.1242	20.70	20.42	0.000064	0.00693
0.1739	29.81	29.38	0.000101	0.01160
0.2236	38.28	37.91	0.000115	0.02360
0.2976	49.77	49.39	0.000161	0.02714
0.3716	59.77	59.24	0.000231	0.03810
0.4456	68.51	67.82	0.000324	0.04984
0.5196	76.06	75.22	0.000429	0.06181
0.5936	82.69	81.86	0.000521	0.07420
0.7928	97.24	96.47	0.000732	0.1076
0.9920	108.26	107.84	0.000826	0.1405
1.1912	117.05	116.24	0.000921	0.1722
1.3904	124.70	124.09	0.001028	0.1998
1.5896	134.10	132.36	0.001521	0.2366
1.7888	144.57	142.63	0.001735	0.2895
1.9880	156.38	153.67	0.002103	0.3565

Table 25 - A

Fluoride Complexing of Copper, Experiment 5 at 35°C

Initial Concentrations

$HClO_4$ = 0.01283M
$Cu(ClO_4)_2$ = 0.04543M
$Fe(ClO_4)_2$ = 0.0002326M
$Fe(ClO_4)_3$ = 0.0007161M
$NaClO_4$ = 0.3396M

Ionic strength = 0.5000
T = 35.00 ± 0.01°C
V_o = 105.09 ml
NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	$(HF)/(H^+)$
0.0497	8.24	8.23	-	-
0.0994	17.84	17.96	-	-
0.1491	28.68	28.63	0.000028	0.01210
0.1988	39.85	39.65	0.000088	0.02010
0.2485	50.45	50.05	0.000154	0.02996
0.2982	60.07	59.67	0.000242	0.04147
0.3479	68.86	68.45	0.000306	0.05429
0.3976	76.58	76.05	0.000375	0.06744
0.4716	87.29	86.63	0.000486	0.08931
0.5456	96.91	96.09	0.000619	0.1129
0.6196	105.52	104.61	0.000841	0.1377
0.6936	113.28	112.29	0.001019	0.1635
0.7676	120.43	119.43	0.001152	0.1905
0.8416	126.89	125.87	0.001286	0.2180
0.9156	132.36	131.39	0.001376	0.2436
0.9896	138.24	137.09	0.001466	0.2725
1.0636	144.72	143.19	0.001667	0.3065
1.1376	150.64	149.15	0.001869	0.3430

Table 26 - A

Fluoride Complexing of Copper, Experiment 6 at 35°C

Initial Concentrations

$HClO_4$ = 0.02260M

$Cu(ClO_4)_2$ = 0.04543M

$Fe(ClO_4)_2$ = 0.0002326M

$Fe(ClO_4)_3$ = 0.0007161M

$HClO_4$ = 0.3361M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V = 105.09 ml

NaF = 0.5000M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)	$\bar{n}$	(HF)/(H^+)
0.0497	7.59	7.59	-	-
0.0994	16.21	16.24	-	-
0.1491	25.40	25.28	0.000028	0.00932
0.1988	34.47	34.32	0.000067	0.01473
0.2485	42.97	42.81	0.000110	0.02117
0.2982	50.70	50.57	0.000154	0.02838
0.3722	59.32	59.00	0.000198	0.03785
0.4462	68.59	68.12	0.000265	0.05034
0.5202	76.75	76.41	0.000331	0.06397
0.5942	84.20	83.77	0.000398	0.07810
0.6682	90.89	90.34	0.000620	0.09254
0.8674	106.56	106.22	0.000710	0.1352
1.0666	119.62	119.01	0.000933	0.1796
1.2658	131.48	130.73	0.001381	0.1950
1.4650	142.88	142.01	0.001540	0.2863
1.6642	154.34	153.11	0.001901	0.3531

Table 27 - A

Fluoride Complexing of Lead, Experiment 1 at 25°C

Initial Concentrations

$HClO_4$ = 0.01089M

$Pb(ClO_4)_2$ = 0.04562M

$Fe(ClO_4)_2$ = 0.0003628M

$Fe(ClO_4)_3$ = 0.0003658M

$NaClO_4$ = 0.3490M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 104.94 ml

NaF = 0.5038M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)
0.0472	22.61	22.67
0.0615	28.33	28.38
0.0758	33.05	33.04
0.1230	47.88	47.88
0.1702	60.92	60.91
0.2174	72.92	72.95
0.2646	83.96	84.00
0.3118	93.62	93.72
0.3590	102.29	102.29
0.4381	114.98	114.95
0.5172	125.71	127.74
0.5963	136.00	136.12
0.6754	143.50	143.58

Table 28 - A

Fluoride Complexing of Lead, Experiment 2 at 25°C

Initial Concentrations

$HClO_4$ = 0.003471M

$Pb(ClO_4)_2$ = 0.01876M

$Fe(ClO_4)_2$ = 0.0003734M

$Fe(ClO_4)_3$ = 0.0003765M

$NaClO_4$ = 0.4366M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 101.94 ml

NaF = 0.5038M

NaF added to Cells A and B (ml)	E_{B-C} (mv)	E_{A-C} (mv)
0.0472	20.70	20.80
0.0944	39.55	39.60
0.1416	58.08	58.09
0.1888	70.42	70.46
0.2360	87.92	87.93
0.2832	101.98	102.00
0.3304	113.18	113.22
0.3776	122.22	122.27
0.4248	132.57	132.54
0.4720	141.18	141.18
0.5192	149.05	149.00
0.5664	156.64	156.43
0.6136	163.94	163.71
0.6608	170.69	170.59
0.7080	176.91	176.74
0.7552	182.70	182.45

Table 29 - A

Fluoride Complexing of Mercury, Experiment 1 at 15°C

Initial Concentrations

$HClO_4$ = 0.01732M

$Hg(ClO_4)_2$ = 0.06980M

$Hg_2(ClO_4)_2$ = 0.008654M

$NaClO_4$ = 0.2648M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 135.02 ml

NaF = 0.5000M

$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.07	0.00279	0.183	0.14	0.14
2.0404	1.0008	0.13	0.00521	0.370	0.29	0.28
3.0606	1.5012	0.19	0.00770	0.535	0.44	0.41
4.0808	2.0016	0.24	0.00979	0.686	0.53	0.55
5.1010	2.5020	0.29	0.01177	0.840	0.70	0.68
6.1212	3.0024	0.34	0.01380	0.979	0.80	0.81
7.1414	3.5028	0.39	0.01588	1.115	0.93	0.94
8.1616	4.0032	0.44	0.01785	1.247	1.07	1.07
9.1818	4.5036	0.49	0.02003	1.372	1.20	1.20
10.202	5.0040	0.54	0.02192	1.490	1.33	1.32
11.222	5.5044	0.59	0.02402	1.608	1.44	1.45
12.242	6.0048	0.63	0.02565	1.718	1.57	1.57
13.263	6.5052	0.67	0.02731	1.828	1.70	1.70
14.283	7.0056	0.71	0.02900	1.931	1.83	1.82
15.303	7.5060	0.75	0.03073	2.037	1.95	1.94
16.323	8.0064	0.78	0.03195	2.137	2.07	2.06
17.343	8.5068	0.80	0.03282	2.237	2.18	2.17
18.364	9.0072	0.83	0.03407	2.336	2.30	2.29
19.384	9.5076	0.86	0.03515	2.427	2.42	2.41
20.404	10.008	0.88	0.03606	2.519	2.54	2.52
21.424	10.508	0.90	0.03698	2.604	2.65	2.63
22.444	11.009	0.93	0.03811	2.695	2.77	2.75
23.465	11.509	0.95	0.03905	2.777	2.89	2.86

Table 30 - A

Fluoride Complexing of Mercury, Experiment 2 at 15°C

Initial Concentrations

$HClO_4$ = 0.01833M	Ionic strength = 0.5000
$Hg(ClO_4)_2$ = 0.1302M	T = 15.00 ± 0.01°C
$Hg_2(ClO_4)_2$ = 0.01610M	V_o = 145.01 ml
$NaClO_4$ = 0.0428M	NaF = 0.5000M
	$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.06	0.00236	0.157	0.14	0.13
2.0404	1.0008	0.10	0.00398	0.310	0.27	0.26
3.0606	1.5012	0.15	0.00645	0.448	0.36	0.38
4.0808	2.0016	0.20	0.00816	0.584	0.50	0.51
5.1010	2.5020	0.25	0.00990	0.713	0.64	0.63
6.1212	3.0024	0.30	0.01253	0.827	0.78	0.76
7.1414	3.5028	0.35	0.01437	0.935	0.86	0.88
8.1616	4.0032	0.40	0.01625	1.055	1.02	1.00
9.1818	4.5036	0.44	0.01817	1.159	1.10	1.12
10.202	5.0040	0.48	0.01923	1.269	1.24	1.24
11.222	5.5044	0.51	0.02032	1.376	1.35	1.35
12.242	6.0048	0.55	0.02234	1.464	1.48	1.47
13.263	6.5052	0.58	0.02349	1.563	1.60	1.59
14.283	7.0056	0.61	0.02464	1.658	1.70	1.70
15.303	7.5060	0.64	0.02581	1.751	1.82	1.81
16.323	8.0064	0.67	0.02700	1.835	1.94	1.93
17.343	8.5068	0.70	0.02822	1.919	2.04	2.04
18.364	9.0072	0.73	0.02947	2.004	2.16	2.15
19.384	9.5076	0.76	0.03071	2.083	2.26	2.25
20.404	10.008	0.79	0.03198	2.160	2.37	2.36

Table 31 - A

Fluoride Complexing of Mercury, Experiment 3 at 15°C

Initial Concentrations

$HClO_4$ = 0.006734M

$Hg(ClO_4)_2$ = 0.03627M

$Hg_2(ClO_4)_2$ = 0.01795M

$NaClO_4$ = 0.3305M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 130.05 ml

NaF = 0.5000M

$HClO_4$ (added) = 0.9080M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.15	0.00607	0.432	0.16	0.15
2.0404	1.0008	0.30	0.01205	0.830	0.30	0.29
3.0606	1.5012	0.44	0.01795	1.198	0.41	0.43
4.0808	2.0016	0.57	0.02311	1.548	0.57	0.57
5.1010	2.5020	0.69	0.02811	1.883	0.71	0.71
6.1212	3.0024	0.80	0.03263	2.208	0.83	0.82
7.1414	3.5028	0.91	0.03727	2.519	0.96	0.98
8.1616	4.0032	1.01	0.04138	2.817	1.11	1.11
9.1818	4.5036	1.10	0.04526	3.115	1.24	1.24
10.202	5.0040	1.18	0.04855	3.401	1.37	1.37
11.222	5.5044	1.25	0.05155	3.663	1.51	1.50
12.242	6.0048	1.33	0.05498	3.953	1.64	1.63
13.263	6.5052	1.42	0.05888	4.202	1.77	1.76
14.283	7.0056	1.51	0.06285	4.505	1.90	1.88
15.303	7.5060	1.61	0.06879	4.695	2.02	2.01
16.323	8.0064	1.71	0.07112	4.950	2.15	2.13
17.343	8.5068	1.80	0.07501	5.181	2.26	2.25
18.364	9.0072	1.88	0.07858	5.405	2.39	2.37
19.384	9.5076	1.96	0.08224	5.618	2.52	2.49
20.404	10.008	2.04	0.08555	5.848	2.63	2.61

Table 32 - A

Fluoride Complexing of Mercury, Experiment 4 at 15°C

Initial Concentrations

$HClO_4$ = 0.01658M	Ionic strength = 0.5000
$Hg(ClO_4)_2$ = 0.03627M	T = 15.00 ± 0.01°C
$Hg_2(ClO_4)_2$ = 0.01795M	V_o = 130.05 ml
$NaClO_4$ = 0.3208M	NaF = 0.5000M
	$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.08	0.00311	0.218	0.14	0.15
2.0404	1.0008	0.14	0.00574	0.398	0.28	0.29
3.0606	1.5012	0.21	0.00845	0.582	0.44	0.43
4.0808	2.0016	0.28	0.01123	0.756	0.57	0.57
5.1010	2.5020	0.34	0.01377	0.920	0.72	0.71
6.1212	3.0024	0.40	0.01639	1.078	0.83	0.82
7.1414	3.5028	0.45	0.01844	1.228	0.98	0.98
8.1616	4.0032	0.50	0.02025	1.376	1.13	1.11
9.1818	4.5036	0.55	0.02238	1.513	1.26	1.24
10.202	5.0040	0.60	0.02459	1.647	1.37	1.37
11.222	5.5044	0.64	0.02618	1.779	1.52	1.50
12.242	6.0048	0.68	0.02780	1.901	1.65	1.63
13.263	6.5052	0.72	0.02944	2.020	1.78	1.76
14.283	7.0056	0.76	0.03113	2.136	1.87	1.88
15.303	7.5060	0.80	0.03286	2.247	2.01	2.01
16.323	8.0064	0.84	0.03426	2.358	2.13	2.13
17.343	8.5068	0.88	0.03604	2.463	2.26	2.25
18.364	9.0072	0.92	0.03785	2.564	2.38	2.37
19.384	9.5076	0.96	0.03933	2.667	2.52	2.49
20.404	10.008	1.00	0.04122	2.762	2.64	2.61
21.424	10.508	1.03	0.04238	2.857	2.74	2.73
22.444	11.009	1.07	0.04394	2.950	2.85	2.84
23.465	11.509	1.10	0.04514	3.040	2.98	2.96
24.485	12.010	1.13	0.04636	3.115	3.09	3.07
25.505	12.510	1.16	0.04800	3.205	3.20	3.18

Table 33 - A

Fluoride Complexing of Mercury, Experiment 9 at 25°C

Initial Concentrations

$HClO_4$ = 0.01732M

$Hg(ClO_4)_2$ = 0.06980M

$Hg_2(ClO_4)_2$ = 0.008654M

$NaClO_4$ = 0.2648M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 135.02 ml

NaF = 0.5000M

$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B}, (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.10	0.00397	0.182	0.14	0.15
2.0404	1.0008	0.13	0.00506	0.382	0.28	0.28
3.0606	1.5012	0.19	0.00740	0.524	0.43	0.42
4.0808	2.0016	0.23	0.00902	0.700	0.58	0.56
5.1010	2.5020	0.28	0.01099	0.852	0.70	0.70
6.1212	3.0024	0.33	0.01301	0.998	0.85	0.84
7.1414	3.5028	0.38	0.01492	1.142	0.98	0.97
8.1616	4.0032	0.43	0.01687	1.277	1.10	1.10
9.1818	4.5036	0.48	0.01886	1.403	1.27	1.24
10.202	5.0040	0.53	0.02091	1.527	1.38	1.37
11.222	5.5044	0.57	0.02249	1.650	1.50	1.50
12.242	6.0048	0.61	0.02409	1.761	1.64	1.63
13.263	6.5052	0.65	0.02556	1.883	1.76	1.75
14.283	7.0056	0.68	0.02688	1.996	1.90	1.88
15.303	7.5060	0.72	0.02840	2.101	1.97	2.00
16.323	8.0064	0.76	0.02995	2.203	2.16	2.13
17.343	8.5068	0.79	0.03116	2.304	2.27	2.25
18.364	9.0072	0.82	0.03239	2.404	2.39	2.37
19.384	9.5076	0.86	0.03402	2.494	2.51	2.49
20.404	10.008	0.90	0.03567	2.584	2.64	2.61
21.424	10.508	0.93	0.03679	2.674	2.74	2.72
22.444	11.009	0.96	0.03811	2.770	2.87	2.84
23.465	11.509	1.00	0.03964	2.841	2.98	2.96

