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SOLUTION REACTIONS OF FLUORO-COMPLEXES  
OF ANTIMONY AND TIN

A THESIS

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SOLUTION REACTIONS OF FLUORO-COMPLEXES  
OF ANTIMONY AND TIN

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## SUMMARY

The purpose of this work was to study the electron exchange reaction between the fluoro-complexes of tin(II) and tin(IV) or antimony(III) and antimony(V). Both these systems are examples of reactions that proceed by the transfer of two electrons.

Several workers have studied the electron exchange between tin(II) and tin(IV) in hydrochloric acid and in dilute sulfuric acid. The exchange reportedly proceeds at a measurable rate in dilute sulfuric acid but due to a complex dependence of the rate on the hydrogen ion and sulfate ion concentration, very little could be concluded about the reaction path. In hydrochloric acid solution, the exchange was viewed as proceeding through the formation of a dimeric intermediate,  $\text{Sn}_2\text{Cl}_{10}^{-4}$ .

The electron exchange between antimony(III) and antimony(V) in sulfuric acid and hydrochloric acid solutions has also been studied by a number of workers. It was found that there was no measurable exchange between antimony(III) and antimony(V) in 3-12F sulfuric acid solutions. The exchange in hydrochloric acid is best represented by a three component system composed of (i) the antimony(III) species, (ii) the exchanging antimony(V) species, and (iii) the hydrolysis product of the exchanging antimony(V) species. The reaction is viewed as proceeding through a chlorine-bridged dimer in which each antimony atom is coordinated to six chlorine atoms.

If the electron exchange reaction between the fluoro-complexes of either tin(II) and tin(IV) or antimony(III) and antimony(V) can be measured,

it should be possible to make some interesting comparisons between the exchange reaction of the fluoro-complexes and that of the corresponding exchange reactions previously studied.

Before any measurements of the rate of exchange can be made, a method for separating the tin(II)-tin(IV) or antimony(III)-antimony(V) fluoro-complexes had to be developed.

Investigations of the tin(II)-tin(IV) fluoro-complex system were undertaken to determine if the separation could be achieved by selective precipitation, solvent extraction, or anion exchange. This work was made more difficult because of the ease with which tin(II) is oxidized. To prevent the oxidation, all work with tin(II) was performed in a glove box which had been converted to a controlled atmosphere box. A stream of nitrogen, purified by passage through a train of bubble jars containing vanadyl sulfate and zinc amalgam, provided the required inert atmosphere.

The reactions of the tin complexes were followed through the use of tin-113 as a tracer. The gamma radiation, resulting from the isomeric transition of the indium-113m daughter, was counted using a well-type scintillation detector and scaler counting apparatus. The detector crystal was of the thallium activated-sodium iodide type.

Although a large number of simple and complex cations were tried, no reliable separation method based on selective precipitation could be found. Solvent extraction using several high molecular weight amines dissolved in petroleum ether extracted less than one percent of either of the tin fluoro-complexes.

Anion exchange using Dowex-1-X10 in both the perchlorate and the fluoride form was investigated at various concentrations of hydrofluoric

acid both in the presence and in the absence of aqueous perchloric acid. The adsorption characteristics of tin(II) and tin(IV) were very similar under the conditions of the experiments. Since no separation method could be found for the tin(II)-tin(IV) fluoro-complexes, the antimony(III)-antimony(V) fluoro-complex system was investigated next.

In the studies with antimony, antimony-124 was used as a tracer. Since antimony-124 yields both beta and gamma radiation upon decay, the antimony-124 can be counted either with an end-window beta detector or a scintillation detector. Both methods were used.

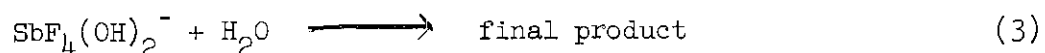
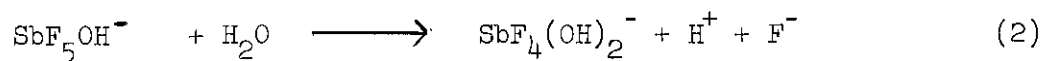
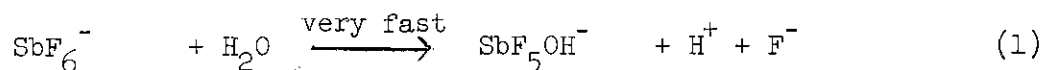
Anion exchange with Dowex-1-X10 showed that both the antimony(III) and antimony(V) fluoro-complexes are strongly adsorbed in 1-15 F hydrofluoric acid solution. The adsorption characteristics were measured by both the equilibrium and flow methods of ion exchange.

It was found that by using paper chromatography with Whatman No. 50 chromatography paper and a developing solution of acetone - 20 percent aqueous trichloroacetic acid solution (9:1), a separation of the antimony(III)-antimony(V) fluoro-complexes could be achieved. The exchange reaction was measured in solutions 0.010 F in antimony(III) and in antimony(V) and 1-10 F in hydrofluoric acid. No exchange was detected after one week at 80° C.

In an attempt to justify this result, the following calculations were made. If an analogy can be made with the chloro-complex exchange reaction, the exchange should proceed through a fluorine-bridged dimer in which each antimony atom is coordinated with six fluorine atoms. An estimate was made of the energy required for the rearrangement of the dimer with normal antimony(III) and antimony(V)-fluorine bond distances to a config-

ration which permits the electron transfer to occur adiabatically. The energy found was 15 kcal/mole for the fluoro-complex and 0.5 kcal/mole for the chloro-complex. The experimental activation energy for the chloro-complex is about 17 kcal/mole. Thus, for the chloro-complex, most of the activation energy results from the formation of the dimer rather than the rearrangement of the dimer. If the same argument holds true for the fluoro-complex, it is easily seen that the reaction could be very slow.

Mazeika and Neumann measured the rate of hydrolysis of  $\text{KSbF}_6$  and from a resolution of a plot of  $\log$  (percent fluoride remaining complexed) versus time, concluded that the reaction proceeded in a step-wise manner. For the hydrolysis in acid solution, they proposed the following sequence of consecutive first order or pseudo-first order reactions:



Since their conclusions were based solely on the graphical resolution of kinetic data and since they did neither prove the number of intermediates involved nor the identity of the intermediates proposed, it was decided to reinvestigate the system.

Using a column chromatographic adaptation of the paper chromatographic technique successfully used for the separation of the antimony(III)-antimony(V) fluoro-complexes, the hydrolysis of  $\text{KSbF}_6$  was studied.

A column containing cellulose powder allowed the separation of the hydrolysis intermediates when eluted with acetone - 20 percent aqueous trichloroacetic acid solution (9:1). It was found that only three intermediates were present to any appreciable extent in the reaction mixture. The rates of reactions (2) and (3) were measured in several buffered solutions.

Using a larger column, macro amounts of the intermediates were separated. Analysis of the fractions corresponding to the proposed intermediates yielded a fluorine/antimony ratio of 5.03 and 5.07 to 1 for the fraction thought to contain the  $\text{SbF}_5\text{OH}^-$  ion, 3.97 and 4.01 to 1 for the fraction thought to contain the  $\text{SbF}_4(\text{OH})_2^-$  ion and 2.10 and 1.94 to 1 for the fraction containing the final product. Thus, the reaction sequence proposed earlier has been proven.

The final product in acid or weakly basic solution has a fluorine/antimony ratio of two to one. It is suggested that this compound is polymeric.

## CHAPTER I

## INTRODUCTION

There has been considerable interest in recent years in elucidating and understanding the mechanisms of oxidation-reduction reactions. The essential feature of such a reaction is the transfer of electrons either between or within chemical species. Reactions involving transfer of one electron are common, and numerous studies of such systems have been made. Reactions involving transfer of two electrons are less common. Furthermore, reactions which from their net equation involve transfer of two electrons, frequently proceed mechanistically in two one-electron steps. Further studies of reactions which proceed in both a net and mechanistic sense by transfer of two electrons would be valuable. To be favorable for such studies an element should have the characteristics: (i) its stable oxidation states differ by two; (ii) the existence of the intermediate oxidation state is very unlikely. Logical choices are regular elements like tin and antimony, whose stable oxidation states are determined by the "inert pair" effect.

The ultimate objective of this work was to study the electron exchange reaction between the fluoro-complexes of either tin(II) and tin(IV), using radioactive tin-113, or antimony(III) and antimony(V), using radioactive antimony-124. The only previous electron exchange studies involving complex anions of these two elements were studies of the chloro- and sulfato-complexes of both tin and antimony. These studies indicated that the chloro-

complexes reacted by means of a chlorine bridged dimer in both cases. The antimony(III)-antimony(V) exchange in aqueous sulfuric acid was too slow to be measured. Although the tin(II)-tin(IV) exchange in dilute sulfuric acid had a measurable rate, very little could be concluded about the reaction path. A study of the electron exchange reaction of the fluoro-complexes would make possible comparisons of the exchange between the fluoro-complexes with that between the chloro- or sulfato-complexes.

Before these reactions could be studied, it was first necessary to establish the chemical behavior of these complexes in solution and to develop methods of separating tin(II) from tin(IV) or antimony(III) from antimony(V) in aqueous hydrofluoric acid solution.



## CHAPTER II

## APPARATUS AND TECHNIQUE

This chapter will be devoted to a discussion of some of the more specialized apparatus and techniques used in the experimental work. These include (i) a description of the controlled atmosphere box used in handling tin(II), (ii) a description of the scintillation counting techniques used in the detection of gamma radiation, and (iii) a description of the paper chromatographic techniques and the apparatus used for subjecting the paper strips to the counting operation.

Use of the Controlled Atmosphere Box

Since tin(II) in solution is very susceptible to air oxidation, it was desirable to perform all work with tin(II) under a nitrogen atmosphere. For this purpose, a glove box (Isolator/Lab, Fisher Scientific Company) was converted to use as a controlled atmosphere box simply by continuously passing a stream of nitrogen through the box. Before entering the box, the nitrogen was passed through a train of three bubble jars. The first two jars contained zinc amalgam and 0.01 F vanadyl sulfate in dilute sulfuric acid solution. These two jars served to remove oxygen from the nitrogen stream. The third jar contained water to remove any vanadium accidentally carried with the nitrogen stream. This nitrogen purification system was devised by Meites and Meites (1), who report that it is an extremely efficient method for removing oxygen from a nitrogen stream.

The box contained a hot plate, a centrifuge, a reagent rack, and all

of the equipment necessary to perform the operations required in the work with tin(II). It was supplied with both a vacuum line and the nitrogen line. Manipulation of the materials in the box was accomplished by means of rubber gloves attached to two ports at the front of the box.

#### Scintillation Counting Techniques

The counting of the gamma radiation resulting from the decay of tin-113 and antimony-124 was performed with a Nuclear-Chicago Corporation Model DS-5 well-type scintillation detector and a Nuclear-Chicago Corporation Model 182 scaler. The crystal of the detector is of the thallium activated-sodium iodide type and is 1-7/8 inches in diameter by 2-1/4 inches thick. The well is 21/32 inch in diameter by .1-1/2 inches deep.

The scaler is designed to indicate and record the number of emitted particles or events detected by an external Geiger-Mueller, proportional, or scintillation detector. The instrument consists of a high gain linear amplifier, pulse forming circuit (scaling factor of 256), and a well regulated high voltage supply continuously variable from 500 to 2500 volts. It features an electrically reset mechanical register and an electrically reset drum-type timer which indicates elapsed time in minutes and hundredths of a minute.

The samples to be counted were placed in two milliliter glass test tubes. The maximum height of the samples in the test tube was 0.5 inch. Since the depth of the well in the detector crystal was 1.5 inches, a high counting geometry that does not depend on the volume of the sample was obtained by placement of the test tubes in the well. In general, a sample was counted in two minute runs with the counting runs alternated

with background runs. This assured that any variation in the background was noticed and the proper correction applied to the counting rate. After correction for background radiation, the counting rates were expressed in counts per minute.

Since pulses caused by radioactive processes have a random distribution in time, the accuracy of a particular measurement is determined by the total number of counts recorded. The counting error is usually expressed in terms of the standard deviation from the "true" average. The standard deviation is equal to the square root of the total number of counts recorded.

#### Paper Chromatographic Techniques and Counting Apparatus

Development of the chromatograms was performed in glass jars 30 cm high and 12 cm in diameter. These jars were fitted with tops that could be sealed by means of a rubber gasket and a clamp. A one hole rubber stopper was placed in a hole in the top and a glass rod bent at a 90° angle placed in the stopper such that the part of the rod parallel to the bottom of the glass jar was inside the jar. These rods were used to suspend the paper chromatograms in the jar and to raise or lower them into the developing solution. The dimensions of the paper strips were 25 × 4 cm. The solvents were placed in the bottom of the glass jar to a depth of about 2 cm. An aliquot of the solution to be chromatographed was delivered by a micro-pipette onto the paper approximately one inch from one end of the paper and 2 cm from either side. The spot was dried and the paper strips were suspended from the glass rod with paper clips. The top of the jar was closed and materials in the jar were allowed to equilibrate with the solvent.

Then the paper strips were lowered until the ends of the papers dipped into the solvent. Care was taken to insure that the spot did not come in contact with the bulk of the solvent. After the solvent had ascended the paper to an appropriate distance, the paper was removed from the jar, the solvent front marked, and the paper air dried. The strips were counted with an end-window Geiger-Mueller tube and a Nuclear-Chicago Model 161A scaler. The end-window tube was fitted into a lead shield which had a series of slides that are used for counting solid beta samples. Each slide has a hole slightly larger in diameter than the end-window tube. When the slide is in place, the hole is directly below the end-window tube. The slide nearest the end-window tube was fitted with a circular piece of lead foil approximately 1/8 inch in thickness, which had a 1/4 inch wide slot cut in the center. The slide immediately below the one containing the lead foil was used to hold the chromatograms. Thus the lead foil served to collimate the beam of beta particles. The two slides were close enough together so that the end-window tube could pick up essentially only those beta particles originating from the narrow region below the slit. Counts were taken at 0.5 cm intervals from the point where the spot was placed to the solvent front. The peaks corresponding to antimony(III) or antimony(V) were detected and the  $R_f$  values calculated.

## CHAPTER III

## SOLUTION CHEMISTRY OF TIN(II)-TIN(IV) FLUORO-COMPLEXES

Introduction

In the general area of electron exchange reactions the two electron exchange systems have been of special interest to a number of workers. One of the prime examples of this type reaction is the tin(II)-tin(IV) system. Four studies of this system have been made: (i) the exchange reaction between tin(II) chloride and tin(IV) chloride in absolute ethanol (2); (ii) the exchange between tin(II) chloride and tin(IV) chloride in absolute methanol (3); (iii) the exchange reaction between the tin(II) and tin(IV) chloro-complexes in hydrochloric acid solution (4); and (iv) the exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid (5).

If a study can be made of the exchange between the tin(II)-tin(IV) fluoro-complexes, it should be possible to compare the exchange reactions between the fluoro-complexes with those between the tin(II) and tin(IV) complexes previously studied.

However, before the exchange reaction could be studied, a method of separating the complexes had to be found. To elucidate this problem, prior studies of the tin fluoro-complexes as solids and in solution will be discussed.

The Structures of Tin(IV) Fluoro-complexes in the SolidState and in Aqueous Solution

The first report on hexafluorostannates(IV) was by Marignac (6,7),

who prepared a large number of complexes of the general formulas  $M_2^I \text{SnF}_6$  and  $M^{II} \text{SnF}_6$ . He showed that the hexafluorostannates(IV) were isomorphous with the corresponding fluosilicates, being salts of a hypothetical fluorostannic acid,  $\text{H}_2\text{SnF}_6$  (8). Although there has been no x-ray structure work on the hexafluorostannates(IV), the isomorphism with the fluosilicates suggests an octahedral configuration for the hexafluorostannate(IV) ion.

Dove (9) studied the x-ray powder pattern of several complex acid fluorides, including  $\text{K}_3\text{HSnF}_8$ . After having indexed the powder patterns by comparison with the known lattice parameters of  $\text{K}_3\text{HNbOF}_7$ , he concluded that  $\text{K}_3\text{HSnF}_8$  was a lattice aggregate of  $\text{K}^+$ ,  $\text{HF}_2^-$ , and  $\text{SnF}_6^-$  ions. He supported this conclusion by a comparison of the infrared spectra of  $\text{KHF}_2$ ,  $\text{NaHF}_2$ , and  $\text{K}_3\text{HNbOF}_7$  with that of  $\text{K}_3\text{HSnF}_8$ .

Kriegsmann and Kessler (10,11), via evaluation of the infrared spectra of  $\text{K}_2\text{SnF}_6 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SnF}_6$ , have shown the assumption of an octahedral configuration for the hexafluorostannate(IV) ion to be correct.

In a polarographic study of the complex ions of tin in fluoride solutions, Schaap, Davis, and Nebergall (12), showed that tin(II) is present as the trifluorostannate(II) ion and tin(IV) as the hexafluorostannate(IV) ion. The anodic waves, arising from the oxidation of the tin(II) species to tin(IV), were reversible in acidic fluoride solutions. A plot of the half-wave potentials of these anodic waves versus the logarithm of the free fluoride ion concentration indicated a difference of three in the number of fluoride ions complexed by the tin(II) and the tin(IV) and that the hexafluorostannate(IV) ion was formed at the electrode. The workers estimated the overall dissociation constant for the hexafluorostannate(IV) ion to be about  $10^{-25}$ .

The Structures of the Solid Tin(II) Fluoro-complexes

The earliest report on complex formation between bivalent tin and fluorine is that of Wagner (13) who described the preparation of  $2\text{NH}_4\text{F} \cdot \text{SnF}_2 \cdot 2\text{H}_2\text{O}$  and  $2\text{KF} \cdot 3\text{SnF}_2 \cdot \text{H}_2\text{O}$ . Muetterties (14) reported that the only solid compounds obtainable from aqueous tin(II) fluoride solutions had the composition  $\text{MSnF}_3$  where  $\text{M} = \text{NH}_4^+$ ,  $\text{K}^+$ , or  $\text{Cs}^+$ .

Pugh (15) prepared hydrazinium salts of the tin fluoro-complexes. From the analysis of the compounds obtained, he proposed the existence of  $(\text{N}_2\text{H}_5)\text{HSnF}_6$  and  $(\text{N}_2\text{H}_5)\text{HSnF}_4$ , indicating that the tin(II) was present as the tetrafluorostannate(II) ion.

In an attempt to prepare  $(\text{NH}_4)_2\text{SnF}_4 \cdot 2\text{H}_2\text{O}$  by the method given by Simons (16), Kriegsmann and Kessler (11) obtained a compound with an empirical formula of  $\text{NH}_4\text{SnF}_3$  as established by analysis. The infrared and raman spectra of  $\text{NH}_4\text{SnF}_3$  compared to that of tin(II) fluoride indicate that the tin is present as the trifluorostannate(II) ion. In the course of the investigations, they also found that the addition of an aqueous sodium fluoride solution to an aqueous tin(II) fluoride solution caused the precipitation of a white crystalline material. Further addition of sodium fluoride solution caused the precipitate to redissolve. Analysis of the precipitate gave an empirical formula of  $\text{NaSn}_2\text{F}_5$ . The infrared spectrum of the compound indicated that trifluorostannate(II) ion was present; the workers proposed  $\text{Na}_3\text{Sn}(\text{SnF}_3)_5$  as the composition of the compound.

Donaldson and O'Donoghue (17) in a study of the systems  $\text{SnF}_2\text{-NaF-H}_2\text{O}$ ,  $\text{SnF}_2\text{-KF-H}_2\text{O}$ , and  $\text{SnF}_2\text{-NH}_4\text{F-H}_2\text{O}$  showed by chemical analysis and x-ray diffraction that two distinct phases,  $\text{MSnF}_3$  and  $\text{MSn}_2\text{F}_5$ , can be obtained from

each system. Addition of portions of a solution of the fluoride salt, MF, to a solution of tin(II) fluoride causes continuous precipitation until the molar ratio of tin(II) fluoride to alkali-metal fluoride or ammonium fluoride is 2:1. Thereafter, the precipitate redissolves on further addition of fluoride solution, until at a molar ratio of 1:1 the precipitate is completely redissolved. It was also found that recrystallization of the  $\text{MSnF}_3$  compounds from water yields  $\text{MSn}_2\text{F}_5$ . X-ray powder data for all the compounds were reported in the study.

McDonald, Larson, and Cromer (18) determined the crystal structure of a compound thought to be  $\text{NaSnF}_3$  from single-crystal x-ray data. The compound had been prepared by mixing equal quantities of 1 F solutions of sodium fluoride and tin(II) fluoride in contact with a small amount of metallic tin. Evaporation of the solution produced the crystals used in the study. It was found that the compound obtained in this way was  $\text{NaSn}_2\text{F}_5$ . The pentafluorodistannate(II) ion consists of two  $\text{SnF}_2$  groups bridged by a fluorine atom lying on a twofold axis. The pentafluorodistannate(II) ion groups are linked by two Sn-F bonds of 2.53 Å so that infinite chains of these groups lie parallel to the c axis. The Sn-F distance in the bridge is 2.22 Å and the other Sn-F distances are 2.07 and 2.08 Å.

The report of Donaldson and O'Donoghue indicates why McDonald and co-workers obtained  $\text{NaSn}_2\text{F}_5$  instead of  $\text{NaSnF}_3$  as was desired. The compound,  $\text{NaF} \cdot 2\text{SnF}_2$ , reported by Kriegsmann and Kessler seems to be identical with the  $\text{NaSn}_2\text{F}_5$  reported by Donaldson and O'Donoghue and, thus, is not  $\text{Na}_3\text{Sn}(\text{SnF}_3)_5$ .

#### The Structures of the Tin(II) Fluoro-complexes in Solution

The form of the fluorostannate(II) ion in solution has been the sub-



ject of much discussion. After studying the effect of fluoride concentration on alloy deposition from a tin-nickel electroplating bath, Davies (19) and Hedges (20) reported the existence of the tetrafluorostannate(II) and hexafluorostannate(IV) ions. Kruglov and Kochergin (21) presented evidence for the presence of the tetrafluorostannate(II) ion in solution. After measuring the density of solutions of varying NaF/SnCl<sub>2</sub> ratios, they found that the density isotherm exhibits a break corresponding to the NaF/SnCl<sub>2</sub> ratio of 4.06 in the presence of 10 g of 12 F hydrochloric acid per liter of solution. The workers interpreted this ratio as indicating that the complex anion was the tetrafluorostannate(II) ion.

As mentioned earlier, Schaap, Davis, and Nebergall (12) presented evidence for the existence of the trifluorostannate(II) ion by a polarographic study of the complex ions of tin in fluoride solutions. They found that at a constant fluoride concentration the half-wave potential of the cathodic wave is independent of the tin(II) concentration and also that changes in pH in the range 5.6 to 7.1 at constant fluoride concentration do not appreciably affect the half-wave potential of the cathodic wave. These observations indicate that the tin(II) complex in fluoride solutions is not polynuclear and that basic complexes are not important in these neutral solutions containing excess fluoride. The slope of a plot of the half-wave potentials of the reversible cathodic waves versus the logarithm of the concentration of fluoride ion indicates that the predominant species in solutions containing excess fluoride is the trifluorostannate(II) ion and that the cathodic reaction is  $\text{SnF}_3^- + 2e \rightarrow \text{Sn}(\text{amalgam}) + 3\text{F}^-$ . In these solutions, the tin(II) concentration was  $6 \times 10^{-4}$  F and the sodium fluoride concentration varied from 0.005 to 0.75 F. The overall

dissociation constant for the trifluorostannate(II) ion is  $1.2 \times 10^{-10}$  at an ionic strength of 0.8.

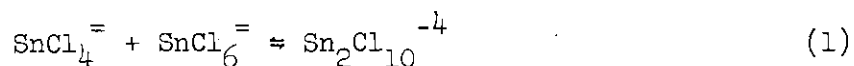
Potentiometric measurements on the tin-tin(II) couple were made by Donaldson and O'Donoghue (17). The cell used consisted of two identical half-cells,  $\text{Sn}/\text{Sn}(\text{ClO}_4)_2$ , 3 F  $\text{HClO}_4$ . A plot of the changes in voltage of the cell on addition of alkali-metal fluoride to one half-cell and of alkali-metal perchlorates to the other versus the ratio of the concentrations of tin(II) and fluoride in the solutions showed one inflection point (at an Sn:F ratio of 1:3) in dilute solutions. In more concentrated solutions (initial concentration of tin  $> 0.3$  F) there was an additional inflection point at an Sn:F ratio of 2:5. Thus, in solutions with an excess of fluoride insufficient for the conversion of all the tin to trifluorostannate(II), a considerable amount of the pentafluorodistannate(II) ion is present.

The only other tin(II) fluoride ion for which there is any evidence is the  $\text{SnF}^+$  ion found by Connick and Poulson (22) during a fluorine-19 nuclear magnetic resonance study. Measurements on a solution 0.8 F in  $\text{SnCl}_2$ , 1 F in NaF, and 0.3 F in HF yielded evidence of  $\text{SnF}^+$  and maybe  $\text{SnF}_2$ .

In conclusion it may be stated that the existence of the trifluorostannate(II) ion has been established by polarography (12), infrared and raman spectroscopy (10,11), and studies of its solid compounds (14,17). Because this evidence was so convincing and because only dilute solutions of tin(II) were used, all references made to the tin(II) fluoro-complex in this study have assumed the presence of the trifluorostannate(II) ion.

The Electron Exchange Reactions Between Tin(II) and Tin(IV)

Brown, Craig, and Davidson (4), in their work in aqueous hydrochloric acid solutions, found that the exchange exhibited second order kinetics at a constant hydrochloric acid concentration. This fact indicates that the slow step in the exchange is an oxidation-reduction reaction involving one tin(II) and one tin(IV) species. The workers suggested that the reaction proceeds via the formation of a dimer by a reaction of the type

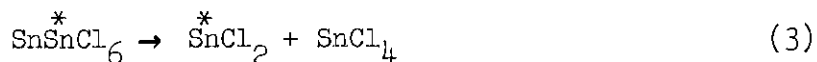
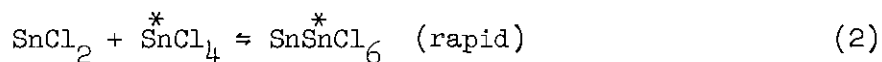


The rate determining step is the reaction of this dimer to form the tetrachlorostannate(II) and hexachlorostannate(IV) ions.

The workers further suggest that the dimer is not symmetrical and that the exchange does not take place with a probability of 0.5 every time the dimer forms and decomposes. Obviously, the work of Brown, Craig, and Davidson (4) does not prove that the dimer is even necessary for the exchange.

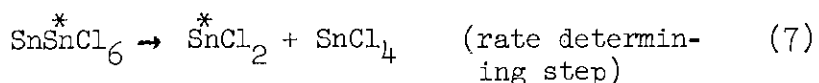
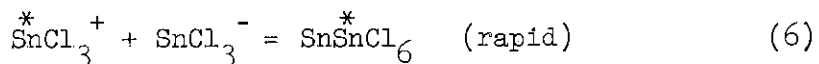
The rate of the exchange reaction in 10 F hydrochloric acid solution is  $7.5 \times 10^5 e^{-10800/RT} [\text{Sn(II)}][\text{Sn(IV)}]$  where the rate is in units of moles liter<sup>-1</sup> sec<sup>-1</sup>.

Meyer and Kahn (2) found that the exchange reaction in absolute alcohol was homogeneous and first order with respect to both the tin(II) chloride and tin(IV) chloride concentrations. They postulated two mechanisms which agree with the experimentally determined rate law. The first mechanism is given by equations (2) and (3).



The activated complex would consist of two tetrahedral tin chloride groups sharing two chlorine atoms along a common edge. Upon dissociation, this complex would yield a radioactive tin atom with either two or four chlorine atoms. If solvated tin chloride molecules are participating in the exchange, the activated complex would be  $\text{SnSnCl}_6^* \cdot 4\text{C}_2\text{H}_5\text{OH}$ . Here, the activated complex would consist of two octahedral  $\text{SnCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$  molecules which share two chlorine atoms along a common edge. Upon dissociation, this complex would also yield the desired products.

The second mechanism involves the same activated complex postulated for the first mechanism. This second mechanism is



This mechanism depends on the existence of the  $\text{SnCl}_3^+$  and  $\text{SnCl}_3^-$  ions in alcohol.

Meyer and Kahn did not favor one of these mechanisms over the other.

The exchange rate was represented by the equation,

$$\text{rate} = 5.02 \times 10^{16} e^{-23700/RT} (\text{SnCl}_2)(\text{SnCl}_4)$$

where the units of the rate are moles liter<sup>-1</sup> hr<sup>-1</sup>.

Meyer and Melnick (3) reported that the exchange reaction in methanol is of first order in both tin(IV) chloride and tin(II) chloride. The rate of exchange was represented by the equation,

$$\text{rate} = 5.5 \times 10^{10} e^{-20900/RT} (\text{SnCl}_2)(\text{SnCl}_4)$$

where the units of the rate are mole liter<sup>-1</sup> sec<sup>-1</sup>. No mechanism for the reaction in this medium was proposed but one could assume mechanisms similar to those given for the reaction in ethanol.

Gordon and Brubaker (5) studied the kinetics of the electron exchange reaction between tin(II) and tin(IV) in aqueous sulfuric acid media. It was found that the reaction is of first order with respect to tin(II) and tin(IV). The effect of hydrogen ion and sulfate on the rate was also studied. The empirical equation,  $r/ab = 0.674(\text{H}^+)^{-2} + 0.0725(\text{SO}_4^{=})_2(\text{H}^+)^{-1}$  was derived, where  $r$  is the rate of exchange,  $a$  is the total tin(II) concentration, and  $b$  is the total tin(IV) concentration. Two possible reaction paths were proposed that conform with this rate law. In the first path, two hydrolysis steps are required to arrive at the exchanging species, and, in the second, one hydrolysis step and one sulfate complexing step. The exchanging species are probably entities such as  $\text{SnO}(\text{SO}_4)_2^{=}$  +  $\text{SnOH}^+$  or

$\text{Sn}(\text{OH})_2\text{SO}_4 + \text{SnOHSO}_4^-$  and  $\text{SnOH}(\text{SO}_4)_2^- + \text{SnOHSO}_4^-$ . Lacking more information concerning the formation of these species, no attempt of a more detailed interpretation was made. The effect of chloride ion on the exchange was also investigated. The addition of chloride to the reaction mixture increases the rate of exchange. Above 0.5 F chloride, the rate corresponds to the equation,

$$\text{rate} = 4.94 [\text{Sn}(\text{II})][\text{Sn}(\text{IV})][\text{Cl}^-],$$

where R is in mole liter<sup>-1</sup> hours<sup>-1</sup>. If it is assumed that the hexachlorostannate(IV) ion is the predominate species of tin(IV) above 0.5 F chloride and that the trichlorostannate(II) ion is the primary tin(II) species, then the experiments indicate that the exchange is between the tetrachlorostannate(II) and the hexachlorostannate(IV) ions which form  $\text{Sn}_2\text{Cl}_{10}^{-4}$  as an intermediate. This is the same mechanism as proposed by Brown, Craig, and Davidson (4) and by Meyer and Kahn (2).

### Experimental

#### Preparation of Active Tin(II)-Tin(IV) Stock Solutions

In performing the experiments designed to find a suitable method for the separation of the hexafluorostannate(IV) ion from the trifluorostannate(II) ion, it was desirable to have stock solutions of these complexes containing tin-113. The tin-113 was obtained from Oak Ridge National Laboratory. The one millicurie sample was contained in about 0.6 ml of 3 F hydrochloric acid.

The tin(IV) stock solution was prepared in the following way. An

aliquot of the one millicurie stock solution was diluted to 5 ml with distilled water in a polyethylene centrifuge cone. About 120 mg  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was added as a carrier. To insure that the tin was in the higher oxidation state, 3 drops of 30 percent hydrogen peroxide was added and the resulting solution heated on a steam bath for several minutes. After cooling, dilute ammonium hydroxide was added to precipitate the tin. The suspension was centrifuged, and the supernatant liquid withdrawn with a transfer pipette. The precipitate was washed twice with dilute ammonium hydroxide and centrifuged. After removal of the supernatant liquid, the precipitate was dissolved in 10 ml of 10.0 F hydrofluoric acid.

For the preparation of a stock solution of the tin(II) fluoro-complex, an aliquot of the hydrochloric acid solution of tin-113 was added to 10 ml of 6 F hydrochloric acid in a 50-ml polyethylene centrifuge cone. About 0.05 g nickel foil was added and the resulting solution heated in a water bath at 80° C for one hour. After cooling, the solution was added to a chromatographic column containing Dowex-1-X10 in the chloride form. Rapid movement of the solvents through the column was obtained by applying suction to the lower end of the column. The nickel(II) was eluted with 5 ml of 6 F hydrochloric acid. Then, the tin(II) was eluted into another container with 15 ml of 2 F perchloric acid. Tin(II) sulfide was precipitated from the perchloric acid solution by addition of ammonium sulfide. The suspension was centrifuged and the supernatant liquid removed with a transfer pipette. The tin(II) sulfide was dissolved in 10 ml of a 5.0 F hydrofluoric acid solution and the hydrogen sulfide driven off by heating in a water bath. The entire operation with tin(II) was conducted in the glove box described earlier.

After preparation, the stock solution remained in the box with the nitrogen stream continuously bubbling through the tin(II) solution. Under these conditions, the tin(II) remained unoxidized for several weeks.

#### Radioactive Properties of Tin-113

Since most of the reactions of the fluoro-complexes of tin investigated in this work were studied via the use of tin-113, it is necessary to discuss some of its radioactive properties. Tin-113 decays with a half-life of 112 days (23) to indium-113m by electron capture. This metastable state of indium-113 decays with a half-life of 10<sup>4</sup> minutes to the ground state with the emission of a 0.392 MeV gamma ray. It is this indium gamma radiation that is actually detected in the process of counting the samples. For the counts to be related to the reactions of tin rather than those of indium, secular equilibrium must be established in the sample. In the case of the tin-113-indium-113 equilibrium, the indium reaches 31/32 of its maximum attainable activity after 8.5 hours. Thus, the samples were always allowed to stand overnight before counting in the manner described earlier.

#### Solvent Extraction

The first separation method considered for the isolation of the tin fluoro-complexes was solvent extraction. Earlier work (24) on the distribution of the tin(II)-tin(IV) fluoro-complexes between (i) diethyl ether and aqueous hydrofluoric acid solutions and (ii) methyl ethyl ketone and aqueous hydrofluoric acid solutions had shown that these systems did not yield a satisfactory separation.

Solvent extraction with a high molecular weight amine dissolved in an inert solvent was investigated. The amines chosen for this experiment were (i) N-N-dimethylcyclohexylamine, (ii) tri-n-butylamine, and



(iii) di-n-hexylamine. The extractant was a 0.100 F solution of the amine in petroleum ether.

An investigation of the behavior of the phase volumes in the extraction process was made. Of a series of 3-ml aliquots at various concentrations of hydrofluoric acid, each was extracted with 3 ml of a solution of the amine in petroleum ether. It was found that there was no volume change for either the aqueous or the organic layer within the precision of the experiment.

The distribution of the tin fluoro-complexes between aqueous hydrofluoric acid solution and amine in petroleum ether solution was measured in the following way. Solutions 0.010 F in tin(II) or tin(IV), but varying in their concentration of hydrofluoric acid, were prepared and placed in polyethylene centrifuge tubes. An aliquot from the appropriate tin-113 stock solution was added to each tube and the resulting solutions allowed to equilibrate overnight. Two-ml aliquots of the amine in petroleum ether solution were added to each centrifuge tube. The tubes were stoppered and shaken for sixty seconds. After centrifugation, an aliquot was withdrawn from each phase with a micropipette and placed in a 2-ml test tube for counting. After waiting for secular equilibrium to be established, the aliquots were counted and the distribution ratio (organic/aqueous) calculated. The hydrofluoric acid solutions used were 1.0, 5.0, 10.0, and 20.0 F hydrofluoric acid. It was found that less than one percent of the tin was extracted with the amine solution.