Table 34 - A

Fluoride Complexing of Mercury, Experiment 10 at 25°C

Initial Concentrations

$HClO_4$ = 0.01833M

$Hg(ClO_4)_2$ = 0.1302M

$Hg_2(ClO_4)_2$ = 0.01610M

$NaClO_4$ = 0.0428M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 145.01 ml

NaF = 0.5000M

$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.07	0.00236	0.159	0.14	0.14
2.0404	1.0008	0.10	0.00398	0.313	0.26	0.26
3.0606	1.5012	0.15	0.00564	0.461	0.41	0.40
4.0808	2.0016	0.20	0.00734	0.599	0.53	0.52
5.1010	2.5020	0.25	0.00990	0.725	0.65	0.65
6.1212	3.0024	0.30	0.01169	0.855	0.77	0.78
7.1414	3.5028	0.35	0.01351	0.970	0.92	0.91
8.1616	4.0032	0.38	0.01452	1.089	1.04	1.03
9.1818	4.5036	0.42	0.01641	1.198	1.15	1.15
10.202	5.0040	0.45	0.01834	1.300	1.29	1.28
11.222	5.5044	0.48	0.01852	1.418	1.40	1.40
12.242	6.0048	0.51	0.01960	1.524	1.53	1.52
13.263	6.5052	0.55	0.02164	1.613	1.65	1.64
14.283	7.0056	0.59	0.02277	1.709	1.78	1.76
15.303	7.5060	0.62	0.02392	1.805	1.88	1.87
16.323	8.0064	0.65	0.02509	1.894	1.99	1.99
17.343	8.5068	0.68	0.02629	1.980	2.11	2.10
18.364	9.0072	0.71	0.02751	2.066	2.23	2.22
19.384	9.5076	0.74	0.02874	2.151	2.36	2.34
20.404	10.008	0.77	0.02998	2.232	2.47	2.45

Table 35 - A

Fluoride Complexing of Mercury, Experiment 11 at 25°C

Initial Concentrations

$HClO_4$ = 0.006734M

$Hg(ClO_4)_2$ = 0.003627M

$Hg_2(ClO_4)_2$ = 0.01795M

$NaClO_4$ = 0.3305M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 130.05 ml

NaF = 0.5000M

$HClO_4$ (added) = 0.9080M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.14	0.00549	0.448	0.16	0.15
2.0404	1.0008	0.28	0.01086	0.870	0.31	0.30
3.0606	1.5012	0.43	0.01673	1.256	0.45	0.45
4.0808	2.0016	0.58	0.02280	1.626	0.59	0.59
5.1010	2.5020	0.69	0.02716	1.992	0.74	0.73
6.1212	3.0024	0.79	0.03134	2.336	0.86	0.87
7.1414	3.5028	0.87	0.03431	2.681	1.01	1.01
8.1616	4.0032	0.95	0.03769	3.012	1.16	1.15
9.1818	4.5036	1.02	0.04048	3.333	1.29	1.28
10.202	5.0040	1.10	0.04369	3.650	1.43	1.42
11.222	5.5044	1.19	0.04732	3.968	1.55	1.55
12.242	6.0048	1.30	0.05175	4.219	1.69	1.68
13.263	6.5052	1.42	0.05669	4.505	1.82	1.82
14.283	7.0056	1.54	0.06173	4.785	1.95	1.95
15.303	7.5060	1.65	0.06619	5.050	2.07	2.07
16.323	8.0064	1.77	0.07112	5.319	2.20	2.20
17.343	8.5068	1.87	0.07540	5.525	2.34	2.33
18.364	9.0072	1.95	0.07897	5.814	2.46	2.45
19.384	9.5076	2.00	0.08102	6.061	2.59	2.57
20.404	10.008	2.05	0.08308	6.329	2.72	2.70

Table 36 - A

Fluoride Complexing of Mercury, Experiment 12 at 25°C

Initial Concentrations

$HClO_4 = 0.01658\underline{M}$

$Hg(ClO_4)_2 = 0.03627\underline{M}$

$Hg_2(ClO_4)_2 = 0.01795\underline{M}$

$NaClO_4 = 0.3208\underline{M}$

Ionic strength = 0.5000

$T = 25.00 \pm 0.01^{\circ}C$

$V_o = 130.05$ ml

$NaF = 0.5000\underline{M}$

$HClO_4$ (added) = $1.0625\underline{M}$

NaF added To Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.07	0.00283	0.207	0.14	0.15
2.0404	1.0008	0.13	0.00517	0.406	0.31	0.30
3.0606	1.5012	0.20	0.00786	0.592	0.46	0.45
4.0808	2.0016	0.26	0.01003	0.772	0.59	0.59
5.1010	2.5020	0.32	0.01256	0.941	0.72	0.73
6.1212	3.0024	0.38	0.01485	1.103	0.86	0.87
7.1414	3.5028	0.44	0.01719	1.258	1.02	1.01
8.1616	4.0032	0.49	0.01930	1.408	1.16	1.15
9.1818	4.5036	0.54	0.02110	1.550	1.28	1.28
10.202	5.0040	0.59	0.02329	1.689	1.44	1.42
11.222	5.5044	0.63	0.02485	1.832	1.56	1.55
12.242	6.0048	0.67	0.02645	1.953	1.70	1.68
13.263	6.5052	0.71	0.02808	2.075	1.84	1.82
14.283	7.0056	0.74	0.02907	2.198	1.97	1.95
15.303	7.5060	0.77	0.03042	2.320	2.08	2.07
16.323	8.0064	0.81	0.03214	2.433	2.21	2.20
17.343	8.5068	0.84	0.03317	2.545	2.35	2.33
18.364	9.0072	0.88	0.03495	2.646	2.47	2.45
19.384	9.5076	0.91	0.03603	2.747	2.59	2.57
20.404	10.008	0.94	0.03713	2.857	2.72	2.70
21.424	10.508	0.97	0.03861	2.950	2.82	2.82
22.444	11.009	1.01	0.04013	3.049	2.95	2.94
23.465	11.509	1.04	0.04167	3.135	3.08	3.06
24.485	12.010	1.08	0.04285	3.226	3.19	3.17
25.505	12.510	1.11	0.04405	3.311	3.31	3.29

Table 37 - A

Fluoride Complexing of Mercury, Experiment 1 at 35°C

Initial Concentrations

$HClO_4$ = 0.01732M

$Hg(ClO_4)_2$ = 0.06980M

$Hg_2(ClO_4)_2$ = 0.008654M

$NaClO_4$ = 0.2648M

Ionic strength = 0.5000M

T = 35.00 ± 0.01°C

V_o = 135.02 ml

NaF = 0.5000M

$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.06	0.00220	0.193	0.14	0.15
2.0404	1.0008	0.12	0.00447	0.389	0.29	0.30
3.0606	1.5012	0.17	0.00648	0.559	0.44	0.44
4.0808	2.0016	0.22	0.00825	0.719	0.59	0.59
5.1010	2.5020	0.26	0.00989	0.877	0.72	0.73
6.1212	3.0024	0.30	0.01142	1.035	0.87	0.87
7.1414	3.5028	0.34	0.01283	1.179	1.01	1.01
8.1616	4.0032	0.39	0.01475	1.317	1.16	1.15
9.1818	4.5036	0.43	0.01639	1.453	1.30	1.28
10.202	5.0040	0.48	0.01823	1.585	1.41	1.42
11.222	5.5044	0.52	0.01977	1.712	1.56	1.55
12.242	6.0048	0.56	0.02134	1.835	1.69	1.68
13.263	6.5052	0.60	0.02277	1.953	1.82	1.81
14.283	7.0056	0.63	0.02405	2.170	1.94	1.94
15.303	7.5060	0.66	0.02518	2.183	2.08	2.07
16.323	8.0064	0.69	0.02633	2.294	2.23	2.20
17.343	8.5068	0.72	0.02750	2.398	2.34	2.33
18.364	9.0072	0.75	0.02868	2.506	2.46	2.45
19.384	9.5076	0.78	0.02990	2.604	2.59	2.57
20.404	10.008	0.80	0.03056	2.703	2.72	2.70
21.424	10.508	0.83	0.03180	2.801	2.84	2.82
22.444	11.009	0.85	0.03249	2.899	2.96	2.94
23.465	11.509	0.88	0.03376	2.985	3.08	3.06

Table 38 - A

Fluoride Complexing of Mercury, Experiment 2 at 35°C

Initial Concentrations

$HClO_4$ = 0.01833M

$Hg(ClO_4)_2$ = 0.1302M

$Hg_2(ClO_4)_2$ = 0.01610M

$NaClO_4$ = 0.0428M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 145.01 ml

NaF = 0.5000 M

$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.05	0.00157	0.167	0.14	0.14
2.0404	1.0008	0.09	0.00318	0.325	0.28	0.28
3.0606	1.5012	0.14	0.00564	0.467	0.40	0.41
4.0808	2.0016	0.18	0.00734	0.610	0.54	0.55
5.1010	2.5020	0.23	0.00907	0.741	0.69	0.68
6.1212	3.0024	0.27	0.01000	0.877	0.81	0.81
7.1414	3.5028	0.32	0.01180	1.003	0.94	0.94
8.1616	4.0032	0.35	0.01279	1.129	1.08	1.07
9.1818	4.5036	0.39	0.01465	1.242	1.21	1.20
10.202	5.0040	0.42	0.01568	1.357	1.32	1.32
11.222	5.5044	0.45	0.01762	1.462	1.45	1.45
12.242	6.0048	0.48	0.01870	1.567	1.58	1.57
13.263	6.5052	0.51	0.01980	1.675	1.71	1.70
14.283	7.0056	0.54	0.02091	1.773	1.83	1.82
15.303	7.5060	0.57	0.02204	1.872	1.95	1.94
16.323	8.0064	0.60	0.02319	1.969	2.07	2.06
17.343	8.5068	0.63	0.02437	2.058	2.20	2.18
18.364	9.0072	0.66	0.02557	2.146	2.31	2.30
19.384	9.5076	0.69	0.02676	2.232	2.42	2.41
20.404	10.008	0.71	0.02700	2.325	2.54	2.53

Table 39 - A

Fluoride Complexing of Mercury, Experiment 3 at 35°C

Initial Concentrations

$HClO_4$ = 0.006734M

$Hg(ClO_4)_2$ = 0.003627M

$Hg_2(ClO_4)_2$ = 0.01795M

$NaClO_4$ = 0.3305M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 130.05 ml

NaF = 0.5000M

$HClO_4$ (added) = 0.9080M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^+}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.13	0.00491	0.470	0.16	0.16
2.0404	1.0008	0.26	0.00998	0.915	0.32	0.31
3.0606	1.5012	0.40	0.01521	1.333	0.45	0.46
4.0808	2.0016	0.53	0.02001	1.739	0.62	0.61
5.1010	2.5020	0.66	0.02526	2.137	0.75	0.75
6.1212	3.0024	0.78	0.02972	2.513	0.90	0.90
7.1414	3.5028	0.89	0.03398	2.882	1.05	1.04
8.1616	4.0032	0.99	0.03803	3.247	1.20	1.19
9.1818	4.5036	1.08	0.04150	3.597	1.34	1.33
10.202	5.0040	1.16	0.04473	3.937	1.48	1.47
11.222	5.5044	1.23	0.04732	4.292	1.62	1.61
12.242	6.0048	1.30	0.05032	4.630	1.75	1.74
13.263	6.5052	1.37	0.05304	4.950	1.88	1.88
14.283	7.0056	1.44	0.05581	5.291	2.02	2.01
15.303	7.5060	1.53	0.05941	5.617	2.15	2.14
16.323	8.0064	1.63	0.06344	5.917	2.29	2.28
17.343	8.5068	1.75	0.06798	6.211	2.41	2.40
18.364	9.0072	1.87	0.07300	6.493	2.54	2.54
19.384	9.5076	1.94	0.07577	6.757	2.66	2.66
20.404	10.008	1.99	0.07777	7.092	2.79	2.79

Table 40 - A

Fluoride Complexing of Mercury, Experiment 4 at 35°C

Initial Concentrations

$HClO_4$ = 0.01658M	Ionic strength = 0.5000
$Hg(ClO_4)_2$ = 0.03627M	T = 35.00 ± 0.01°C
$Hg_2(ClO_4)_2$ = 0.01795M	V_o = 130.05 ml
$NaClO_4$ = 0.3208M	NaF = 0.5000M
	$HClO_4$ (added) = 1.0625M

NaF added to Cells A and B (ml)	$HClO_4$ added to Cells A and B (ml)	ΔE_{A-B} (mv)	$\left(\frac{HgF^{++}}{Hg^{++}}\right)$	$\left(\frac{HF}{H^+}\right)$	ΔE_{B-C} (mv)	$\frac{RT}{2F} \ln \frac{(Hg_2^{++})_B}{(Hg_2^{++})_C}$
1.0202	0.5004	0.06	0.00226	0.212	0.16	0.16
2.0404	1.0008	0.12	0.00459	0.414	0.32	0.31
3.0606	1.5012	0.18	0.00669	0.606	0.45	0.46
4.0808	2.0016	0.24	0.00914	0.789	0.62	0.61
5.1010	2.5020	0.30	0.01135	0.966	0.75	0.75
6.1212	3.0024	0.35	0.01362	1.133	0.91	0.90
7.1414	3.5028	0.40	0.01532	1.294	1.05	1.04
8.1616	4.0032	0.45	0.01708	1.451	1.19	1.19
9.1818	4.5036	0.49	0.01853	1.603	1.34	1.33
10.202	5.0040	0.53	0.02003	1.748	1.48	1.47
11.222	5.5044	0.57	0.02156	1.887	1.62	1.61
12.242	6.0048	0.61	0.02311	2.024	1.74	1.74
13.263	6.5052	0.65	0.02470	2.155	1.90	1.88
14.283	7.0056	0.69	0.02632	2.283	2.02	2.01
15.303	7.5060	0.73	0.02798	2.398	2.15	2.14
16.323	8.0064	0.77	0.02932	2.525	2.30	2.28
17.343	8.5068	0.80	0.03068	2.639	2.42	2.41
18.364	9.0072	0.83	0.03171	2.755	2.56	2.54
19.384	9.5076	0.86	0.03275	2.865	2.68	2.66
20.404	10.008	0.89	0.03382	2.967	2.80	2.79
21.424	10.508	0.91	0.03488	3.077	2.93	2.91
22.444	11.009	0.94	0.03597	3.175	3.06	3.04
23.465	11.509	0.96	0.03670	3.279	3.18	3.16
24.485	12.010	0.99	0.03782	3.367	3.31	3.28
25.505	12.510	1.01	0.03897	3.472	3.43	3.40

Table 41 - A

Fluoride Complexing of Silver, Experiment 1 at 15°C

Initial Concentrations

$HClO_4$ = 0.02145M

$AgClO_4$ = 0.04190M

$NaClO_4$ = 0.4368M

Ionic strength = 0.5000M

T = 15.00 ± 0.01°C

V_o = 100.11 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.00	19.388	1.14
2.0408	0.02	20.408	1.20
3.0612	0.04	21.428	1.26
4.0816	0.08	22.449	1.32
5.1020	0.13	23.469	1.38
6.1224	0.20	24.490	1.44
7.1428	0.27	25.510	1.50
8.1632	0.34	26.530	1.56
9.1836	0.42	27.551	1.62
10.204	0.49	28.571	1.68
11.224	0.57	29.592	1.74
12.245	0.65	30.612	1.80
13.265	0.72	31.632	1.85
14.286	0.80	32.653	1.91
15.306	0.87	33.673	1.96
16.326	0.95	34.694	2.01
17.347	1.02	35.714	2.06
18.367	1.08		

Table 42 - A

Fluoride Complexing of Silver, Experiment 2 at 15°C

Initial Concentrations

$HClO_4$ = 0.004849M

$AgClO_4$ = 0.21001M

$NaClO_4$ = 0.2851M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 100.11 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.03	21.428	1.35	41.836	2.33
2.0408	0.09	22.449	1.40	42.857	2.37
3.0612	0.17	23.469	1.45	43.877	2.41
4.0816	0.25	24.490	1.50	44.898	2.45
5.1020	0.32	25.510	1.55	45.918	2.49
6.1224	0.39	26.530	1.60	46.938	2.52
7.1428	0.46	27.551	1.65	47.959	2.56
8.1632	0.53	28.551	1.70	48.979	2.59
9.1836	0.60	29.592	1.75	50.000	2.63
10.204	0.67	30.612	1.80	51.020	2.66
11.224	0.74	31.632	1.85	52.040	2.69
12.245	0.81	32.653	1.90	53.061	2.72
13.265	0.87	33.673	1.95	54.081	2.75
14.286	0.93	34.694	2.00	55.102	2.78
15.306	1.00	35.714	2.05	56.122	2.81
16.326	1.06	36.734	2.10	57.142	2.84
17.347	1.13	37.755	2.15	58.163	2.87
18.367	1.19	38.775	2.19	59.183	2.90
19.388	1.25	39.796	2.24	60.204	2.93
20.408	1.30	40.816	2.28	61.224	2.96

Table 43 - A

Fluoride Complexing of Silver, Experiment 3 at 15°C

Initial Concentrations

$HClO_4$ = 0.0009675M

$AgClO_4$ = 0.04190M

$NaClO_4$ = 0.4571M

Ionic strength = 0.5000

T = 15.00 ± 0.01°C

V_o = 100.11 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.08	19.388	1.44
2.0408	0.17	20.408	1.50
3.0612	0.26	21.428	1.56
4.0816	0.34	22.449	1.63
5.1020	0.42	23.469	1.69
6.1224	0.51	24.490	1.75
7.1428	0.59	25.510	1.81
8.1632	0.67	26.530	1.87
9.1836	0.74	27.551	1.93
10.204	0.81	28.571	1.98
11.224	0.88	29.592	2.03
12.245	0.95	30.612	2.08
13.265	1.02	31.632	2.13
14.286	1.09	32.653	2.17
15.306	1.16	33.673	2.21
16.326	1.23	34.694	2.26
17.347	1.30	35.714	2.30
18.367	1.37		

Table 44 - A

Fluoride Complexing of Silver, Experiment 1 at 25°C

Initial Concentrations

$HClO_4$ = 0.04126M

$AgClO_4$ = 0.10528M

$NaClO_4$ = 0.3534M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 99.95 ml

NaF = 0.5004M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.020	0.00	16.320	0.57
2.040	0.00	17.340	0.63
3.060	0.00	18.360	0.69
4.080	0.00	19.380	0.75
5.100	0.00	20.400	0.80
6.120	0.03	21.420	0.86
7.140	0.06	22.440	0.92
8.160	0.10	23.460	0.97
9.180	0.15	24.480	1.02
10.200	0.19	25.500	1.07
11.220	0.26	26.520	1.13
12.240	0.32	27.540	1.18
13.260	0.38	28.560	1.23
14.280	0.44	29.580	1.28
15.300	0.50	30.600	1.34

Table 45 - A

Fluoride Complexing of Silver, Experiment 2 at 25°C

Initial Concentrations

$HClO_4$ = 0.004862$\underline{M}$

$AgClO_4$ = 0.21056$\underline{M}$

$NaClO_4$ = 0.2846$\underline{M}$

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 99.95

NaF = 0.5004$\underline{M}$

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.020	0.03	21.420	1.29	41.820	2.20
2.040	0.08	22.440	1.34	42.840	2.25
3.060	0.15	23.460	1.40	43.860	2.28
4.080	0.23	24.480	1.44	44.880	2.31
5.100	0.30	25.500	1.48	45.900	2.35
6.120	0.36	26.520	1.52	46.920	2.38
7.140	0.43	27.540	1.55	47.940	2.41
8.160	0.49	28.560	1.58	48.960	2.44
9.180	0.57	29.580	1.61	49.980	2.47
10.200	0.63	30.600	1.66	51.000	2.50
11.220	0.70	31.620	1.71	52.020	2.54
12.240	0.76	32.640	1.76	53.040	2.58
13.260	0.82	33.660	1.82	54.060	2.62
14.280	0.87	34.680	1.87	55.080	2.65
15.300	0.95	35.700	1.92	56.100	2.68
16.320	1.00	36.720	1.97	57.120	2.72
17.340	1.06	37.740	2.03	58.140	2.75
18.360	1.12	38.760	2.08	59.160	2.79
19.380	1.17	39.780	2.12	60.180	2.82
20.400	1.23	40.800	2.16	61.200	2.85

Table 46 - A

Fluoride Complexing of Silver, Experiment 3 at 25°C

Initial Concentrations

$HClO_4$ = 0.0009704M

$AgClO_4$ = 0.04203M

$NaClO_4$ = 0.4571M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 99.95 ml

NaF = 0.5004M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.021	0.07	16.336	1.10
2.042	0.15	17.357	1.16
3.063	0.23	18.378	1.21
4.084	0.30	19.399	1.27
5.105	0.39	20.420	1.33
6.126	0.46	21.441	1.38
7.147	0.53	22.462	1.43
8.168	0.60	23.483	1.47
9.189	0.66	24.504	1.52
10.210	0.72	25.523	1.57
11.231	0.79	26.546	1.63
12.252	0.86	27.567	1.68
13.273	0.92	28.588	1.72
14.294	0.99	29.609	1.76
15.315	1.05	30.630	1.81

Table 47 - A

Fluoride Complexing of Silver, Experiment 1 at 35°C

Initial Concentrations

$HClO_4$ = 0.02145M

$AgClO_4$ = 0.04190M

$NaClO_4$ = 0.4368M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 100.11 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.00	19.388	0.87
2.0408	0.01	20.408	0.93
3.0612	0.02	21.428	0.98
4.0816	0.05	22.449	1.03
5.1020	0.09	23.469	1.08
6.1224	0.14	24.490	1.13
7.1428	0.19	25.510	1.17
8.1632	0.25	26.530	1.21
9.1836	0.32	27.551	1.25
10.204	0.39	28.571	1.29
11.224	0.45	29.592	1.34
12.245	0.50	30.612	1.39
13.265	0.55	31.632	1.43
14.286	0.60	32.653	1.48
15.306	0.65	33.673	1.52
16.326	0.71	34.694	1.56
17.347	0.76	35.714	1.60
18.367	0.82		

Table 48 - A

Fluoride Complexing of Silver, Experiment 2 at 35°C

<u>Initial Concentrations</u>

$HClO_4 = 0.004849\underline{M}$

$AgClO_4 = 0.21001\underline{M}$

$NaClO_4 = 0.2851\underline{M}$

Ionic strength = 0.5000

$T = 35.00 \pm 0.01^{\circ}C$

$V_o = 100.11$ ml

$NaF = 0.5000\underline{M}$

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.03	21.428	1.10	41.836	1.89
2.0408	0.08	22.449	1.15	42.857	1.92
3.0612	0.14	23.469	1.19	43.877	1.95
4.0816	0.20	24.490	1.24	44.898	1.99
5.1020	0.26	25.510	1.28	45.918	2.02
6.1224	0.32	26.530	1.33	46.938	2.06
7.1428	0.38	27.551	1.37	47.959	2.09
8.1632	0.43	28.571	1.42	48.979	2.13
9.1836	0.49	29.592	1.46	50.000	2.16
10.204	0.54	30.612	1.50	51.020	2.19
11.224	0.60	31.632	1.54	52.040	2.23
12.245	0.66	32.653	1.58	53.061	2.26
13.265	0.71	33.673	1.62	54.081	2.30
14.286	0.76	34.694	1.65	55.102	2.33
15.306	0.82	35.714	1.69	56.122	2.36
16.326	0.87	36.734	1.72	57.142	2.39
17.347	0.92	37.755	1.76	58.163	2.43
18.367	0.97	38.775	1.79	59.183	2.46
19.388	1.02	39.796	1.82	60.204	2.48
20.408	1.06	40.816	1.86	61.224	2.50

Table 49 - A

Fluoride Complexing of Silver, Experiment 3 at 35°C

Initial Concentrations

$HClO_4$ = 0.0009675M

$AgClO_4$ = 0.04190M

$NaClO_4$ = 0.4571M

Ionic strength = 0.5000

T = 35.00 ± 0.01°C

V_o = 100.11 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
1.0204	0.06	19.388	1.13
2.0408	0.13	20.408	1.18
3.0612	0.20	21.428	1.23
4.0816	0.27	22.449	1.28
5.1020	0.34	23.469	1.32
6.1224	0.40	24.490	1.37
7.1428	0.46	25.510	1.41
8.1632	0.52	26.530	1.45
9.1836	0.58	27.551	1.49
10.204	0.64	28.571	1.53
11.224	0.70	29.592	1.57
12.245	0.75	30.612	1.60
13.265	0.81	31.632	1.64
14.286	0.86	32.653	1.67
15.306	0.92	33.673	1.71
16.326	0.97	34.694	1.74
17.347	1.02	35.714	1.77
18.367	1.08		

Table 50 - A

Fluoride Complexing of Sn(II), Experiment 4 at 25°C

Initial Concentrations

$HClO_4$ = 0.1605M

$Sn(ClO_4)_2$ = 0.03947M

$NaClO_4$ = 0.2214M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 133.15 ml

NaF = 0.5000

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1995	0.15	4.3890	4.93	13.363	17.58	29.813	41.67
0.3990	0.32	4.5885	5.18	13.861	18.34	30.810	43.03
0.5985	0.51	4.7880	5.44	14.360	19.13	31.807	44.39
0.7980	0.70	4.9875	5.69	14.858	19.92	32.804	45.73
0.9975	0.94	5.1870	5.94	15.357	20.67	33.801	47.11
1.1970	1.16	5.3865	6.17	15.855	21.44	34.798	48.50
1.3965	1.38	5.8850	6.79	16.354	22.21	35.795	49.88
1.5960	1.61	6.3835	7.47	16.852	22.98	36.792	50.25
1.7955	1.85	6.8820	8.12	17.351	23.75	37.789	52.63
1.9950	2.08	7.3805	8.79	17.849	24.52	38.786	54.02
2.1945	2.31	7.8790	9.47	18.846	26.02	39.783	55.42
2.3940	2.55	8.3775	10.16	19.843	27.51	40.780	56.87
2.5935	2.78	8.8760	10.85	20.840	29.00	41.777	58.31
2.7930	3.00	9.3745	11.57	21.837	30.45	42.774	59.75
2.9925	3.22	9.8730	12.31	22.834	31.90	43.771	61.25
3.1920	3.43	10.372	13.07	23.831	33.34	44.768	62.76
3.3915	3.65	10.870	13.81	24.828	34.73	45.765	64.28
3.5910	3.89	11.369	14.55	25.825	36.15	46.762	65.86
3.7905	4.16	11.867	15.30	26.822	37.52	47.759	67.42
3.9900	4.42	12.366	16.04	27.819	38.90	48.756	69.04
4.1895	4.68	12.864	16.81	28.816	40.28	49.753	70.68

Table 51 - A

Fluoride Complexing of Sn(II), Experiment 5 at 25°C

Initial Concentrations

$HClO_4$ = 0.1633M

$Sn(ClO_4)_2$ = 0.09541M

$NaClO_4$ = 0.0506M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 136.85 ml

NaF = 0.5000M

NaF added (ml)	ΔE (ml)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1994	0.11	12.263	6.66	25.224	15.94	38.185	27.23
0.3988	0.22	12.762	6.99	25.723	16.35	38.684	27.69
0.5982	0.31	13.260	7.31	26.221	16.76	39.182	28.14
0.7976	0.40	13.759	7.61	26.720	17.17	39.681	28.58
1.2961	0.65	14.257	7.94	27.218	17.59	40.179	29.03
1.7946	0.87	14.756	8.26	27.717	18.00	40.678	29.49
2.2931	1.11	15.254	8.57	28.215	18.44	41.176	29.95
2.7916	1.37	15.753	8.90	28.714	18.86	41.675	30.41
3.2901	1.64	16.251	9.26	29.212	19.28	42.173	30.85
3.7886	1.90	16.750	9.58	29.711	19.70	42.672	31.30
4.2871	2.16	17.248	9.90	30.209	20.13	43.170	31.75
4.7856	2.41	17.747	10.24	30.708	20.56	43.669	32.21
5.2841	2.66	18.245	10.59	31.206	21.00	44.167	32.67
5.7826	2.92	18.744	10.94	31.705	21.44	44.666	33.11
6.2811	3.18	19.242	11.32	32.203	21.88	45.164	33.56
6.7796	3.45	19.741	11.70	32.702	22.32	45.663	34.01
7.2781	3.74	20.239	12.06	33.200	22.76	46.161	34.46
7.7766	4.03	20.738	12.44	33.699	23.20	46.660	34.91
8.2751	4.29	21.236	12.82	34.197	23.64	47.158	35.36
8.7736	4.57	21.735	13.20	34.696	24.09	47.657	35.80
9.2721	4.85	22.233	13.59	35.194	24.53	48.155	36.25
9.7706	5.13	22.732	13.98	35.693	24.98	48.654	36.70
10.269	5.41	23.230	14.35	36.191	25.43	49.152	37.14
10.768	5.68	23.729	14.74	36.690	25.88	49.651	37.59
11.266	5.98	24.227	15.13	37.188	26.33	50.149	38.03
11.765	6.33	24.726	15.54	37.687	26.79		