#### Precipitation Reactions for Tin(II)-Tin(IV)

It was hoped that the hexafluorostannate(IV) ion could be separated from the trifluorostannate(II) ion by selective precipitation. A number of

metal ions, complex and simple, as well as several organic cations were used to test this possibility. The general method was to prepare a concentrated solution of the cation in either 5.0 or 10.0 F hydrofluoric acid and to add the resulting solution dropwise to a solution 0.010 F in tin(II) or tin(IV) and 5.0 or 10.0 F in hydrofluoric acid. The following cations were used:

- potassium (as fluoride)
- cesium (as chloride)
- thallium (as thallium(I) sulfate)
- lithium (as carbonate)
- barium (as hydroxide)
- iron (as iron(III) nitrate)
- zinc (as nitrate)
- copper (as copper(II) nitrate)
- cobalt (as cobalt(II) chloride and as cobalt(III) nitrate)
- tetraphenylarsonium (as chloride)
- tetraethylammonium (as bromide)
- pyridinium (as hydrochloride)
- quinolinium (as hydrofluoride - prepared from quinoline)
- brucine (as sulfate)
- benzoguanamine
- benzocaine
- hexamminecobalt(III) (as chloride)
- cis-dichlorobis(ethylenediamine)cobalt(III) (as chloride - prepared by the method of Tupizina (25))

trans-dichlorobis(ethylenediamine)cobalt(III) (as chloride - prepared by the method of Tupizina (25))

hexaureachromium(III) chloride (prepared by the method of Pfeiffer (26))

hexa(1-phenyl-3-methylpyrazolone-5)chromium(III) chloride (prepared by the method of Wilke-Dörfurt (27))

hydrazinium (as hydrofluoride)

The complex prepared by Wilke-Dörfurt was actually hexaantipyrine-chromium(III) chloride. Antipyrine is 1-phenyl-2-methylpyrazolone-5 and differs from the compound used here only in that antipyrine has the methyl group in the position two instead of three. However, this difference did not affect the synthesis of the complex. With the exception of hydrazinium, none of the cations mentioned gave precipitates with either tin(II) or tin(IV) under the conditions of the experiment.

Solutions of hydrazine in hydrofluoric acid of varying concentration were used to test the tin(II)-tin(IV) solutions. Solutions containing only a small amount of hydrazine gave crystalline precipitates with both oxidation states. Since no separation was achieved, the precipitates were not analyzed. Solutions containing an excess of hydrazine in hydrofluoric acid such that the final tin solutions were neutral (hydrion paper) gave no precipitate for either oxidation state while solutions containing enough excess hydrazine to make the tin solutions basic gave a precipitate only with tin(II). The precipitate was extremely fine and could be separated by filtration only with difficulty. When the precipitate was dissolved in dilute hydrochloric acid and the resulting solution treated with a mercuric chloride solution, mercurous chloride formed indicating the presence

of tin(II). The precipitation with hydrazine was deemed unsatisfactory for the separation of tin(II)-tin(IV) fluoro-complexes because of the difficulty in isolating the precipitate.

#### Anion Exchange - Equilibrium Method

The next separation method tried was anion exchange. Faris (28) reported the elution curves of a number of elements from a column of Dowex-1-X10 with hydrofluoric acid. He concluded that tin(II) and tin(IV) gave identical elution curves but that tin(II) was probably oxidized during the experiment. Since our work was performed in a dry box under a nitrogen atmosphere, it was hoped that this difficulty could be avoided.

The resin used in the following experiments was a Dowex-1-X10, (200-300 mesh size) strong base anion exchange resin, with a rated capacity of 2.7 meq per gram of dry resin.

Since the resin was obtained in the chloride form, it was necessary to convert it to another form to avoid any possible influence of chloride on the reactions of the fluoro-complexes. It was converted to the perchlorate form by treatment with dilute perchloric acid until the washing no longer gave a positive silver nitrate test for chloride. Conversion from the chloride form to the fluoride form was accomplished similarly by washing the resin with dilute hydrofluoric acid. It was found that it was difficult to convert from the perchlorate form to any other form and that any resin which had been in contact with perchloric acid was best discarded unless the perchlorate form was desired.

The adsorbability of the hexafluorostannate(IV) and trifluorostannate(II) ions was studied by the equilibrium method. In the equilibrium method, measured amounts of resin and solution are intermixed and

the resulting decrease in concentration of the metal in the solution is used to calculate the distribution between the solution and the resin according to the following expression (29):

$$D = \frac{A - A_t}{A_t}$$

where  $A$  = activity of solution before resin is added, in counts per minute

$A_t$  = activity of solution at a particular time  $t$ , in counts per minute.

The distribution coefficient  $K_d$  (amount of adsorbed material per kg. resin/amount of adsorbable material per liter solution) is related to  $D$  by the relationship  $K_d = D \times \frac{v}{m}$  (29)

where  $v$  = volume of liquid phase in liters

$m$  = mass of resin in kilograms.

Since a solution volume of 5.00 ml and resin weight of 0.500 g were used in each experiment,  $v/m = 10$ , and therefore,  $K_d = 10 D$ .

All distribution data have been calculated with resin weights expressed in terms of resin dried to constant weight at 60° C over Anhydrone (J. T. Baker Chemical Company). Kraus, Nelson, and Smith (30) reported that such drying yields constant weights within twenty-four hours and an apparently water-free product. The drying was accomplished in a pistol drying tube over Anhydrone at the boiling point of chloroform.

The distribution coefficients of tin in solutions of varying perchloric acid and hydrofluoric acid concentrations were determined with the resin in the perchlorate and fluoride form in the following way. The resin (0.500 g) was weighed and placed in a polyethylene centrifuge cone. Water was added and the resin allowed to equilibrate with water for a few

hours. The mixture was centrifuged and the water removed with a transfer pipette. A solution (5.00 ml) containing tin in the appropriate acid media was prepared by dissolving either tin(II) oxide (Baker A. R.) or sodium stannate(IV) (Baker A. R.) in the acid solution. An aliquot from the appropriate tin stock solution was added as a tracer yielding a final tin concentration of 0.010 F. Solutions containing tin(II) were outgassed with nitrogen and the work performed in the glove box under nitrogen. An aliquot was removed for counting, and the remaining solution was added to the cone containing the resin. After equilibration for twenty-four hours, the solution above the resin was sampled with a micropipette, the aliquot was placed in a 2-ml test tube and counted, and the distribution,  $D$ , calculated. The results are tabulated in Table 1 and presented graphically in Figure 1. It can be seen that the distribution,  $D$ , decreases rapidly with increasing hydrofluoric acid concentration for both tin(II) and tin(IV). The plot in Figure 1 holds for the resin in the perchlorate form. Figures 2, 3, and 4 show the effect on the distribution of the fluoro-complexes between perchloric acid - hydrofluoric acid solutions and the resin in the fluoride form when holding the perchloric acid concentration constant and varying the hydrofluoric acid concentration. Figure 3 shows that the distribution in 0.30 F perchloric acid increases with increasing hydrofluoric acid concentration in the range 0.05-0.50 F and decreases thereafter in agreement with Figure 1. Figure 4 shows the situation with 0.03 to 0.10 F hydrofluoric acid and 0.10 F perchloric acid. As can be seen, the distribution goes through a minimum between 0.05-0.06 F hydrofluoric acid and rapidly increases to strong adsorption at 0.10 F. Presumably, as the hydrofluoric acid is further increased,  $D$ , will go through a maximum and start to de-

Table 1. Distribution (D) Between Resin and Fluoride Solution

F HClO <sub>4</sub>	F HF	D-Sn(II)	D-Sn(IV)	Resin Form
	0.10	2.80	10.9	ClO <sub>4</sub>
	0.20	2.60	5.70	ClO <sub>4</sub>
	1.00	1.79	1.58	ClO <sub>4</sub>
	5.00	0.70	0.68	ClO <sub>4</sub>
	10.00	0.28	0.33	ClO <sub>4</sub>
	0.10	st. ads.	st. ads.	F
	0.20	st. ads.	st. ads.	F
	1.00	st. ads.	st. ads.	F
	5.00	17.5	13.5	F
	10.00	2.51	2.25	F
3.00	1.50	0.00	0.00	ClO <sub>4</sub>
2.00	1.00	0.00	0.00	ClO <sub>4</sub>
1.00	0.50	0.00	0.00	ClO <sub>4</sub>
0.50	0.25	0.00	0.00	ClO <sub>4</sub>
0.10	0.05	4.13	7.10	F
0.20	0.05	0.60	1.05	F
0.30	0.05	0.17	0.23	F
0.40	0.05	0.05	0.06	F
0.10	0.10	st. ads.	st. ads.	F
0.20	0.10	5.80	21.5	F
0.30	0.10	0.29	1.04	F

Table 1. Distribution (D) Between Resin and Fluoride Solution  
(Concluded)

F HClO <sub>4</sub>	F HF	D-Sn(II)	D-Sn(IV)	Resin Form
0.40	0.10	0.22	0.13	F
0.50	0.10	0.04	0.03	F
0.10	0.20	st. ads.	st. ads.	F
0.20	0.20	11.7	35.0	F
0.30	0.20	0.55	2.3	F
0.40	0.20	0.22	0.20	F
0.50	0.20	0.02	0.01	F
0.10	0.03	17.9	10.4	F
0.10	0.04	5.07	10.0	F
0.10	0.06	3.75	7.10	F
0.10	0.07	5.65	8.70	F
0.30	0.50	9.20	3.75	F
0.30	1.00	6.00	3.25	F
0.30	5.00	1.85	1.55	F

All solutions are 0.001 F in tin except for the solutions using the resin in the ClO<sub>4</sub><sup>-</sup> form. The latter solutions are 0.010 F in tin.



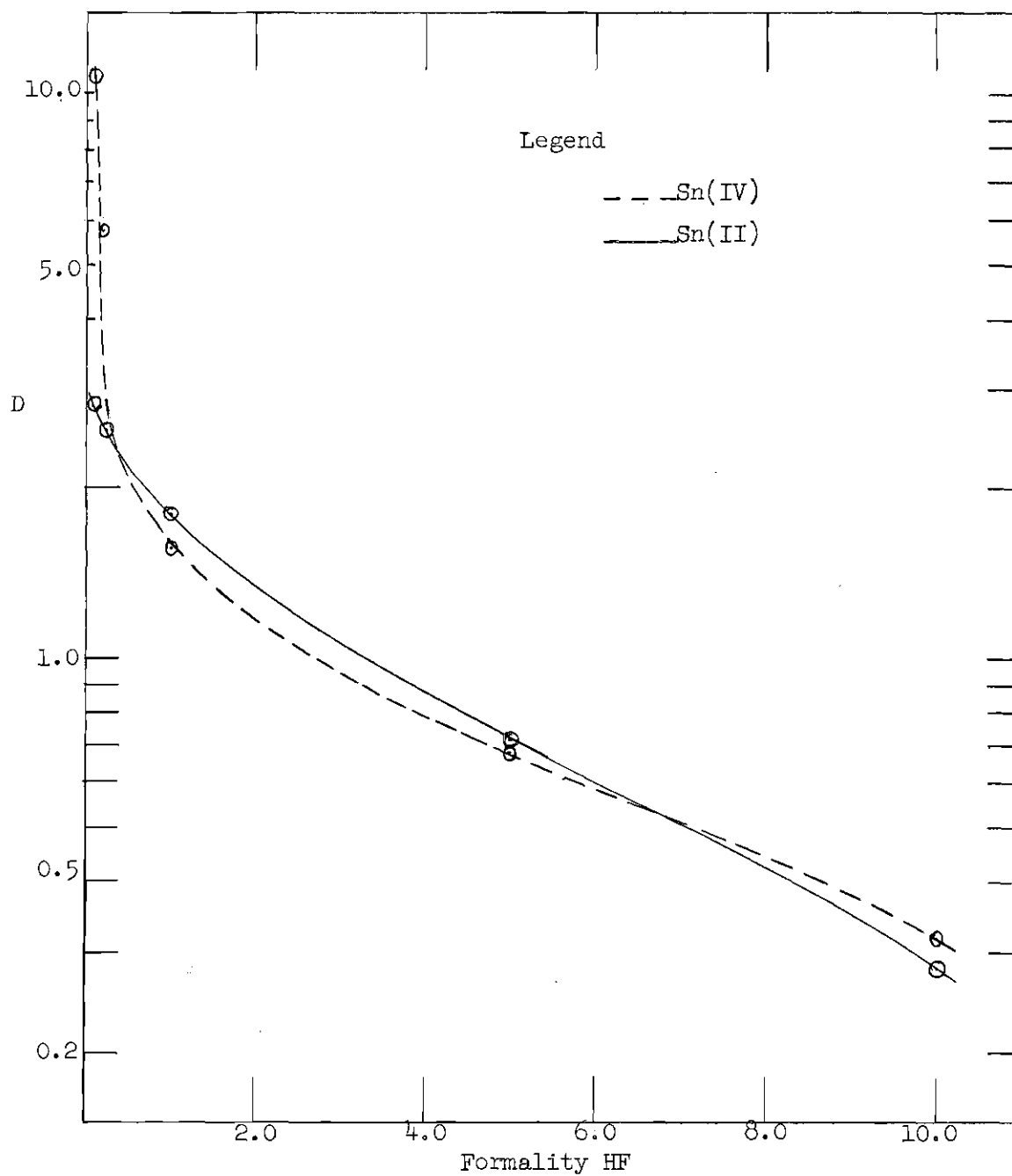


Figure 1. Plots of the Distribution (Resin/Solution) versus Concentration of HF (Perchlorate Form of Resin)

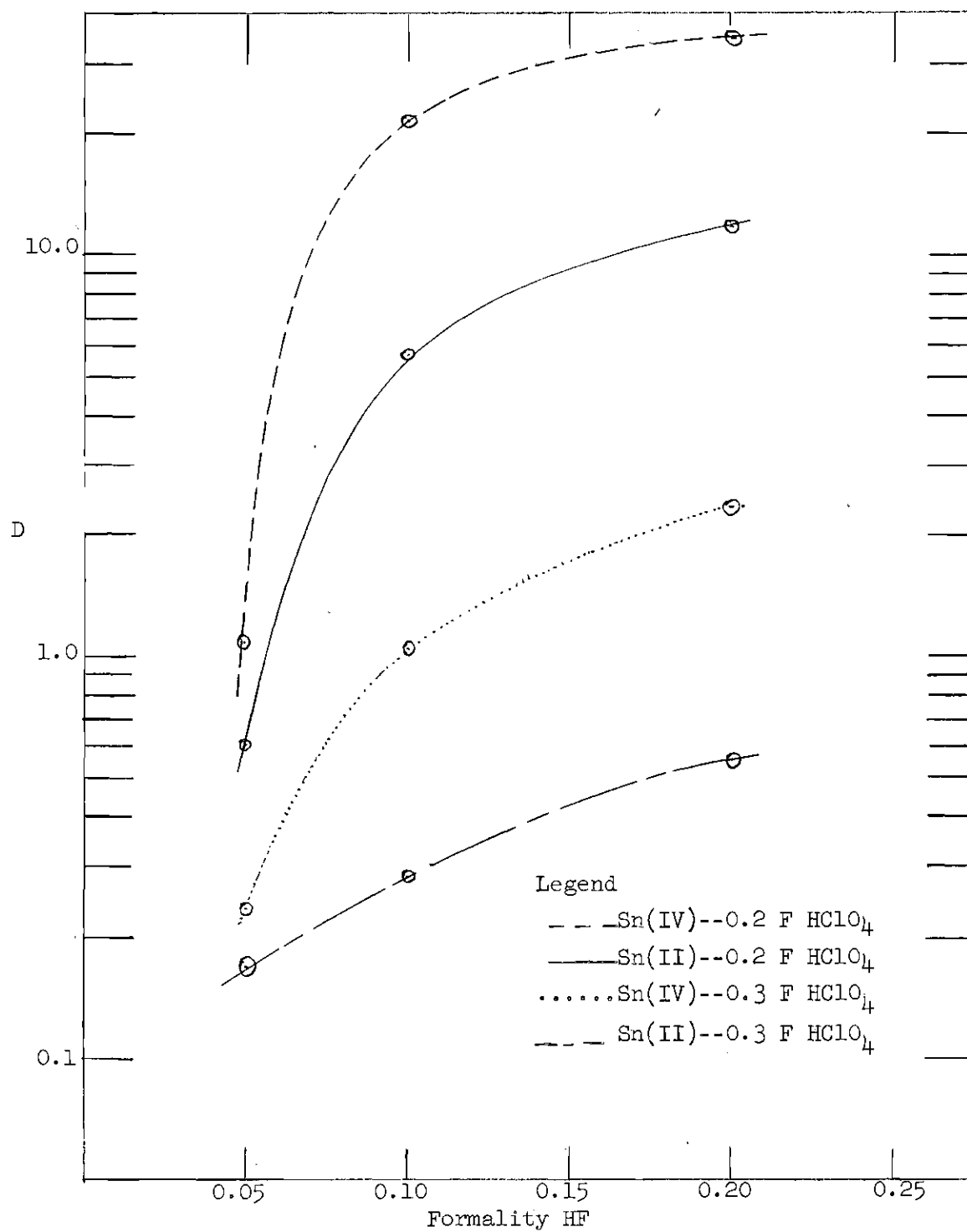


Figure 2. Plots of Distribution (Resin/Solution) versus HF Concentration at Constant HClO<sub>4</sub> Concentration (Fluoride Form of Resin)