Table 52 - A

Fluoride Complexing of Sn(II), Experiment 7 at 25°C

Initial Concentrations

$HClO_4$ = 0.08965M

$Sn(ClO_4)_2$ = 0.06849M

$NaClO_4$ = 0.2047M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 126.16 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1994	0.16	7.4780	6.43	21.937	22.96	36.397	43.33
0.3988	0.31	7.9766	6.92	22.436	23.62	36.895	44.10
0.5982	0.45	8.4752	7.41	22.935	24.30	37.394	44.88
0.7976	0.60	8.9738	7.90	23.433	24.98	37.893	45.66
0.9970	0.76	9.4724	8.41	23.932	25.64	38.391	46.45
1.1964	0.92	9.9710	8.93	24.430	26.29	38.890	47.24
1.3958	1.08	10.470	9.46	24.929	26.97	39.388	48.04
1.5952	1.24	10.968	9.99	25.428	27.64	39.887	48.84
1.7946	1.36	11.467	10.50	25.926	28.31	40.386	49.64
1.9940	1.54	11.965	11.03	26.425	28.98	40.884	50.47
2.1934	1.71	12.464	11.58	26.923	29.66	41.383	51.30
2.3928	1.86	12.963	12.11	27.422	30.33	41.881	52.13
2.5922	2.01	13.461	12.66	27.921	31.01	42.380	52.97
2.7916	2.17	13.960	13.22	28.419	31.70	42.879	53.81
2.9910	2.35	14.458	13.77	28.918	32.40	43.377	54.67
3.1904	2.52	14.957	14.32	29.416	33.09	43.876	55.53
3.3898	2.69	15.456	14.91	29.915	33.78	44.374	56.40
3.5892	2.86	15.954	15.48	30.414	34.47	44.873	57.28
3.7886	3.02	16.453	16.06	30.912	35.18	45.372	58.16
3.9880	3.20	16.951	16.64	31.411	35.90	45.870	59.06
4.1874	3.38	17.450	17.23	31.909	36.61	46.369	59.96
4.3864	3.55	17.949	17.84	32.408	37.34	46.867	60.87
4.5862	3.73	18.447	18.47	32.907	38.08	47.366	61.78
4.7856	3.91	18.946	19.11	33.405	38.82	47.865	62.70
4.9850	4.09	19.444	19.73	33.904	39.55	48.363	63.63
5.4836	4.56	19.943	20.38	34.402	40.29	48.862	64.57
5.9822	5.01	20.442	21.00	34.901	41.05	49.360	65.55
6.4808	5.48	20.940	21.65	35.400	41.81	49.859	66.55
6.9794	5.95	21.439	22.29	35.898	42.56	50.358	67.55

Table 53 - A

Fluoride Complexing of Sn(II), Experiment 8 at 25°C

Initial Concentrations

$HClO_4$ = 0.4225M

$Sn(ClO_4)_2$ = 0.01580M

$NaClO_4$ = 0.00M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 110.57 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1983	0.21	4.9575	8.04	12.441	18.49	24.465	30.27
0.3966	0.48	5.1558	8.36	12.942	19.07	24.966	30.69
0.5949	0.77	5.3541	8.67	13.443	19.65	25.467	31.11
0.7932	1.03	5.5524	8.99	13.944	20.22	25.968	31.52
0.9915	1.35	5.7507	9.31	14.445	20.78	26.469	31.93
1.1898	1.67	5.9490	9.62	14.946	21.32	26.970	32.33
1.3881	2.01	6.1473	9.93	15.447	21.86	27.471	32.73
1.5864	2.33	6.3456	10.24	15.948	22.38	27.972	33.12
1.7847	2.68	6.5439	10.54	16.449	22.90	28.473	33.51
1.9830	3.02	6.7422	10.85	16.950	23.41	28.974	33.89
2.1813	3.37	6.9405	11.15	17.451	23.92	29.475	34.28
2.3796	3.71	7.1388	11.45	17.952	24.42	29.976	34.67
2.5779	4.06	7.3371	11.75	18.453	24.92	30.477	35.05
2.7762	4.41	7.5354	12.04	18.954	25.39	30.978	35.42
2.9745	4.75	7.7337	12.34	19.455	25.86	31.479	35.80
3.1728	5.09	7.9320	12.64	19.956	26.32	31.980	36.17
3.3711	5.43	8.4330	13.35	20.457	26.78	32.481	36.55
3.5694	5.76	8.9340	14.06	20.958	27.23	32.982	36.92
3.7677	6.10	9.4350	14.71	21.459	27.68	33.483	37.28
3.9660	6.43	9.9360	15.38	21.960	28.12	33.984	37.65
4.1643	6.74	10.437	16.02	22.461	28.56	34.485	38.01
4.3626	7.06	10.938	16.66	22.962	29.00	34.986	38.36
4.5609	7.40	11.439	17.28	23.463	29.42		
4.7592	7.72	11.940	17.89	23.964	29.85		

Table 54 - A

Fluoride Complexing of Sn(II), Experiment 9 at 25°C

Initial Concentrations

$HClO_4$ = 0.3998M

$Sn(ClO_4)_2$ = 0.03359M

$NaClO_4$ = 0.00M

Ionic strength = 0.5000

T = 25.00 ± 0.01°C

V_o = 130.20 ml

NaF = 0.5000M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1982	0.16	4.9550	4.52	16.866	16.50	28.777	26.38
0.3964	0.32	5.4513	5.01	17.363	16.96	29.274	26.74
0.5946	0.48	5.9476	5.50	17.859	17.42	29.770	27.11
0.7928	0.65	6.4439	6.01	18.355	17.88	30.266	27.46
0.9910	0.82	6.9402	6.52	18.851	18.32	30.763	27.81
1.1892	0.99	7.4365	7.04	19.348	18.76	31.259	28.16
1.3874	1.16	7.9328	7.55	19.844	19.19	31.755	28.51
1.5856	1.34	8.4291	8.07	20.340	19.62	32.252	28.76
1.7838	1.52	8.9254	8.58	20.837	20.06	32.748	29.21
1.9820	1.69	9.4217	9.09	21.333	20.49	33.244	29.56
2.1802	1.87	9.9180	9.61	21.829	20.91	33.740	29.91
2.3784	2.05	10.414	10.13	22.326	21.31	34.237	30.25
2.5766	2.22	10.911	10.64	22.822	21.72	34.733	30.60
2.7748	2.41	11.407	11.15	23.318	22.13	35.229	30.95
2.9730	2.60	11.903	11.65	23.814	22.54	35.726	31.29
3.1712	2.79	12.400	12.17	24.311	22.94	36.222	31.63
3.3694	2.98	12.896	12.65	24.807	23.33	36.718	31.97
3.5676	3.16	13.392	13.13	25.303	23.73	37.215	32.30
3.7658	3.35	13.888	13.62	25.800	24.12	37.711	32.63
3.9640	3.55	14.385	14.11	26.296	24.51	38.207	32.95
4.1622	3.74	14.881	14.60	26.792	24.89	38.703	33.26
4.3604	3.94	15.377	15.09	27.289	25.26	39.200	33.56
4.5586	4.13	15.874	15.57	27.785	25.64	39.696	33.86
4.7568	4.33	16.370	16.04	28.281	26.11		

Table 55 - A

Fluoride Complexing of Sn(II), Experiment 11 at 25°C

Initial Concentrations

$HClO_4$ = 1.6936M

$Sn(ClO_4)_2$ = 0.01603M

$NaClO_4$ = 0.2584M

Ionic strength = 2.000

T = 25.00 ± 0.01°C

V_o = 108.97 ml

NaF = 0.8561M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1995	0.07	8.5665	5.07	17.531	9.62
0.3990	0.14	9.0645	5.36	18.029	9.84
0.5985	0.22	9.5625	5.61	18.527	10.05
1.0965	0.52	10.061	5.89	19.025	10.27
1.5945	0.85	10.559	6.17	19.523	10.48
2.0925	1.17	11.057	6.45	20.021	10.71
2.5905	1.49	11.555	6.72	20.519	10.93
3.0885	1.80	12.053	6.97	21.017	11.14
3.5865	2.11	12.551	7.23	21.515	11.34
4.0845	2.42	13.049	7.47	22.013	11.55
4.5825	2.73	13.547	7.72	22.511	11.76
5.0805	3.04	14.045	7.97	23.009	11.97
5.5785	3.34	14.543	8.22	23.507	12.17
6.0767	3.64	15.041	8.46	24.005	12.37
6.5745	3.93	15.539	8.70	24.503	12.58
7.0725	4.21	16.037	8.93	25.001	12.78
7.5705	4.50	16.535	9.16	25.499	12.98
8.0685	4.79	17.033	9.39	25.997	13.18

Table 56 - A

Fluoride Complexing of Sn(II), Experiment 12 at 25°C

Initial Concentrations

$HClO_4$ = 1.6723M

$Sn(ClO_4)_2$ = 0.1044M

$NaClO_4$ = 0.0210M

Ionic strength = 2.000

T = 25.00 ± 0.01°C

V_o = 125.00 ml

NaF = 0.8561M

NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.498	0.09	12.948	3.58	25.398	7.22	37.848	10.67
0.996	0.21	13.446	3.74	25.896	7.35	38.346	10.80
1.494	0.32	13.944	3.89	26.384	7.50	38.844	10.93
1.992	0.46	14.442	4.04	26.892	7.64	39.342	11.06
2.490	0.59	14.940	4.18	27.390	7.77	39.840	11.19
2.988	0.72	15.438	4.33	27.888	7.91	40.338	11.32
3.486	0.85	15.936	4.47	28.386	8.05	40.836	11.45
3.984	0.99	16.434	4.61	28.884	8.20	41.334	11.58
4.482	1.13	16.932	4.75	29.382	8.33	41.832	11.71
4.980	1.27	17.430	4.90	29.880	8.47	42.330	11.84
5.478	1.41	17.928	5.05	30.378	8.61	42.828	11.97
5.976	1.55	18.426	5.20	30.876	8.75	43.326	12.10
6.474	1.70	18.924	5.35	31.374	8.90	43.824	12.23
6.972	1.84	19.422	5.50	31.872	9.05	44.322	12.36
7.470	1.99	19.920	5.65	32.370	9.19	44.820	12.49
7.968	2.13	20.418	5.80	32.868	9.32	45.318	12.62
8.466	2.26	20.916	5.93	33.366	9.46	45.816	12.74
8.964	2.40	21.414	6.08	33.864	9.60	46.314	12.87
9.462	2.55	21.912	6.22	34.362	9.73	46.812	13.00
9.960	2.70	22.410	6.36	34.860	9.86	47.310	13.12
10.458	2.85	22.908	6.51	35.358	10.00	47.808	13.25
10.956	2.99	23.406	6.66	35.856	10.14	48.306	13.37
11.454	3.14	23.904	6.81	36.354	10.27	48.804	13.50
11.952	3.29	24.402	6.95	36.852	10.40	49.302	13.62
12.450	3.44	24.900	7.09	37.350	10.54	49.800	13.74