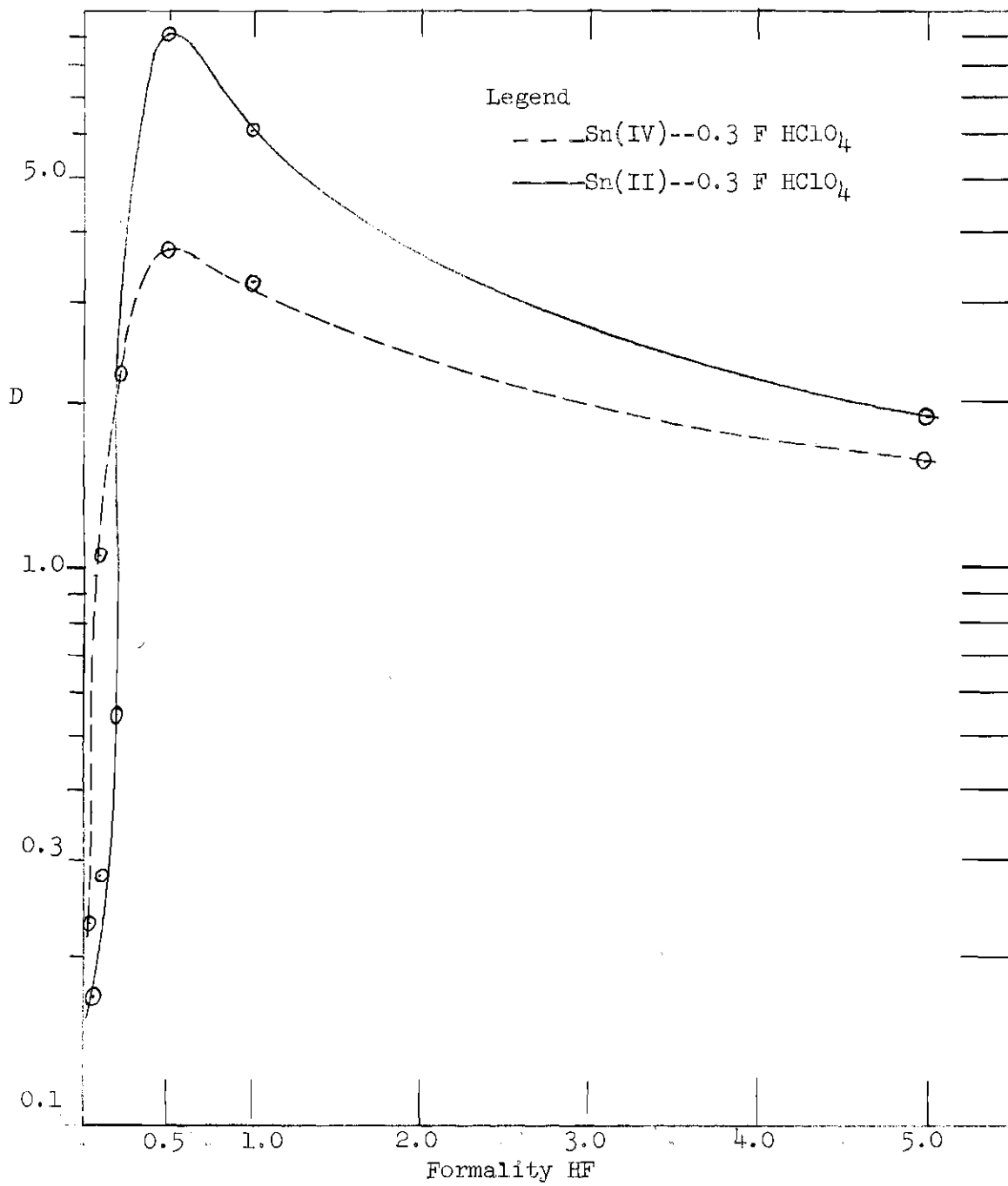


Figure 3. Plots of the Distribution (Resin/Solution) versus HF Concentration at Constant HClO<sub>4</sub> Concentration (Fluoride Form of Resin)

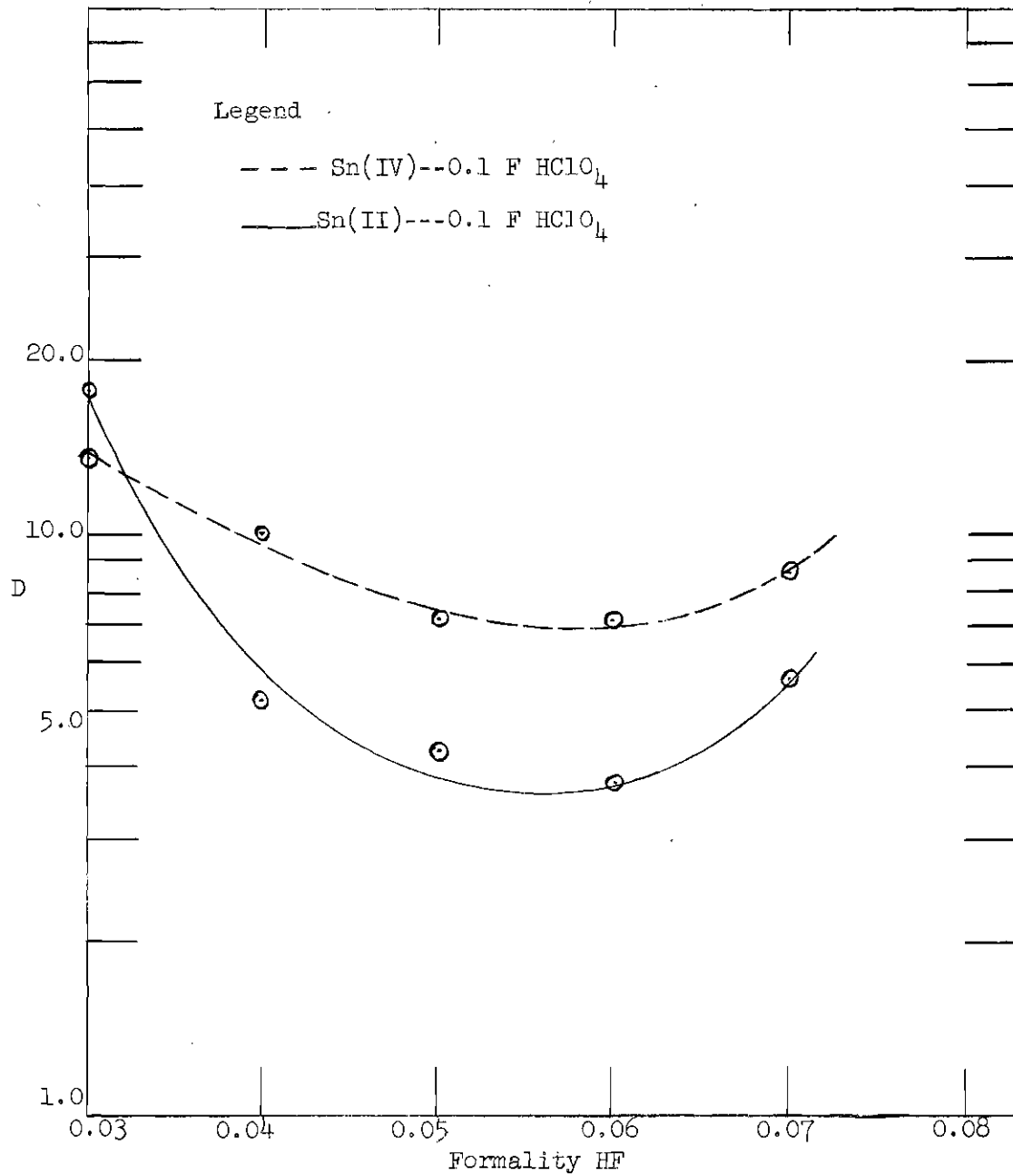


Figure 4. Plots of Distribution (Resin/Solution) versus HF Concentration at Constant HClO<sub>4</sub> Concentration (Fluoride Form of Resin)

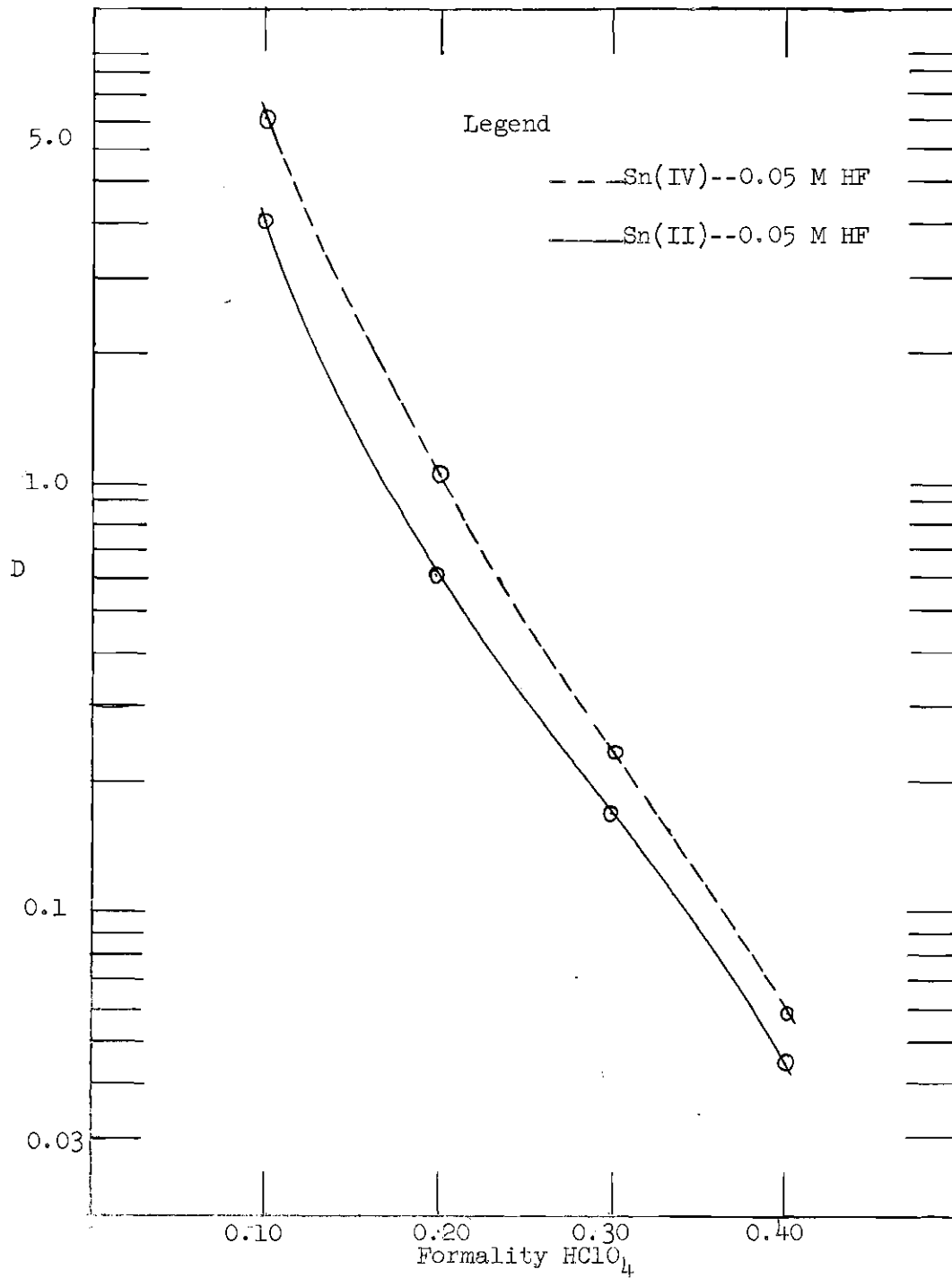


Figure 5. Plot of Distribution (Resin/Solution versus  $\text{HClO}_4$  Concentration at Constant HF Concentration (Fluoride Form of Resin)

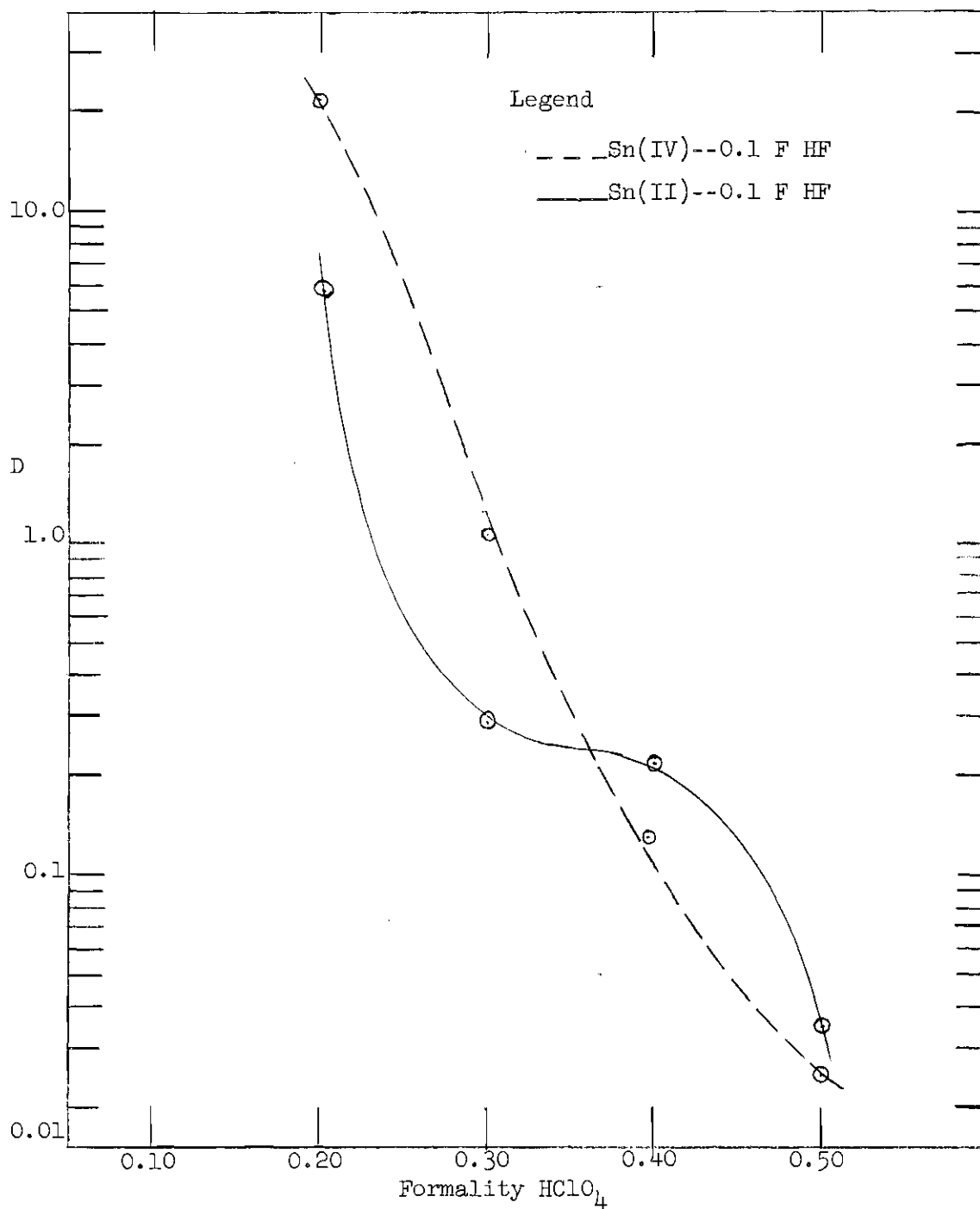


Figure 6. Plots of Distribution (Resin/Solution) versus  $\text{HClO}_4$  Concentration at Constant HF Concentration (Fluoride Form of Resin)

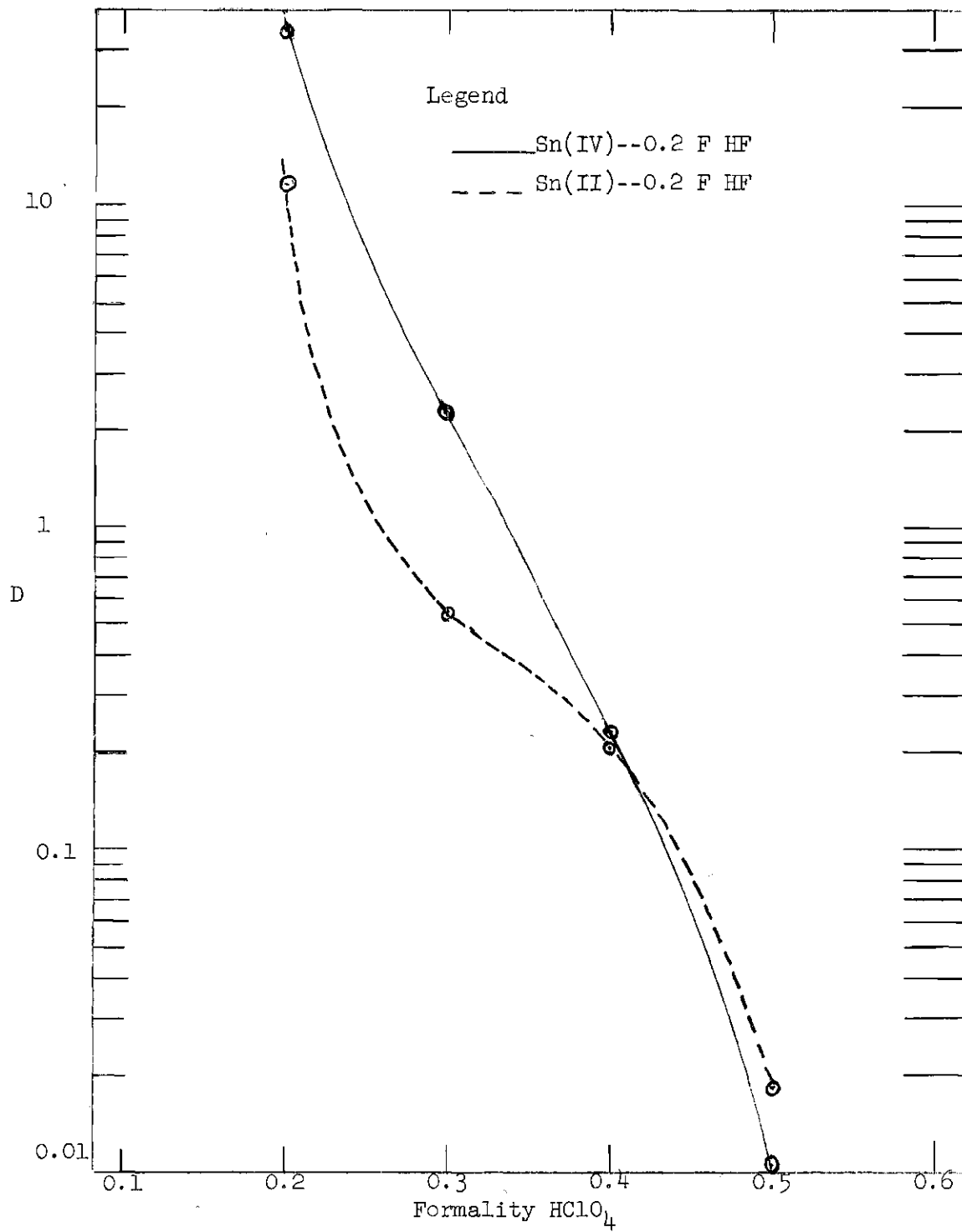


Figure 7. Plots of Distribution (Resin/Solution) versus  $\text{HClO}_4$  Concentration at Constant HF Concentration (Fluoride Form of Resin)

crease with increasing hydrofluoric acid concentration.

Figures 5, 6, and 7 show much of the same data with the hydrofluoric acid concentration being held constant and the perchloric acid concentration varied. The values of D are extremely close in all cases and in Figures 6 and 7 the curves for tin(II) and tin(IV) actually cross. Thus, under none of the conditions studied is a separation possible.



## CHAPTER IV

ELECTRON EXCHANGE REACTION BETWEEN  
ANTIMONY(III)-ANTIMONY(V) FLUORO-COMPLEXESIntroduction

Since no method could be found for separating the trifluorostannate-(II) ion from the hexafluorostannate(IV) ion, it was decided to investigate the antimony(III)-antimony(V) fluoro-complex system. If the antimony(III) could be separated from the antimony(V), the electron exchange reaction could be studied. This system would also be an example of a reaction that proceeds through the transfer of two electrons.

Before going into the details of the separation method, the general solution chemistry and the structures in the solid state of the antimony fluoro-complexes will be discussed.

The Structures of the Antimony(V) Fluoro-complexes  
in the Solid State

The first preparation of an antimony(V) fluoro-complex was reported by M. C. Marignac (31). He prepared  $MSbF_6$ , where  $M = K^+$ ,  $Na^+$ , and  $NH_4^+$ . Marignac (32) also prepared what were apparently the heptafluoroantimonates-(V) of potassium and ammonium and a compound  $NaF \cdot SbOF_3 \cdot H_2O$ .

The crystal structure has been studied by x-ray methods for a number of hexafluoroantimonates(V). For those compounds in which the cation has a single positive charge, the lattice is essentially of the sodium chloride or cesium chloride type.

Schrewelius (33) determined the crystal structure of  $\text{NaSbF}_6$ . Although the exact positions of the fluorine atoms could not be determined, he concluded that the structure was a sodium chloride type lattice. Assuming an Sb-F distance of 1.95 Å, he was able to deduce the following atom to atom distances (in Å): Sb-F, 1.95; Na-F, 2.32; F-F within  $\text{SbF}_6^-$  octahedra, 2.67 and 2.78; and F-F in adjacent octahedra, 2.72. The F-F distances within one octahedron are not all the same and, thus, indicate that the octahedron is distorted.

In the same paper, Schrewelius reported the structure of Marignac's salt,  $\text{NaF} \cdot \text{SbOF}_3 \cdot \text{H}_2\text{O}$ . Schrewelius assumed that this compound was  $\text{NaSbF}_4(\text{OH})_2$  and described the  $\text{SbF}_4(\text{OH})_2^-$  ion as octahedral with an Sb-F distance of 1.95 Å. In a later study of the hydroxofluoro complexes of antimony(V), Kolditz and Rehak (34) identified Marignac's salt as  $\text{NaSbF}_5\text{OH}$ . Marignac reported  $\text{NaF} \cdot \text{SbOF}_3 \cdot \text{H}_2\text{O}$  as hexagonal prisms, but Kolditz and Rehak found that  $\text{NaSbF}_5\text{OH}$  crystallizes as hexagonal prisms while  $\text{NaSbF}_4(\text{OH})_2$  is formed as a thick hygroscopic mass. They also found that the powder pattern of  $\text{NaSbF}_5\text{OH}$  is identical with that taken by Schrewelius and ascribed to  $\text{NaSbF}_4(\text{OH})_2$ . Thus, the structure determined by Schrewelius corresponds to  $\text{NaSbF}_5\text{OH}$  rather than to  $\text{NaSbF}_4(\text{OH})_2$ .

Schrewelius (35) reported distortions of the octahedral anions in  $\text{CsSbF}_6$ ,  $\text{RbSbF}_6$ ,  $\text{NH}_4\text{SbF}_6$ , and  $\text{TlSbF}_6$  in addition to distortions of the CsCl type lattice to resemble that of the  $\text{BaSiF}_6$  lattice. Again, an Sb-F distance of 1.97 Å was assumed.

Bode and Voss (36) found that the Sb-F distance in  $\text{KSbF}_6$  was 1.77 Å. Other distances reported are: F-F distance within octahedra 2.38 and 2.60; F-F distance between octahedra, 2.74; and K-F distance, 2.74 Å.

The central angle of the  $\text{SbF}_6^-$  octahedra was found to be  $97^\circ$ . These data could be explained by assuming a compression of the octahedra along the three-fold axis. In a later work, Bode (37) found that the  $\text{SbF}_6^-$  octahedra in  $\text{AgSbF}_6$  have distortions very similar to those in  $\text{KSbF}_6$ .

In a reinvestigation of the structure of  $\text{NaSbF}_6$ , Teufer (38) found that the powder pattern had a maximum for the fluorine atom corresponding to an Sb-F distance of 1.78 Å. Using this distance instead of the 1.95 Å used by Schrewelius, he found that the  $\text{SbF}_6^-$  octahedra have distortions like those reported by Bode and Voss in  $\text{KSbF}_6$ .

After a single crystal study of  $\text{LiSbF}_6$ , Burns (39) was able to re-interpret much of the older x-ray crystal data. He found that  $\text{LiSbF}_6$  consists of regular  $\text{SbF}_6^-$  octahedra with each lithium atom octahedrally coordinated by fluorine atoms from six  $\text{SbF}_6^-$  groups. The Sb-Li bonds are longer than the Sb-F bonds and discrete  $\text{SbF}_6^-$  octahedra exist in the lattice. The following distances were observed (in Å): Sb-F distance,  $1.877 \pm 0.006$ ; Li-F distance,  $2.032 \pm 0.006$ ; F-F distance within  $\text{SbF}_6^-$  octahedra,  $2.65 \pm 0.01$ , and F-F distance within  $\text{LiF}_6^-$  octahedra,  $2.87 \pm 0.01$ . The F-Sb-F bond angles of  $89.9 \pm 0.2^\circ$  and  $90.1 \pm 0.2^\circ$  show that the  $\text{SbF}_6^-$  octahedra are regular within the experimental errors. All the reported structures of the fluoroantimonates(V) can be classified as having either a NaCl or CsCl arrangement of  $\text{M}^+$  and  $\text{SbF}_6^-$  ions with various forms of distortion. The two compounds in the NaCl category,  $\text{LiSbF}_6$  and  $\text{NaSbF}_6$ , have very similar crystal structures. This similarity adds credibility to the fluorine atom positions in  $\text{NaSbF}_6$  reported by Schrewelius.

The fluoroantimonates(V) of  $\text{Ag}^+$ ,  $\text{K}^+$ ,  $\text{Tl}^+$ ,  $\text{Rb}^+$ ,  $\text{NH}_4^+$ , and  $\text{Cs}^+$  may be described in terms of the CsCl structure. All but the first two of these

compounds have the  $\text{BaSiF}_6$  structure described by Hoard and Vincent (40). The other two, with  $\text{Ag}^+$  and  $\text{K}^+$ , are cubic with adjacent  $\text{SbF}_6^-$  octahedra oriented differently thus resulting in a superlattice of eight CsCl-like cubes. Bode and Voss (36) claimed that the  $\text{SbF}_6^-$  octahedron in these two compounds is compressed along its three-fold axis causing the F-Sb-F angle to be  $96^\circ$ , and suggested that the rhombohedral fluoroantimonates(V) result from the periodic arrangement of these distorted octahedra. However, Burns pointed out that the rhombohedral angle in the  $\text{BaSiF}_6$  structure is a consequence of the regular 12-fold coordination of fluorine atoms around the  $\text{Ba}^{++}$  (the  $\text{SiF}_6^{=}$  show little or no distortion). He suggested the assumption that there is an inherent distortion of  $\text{SbF}_6^-$  in these fluoroantimonates(V) is probably incorrect.

As mentioned earlier, Marignac obtained the hydrated heptafluoroantimonates(V) of potassium and ammonium. Other salts containing seven fluoride atoms are  $\text{K}_2\text{SbF}_7 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{SbF}_7 \cdot 1/2\text{H}_2\text{O}$ , and  $(\text{quinine} \cdot \text{H})_2\text{SbF}_7$  (41). The structures of these salts are unknown and it is not certain that the antimony is seven coordinate. Data on the formally analogous heptachloroantimonates(V) indicate that antimony(V) is not seven coordinate in these compounds.

Several polymeric fluoroantimonates(V) have been prepared by Kolditz (34, 42). Crystalline  $\text{NaSbF}_5\text{OH}$  was thermally decomposed with the loss of hydrofluoric acid and the formation of a chainlike polymeric tetrafluoroantimonate(V). A dimeric salt,  $\text{K}_2\text{Sb}_2\text{OF}_{10}$ , was obtained by heating the carbonato complex of  $\text{SbF}_5$  with  $\text{SbF}_5$  to  $125^\circ \text{C}$ . Kolditz postulated that antimony(V) is six-coordinate and that these condensed fluoroantimonates(V) are of octahedral structure.

In all cases for which x-ray crystal structure data are available, it is found that the antimony(V) fluoro-complexes have an octahedral structure.

#### The Structures of Antimony(V) in the Solution

All the evidence on the nature of the hexafluoroantimonate(V) ion in solution indicates it has an octahedral structure.

In a fluorine-19 nuclear magnetic resonance study of liquid antimony(V) fluoride, Hoffman, Holder, and Jolly (43) found that it consists of long chains of octahedral  $\text{SbF}_6^-$  groups, each group sharing two of its fluorine atoms with two neighbors.

The hydrogen fluoride-antimony(V) fluoride system has been studied by several workers. Clifford, Beachell, and Jack (44) observed that antimony(V) fluoride was the strongest acid among the twenty-odd fluorides investigated. Their method of investigation consisted of determining the solubility of the fluorides in liquid hydrogen fluoride, observing the ability of the hydrofluoric acid solution to dissolve various metals and then classifying the fluorides according to their acid strength. Hyman, Quarterman, Kilpatrick, and Katz (45) concluded from conductivity measurements on the hydrogen fluoride-antimony(V) fluoride system that antimony(V) fluoride is a strong acid in that acid. Infrared and raman spectra indicated that the following species are present in the system: antimony(V) fluoride, hydrogen fluoride, a highly symmetrical species, presumably the hexafluoroantimonate(V) ion, and a more complex species, possibly the ion pair  $\text{H}_2\text{F}^+\text{SbF}_6^-$ . At low antimony(V) fluoride concentrations, the hexafluoroantimonate(V) ion predominates and the spectrum is that expected for an

octahedral ion. At high concentrations, the more complex species predominates. Clifford and Kongpricha (46) supported the conclusion that antimony(V) fluoride is a strong acid in liquid hydrogen fluoride from their studies of the solvolysis of the hexafluoroantimonate(V) ion.

Meuwsen and Mögling (47) reported that they have succeeded in isolating the free acid,  $\text{HSbF}_6 \cdot \text{H}_2\text{O}$ , by treating antimony(V) oxide with 40 percent hydrofluoric acid solution and concentrating the solution on a steam bath. The compound is very soluble in water, ether, and acetone but only slightly soluble in benzene, chloroform, and carbon tetrachloride. An aqueous solution of  $\text{HSbF}_6$  does not yield a precipitate of antimony(V) hydrous oxide on heating and freshly prepared solutions do not indicate the presence of free fluoride ions when tested with zirconium alizarin paper. Using this compound they were able to prepare hexafluoroantimonates(V) of a number of complex cations.

Hatton, Saito, and Schneider (48) investigated an aqueous 48 percent hydrofluoric acid solution of  $^{121}\text{SbF}_5$  and  $^{123}\text{SbF}_5$  by nuclear magnetic resonance techniques. They found that the  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$  resonances consist of a symmetrical septet which they claim corresponds to the hexafluoroantimonate(V) ion.

Thus, the existence of the hexafluoroantimonate(V) ion seems to be well established in both the solid state and in solutions.

#### The Structures of Fluoroantimonates(III) in the Solid State and in Aqueous Solution

Flückiger reported the preparation of the first known fluoro-complexes of antimony(III) in 1852 (49). By the turn of the century, a complete se-

ries of antimony(III) fluoro-complexes had been prepared by a number of workers. A particular member of this series had the empirical formula of an addition compound of an alkali metal or ammonium or thallium fluoride with antimony(III) fluoride. Compounds corresponding to the following ratios of MF to  $\text{SbF}_3$  were found (49,50,51,52): 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, and 4:7.

Byström and Westgren (53) studied the crystal structure of solid antimony(III) fluoride by x-ray methods. It was found to consist of discrete  $\text{SbF}_3$  groups with each antimony atom situated on top of an approximately equilateral fluorine triangle. The Sb-F distances are 2.0 Å. There is one bond angle of  $81.9^\circ$  and two of  $104.3^\circ$ . Byström and co-workers then undertook the monumental task of studying the crystal structure of the various fluoroantimonates(III).

Byström and Wilhelmi (54) studied the crystal structure of the isomorphous series  $\text{MSb}_4\text{F}_{13}$ , where  $\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{and } \text{Tl}^+$  and obtained the following results. Each antimony atom is surrounded by six fluorine atoms in the form of a strongly distorted octahedron. The Sb-F distances are: three distances of 2.0, one distance of 2.9, and two distances of 3.0 Å. Thus, there are three strong Sb-F bonds and three secondary bonds. The longer Sb-F bonds link the  $\text{SbF}_3$  groups together to form finite  $\text{Sb}_4\text{F}_{13}^-$  groups in which four  $\text{SbF}_3$  groups are arranged around the thirteenth fluorine atom.

Byström and Wilhelmi (55) found that the  $\text{MSb}_2\text{F}_7$  series does not form an isomorphous series. In  $\text{CsSb}_2\text{F}_7$ , the antimony atoms are surrounded by four fluorine atoms situated at the corners of an irregular tetrahedron. Two tetrahedra share one fluorine atom to form discrete  $\text{Sb}_2\text{F}_7^-$  groups.

The Sb-F-Sb bridge distance is the only distance known very accurately and is  $2.22 \pm 0.03 \text{ \AA}$ . The F-F distances are approximately 2.59 and 2.75  $\text{\AA}$ .

For the isomorphous series  $M_2SbF_5$ , where  $M = K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $NH_4^+$ , and  $Tl^+$ , Byström and Wilhelmi (56) found that the antimony atom is surrounded by five fluorine atoms arranged at five corners of an octahedron with an inert electron pair occupying the sixth corner. The antimony atom is displaced from the center of the octahedron in a direction away from the five fluorine atoms. The Sb-F distances are  $2.68 \pm 0.1$  and  $2.77 \pm 0.1 \text{ \AA}$ .

Byström, Bäcklund, and Wilhelmi (57) studied the crystal structure of  $KSbF_4$ . In this compound, each antimony atom is in contact with five fluorine atoms at a distance of 2.0-2.3  $\text{\AA}$ . As with  $K_2SbF_5$ , the five fluorine atoms occupy five of the six corners of an octahedron with the antimony atoms displaced from the center and in a direction away from the fluorine atoms. Two of the five fluorine atoms are shared between two antimony atoms and thus large tetranuclear complexes of the formula  $Sb_4F_{16}^{-4}$  are formed. The metal atoms are situated in the corners of a tetrahedron with the bridge-forming fluorine atoms located closely to four of the six edges of the tetrahedron and the twelve remaining fluorine atoms at the corners of four triangles, each triangle situated outside one of the four corners of the metal tetrahedron. Since the Sb-Sb distance is 4.4  $\text{\AA}$  or larger, no metal-metal bonding is postulated. The mean Sb-F distance for non-bridge fluorine atoms is  $2.01 \pm 0.1 \text{ \AA}$  and that for bridge fluorine atoms  $2.24 \pm 0.1 \text{ \AA}$ .

An investigation of the system  $NaF \cdot SbF_3$  by Byström, Bäcklund, and Wilhelmi (58) yielded only  $NaSbF_4$  and  $Na_2SbF_5$ . They were not able to prepare the  $Na_3SbF_6$  reported by Flückiger (49) and concluded that the compound



reported by Flückiger must actually have consisted of a compound with a lower NaF content. As further evidence, Fluckiger's description of the  $\text{Na}_3\text{SbF}_6$  crystals agrees well with the appearance of  $\text{Na}_2\text{SbF}_5$ .

In  $\text{NaSbF}_4$ , each antimony atom is bonded to five fluorine atoms which surround the antimony atom in the same manner as in  $\text{K}_2\text{SbF}_5$  and  $\text{KSbF}_4$ . The structure is built up by double  $[\text{SbF}_4^-]_\infty$  chains. The mean Sb-F distance for the unshared fluorine atoms is  $2.02 \pm 0.1 \text{ \AA}$  which is very close to the corresponding distance in  $\text{K}_2\text{SbF}_5$  (2.03) and in  $\text{KSbF}_4$  (2.01). The Sb-F bridge distances are  $2.19 \pm 0.1$  and  $2.51 \pm 0.1 \text{ \AA}$ .

The compound  $4\text{CsF} \cdot 7\text{SbF}_3$  was reported by Wells and Metzger (51) but its existence has not been verified by later work.

The remaining member of the series,  $\text{MF} \cdot 3\text{SbF}_3$ , namely the rubidium salt, has been studied by Wilhelmi (59). The results were mentioned in an abstract of a paper presented by the author to the Third General Assembly and International Congress of the International Union of Crystallography, but apparently the complete data have never been published.

Thus, it can be seen that the chemistry of the fluoroantimonates(III) is extremely complicated. Although the polynuclear anions might exist only in solids due to a stabilization by the crystal lattice, the possibility of their existence in solutions containing a high concentration of antimony(III) must be considered.