Table 57 - A

Fluoride Complexing of Sn(II), Experiment 14 at 25°C

Initial Concentrations

$HClO_4$ = 1.7085M

$Sn(ClO_4)_2$ = 0.003995M

$NaClO_4$ = 0.2794M

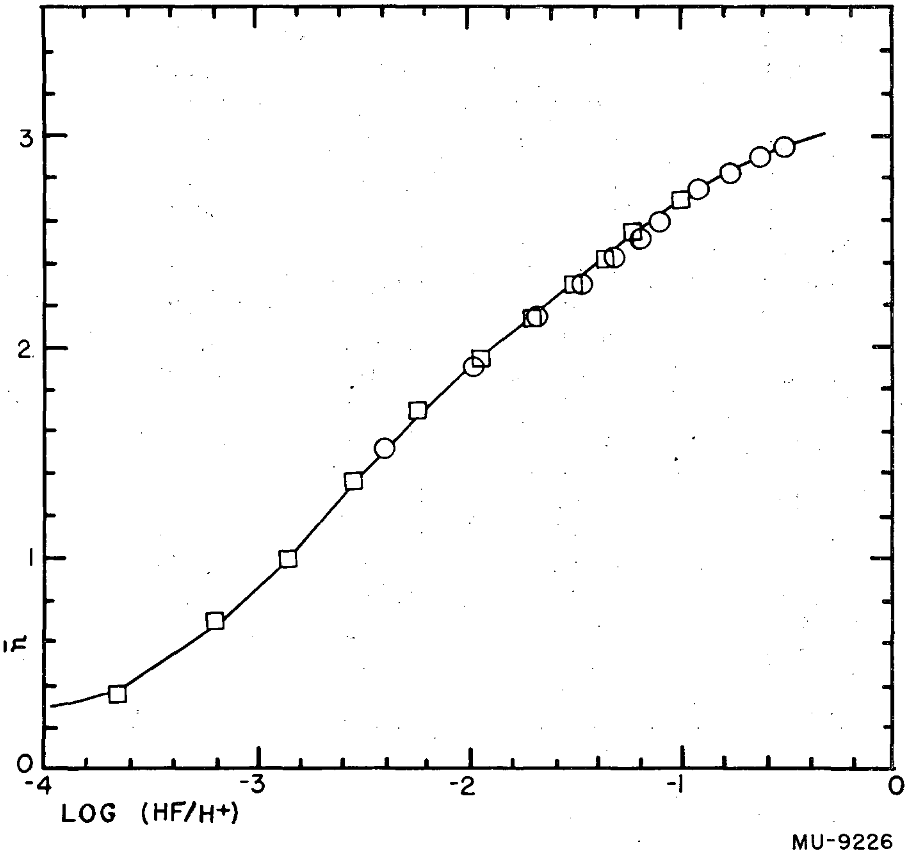
Ionic strength = 2.000

T = 25.00 ± 0.01°C

V_o = 107.92 ml

NaF = 0.8561M

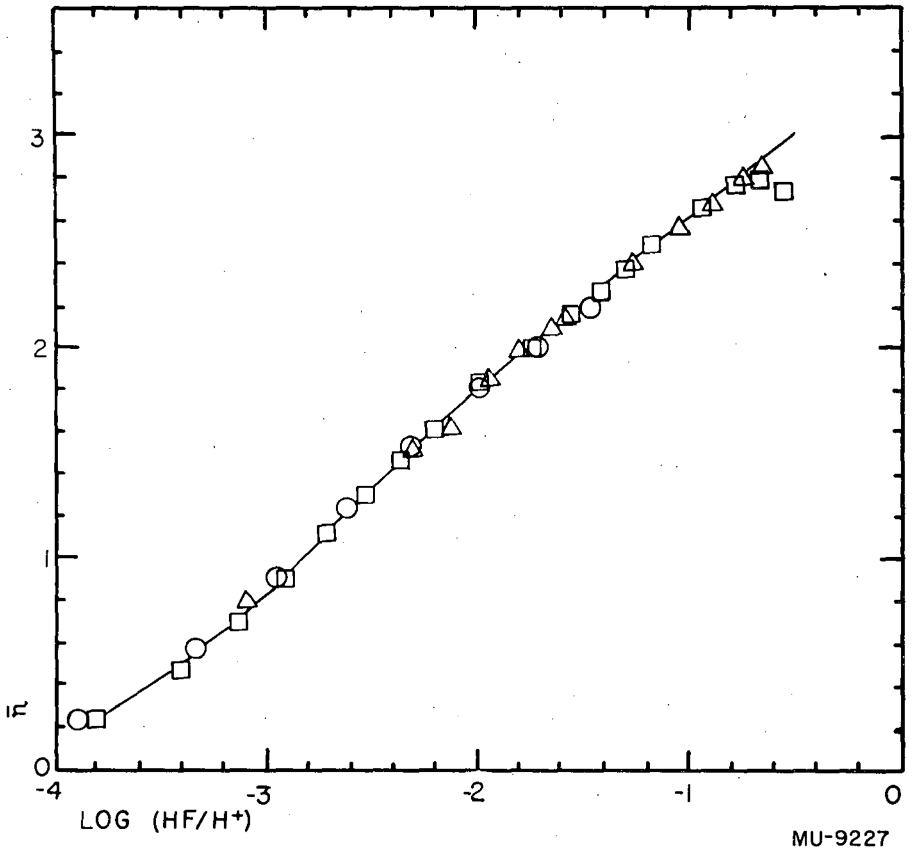
NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)	NaF added (ml)	ΔE (mv)
0.1991	0.11	3.5838	2.43	11.445	7.36
0.3982	0.22	3.7829	2.57	11.942	7.63
0.5973	0.33	3.9820	2.72	12.440	7.89
0.7964	0.44	4.4795	3.05	12.937	8.15
0.9955	0.56	4.9770	3.37	13.435	8.41
1.1946	0.69	5.4745	3.71	13.932	8.67
1.3937	0.85	5.9720	4.04	14.927	9.22
1.5928	1.00	6.4695	4.38	15.922	9.72
1.7919	1.15	6.9670	4.71	16.917	10.20
1.9910	1.30	7.4645	5.02	17.912	10.65
2.1901	1.44	7.9620	5.33	18.907	11.10
2.3892	1.58	8.4595	5.63	19.902	11.56
2.5883	1.72	8.9570	5.93	20.897	12.02
2.7874	1.86	9.4545	6.22	21.892	12.45
2.9865	2.01	9.9520	6.51	22.887	12.87
3.1856	2.15	10.450	6.79	23.882	13.30
3.3847	2.29	10.947	7.08	24.877	13.72



○ Experiment 1 $\Sigma H_o^+ = 0.05277\ \underline{M}$ $\Sigma Sc_o^{+3} = 0.001387\ \underline{M}$

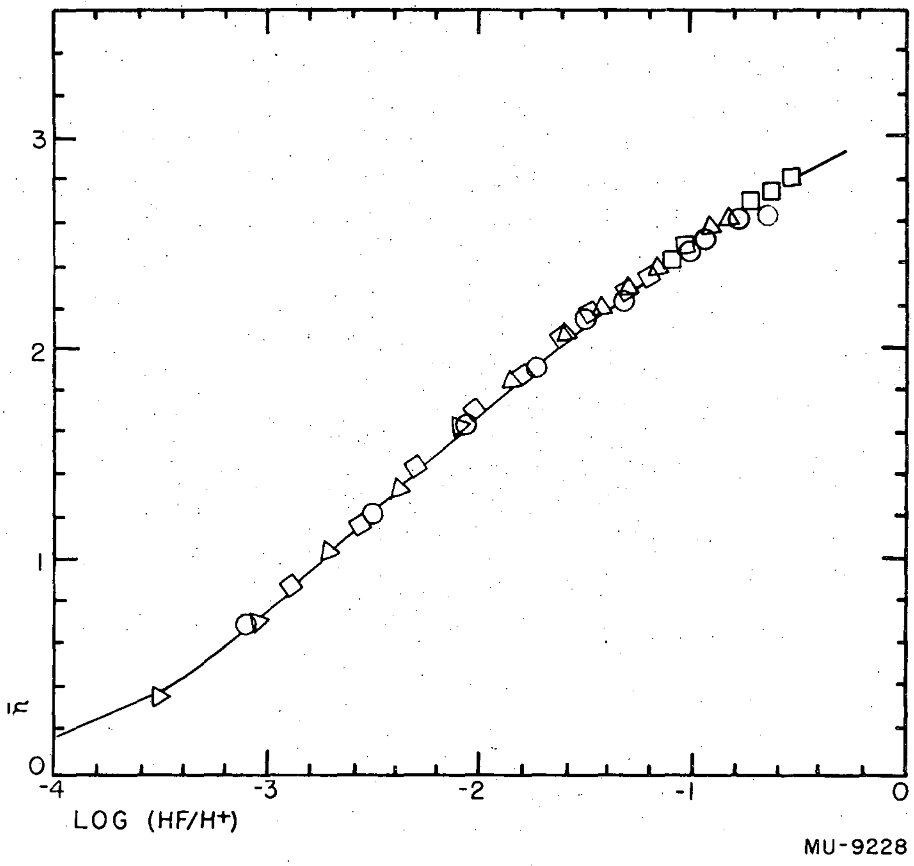
☐ Experiment 3 $\Sigma H_o^+ = 0.1065\ \underline{M}$ $\Sigma Sc_o^{+3} = 0.006665\ \underline{M}$

Fig. 1A Fluoride Complexing of Scandium at 15°C: $\bar{n}$ vs. (HF)/(H$^+$)



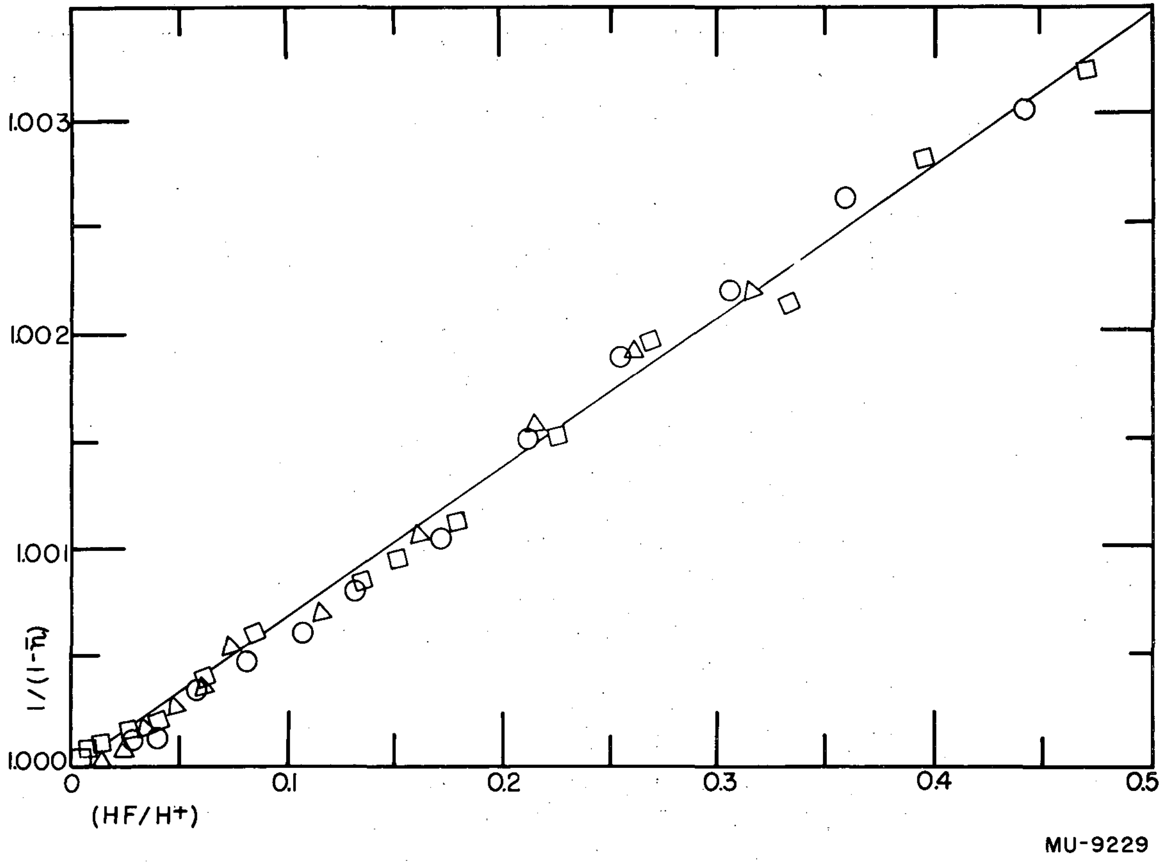
○ Experiment 1 $\Sigma H_o^+ = 0.1122$ M $\Sigma Sc_o^{+3} = 0.01273$ M
□ Experiment 2 $\Sigma H_o^+ = 0.05287$ M $\Sigma Sc_o^{+3} = 0.001387$ M
△ Experiment 3 $\Sigma H_o^+ = 0.05457$ M $\Sigma Sc_o^{+3} = 0.002741$ M

Fig. 2A Fluoride Complexing of Scandium at 25°C: π vs. $(HF)/(H^+)$



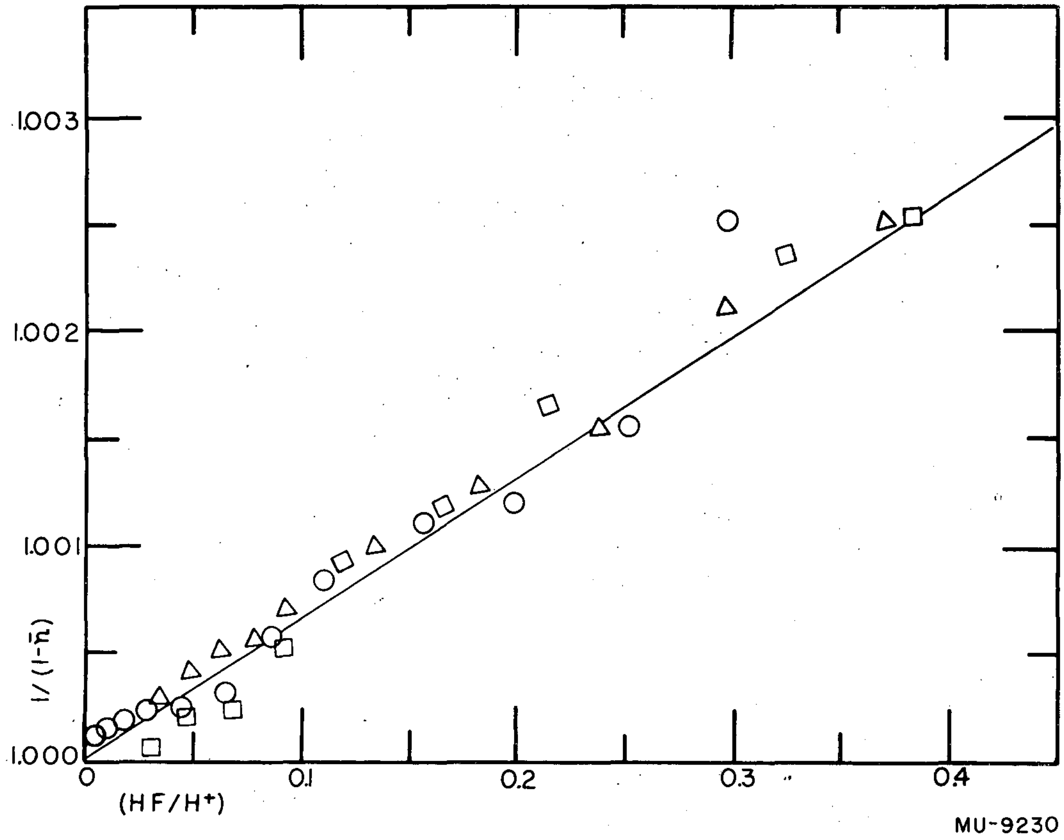
○Experiment 1 $\Sigma H_o^+ = 0.05277$ M $\Sigma Sc_o^{+3} = 0.001387$ M
□Experiment 2 $\Sigma H_o^+ = 0.05493$ M $\Sigma Sc_o^{+3} = 0.002741$ M
△Experiment 3 $\Sigma H_o^+ = 0.1065$ M $\Sigma Sc_o^{+3} = 0.006665$ M

Fig. 3A Fluoride Complexing of Scandium at $35^{\circ}C$: $\bar{n}$ vs. $(HF)/(H^+)$



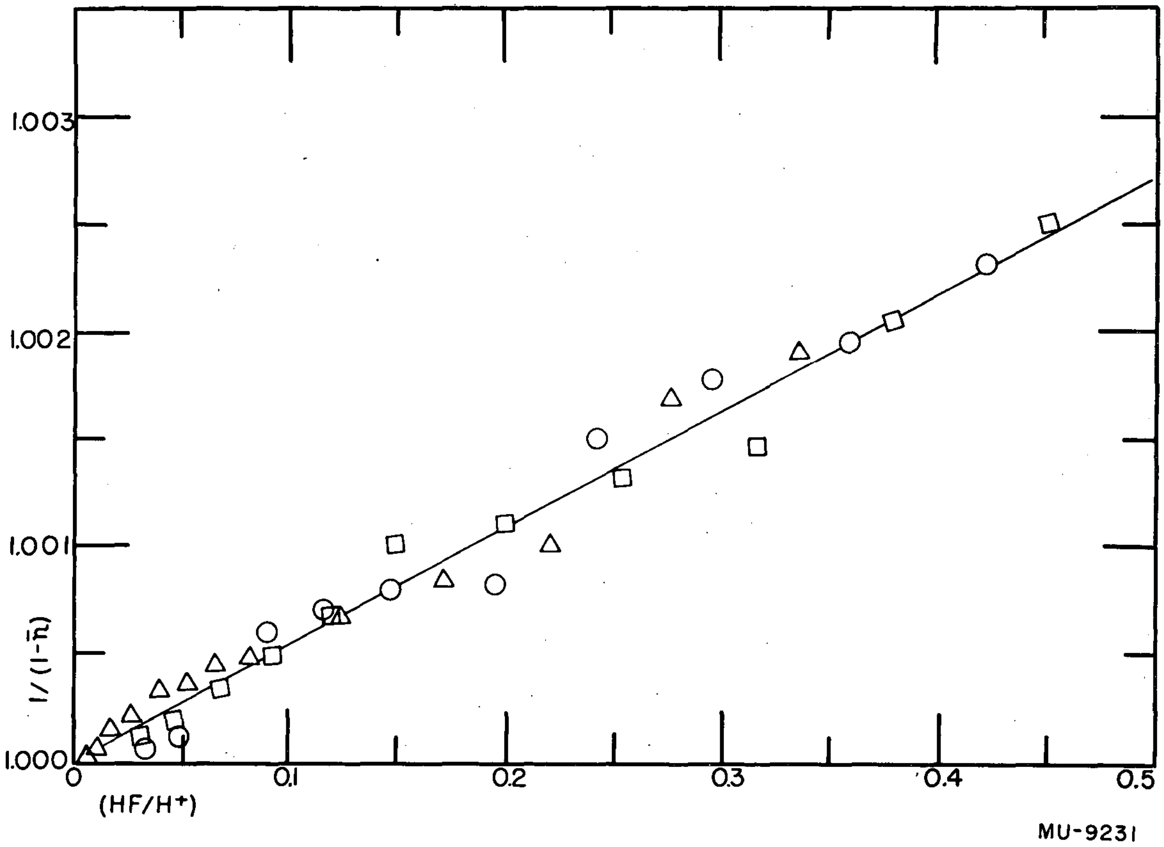
○ Experiment 4 $\Sigma H_o^+ = 0.005338\ \underline{M}$ $\Sigma Zn_o^{++} = 0.08676\ \underline{M}$
□ Experiment 5 $\Sigma H_o^+ = 0.005699\ \underline{M}$ $\Sigma Zn_o^{++} = 0.02797\ \underline{M}$
△ Experiment 6 $\Sigma H_o^+ = 0.02164\ \underline{M}$ $\Sigma Zn_o^{++} = 0.02779\ \underline{M}$