The evidence on the nature of the fluoroantimonates(III) in solution is very sketchy. Guntz (60) measured the heat of solution of antimony(III) fluoride in aqueous hydrofluoric acid solutions and postulated the existence of  $\text{H}_3\text{SbF}_6$ . A study was made of aqueous solutions of antimony(III) fluoride by Grünbaum and Rosenheim (61). They found that saturated

aqueous antimony(III) fluoride solutions hydrolyze to only a very small extent. In the presence of hydrofluoric acid or potassium fluoride, the solubility of antimony(III) fluoride is increased above that in water. The increased solubility and measurements of the electrical conductivity of the solution indicate complex formation.

Naumov, Dukhovnin, and Mandel (62) in a study of the solid phases obtained from the system  $\text{SbF}_3 \cdot \text{NH}_4\text{F} \cdot \text{H}_2\text{O}$  suggested the existence of the tetrafluoroantimonate(III) ion in solution.

A polarographic study by Pavlov and Lazarov (63) indicated the formation of the hexafluoroantimonate(III) ion in acidic solutions.

Since the information concerning the antimony(III) fluoro-complexes in solution is scarce and contradictory, no conclusion as to the nature of the species in solution can be drawn at the present time. From the work with the solid fluoro-complexes it is seen that condensation reactions are prevalent at high antimony concentrations. The crystal structure work also indicates that the  $\text{SbF}_5^-$  group has a special stability in the solid state, as can be seen from its existence in a large number of the condensed fluoroantimonates(III).

Kolditz and Sarrach (64), two of the more recent workers in the field, assumed the existence of the tetrafluoroantimonate(III) ion in their paper chromatographic study of the fluoro-complexes of antimony(III) and antimony(V). This assumption was supported by the fact that oxidation of the antimony(III) fluoro-complex with bromine gave the dihydroxotetrafluoroantimonate(V) ion.

Although the evidence does not decidedly favor any one of the possible alternatives, it will be assumed here that antimony(III) is present

as the tetrafluoroantimonate(III) ion in fluoride solutions.

### The Electron Exchange Reactions

The electron exchange between the chloro-complexes of antimony(III) and antimony(V) in hydrochloric acid solution has been the subject of extensive investigation by a number of workers. The first was Bonner (65). A study of the exchange in 6.0 F hydrochloric acid solution yielded the empirical rate law

$$\text{rate} = 8.8 \times 10^{-11} [\text{Sb(III)}]^{0.6} [\text{Sb(V)}]^{1.1} [\text{H}^+]^4 [\text{Cl}^-]^9$$

where the rate has the units mole liter<sup>-1</sup> hour<sup>-1</sup>. Cheek, Bonner, and Wahl (66) measured the rate of exchange in 6.0 to 12.0 F hydrochloric acid. The reaction was found to be first order in both antimony(III) and antimony(V) in 12 F hydrochloric acid. They suggested that not all forms of antimony(V) are capable of exchanging with antimony(III), and that the rate of formation of the exchanging form might be the rate determining step in the observed exchange.

Neumann and Brown (67) performed a series of non-equilibrium exchange experiments and demonstrated that the hexachloroantimonate(V) ion was the exchanging form of antimony(V). They proposed two possible intermediates for the exchange of the form,  $\text{Sb}_2\text{Cl}_9^-$ . These two forms differ in that one has two chlorine bridge atoms while the other has three.

Bonner and Goishi (68) studied the exchange in 7-8 F hydrochloric acid solution and correlated all the previous data for the exchange in hydrochloric acid.

The exchange system can be represented by a three component system composed of (i) the antimony(III) species, (ii) the exchanging antimony(V) species, and (iii) the hydrolysis product of the exchanging antimony(V) species. The following conclusions were drawn.

1. The exchanging species of antimony(V) is the hexachloroantimonate(V) ion.

2. The antimony(III) catalyzed hydrolysis of antimony(V) reported by Neumann and Ramette (69) does not cause exchange. This suggests that the antimony atom which was in the +3 state before exchange must have six chloride ions attached to it in the activated complex.

3. The exchange does not cause hydrolysis of the antimony(V).

Turco and Faraone (70) found that the exchange between antimony(III) and antimony(V) in 3.2 F hydrochloric acid takes place at a greater rate in the presence of bromide ion. Turco reinvestigated the system (71) and established the empirical rate law,

$$\text{rate} = 5.4 \times 10^{-4} [\text{Sb(III)}]^{0.18} [\text{Sb(V)}]^{1.1} [\text{H}^+]^{4.2} [\text{Br}^-]^{3.5}$$

for 3.2 F hydrochloric acid and 1.5 F potassium bromide. They suggested that the exchange occurs through a complex mechanism involving various parallel reactions in which a zero order reaction with respect to antimony(III) predominates. The zero order with respect to antimony(III) results from the reduction of antimony(V) to antimony(III) by bromide.

Barker and Kahn (72) measured the rate of exchange between antimony(III) chloride and antimony(V) chloride in carbon tetrachloride. They found the empirical rate law,

$$\text{rate} = 1.6 \times 10^{-7} [\text{SbCl}_5] + 1.8 \times 10^{-4} [\text{SbCl}_3][\text{SbCl}_5]^2,$$

where the units of the rate are mole liter<sup>-1</sup> sec<sup>-1</sup>. The rate law suggests a dissociative path:  $\text{SbCl}_5 \rightarrow \text{SbCl}_3 + \text{Cl}_2$ , and a path involving a complex  $\text{Sb}_3\text{Cl}_{13}$ , formed from one molecule of antimony(III) chloride and two of antimony(V) chloride. Price and Brubaker (73) investigated the system in the presence of hydrogen chloride and were able to fit their data to the Barker and Kahn rate law plus an additional term,  $2.07 \times 10^{-5} [\text{SbCl}_3][\text{HSbCl}_6]$ . This path was found to be about twice as fast as the combined paths of the Barker and Kahn rate law. They proposed an activated complex identical to that proposed by Neumann and Ramette.

Brubaker and Sincius (74) studied the exchange in aqueous sulfuric acid. No exchange was found to take place in 3.0 to 12.0 F sulfuric acid. When chloride ion is added to the solutions at a constant hydrogen ion concentration, exchange occurs and the rate increases as the concentration of chloride ion increases. The dependence of the rate of exchange on hydrogen ion and sulfate ion concentrations is very complex. The workers concluded that the transition state contains two chloride ions when the concentration of chloride ion is less than 0.200 F.

Kolditz and Roensch (75) studied the rate of antimony exchange in acetonitrile for the following systems:  $\text{Cl}^-$ - $\text{SbCl}_3$ - $\text{SbCl}_6^-$ ;  $\text{SbCl}_3$ - $\text{SbCl}_5\text{OEt}^-$ ;  $\text{SbCl}_4^-$ - $\text{SbCl}_5\text{Ph}$ ;  $\text{Cl}^-$ - $\text{SbCl}_3$ - $\text{SbCl}_4(\text{OEt})_2$ . Antimony exchange occurred only for the first system. No rate law was given.

It should be noted that, with the exception of the exchange reaction studied in carbon tetrachloride and the one studied in the presence of bromide, all the evidence suggests that exchange occurs via bridging mechanisms

rather than outer sphere mechanisms.

### Experimental

#### Preparation of Active Antimony Stock Solutions

In order to find a method to separate the hexafluoroantimonate(V) ion from the tetrafluoroantimonate(III) ion, it was necessary to have stock solutions of antimony-124 in both oxidation states. To eliminate any influence of chloride upon the system, the radioactive antimony as obtained from Oak Ridge National Laboratory in 2 F hydrochloric acid was converted into the corresponding fluoro-complex. The procedure used to perform this operation is described in the following paragraphs.

For the preparation of the hexafluoroantimonate(V) ion in solution, an aliquot from the antimony-124 solution received from Oak Ridge National Laboratory was added to 10 ml of 6 F hydrochloric acid. To this was added 27.2 mg inactive  $\text{KSb}(\text{OH})_6 \cdot \text{H}_2\text{O}$  (Amend Drug and Chemical Company).

The resulting solution was treated with chlorine for thirty minutes and then degassed with nitrogen for ten minutes. After being neutralized with dilute ammonium hydroxide, the solution was heated on a steam bath for several minutes. The resulting precipitate was separated by filtration and washed with distilled water. Dissolution of the solid in 10 ml of 5 F hydrofluoric acid yielded a solution approximately 0.01 F in antimony(V).

The antimony(III) stock solution was prepared via reduction with iodide. An aliquot from the original solution was added to 3 ml of 3 F hydrochloric acid and 29.2 mg of antimony(III) oxide was added to the resulting solution as a carrier. Treatment with excess potassium iodide

solution, followed by heating on a steam bath, insured reduction of any antimony(V) to antimony(III).

Distilled water was then added until antimony oxychloride precipitated. After cooling in an ice bath, the precipitate was allowed to settle out and the supernatant liquid was removed with a pipette; the solid was washed with water. The antimony oxychloride was dissolved in 10 ml of 1.0 F hydrofluoric acid.

#### Radioactive Properties of $^{124}\text{Sb}$

Many of the fluoro-complexes of antimony have been studied most conveniently by use of antimony- $^{124}$  as a tracer. Antimony- $^{124}$  is a radioactive isotope with a half-life of 60 days. This half-life is an excellent one for radiochemical purposes since it is short enough to give samples with high specific activity and long enough for use in experiments requiring days or weeks for their completion. Antimony- $^{124}$  decays by beta emission to an excited state of tellurium- $^{124}$ . The tellurium then decays immediately to its ground state with emission of gamma radiation. The ground state of tellurium- $^{124}$  is stable with respect to radioactive decay. The full decay scheme of antimony- $^{124}$  as given by Zolotavin, Grigor'ev, and Abroyan (76) is shown in Figure 8. Note that five beta and nine gamma rays are involved in the scheme.

Since the gamma emission is effectively coincident with the beta emission, the presence of antimony- $^{124}$  can be determined by detecting either the beta or the gamma radiation. Thus, in some experiments the antimony- $^{124}$  was counted with a well-type scintillation detector designed to detect the gamma radiation while in others an end-window Geiger tube was employed to detect the beta radiation. Finally, the energies of most of the betas

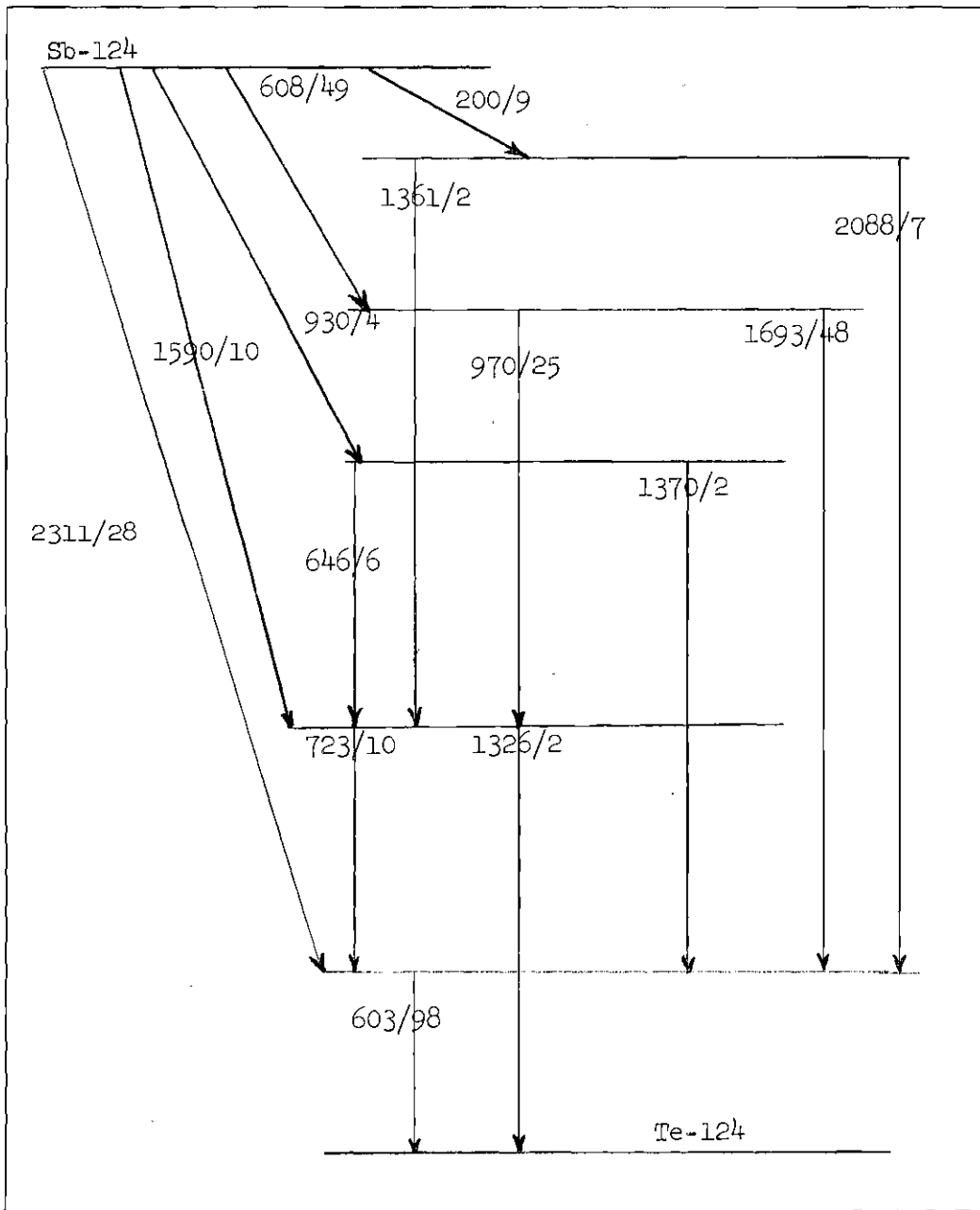


Figure 8: Radioactive Decay Scheme for Sb-124

Notation a/b: a is the energy of the transition in kev and  
b is the percent occurrence of the transition.



and gammas involved are sufficiently high enough to permit counting of the antimony either in solution or adsorbed on paper.

#### Anion Exchange Reactions of Antimony(III)-Antimony(V) Fluoro-complexes

The first attempt at devising a scheme for the separation of the antimony(III)-antimony(V) fluoro-complexes involved the ion exchange technique previously discussed in connection with the tin(II)-tin(IV) fluoro-complexes. Work by J. P. Faris (28) seemed to indicate that the antimony(III)-antimony(V) fluoro-complexes could be readily separated by selective adsorption on Dowex-1-X10 anion exchange resin. Faris reported that antimony(V) was strongly adsorbed at all hydrofluoric acid concentrations, that is, the distribution coefficient for antimony(V) was greater than  $10^2$  at all hydrofluoric acid concentrations investigated. The adsorption of antimony(III) decreased with increasing hydrofluoric acid concentration, and the distribution coefficient approached unity in approximately 12 F hydrofluoric acid. Thus, the separation should be possible in about 10 F hydrofluoric acid. The feasibility of this separation was investigated by both the equilibrium method and the column method of ion exchange.

In the equilibrium method 5.0 ml of the appropriate antimony fluoro-complex solution was placed in a 50-ml polyethylene centrifuge cone. A 200  $\mu$ l aliquot of the radioactive antimony(III) or antimony(V) stock solution was added with a micropipette.

The resulting solution was allowed to stand for two days so that the radioactive antimony and the bulk of the antimony would be present as the same species. A 200  $\mu$ l aliquot was withdrawn for counting and the activity in the solution determined before adding the resin. Then, 0.500 g of dry anion exchange resin was added. Aliquots were withdrawn from the solution

at the required intervals and were placed in 2-ml glass test tubes for counting. Extreme care was taken not to withdraw any of the resin with the solution. After counting the aliquots, distribution coefficients were calculated exactly in the same way as those for the tin(II)-tin(IV) system. The concentration of antimony was 0.010 F in each solution. Hydrofluoric acid solutions of the following concentrations were employed: 1.0, 5.0, 10.0, 15.0 F. The values obtained for the distribution coefficients are shown in Table 2. These distribution coefficients were determined after resin and solution had been in contact for 24 hours. It should be noted that all of these values correspond to "strong adsorption" according to the nomenclature used by Faris. Henceforth, all distribution coefficients greater than  $10^2$  will be reported only as "strong adsorption."

Table 2. Distribution Coefficients ( $K_d$ ) for HF Solutions

F HF	$K_d$ for Sb(III)	$K_d$ for Sb(V)
1.0	1120	1170
5.0	720	710
10.0	440	570
15.0	410	410

It was thought that the discrepancies between these values and those reported by Faris were due to some kind of time phenomenon. The following experiment was performed to test this possibility. A solution 0.010 F in antimony(III) and 10.0 F in hydrofluoric acid was prepared by adding

antimony(III)-124 stock solution to 50 ml of 10 F hydrofluoric acid and the time noted. At various intervals, 5-ml portions were withdrawn, sampled for counting, and then treated with dry resin in the usual way. After the resin was added, the solution above the resin was sampled at various intervals. It was found that strong adsorption resulted after one hour of equilibration and within one minute after the resin was added to the pre-equilibrated solution.

Finally, it was decided to reproduce Faris' work in detail. A polyethylene tube 1/4 inch in inside diameter, containing 2.80 g of dry resin, was used for the experiment. Dowex-1-X10, 200 mesh anion exchange resin, was converted to the fluoride form and dried in the usual way. The resin was added as a slurry with dilute hydrofluoric acid; the height of the settled bed was 21 cm. Solutions were allowed to flow through the column by gravity and a flow rate of 9-10 ml per hour was obtained. An antimony(III) solution was prepared to contain 60  $\mu$ g of antimony in a 50  $\mu$ l aliquot. The solution contained sufficient antimony-124 to allow the movement of the solution through the column to be followed with a survey meter. A 50  $\mu$ l aliquot of the solution was added to 3 ml of 10.0 F hydrofluoric acid and placed onto the column. After the level of the liquid reached the top of the resin bed, 10.0 F hydrofluoric acid was added to the column. The effluent was collected in calibrated polyethylene containers. After having collected 75 ml of effluent, the elution was discontinued because at that time the activity had moved only a few centimeters into the resin. According to the value obtained by the equilibrium method, about 1150 ml should have been required to elute the antimony(III). Since it was found that the antimony(III) scarcely moved when eluted with

75 ml of solution, it appears that our value is more reasonable than that reported by Faris (28). Thus, it appears that ion exchange with Dowex-1-X10 is not applicable as a separation method for antimony(III)-antimony(V) fluoro-complexes.