Fig. 4A Fluoride Complexing of Zinc at 15°C: $1/(1-\bar{n})$ vs. $(HF)/(H^+)$



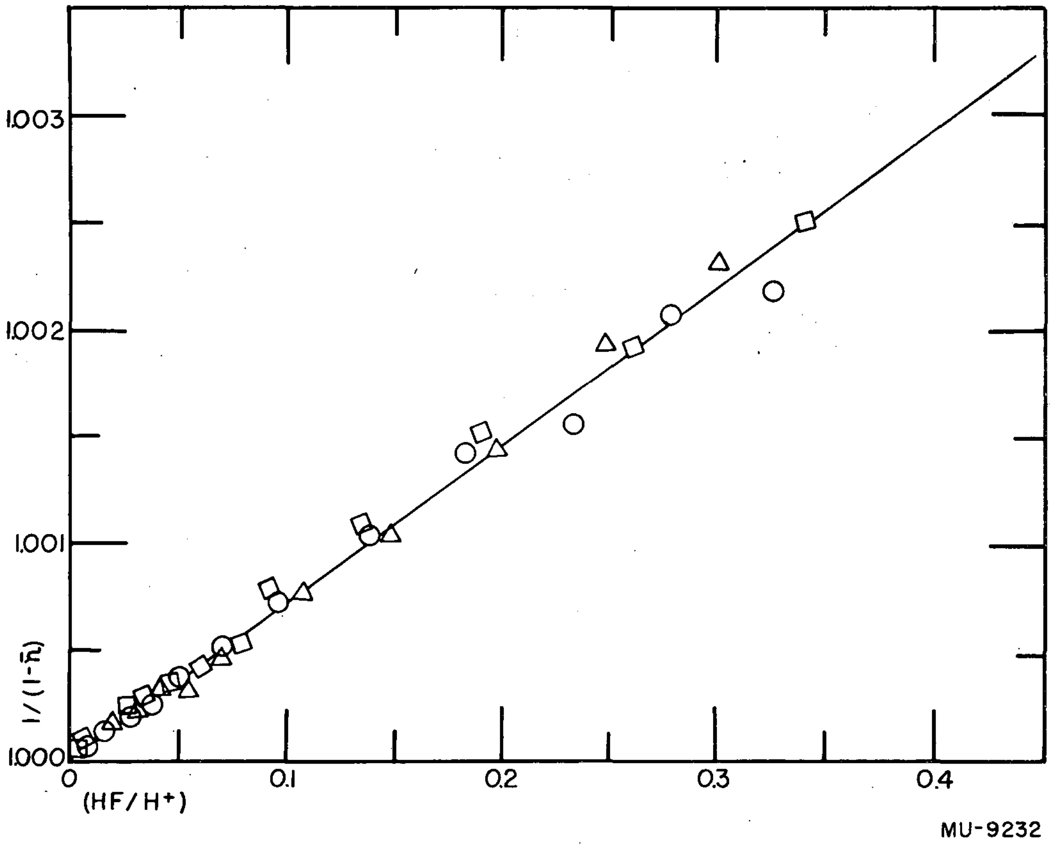
○Experiment 5 ΣH_o^+ = 0.005338 M ΣZn_o^{++} = 0.08676 M
□Experiment 6 ΣH_o^+ = 0.005699 M ΣZn_o^{++} = 0.02779 M
△Experiment 7 ΣH_o^+ = 0.02164 M ΣZn_o^{++} = 0.02779 M

Fig. 5A Fluoride Complexing of Zinc at 25°C: $1/(1-\bar{n})$ vs. (HF)/(H$^+$)



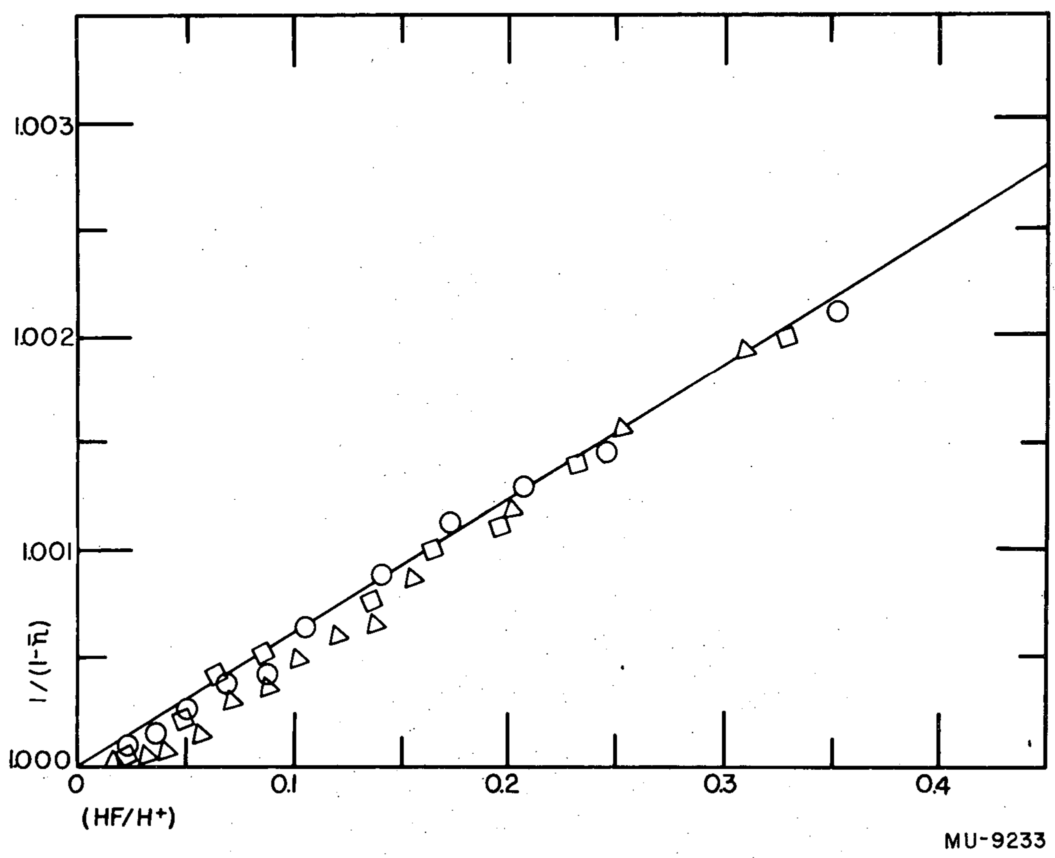
○ Experiment 4 $\Sigma H_0^+ = 0.005338$ M $\Sigma Zn_0^{++} = 0.8676$ M
□ Experiment 5 $\Sigma H_0^+ = 0.005699$ M $\Sigma Zn_0^{++} = 0.02779$ M
△ Experiment 6 $\Sigma H_0^+ = 0.02164$ M $\Sigma Zn_0^{++} = 0.02779$ M

Fig. 6A Fluoride Complexing of Zinc at 35°C: $1/(1-\bar{n})$ vs. $(HF)/(H^+)$



○ Experiment 3 $\Sigma H_o^+ = 0.02285$ M $\Sigma Cu_o^{++} = 0.08667$ M
□ Experiment 4 $\Sigma H_o^+ = 0.01283$ M $\Sigma Cu_o^{++} = 0.04543$ M
△ Experiment 5 $\Sigma H_o^+ = 0.02260$ M $\Sigma Cu_o^{++} = 0.04543$ M

Fig. 7A Fluoride Complexing of Copper at 15°C: $1/(1-\bar{n})$ vs. (HF)/(H^+)

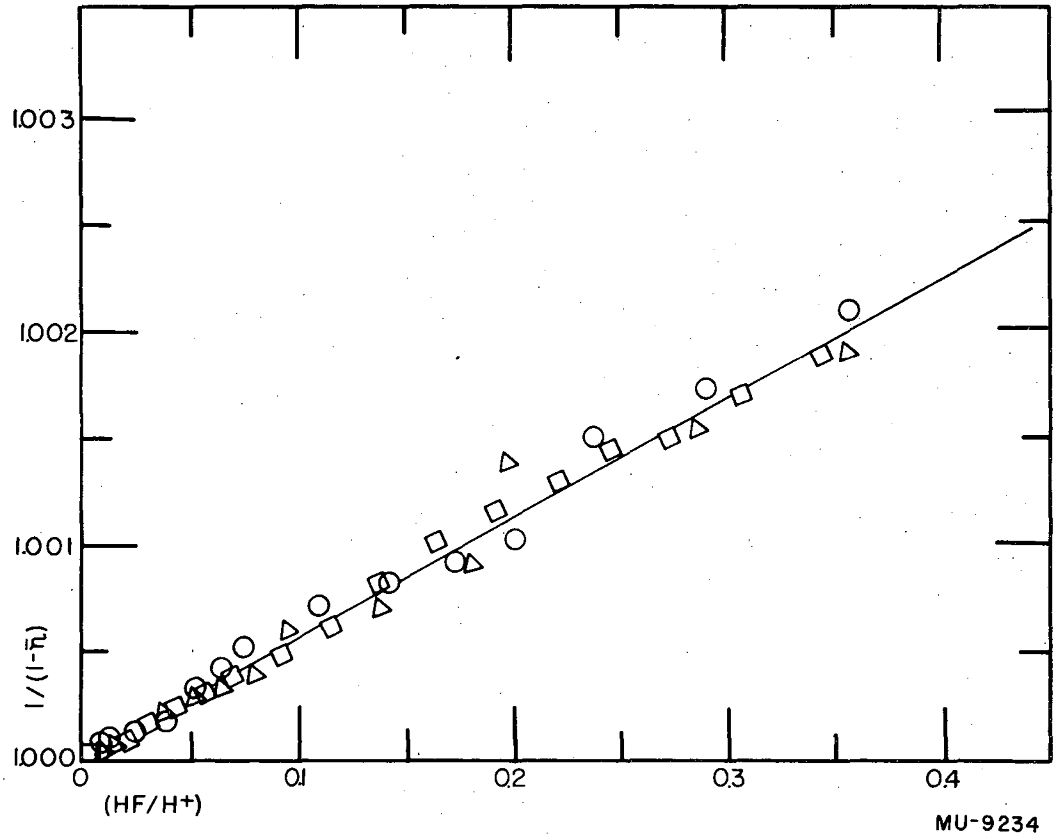


○Experiment 1 $\Sigma H_o^+ = 0.009988 \underline{M}$ $\Sigma Cu_o^{++} = 0.01874 \underline{M}$

□Experiment 2 $\Sigma H_o^+ = 0.01263 \underline{M}$ $\Sigma Cu_o^{++} = 0.04558 \underline{M}$

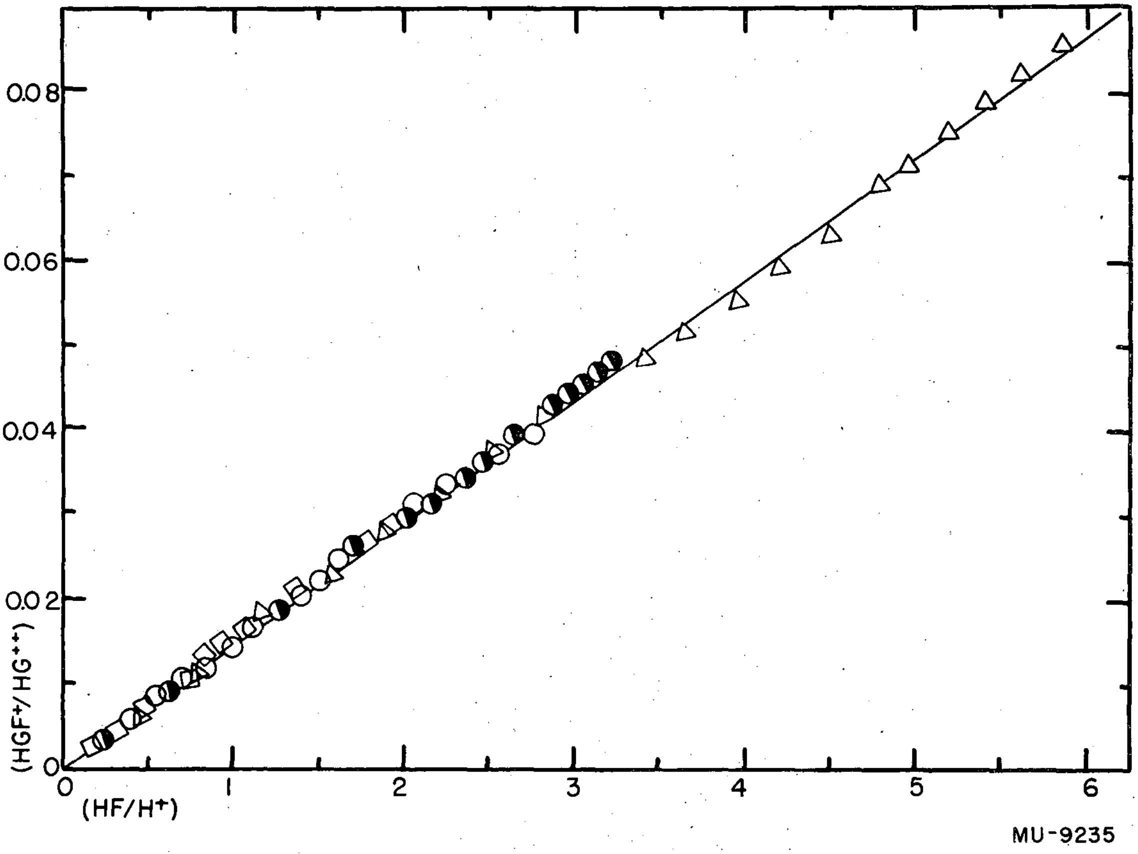
△Experiment 4 $\Sigma H_o^+ = 0.02324 \underline{M}$ $\Sigma Cu_o^{++} = 0.08703 \underline{M}$