#### Paper Chromatography of Antimony(III)-Antimony(V) Fluoro-complexes

The next technique investigated to achieve separation was paper chromatography. Kolditz and Sarrach (64) reported the  $R_F$  values for the  $\text{SbF}_{6-N}(\text{OH})_N^-$  ion with  $N = 0, 1, 2, 3, 4, 5$  and for  $\text{SbF}_4^-$  ion using the solvent system devised by Grunze and Thilo (77). However, Kolditz and Sarrach did not specify what paper they used for the chromatograms. Thus, a number of different chromatography papers as well as several different solvent systems were tried before obtaining a satisfactory separation method.

The general method used in the chromatographic procedure has been described in the Apparatus and Technique section. Solutions chromatographed were 0.01 F antimony(III) in 5.0 F hydrofluoric acid, 0.01 F antimony(V) in 5.0 F hydrofluoric acid, and 1:1 mixtures of antimony(III)-antimony(V) in 5.0 F hydrofluoric acid. The solvent system used was that reported by Grunze and Thilo (77); that is, isopropyl alcohol, 20 percent aqueous trichloroacetic acid solution, and water (7:2:1). The papers used were by Schleicher and Schuell, and by Whatman. The resulting  $R_F$  values are shown in Table 3.

Qureshi and Khan (78) reported that the antimony(III)-antimony(V) chloro-complexes can be separated using a solvent system of glacial acetic acid-water-ethyl acetate (1:1:1). They also gave  $R_F$  values for antimony(III) and antimony(V) in various pure solvents. Since one of the more promising of these was acetone, it was decided to apply a solvent system

Table 3.  $R_F$  Values of Sb(III) and Sb(V) on Various Papers

Paper	Isopropyl alcohol		70 percent acetone		90 percent acetone	
	Sb(III)	Sb(V)	Sb(III)	Sb(V)	Sb(III)	Sb(V)
W 1	0.47	0.76	0.78	0.91	0.83	0.95
W 31 DT	0.49	0.73	tails	0.95	0.78	1.00
W 50			0.64	0.89	0.15	0.85
W 54	0.53	0.53	0.80	0.92	0.47T	0.95
W 3mm			0.82	0.93	0.69	0.99
S&S 576	0.49T	0.61	0.70	0.97		
S&S 598	0.62	0.81	0.84	0.95		
S&S 470A	0.55	0.78				
S&S 2045a	0.20	0.44				
S&S 2040b	0.39	0.66				

- (a) W refers to Whatman paper.
- (b) S&S refers to Schleicher and Schuell paper.
- (c) The symbol T means that the peak tailed.

based on acetone. Acetone has the additional advantage that it will rapidly develop the paper; this fact is of great importance if the exchange reaction is relatively rapid. Acetone alone would not be expected to be sufficiently polar (78) to allow separation and, at first, a system using acetone - 20 percent aqueous trichloroacetic acid solution - water (7:2:1) was tried. The results are presented in Table 3. It can be seen that the difference between the  $R_f$  values of antimony(III) and antimony(V) is small for this system.

Finally, a solvent system of acetone - 10 percent aqueous trichloroacetic acid solution (9:1) was tried. The results obtained with this system are presented in Table 3.

From the tabulated  $R_f$  values it can be seen that the papers offering the best separation are: Whatman No. 50 and 54. Considering only the  $R_f$  values, neither paper seems to have a distinct advantage over the other. A plot of counts per minute versus the distance from the spotting point for each paper should give a better basis for deciding which paper to use. A solution 0.005 F in antimony(III) and 0.005 F in antimony(V) in 5.0 F hydrofluoric acid was prepared. A chromatogram of the solution was made with both papers, the papers counted, and the curves plotted. Figure 9 shows that the Whatman No. 50 is the better choice for the separation of the antimony(III)-antimony(V) fluoro-complexes.

#### The Electron Exchange Reaction

Using the separation procedure described above, the following experiments designed to measure the rate of electron exchange were performed. An antimony(V) stock solution was prepared by dissolving  $\text{KSb}(\text{OH})_6 \cdot 1/2\text{H}_2\text{O}$  in 50 ml of the appropriate hydrofluoric acid solution to give a solution

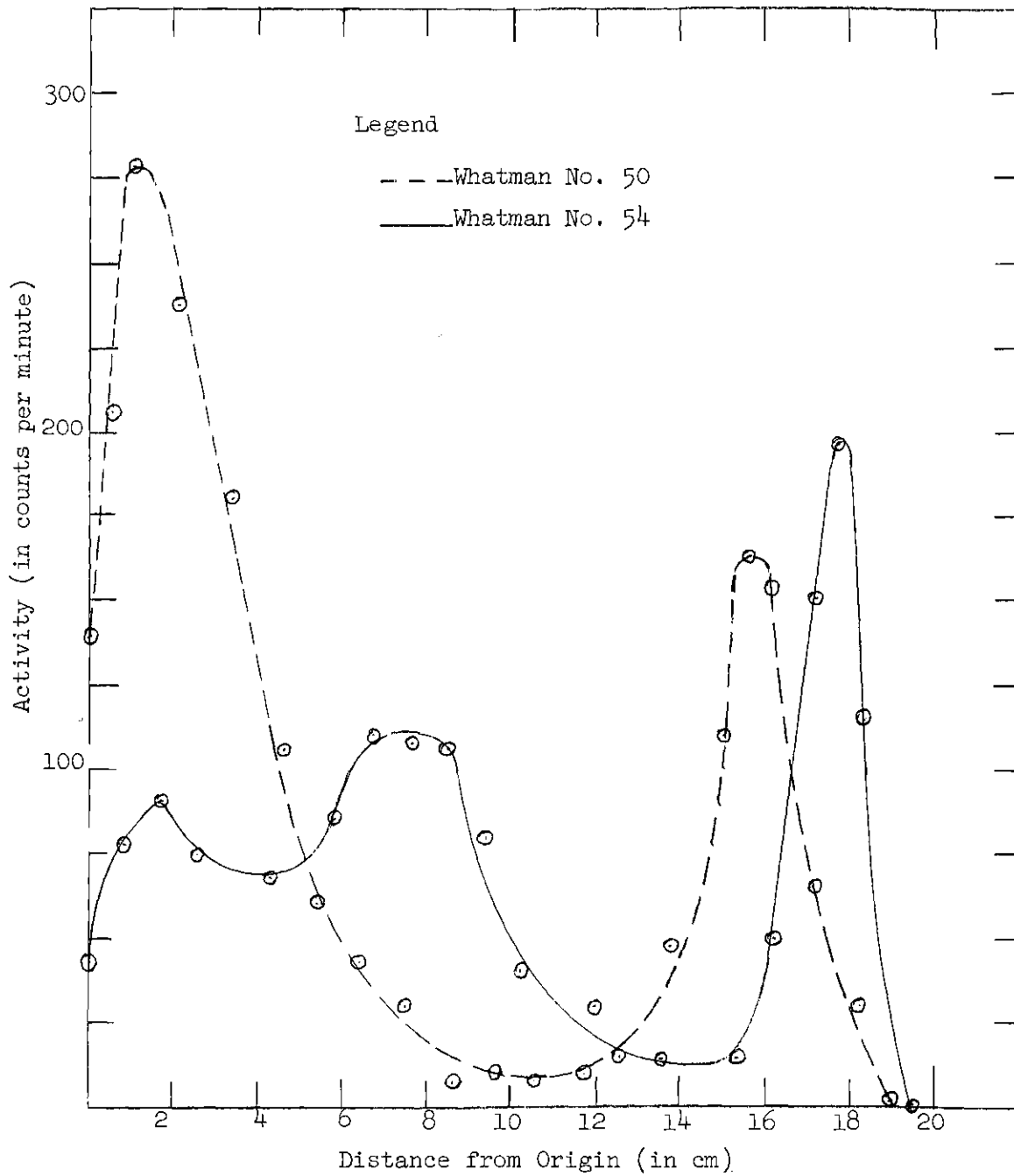


Figure 9. Plot of Activity versus Distance for Two Whatman Papers

0.020 F in antimony(V). An antimony(III) stock solution was prepared by dissolving antimony trioxide in 10.0 ml of the appropriate hydrofluoric acid solution and adding an aliquot from the radioactive antimony(III) stock solution. These stock solutions were allowed to stand overnight to equilibrate. The exchange reaction was started by the addition of 1.0 ml of the antimony(V) stock solution to 1.0 ml of the antimony(III) stock solution contained in a small polyethylene test tube. Zero time for the kinetic run was defined as the time of the addition of the antimony(V) solution to the antimony(III) solution. Aliquots (10  $\mu$ l) were taken from the solution in the reaction vessel and placed on strips of Whatman No. 50 chromatography paper. The strips were then developed with the acetone - 20 percent aqueous trichloroacetic acid (9:1) solution. The solvent front was allowed to advance about 18.5 cm on each strip. The time required for the solvent to move this distance was about two hours. The strips were dried and cut in a standard way for counting: for antimony(III) the section from -0.5 to 4.5 cm, for antimony(V) the section from 13.5 to 18.5 cm. By reference to Figure 9, it can be seen that these sections will account for more than 90 percent of the activity present on the paper. The sections were mounted in a standard way upon a slide and counted with the end-window Geiger tube apparatus. The solutions studied are listed in Table 4. Runs were made both at room temperature and in an 80° C oil bath. In the first four runs, the activity was added as antimony(III) and in the fifth case it was added as antimony(V). Data points were taken at intervals up to seven days. In no case was any exchange detected.



Table 4. Solutions Used in Exchange Study

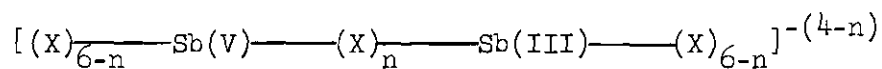
Run	F Sb(III)	F Sb(V)	F HF	Temp.	Time of Final Sampling
1	0.01	0.01*	1.00	25° C	7 days
2	0.01	0.01*	1.00	80° C	7 days
3	0.01	0.01*	0.30	80° C	3 days
4	0.01	0.01*	10.0	80° C	3 days
5	0.01*	0.01	1.25	80° C	3 days

\*Indicates oxidation state of antimony-124.

### Conclusion

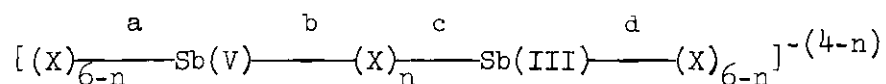
To justify the extremely slow rate found for the electron exchange reaction between the antimony(III)-antimony(V) fluoro-complexes, the reaction mechanism must be considered.

On the basis of evidence from similar systems, the reaction probably proceeds in the following steps: (i) formation of a relatively stable dimer which exists in equilibrium with monomeric species of antimony(III) and antimony(V), (ii) rearrangement of the dimer to a configuration which permits the electron transfer to occur adiabatically, and (iii) transfer of the electrons. The dimer formed in step (i) is assumed to have a structure in which each antimony atom is octahedrally coordinated by six fluorine atoms, some of which are bonded to both antimony atoms. This assumption is based on the following arguments. Antimony(V) invariably exists as the octahedral hexafluoroantimonate(V) ion both in solution and in solid compounds, indicating that coordination numbers other than six are energetically unfavorable. Fluoro-complexes of antimony(III) with coordination numbers four, five, and six are known, indicating no great energy advantage for a particular coordination number. However, for the exchange to occur with a minimum of energy, the antimony(III) atom must be coordinated by six fluorine atoms in the dimer so that after exchange the antimony(V) will still be present as the hexafluoroantimonate(V) ion. The dimer can be represented as

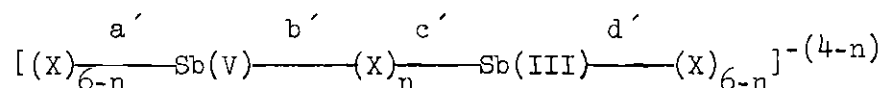


where n is the number of bridging fluorine atoms.

Formation of a dimer is not sufficient to allow electron transfer. The dimer must exist in a configuration with enough symmetry to allow electron transfer to proceed adiabatically with conservation of energy. It was recognition of this requirement, although not stated in these terms, which led to the dimer suggested in the previous paragraph. This dimer still lacks sufficient symmetry if the Sb(V)-F bond distances are different from the corresponding Sb(III)-F bond distances. Thus, step (ii) is the rearrangement of the antimony(III) and antimony(V)-fluorine bonds of the dimer



to form the dimer



where a is the antimony(V)-fluorine bond distance for non-bridging fluorines  
 b is the antimony(V)-fluorine bond distance for bridging fluorines  
 c is the antimony(III)-fluorine bond distance for bridging fluorines  
 d is the antimony(III)-fluorine bond distance for non-bridging fluorines

a' and d' are the arithmetic averages of a and d

b' and c' are the arithmetic averages of b and c.

The energy required for the rearrangement can be readily calculated using the equation for a simple harmonic oscillator:

$$E = 1/2K(\Delta x)^2$$

where  $K$  is the stretching force constant

$\Delta x$  is change in bond distance.

The distances  $a$ ,  $c$ , and  $d$  can be estimated with confidence from the structural data presented previously. Distance  $b$  has been estimated by assuming that the bridge bond is lengthened by an amount similar to the lengthening experimentally observed for the antimony(III)-fluorine bond. Thus, the distances used are  $a = 1.88$ ,  $b = 2.07$ ,  $c = 2.20$ , and  $d = 2.00 \text{ \AA}$ .

The energy for the rearrangement was taken to be the work required to expand or compress bonds  $a$ ,  $b$ ,  $c$ , and  $d$  so that the corresponding bond lengths  $a'$ ,  $b'$ ,  $c'$ , and  $d'$  result. The necessary stretching force constants are listed in Table 5. In all but two cases the values are taken directly from the literature.

The estimate of the Sb(V)-F stretching force constants in  $\text{SbF}_6^-$  was made using the infrared spectral data of Kolditz (79). The calculations were made using the equation for the simple harmonic oscillator approximation

$$K = (2 \tilde{\nu} c)^2 \mu$$

where

$\tilde{\nu}$  is the frequency of the vibration in  $\text{cm}^{-1}$

$c$  is the velocity of light

$\mu$  is the reduced mass

$K$  is the force constant.

Assuming that  $\text{SbF}_5$  is vibrating against F, the Sb(V)-F stretching force constant was estimated to be 4.60 millidynes/ $\text{\AA}$ . A similar calculation for  $\text{SnF}_6^-$  and  $\text{SnF}_3^-$  yields 4.03 and 3.06 millidynes/ $\text{\AA}$ , respectively. A comparison of these values with those in Table 5 shows that the values

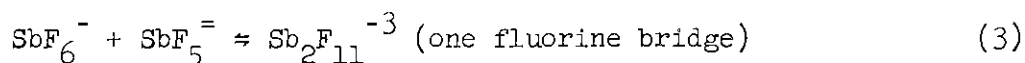
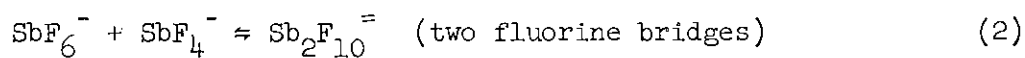
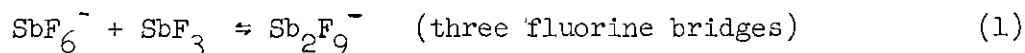
Table 5. Stretching Force Constants (K)

Compound	K in md/Å	Reference
$\text{SbF}_6^-$	5.06	(estimated)
$\text{SbF}_5$	5.20	(80)
$\text{SbF}_3$	3.69	(estimated)
$\text{SnF}_6^{=}$	4.42	(81)
$\text{SnF}_3^-$	3.40	(81)
$\text{SbCl}_6^-$	2.37	(82)
$\text{SbCl}_3$	1.68	(83)
$\text{SnCl}_6^{=}$	1.46	(84)
$\text{SnCl}_3^-$	0.79	(84)

calculated in this way are too low by a factor of 1.10. Application of this factor to the case of the Sb(V)-F bond yields a force constant of 5.06 millidynes/Å. Note that this is in good agreement with the force constant for the  $\text{SbF}_5$  stretching vibration obtained by Condrate and Nakamoto (80), i.e., 5.20 millidynes/Å.

For the Sb(III)-F stretching force constant, the calculations are less certain since no infrared spectral data are available. This force constant,  $K_{\text{Sb(III)-F}}$  can be estimated in two ways; by assuming that the ratios  $K_{\text{SbF}_6^-} / K_{\text{SbCl}_6^-}$  and  $K_{\text{Sb(III)-F}} / K_{\text{SbCl}_3}$  are equal or by assuming that the ratios  $K_{\text{SbF}_6^-} / K_{\text{Sb(III)-F}}$  and  $K_{\text{SnF}_6^{2-}} / K_{\text{SnF}_3}$  are equal. Fortunately, both methods yield the same value,  $K_{\text{Sb(III)-F}} = 3.69$  millidynes/Å.

Using these values of the force constants, the energy of step (ii) was calculated for one, two, and three fluorine bridges. The formation of the bridged intermediates could take place via the following reactions:



The energy obtained for step (ii) is 14.7 kcal/mole for three fluorine bridges, 14.3 kcal/mole for two fluorine bridges and 14.0 kcal/mole for one fluorine bridge.

It can be seen that the energy has very little dependence on the number of fluorine bridges present in the dimer.

Since the force constants were estimated, a calculation of the sensitivity of the energy calculation to changes in the force constants was made for the intermediate with three fluorine bridge atoms. If the force constants for both the antimony(V) and the antimony(III)-fluorine bonds are decreased by 10 percent, i.e., from 5.06 and 3.69 to 4.55 and 3.32 millidynes/Å respectively, the energy is decreased by only six percent. If the actual force constants are larger than those used, the energy will be greater than that calculated and the argument will be strengthened.