Fig. 8A Fluoride Complexing of Copper at 25°C: $1/(1-\bar{n})$ vs. $(HF)/(H^+)$



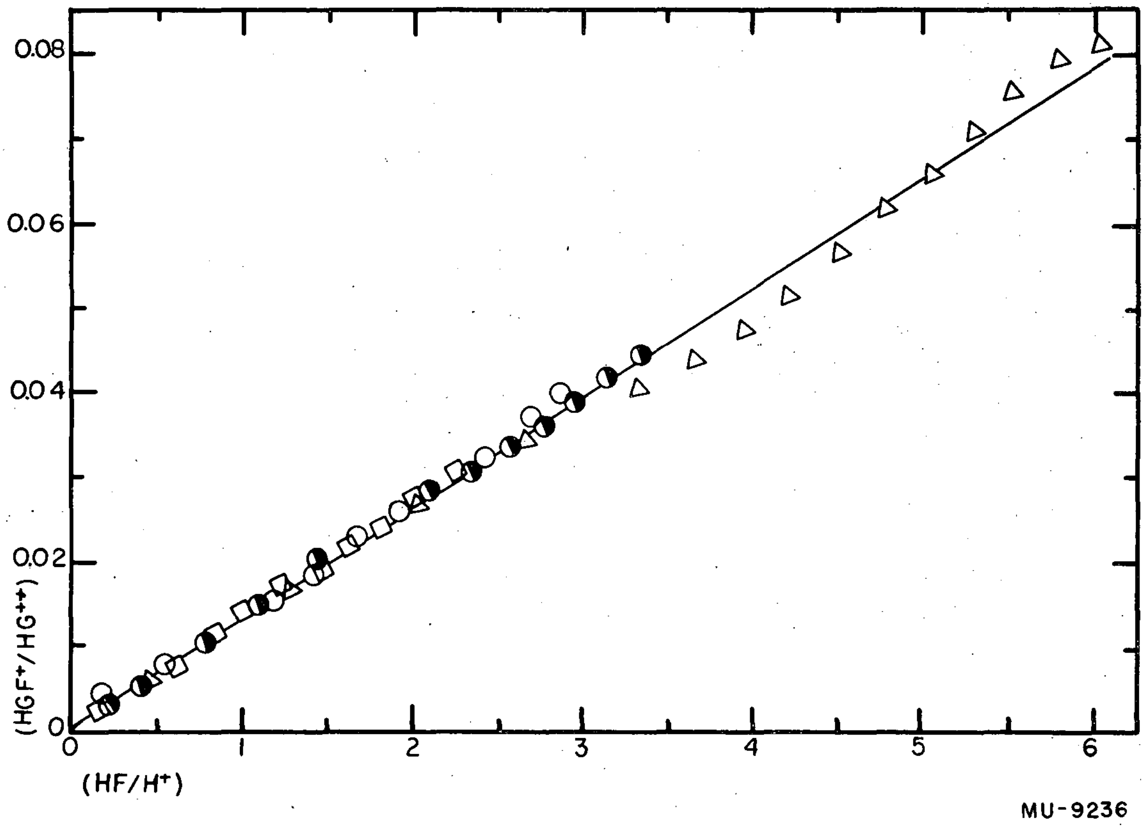
○ Experiment 4 $\Sigma H_0^+ = 0.02285$ M $\Sigma Cu_0^{++} = 0.08667$ M
□ Experiment 5 $\Sigma H_0^+ = 0.01283$ M $\Sigma Cu_0^{++} = 0.04543$ M
△ Experiment 6 $\Sigma H_0^+ = 0.02260$ M $\Sigma Cu_0^{++} = 0.04543$ M

Fig. 9A Fluoride Complexing of Copper at 35°C: $1/(1-\bar{n})$ vs. $(HF)/(H^+)$



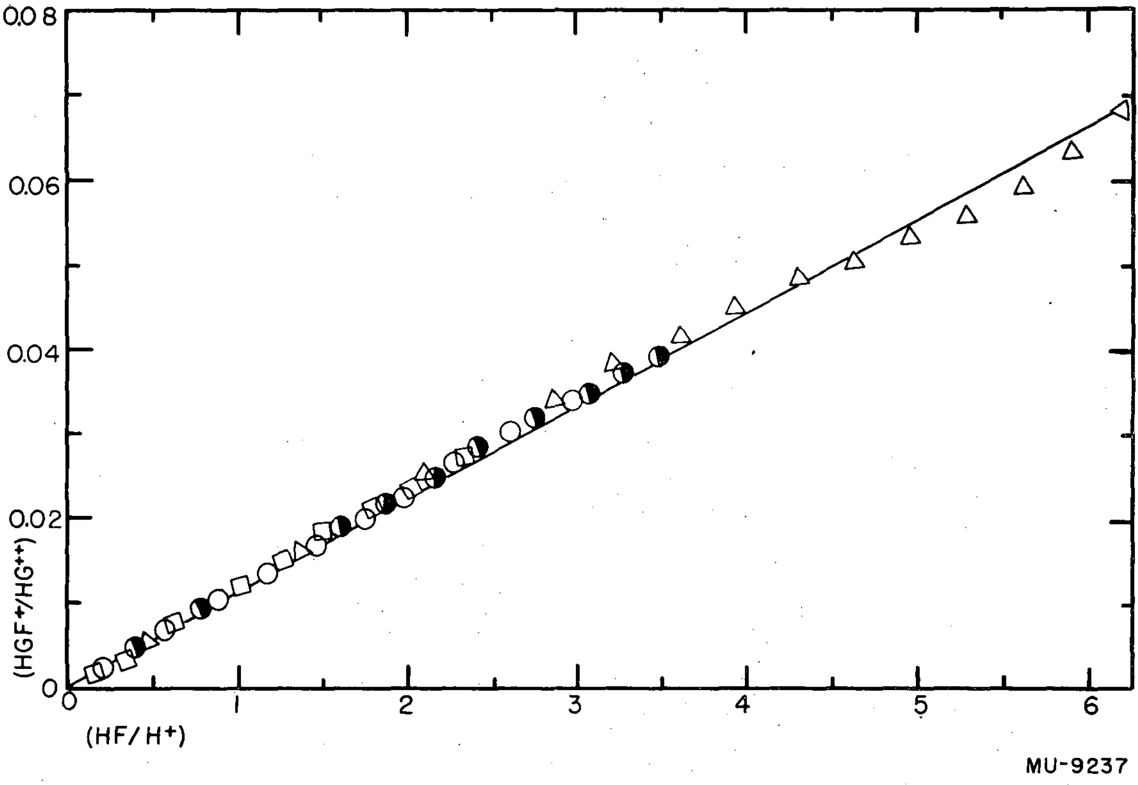
○ Experiment 1	$\Sigma H_o^+ = 0.01732$ M	$\Sigma Hg_o^{++} = 0.06980$ M
□ Experiment 2	$\Sigma H_o^+ = 0.01833$ M	$\Sigma Hg_o^{++} = 0.1302$ M
△ Experiment 3	$\Sigma H_o^+ = 0.006734$ M	$\Sigma Hg_o^{++} = 0.03627$ M
◐ Experiment 4	$\Sigma H_o^+ = 0.01658$ M	$\Sigma Hg_o^{++} = 0.03627$ M

Fig. 10A Fluoride Complexing of Hg(II) at 15°C: $(HgF^+)/(Hg^{++})$ vs. $(HF)/(H^+)$



○ Experiment 9 $\Sigma H_o^+ = 0.01732$ M $\Sigma Hg_o^{++} = 0.06980$ M
□ Experiment 10 $\Sigma H_o^+ = 0.01833$ M $\Sigma Hg_o^{++} = 0.1302$ M
△ Experiment 11 $\Sigma H_o^+ = 0.006734$ M $\Sigma Hg_o^{++} = 0.03627$ M
◐ Experiment 12 $\Sigma H_o^+ = 0.01658$ M $\Sigma Hg_o^{++} = 0.03627$ M

Fig. 11A Fluoride Complexing of Hg(II) at 25°C: $(HgF^+)/(Hg^{++})$ vs. $(HF)/(H^+)$



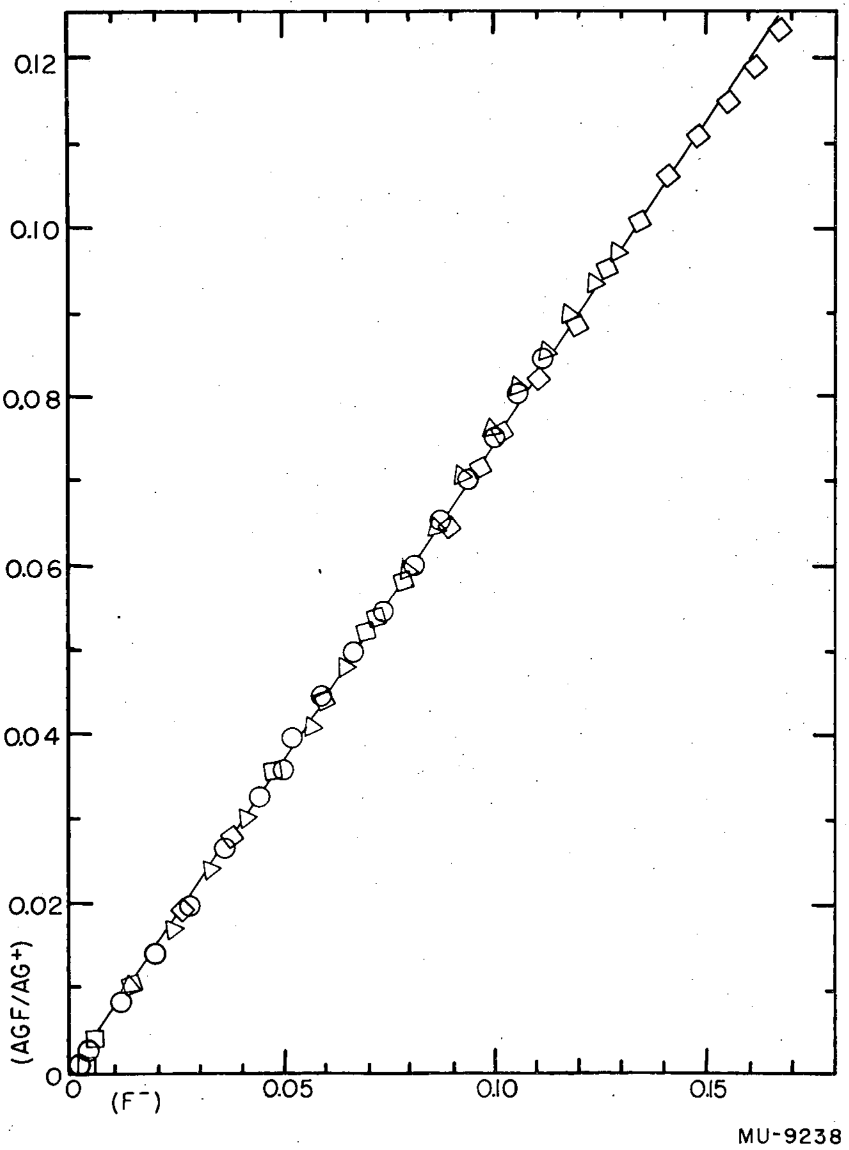
○ Experiment 1 $\Sigma H_o^+ = 0.01732\ \underline{M}$ $\Sigma Hg_o^{++} = 0.06980\ \underline{M}$

□ Experiment 2 $\Sigma H_o^+ = 0.01833\ \underline{M}$ $\Sigma Hg_o^{++} = 0.1302\ \underline{M}$

△ Experiment 3 $\Sigma H_o^+ = 0.006734\ \underline{M}$ $\Sigma Hg_o^{++} = 0.03627\ \underline{M}$

◐ Experiment 4 $\Sigma H_o^+ = 0.01658\ \underline{M}$ $\Sigma Hg_o^{++} = 0.03627\ \underline{M}$

Fig. 12A Fluoride Complexing of Hg(II) at 35°C: $(HgF^+)/(Hg^{++})$ vs. $(HF)/(H^+)$

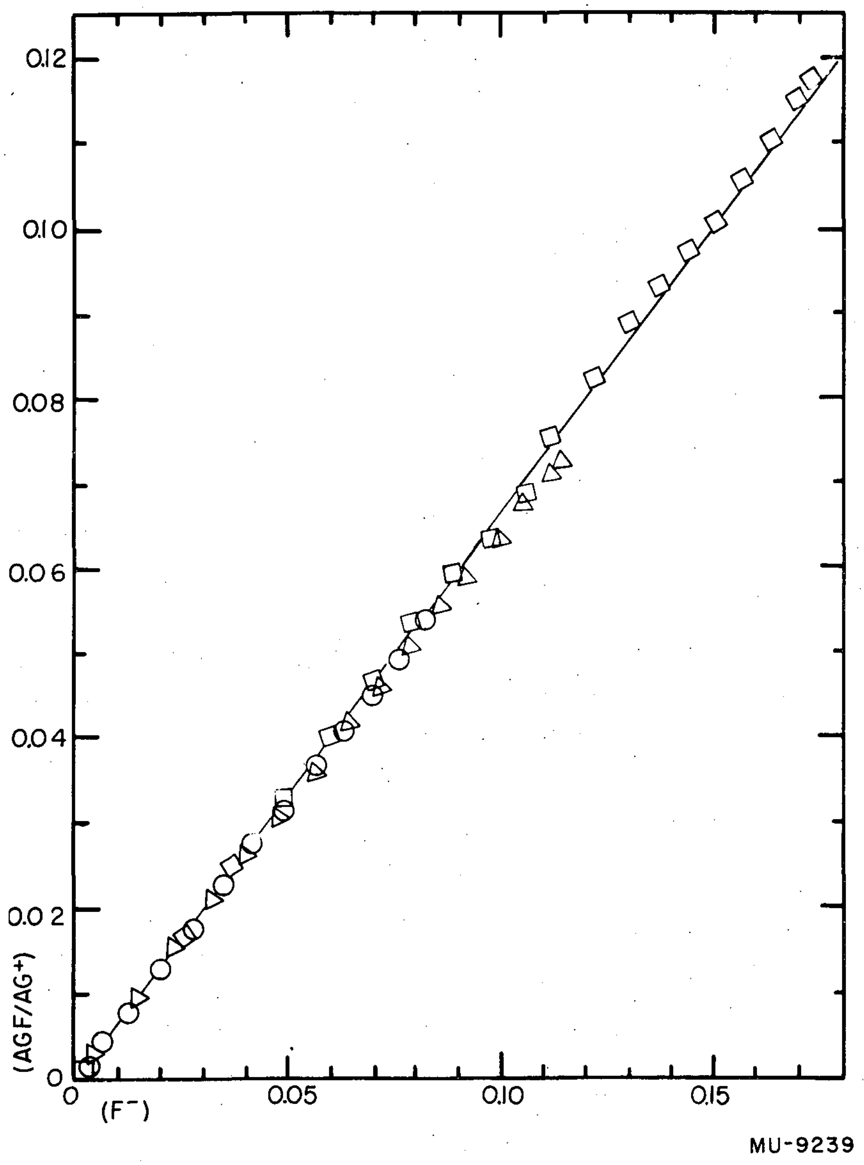


○ Experiment 1 ΣH^+_o = 0.02145 M ΣAg^+_o = 0.04190 M

□ Experiment 2 ΣH^+_o = 0.004849 M ΣAg^+_o = 0.2100 M

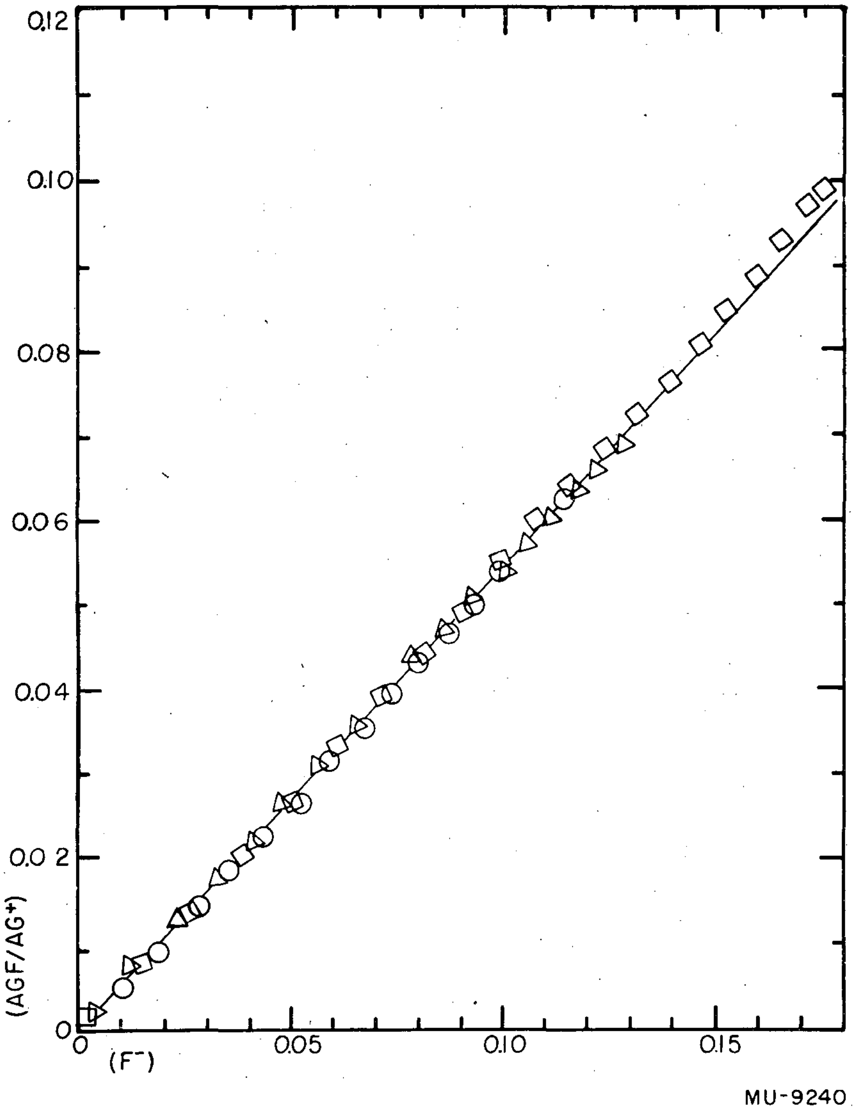
△ Experiment 3 ΣH^+_o = 0.0009675 M ΣAg^+_o = 0.04190 M

Fig. 13A Fluoride Complexing of Silver at 15°C: (AgF)/(Ag$^+$) vs. (F$^-$)



○ Experiment 1 $\Sigma H_0^+ = 0.04126$ M $\Sigma Ag_0^+ = 0.1053$ M
□ Experiment 2 $\Sigma H_0^+ = 0.004862$ M $\Sigma Ag_0^+ = 0.2106$ M
△ Experiment 3 $\Sigma H_0^+ = 0.0009704$ M $\Sigma Ag_0^+ = 0.04203$ M

Fig. 14A Fluoride Complexing of Silver at 25°C: $(AgF)/(Ag^+)$ vs. (F^-)

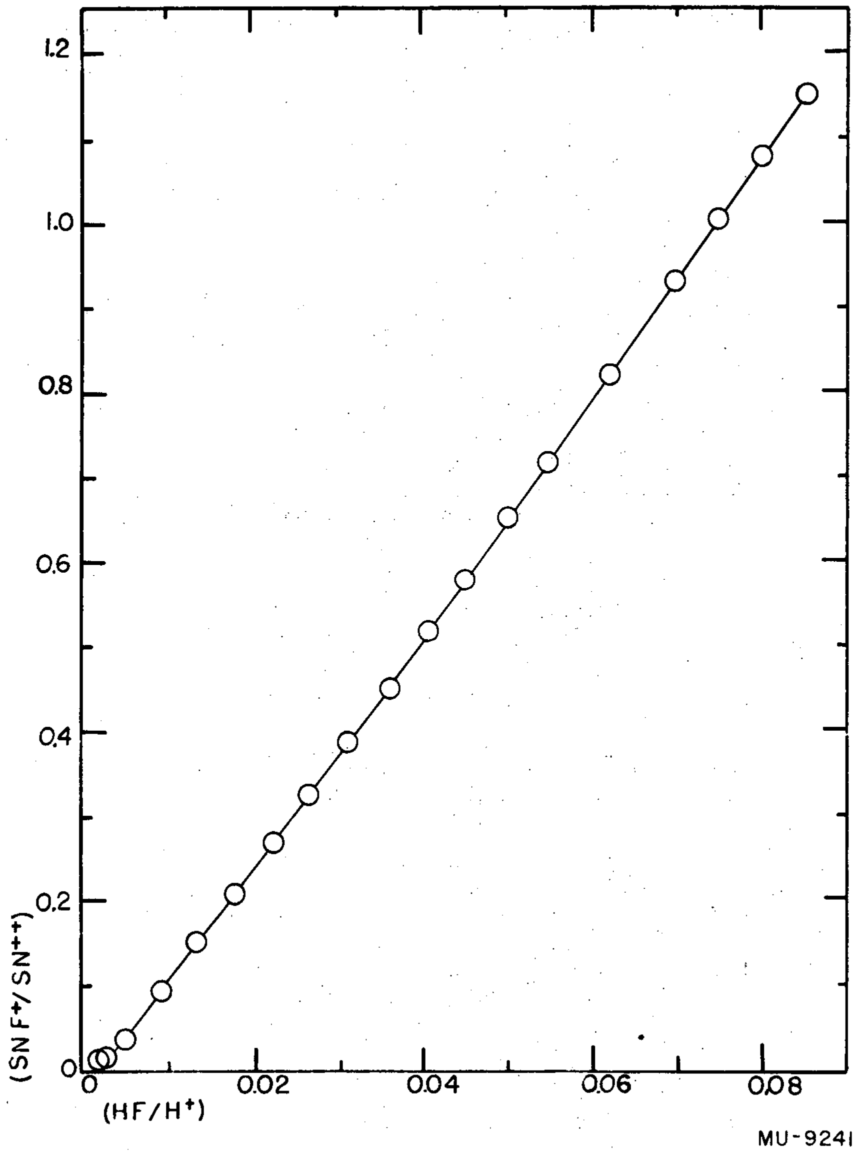


○ Experiment 1 $\Sigma H_o^+ = 0.02145$ M $\Sigma Ag_o^+ = 0.04190$ M

□ Experiment 2 $\Sigma H_o^+ = 0.004849$ M $\Sigma Ag_o^+ = 0.21001$ M

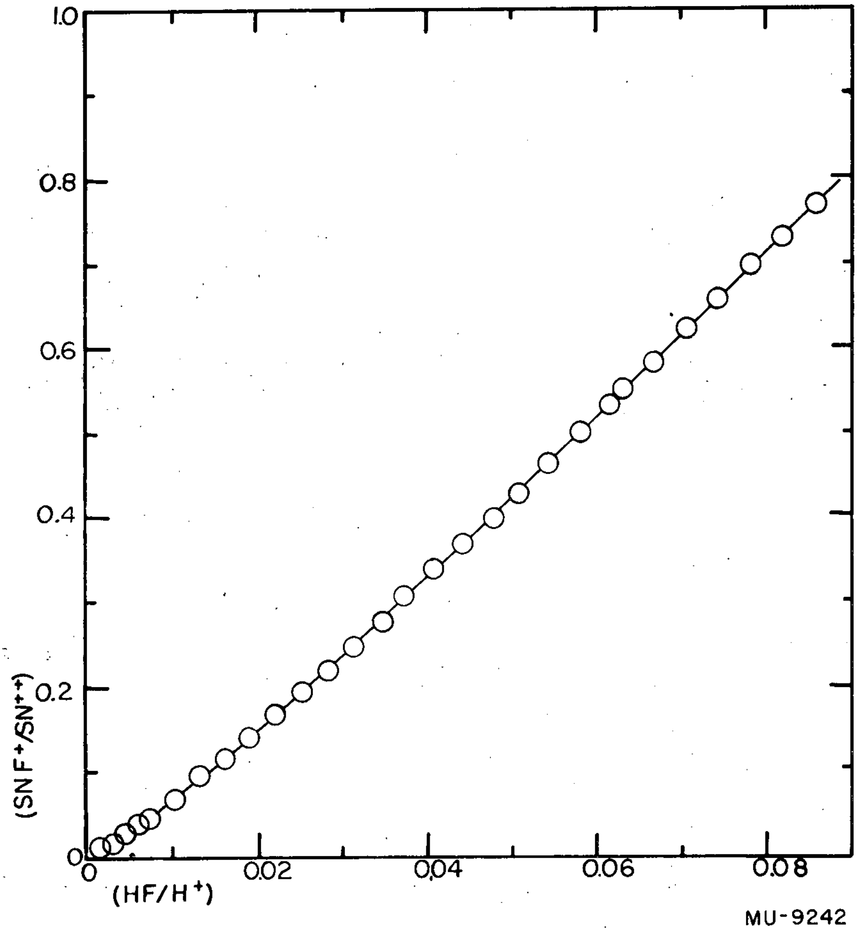
△ Experiment 3 $\Sigma H_o^+ = 0.0009675$ M $\Sigma Ag_o^+ = 0.04190$ M

Fig. 15A Fluoride Complexing of Silver at 35°C: (AgF)/(Ag$^+$) vs. (F$^-$)



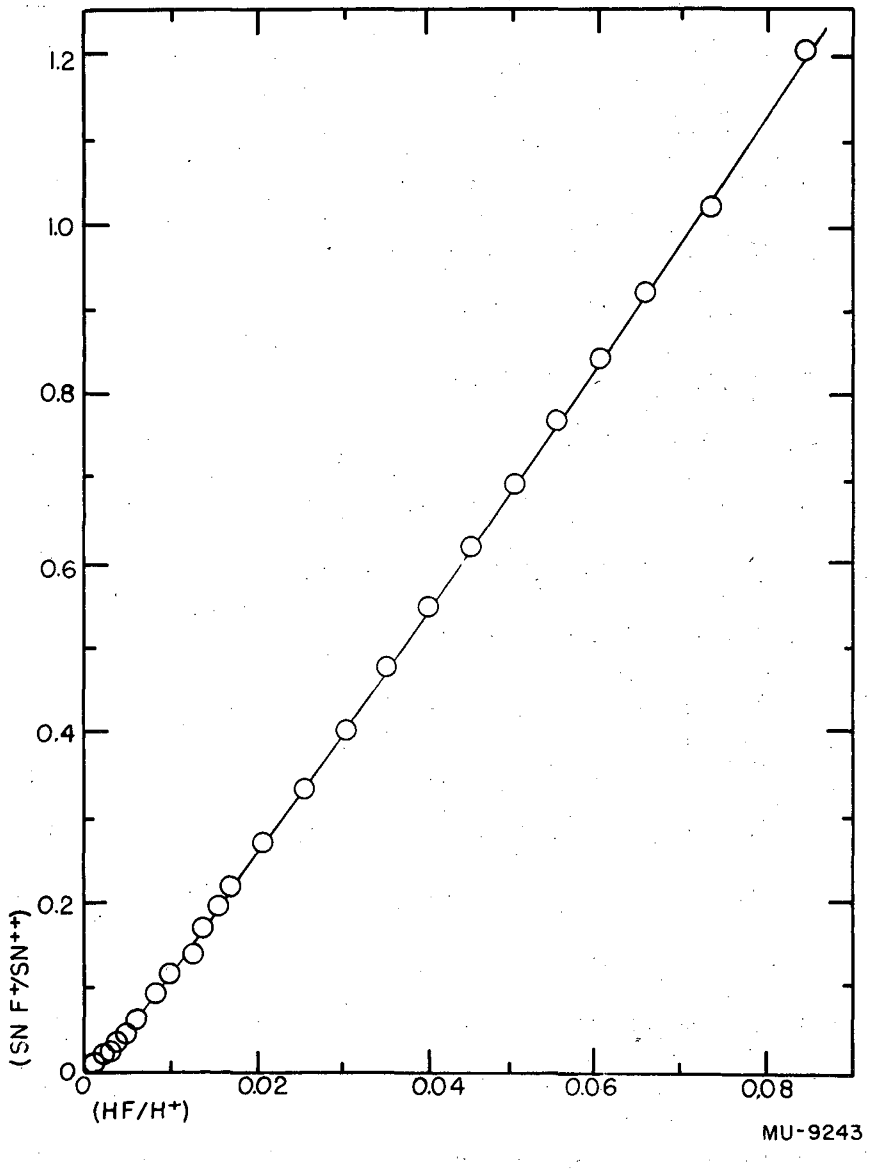
$\Sigma\, Sn_0^{++}$ = 0.01603 M
$\Sigma\, H_0^{+}$ = 1.6936 M

Fig. 16A Fluoride Complexing of Sn(II), Experiment 11 at 25°C: $(SnF^+)/(Sn^{++})$ vs. $(HF)/(H^+)$



$\Sigma Sn_0^{++} = 0.1044\ \underline{M}$
$\Sigma H_0^{+} = 1.6723\ \underline{M}$

Fig. 17A Fluoride Complexing of Sn(II), Experiment 12 at 25°C: $(SnF^+)/(Sn^{++})$ vs. $(HF)/(H^+)$



ΣSn_o^{++} = 0.003995 M
ΣH_o^+ = 1.7085 M

Fig. 18A Fluoride Complexing of Sn(II), Experiment 14 at 25°C: $(SnF^+)/(Sn^{++})$ vs. $(HF)/(H^+)$

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