The energy of step (ii) was also calculated where X is chloride and n is three. The force constants are shown in Table 5. In this case, the bond distances are not well known. Distance d is 2.36 Å from studies of  $(\text{NH}_4)_2\text{SbCl}_5$  (85) and solid  $\text{SbCl}_3$  (86). Distance a was taken as 2.32 Å, since this is the mean Sb-Cl distance in solid  $\text{SbCl}_5$  (87). The only polynuclear chloroantimonate studied is  $\text{Rb}_2\text{SbCl}_6$ , which consists of alternate antimony(V) and antimony(III) atoms. Since Jensen (88) found only one Sb-Cl distance, it is necessary to assume that the normal Sb(III)-Cl and Sb(V)-Cl bridge distances are equal. Using these values, the energy for the chloro-case is found to be 0.4 kcal/mole. The experimentally observed activation energy for the electron exchange reaction is about 17 kcal/mole. Thus, it can be assumed that most of the observed activation energy is due to the formation of the dimer rather than the reaction of the dimer to form the intermediate required for exchange. If this is also true for the fluoro-complex case, it follows that the activation energy for the exchange will be considerably higher than the 15 kcal/mole calculated earlier. The

resulting high activation energy would tend to make the exchange reaction extremely slow and the considerations would support the results found experimentally.

Calculations of the rearrangement energy have been made for other systems. For example, Basolo and Pearson (89) attempted to calculate the rearrangement energy for the electron exchange reaction between the iron(II) and iron(III) aquo-complexes. Using a simple electrostatic model and assuming an outer sphere reaction mechanism, they calculated the energy required to rearrange the hydration shells of the ions to intermediate positions. The calculated rearrangement energy was 14 kcal/mole. The experimentally observed activation energy for the electron exchange reaction between the iron(II) and iron(III) aquo-complexes is 9.9 kcal/mole (90). This apparent discrepancy is not meaningful, since the exchange most probably proceeds by a bridging mechanism rather than by an outer sphere mechanism. It is likely that a calculation similar to that used with the antimony system would give a more realistic value for the rearrangement energy.

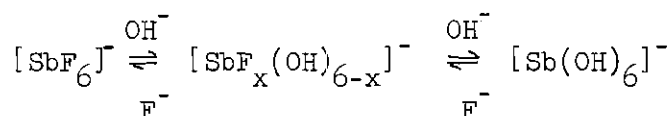


## CHAPTER V

## HYDROLYSIS OF THE HEXAFLUOROANTIMONATE(V) ION

Introduction

Lange and Askitopoulos (91) dissolved various alkali salts of  $\text{HSbF}_6$  in water and found that the solutions were acidic; therefore, they concluded that hydrolysis took place and that the system would be expected to react according to the following scheme:

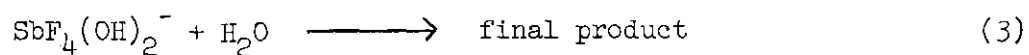
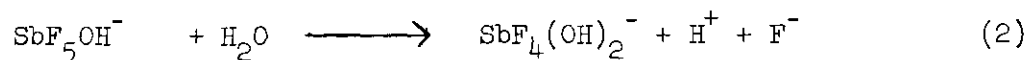
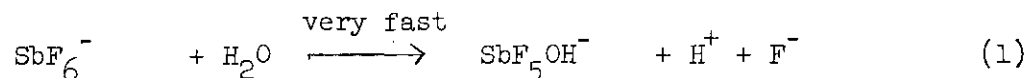


Kolditz and co-workers (34, 64) have studied the formation of many of the hydroxofluoroantimonates(V). They isolated the  $\text{MSbF}_5\text{OH}$  and  $\text{MSbF}_4(\text{OH})_2$  salts (where  $\text{M} = \text{K}^+$ ,  $\text{Cs}^+$ , and  $\text{Na}^+$ ) by reacting  $\text{MSb}(\text{OH})_6$  and hydrofluoric acid in stoichiometric amounts. In a chromatographic study, they prepared the series  $[\text{SbF}_N(\text{OH})_{6-N}]^-$ , with  $N = 2, 3, 4,$  and  $5$  by reacting either  $\text{KSbF}_6$  or  $\text{KSbF}_4(\text{OH})_2$  with stoichiometric amounts of base and determined the  $R_f$  values for each member of the series.

Kolditz and Sarrach (64) showed that an aqueous solution of  $\text{KSbF}_6$  does not contain hexafluoroantimonate(V) ions but hydroxopentafluoroantimonate(V) ions. In a 40 percent hydrofluoric acid solution, the antimony(V) is present as the hexafluoroantimonate(V).

The kinetics of the hydrolysis of the hexafluoroantimonate(V) ion have been studied by Mazeika and Neumann (92). They measured the rate of

hydrolysis of  $\text{KSbF}_6$  via titration of the liberated fluoride ion. From a resolution of a plot of  $\log$  (percent fluoride remaining complexed) versus time, they concluded that the reaction proceeded in a step-wise manner. For the hydrolysis in acid solution, they proposed the following sequence of consecutive first order or pseudo-first order reactions:



Reaction (1) is very rapid and occurs within the time of dissolution of the solid  $\text{KSbF}_6$ . Reactions (2) and (3) are slow and their rates were measured in 0.0100-1.000 F perchloric acid and 0.0100-1.000 F sodium hydroxide. The rate of reaction in the basic solutions increased rapidly with increasing base concentration. It was found that in solutions of pH 12 or higher, the final product of the reactions was the hexahydroxoantimonate(V). The final product in acid solution could not be identified.

Since the conclusions drawn by Mazeika and Neumann were based solely on the graphical resolution of kinetic data and since the workers ascertained neither the number of intermediates involved nor the identity of the intermediates proposed, it was decided to reinvestigate this system using a chromatographic technique. It was hoped that several things could be accomplished using this method: (i) the measurement of the rate of reaction of the various hydrolytic steps in solutions buffered in the pH range

not previously studied, (ii) the establishment of the number of intermediates present to any appreciable extent in the reaction medium, and (iii) the identification of the intermediates by determining the fluoride/antimony ratio.

### Experimental

#### Preparation of $K^{124}SbF_6$

In order to study the hydrolysis reaction, it was necessary to prepare solid  $KSbF_6$  containing antimony-124. A 3.0-mc aliquot of antimony-124 was withdrawn from the stock solution obtained from Oak Ridge National Laboratory and placed in a polyethylene centrifuge cone. Chlorine gas was bubbled through the solution for ten minutes to insure that only antimony(V) was present. Inactive  $KSb(OH)_6 \cdot 1/2H_2O$  (1.80 g) was added to the solution and the resulting gummy mass was dissolved in a minimum amount of hot concentrated hydrofluoric acid. The solution was heated on a steam bath for a few minutes and then cooled in an ice bath. The resulting crystals were separated by filtration and placed in a vacuum desiccator over a mixture of potassium hydroxide and Anhydrone. The resulting material had a specific activity of approximately 1.6  $\mu\text{c}/\text{mg}$ . Analysis of the salt yielded the following data:

	<u>Calculated %</u>	<u>Found %</u>	<u>Average</u>
Sb	44.30	43.70, 44.40	44.05
F	41.50	41.40, 41.51	41.45
Ratio F/Sb	6.0		6.0

### Analytical Methods

Analysis for Antimony in Isolated Compounds. The method used for determination of antimony(V) was essentially that described by Willard and Diehl (93), in which antimony(V) oxidizes iodine in strong acid, and the liberated iodine is titrated with thiosulfate. The antimony containing compound was dissolved in enough concentrated hydrochloric acid to maintain a concentration in the vicinity of 3.0 F at the end of the titration. Approximately 1 g of sodium hydrogen carbonate was added in several portions to create a carbon dioxide atmosphere. This step was followed by the immediate addition of 1 g of potassium iodide dissolved in 3 ml of distilled water. The flask was stoppered to prevent air oxidation of the iodide. The resulting solution was titrated with a standard sodium thiosulfate solution to the disappearance of the iodine-starch blue color with the stopper being replaced after each addition of reagent. Mazeika and Neumann (94) found that, when the solutions for titration were prepared from the fluoro-complexes of antimony, the observed end point always gave a low value for antimony and was not reproducible. The low value was obtained because iodide ion reacts slowly with the antimony fluoro-complexes but reacts rapidly with the antimony chloro-complexes. The addition of boric acid to the solution eliminates the slow reaction with antimony fluoro-complexes by aiding in the decomposition of the antimony fluoro-complex. It will be seen later that we disposed of this difficulty in yet another way; namely, by removing the fluoride before the titration.

Analysis for Fluoride in Isolated Compounds. Belcher and Clark (95) found that fluoride could be determined by a method in which fluoride is precipitated as calcium fluoride by the addition of an excess of calcium

chloride solution and the unconsumed calcium ions back-titrated with EDTA. This method is applicable over the range 5-65 mg of fluorine, and halides, sulphate, phosphate, and arsenate do not interfere under the recommended conditions.

The actual procedure is as follows. The fluoride solution, containing between five and 65 mg of fluorine in a volume of 50 ml, was made slightly acid with dilute hydrochloric acid, using methyl red as an indicator. A 20-ml volume of 0.1000 F calcium chloride solution was added and the pH of the solution adjusted by careful addition of 0.1 F ammonium hydroxide solution until the red color of the indicator was just discharged. The pH was brought to approximately 4.5 by dropwise addition of 0.02 F hydrochloric acid until the indicator showed a faint pink. The solution was boiled for about 15 seconds and allowed to stand overnight at room temperature. Then the precipitate was filtered and washed with three 10-ml portions of a five percent solution of ammonium nitrate. Buffer solution (1 ml), prepared as described by Belcher and Clark, and a few drops of Eriochrome Black T (0.5 g dissolved in 100 ml ethanol) were added, and the solution titrated with a standard 0.05 F EDTA solution.

Analysis for Both Antimony and Fluoride in Isolated Compounds. By using a combination of the Willard and Diehl method for antimony and the Belcher and Clark method for fluoride, we were able to develop a method for determining both antimony and fluoride in a single sample. In this method about 140 mg of the appropriate fluoro-complex of antimony was dissolved in 20 ml of 0.2 F sodium hydroxide and heated on a steam bath for about one hour. The solution was cooled and the  $\text{NaSb(OH)}_6$  removed by filtration with a sintered glass funnel. The filtrate was then subjected to

the Belcher and Clark procedure for fluoride. The precipitate was dissolved directly from the funnel by the addition of 6 F hydrochloric acid, and the resulting solution treated according to Willard and Diehl's method for antimony. It is found that the precipitation of the  $\text{NaSb}(\text{OH})_6$  is quantitative. It can readily be seen that this method has the following advantages compared to the usual method of analyzing fluoro-complexes of antimony: (i) the complex is decomposed in a simpler manner, (ii) the freeing of the fluoride prior to analysis is much easier than the usual volatilization as fluosilicic acid, (iii) the end point in the EDTA titration of calcium is much sharper than the end point in the thorium(IV) nitrate titration of fluoride, and (iv) both fluoride and antimony can be readily determined in the same sample.

#### The Hydrolysis Reaction

The salt  $\text{KSbF}_6$ , previously prepared with antimony-124 as a tracer, was used as a source of hexafluoroantimonate(V) ions. The reaction was begun by dissolving a weighed sample of  $\text{KSbF}_6$  in the appropriate solvent. The solution was stirred with a teflon stirring rod to achieve rapid dissolution, and the dissolution was judged to be complete after about one minute. The time taken for the start of the reaction was the time of the addition of the solvent to the salt in a polyethylene test tube. The reaction vessel was then thermostated at 25° C and aliquots removed at appropriate intervals for analysis. The first aliquot for analysis was taken as soon as possible after dissolution of the  $\text{KSbF}_6$ . The time intervals for subsequent aliquots were determined by the rate of the reaction. For slow reactions, aliquots were taken over a period of several hours. In the case of the most rapid reactions, namely those in the basic regions, it

was necessary to quench the reaction in the aliquots. This was done simply by adding the aliquot to an excess of the acidic eluting agent. This quenching was made possible because the amount of base in the aliquot was negligible compared to the amount of acid in the volume of eluting agent used and because the rate of reaction in the resulting acidic solution was negligible compared to that in the bulk of the basic solution. The quenching was necessary because the analytical procedure employed required several minutes for preparation, and this time was a significant interval of reaction time.

The method of analysis involved a column chromatography adaptation of the paper chromatography method successfully used to separate antimony-(III)-antimony(V) fluoro-complexes. The column was prepared by adding a slurry of acetone and Whatman cellulose powder CF 11 to a glass buret. The column was tightly packed by stamping with a glass rod and topped with a layer of glass wool several centimeters high. It was found that the first species appearing in the hydrolysis (i.e.,  $\text{KSbF}_5\text{OH}$ ) could be separated from the second species (i.e.,  $\text{KSbF}_4(\text{OH})_2$ ) using a cellulose column of about 40 cm in height and an elutant of 90 percent v/v acetone - 20 percent aqueous trichloroacetic acid solution (9:1). The next species which appears to any extent in the reaction is eluted only slowly with the acetone-trichloroacetic acid system and is retained on the column during the usual elution process. It is then removed by treatment of the column with 2.0 F hydrochloric acid. For the later stages of the hydrolysis when only  $\text{KSbF}_4(\text{OH})_2$  and  $\text{KSbF}_2(\text{OH})_4$  are present, a column of about six cm in height is sufficient for the separation.

In a kinetic study, a 200- $\mu\text{l}$  aliquot of the solution in the reaction

vessel was taken with a micropipette and added to 2 ml of the elutant. The resulting solution was added to the column and allowed to flow into the column until it reached the top of the cellulose bed. The elutant was then added and the elution begun. The collection of the effluent was accomplished with an automatic fraction collector. A 1.0-ml portion was taken from each of the collected fractions and the total volume of that fraction measured. These aliquots were then counted on the scintillation detector-scaler equipment previously described.

The rate of hydrolysis was determined in solutions which were 0.0101 F in  $\text{KSbF}_6$  and of varying pH. Three solutions were chosen: (i) 0.2004 F perchloric acid, (ii) acetic acid - potassium acetate solution of pH 5.00, and (iii) potassium hydrogen carbonate - potassium carbonate solution of pH 10.95. All pH values were measured with a Beckman Research pH Meter, standardized against buffers in the appropriate ranges.

### Results

The half-times for reactions (2) and (3) are presented in Table 6.

It should be noted that no evidence was found for the presence of the  $\text{SbF}_3(\text{OH})_3^-$  ion in the reaction mixture. The  $R_f$  values given by Kolditz and Sarrach (64) for the various hydroxofluoroantimonate(V) ions indicate that the separation of the  $\text{SbF}_3(\text{OH})_3^-$  from the other complexes should be possible. Thus, it could be concluded that, under the conditions studied, only three intermediates are involved in the hydrolysis reaction.

### Identification of Hydrolysis Intermediates

Since the hydrolysis intermediates can be separated on a cellulose column, an attempt was made to perform the separation using macro amounts



Table 6. Half-times for Hydrolysis of  $\text{SbF}_6^-$  in Various Solutions

pH	Solution	$t_{1/2}(2)$	$t_{1/2}(3)$
	0.2004 M $\text{HClO}_4$	5.1 hrs	12.1 days
5.00	$\text{KC}_2\text{H}_3\text{O}_2$ - $\text{HC}_2\text{H}_3\text{O}_2$	5.5 hrs	5.8 days
10.95	$\text{K}_2\text{CO}_3$ - $\text{KHCO}_3$	11.0 min	1.9 hrs

- (a) All solutions are 0.0101 M in  $\text{KSbF}_6$ .
- (b) All reactions are at a temperature of  $25 \pm 0.1^\circ \text{C}$ .
- (c)  $t_{1/2}(2)$  refers to the half-time for reaction (2).
- (d)  $t_{1/2}(3)$  refers to the half-time for reaction (3).

of material. The separated material was then analyzed for fluorine and antimony to determine the composition of the intermediates. The separation and identification were performed in the following way.

A glass tube one inch in diameter and six feet in length was fitted with a sintered glass filter and stopcock at the lower end for use as the chromatographic column. The column was packed with cellulose powder to a height of 50 cm using the procedure described earlier.

For the identification of the first intermediate in the hydrolysis reaction, a solution containing about 200 mg of active and inactive  $\text{KSbF}_6$  in enough distilled water to make the solution approximately 0.1 F in antimony(V) was prepared. The elution was accomplished in the usual way and the effluents collected with an automatic fraction collector. Using the antimony-124 as a guide the appropriate fractions were selected and combined. The acetone was evaporated on a steam bath and the remaining solution analyzed for antimony and fluoride as described earlier. The F/Sb ratio obtained was 5.03, 5.07 to 1 proving that the peak thought to be caused by  $\text{KSbF}_5\text{OH}$  indeed had to be ascribed to that compound.

A short column similar to the long one was prepared for the identification of the other two intermediates. A solution containing approximately 200 mg of active and inactive  $\text{KSbF}_6$  in the potassium hydrogen carbonate - potassium carbonate buffer was prepared. After standing for the appropriate length of time to allow the reaction to proceed to the point where the only species present were  $\text{KSbF}_4(\text{OH})_2$  and  $\text{KSbF}_2(\text{OH})_4$ , the solution was placed onto the column and eluted with the acetone - trichloroacetic acid solution. The elution of a compound, proposed to be  $\text{KSbF}_4(\text{OH})_2$ , was followed by means of a survey meter and when no further activity was observed

to be coming off the column, the column was treated with 2.0 F hydrochloric acid. This caused the elution of a compound which was the final product observed in the hydrolysis of the  $\text{KSbF}_6$ . The acetone fractions were concentrated on a steam bath and analyzed for fluoride and antimony. The F/Sb ratio was found to be 3.97, 4.01 to 1 indicating that this compound was  $\text{KSbF}_4(\text{OH})_2$ . Treated in a similar way, the appropriate acid fractions yielded an F/Sb ratio of 2.10, 1.94 to 1.

#### Conclusion

From the isolation and analysis of the intermediates, the reaction sequence for the hydrolysis of the hexafluoroantimonate(V) ion proposed by Mazeika and Neumann has been proven. In acidic or slightly basic solution, the final product has an F/Sb ratio of 2.0. It is thought that this is probably a polymeric material.

Using the chromatographic technique described, it should be possible to extend the study of the rate of hydrolysis of the hexafluoroantimonate(V) ion to any pH region, except the strongly basic region. In this region, the rate of reaction would probably be too rapid to be measured by the technique developed.

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