LIQUID-SOLID EQUILIBRIA, IN THE STANNOUS FLUORIDE-HYDROGEN FLUORIDE SYSTEM

By

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PREFACE

In the manufacture of stannous fluoride from powdered tin and anhydrous hydrofluoric acid, the stannous fluoride is dissolved in an excess of hydrofluoric acid. It would be desirable to crystallize the stannous fluoride from the stannous fluoride-hydrofluoric acid solution.

This study was undertaken to determine how stannous fluoride may be crystallized and separated from hydrofluoric acid. This objective was accomplished by developing a part of the freezing point-concentration diagram for the stannous fluoride-hydrogen fluoride system.

The freezing point-concentration diagram was developed using data obtained from cooling curve experiments on stannous fluoride-hydrogen fluoride mixtures of different compositions. Solubility determinations were made to help confirm the freezing point curve. Boiling point data were obtained in the region where the boiling point at one atmosphere and the freezing point coincide.

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CHAPTER I

INTRODUCTION

Stannous fluoride was first described by Scheele (27) in 1771. However, it became of commercial importance only in 1955 when it was incorporated into a tooth paste as an additive to reduce dental caries.

During commercial development, SnF_2 was produced by the reaction of SnO with aqueous HF. (20). Later, a process was developed to produce SnF_2 directly from metallic tin which is a somewhat cheaper raw material. (12).

To produce SnF_2 from elemental tin and HF, powdered tin is placed in a reactor with an excess of anhydrous HF and allowed to react for approximately eight hours according to the following equation:

$$Sn + 2HF \rightarrow SnF_2 + H_2$$

A reflux condenser is attached to the reactor to permit the escape of H_2 and retain the HF in the reactor. After the reaction has gone to completion, the liquid mixture of SnF_2 and HF is discharged into a dissolving tank containing aqueous recycle mother liquor. Purification is carried out by heating the mother liquor to dissolve the SnF_2, filtering the hot concentrated solution, and then cooling this solution to recrystallize SnF_2.

To prevent a build-up of free HF in the dissolving tank, it is necessary to add sufficient SnO to neutralize the HF discharged from the reactor with the SnF_2. Even though elemental tin is used for the bulk of the reaction, a considerable amount of SnO is consumed in neutralizing the excess HF. If SnF_2 could be crystallized and separated from the excess HF, addition of SnO would be eliminated; and a 25 per cent reduction in raw material cost would be realized.

This study was undertaken to determine how SnF_2 may be crystallized and separated from HF. This objective was accomplished by developing a part of the freezing point-concentration diagram for the SnF_2-HF system.

CHAPTER II

REVIEW OF THE LITERATURE

Freezing Point Diagrams

Relatively few freezing point diagram studies of HF with other inorganic fluorides in binary systems have been reported in the literature.

Ruff and Staub (25) reported on a study of the NH_4-HF system in 1933. They reported evidence of $NH_4F \cdot HF$, $NH_4F \cdot 3HF$, and $NH_4F \cdot 5HF$. The diagram was incomplete in the neighborhood of $NH_4F \cdot 2HF$. In 1934, Cady (5) made a study of the KF-HF system. His study indicated the formation of $KF \cdot HF$ (two crystalline forms), $KF \cdot 2HF$, $2KF \cdot 5HF$, $KF \cdot 3HF$, and $KF \cdot 4HF$. The RbF-HF system was investigated in 1939 by Webb and Prideaux. (31). Their studies show the formation of $RbF \cdot 2HF$, $RbF \cdot 3HF$, $RbF \cdot 3.5HF$, and $RbF \cdot 4.5HF$. In 1948, Winsor and Cady (33) made a study of the CsF-HF system and obtained indications of the formation of $CsF \cdot HF$, $CsF \cdot 2HF$, $CsF \cdot 3HF$, and $CsF \cdot 6HF$.

With the development of atomic energy has come an increase in activity on systems of this type. The UF_6-HF system was reported by Rutledge, Jarry, and Davis (26) in 1953. Only a single eutectic was observed with no indication of compound formation. Studies of the systems BrF_5-HF and IF_5-HF were reported by Rogers, et al. (23, 24) in 1956. These two systems resemble the UF_6-HF system.

No previous study of the SnF_2-HF system was found. Solubility determinations reported in Simons (28) and by Clifford (8) indicated SnF_2 is only very slightly soluble in HF.

The experimental procedure in all the above studies was essentially the same. A series of cooling curve experiments were conducted on mixtures of different composition. The first significant change in slope of the cooling curve was interpreted as being the temperature at which initial crystal formation occurred. Long halts were assumed to indicate some type of phase change was taking place, usually a eutectic or peritectic point.

Equipment usually consisted of a small vessel (about 100 milliliter capacity), a Dewar flask or other well insulated vessel, and some means of measuring temperature, usually a thermocouple. The small vessel was totally enclosed and equipped with a thermal well and a small outlet pipe for adding or withdrawing materials. The mixture was agitated by shaking the whole vessel or using a small mixer. If a small mixer was installed, great care was taken in keeping the vessel leak-proof. Vessels used in earlier work were constructed of some suitable metal such as monel, silver, or platinum. The more recent studies made in the atomic energy field used fluorinated plastics for all surfaces exposed to the fluoride mixtures.

The experimental procedure was to place a given amount of the pure inorganic fluoride in the vessel. The inorganic fluoride was prepared or purified by the investigator. A cylinder of HF was bled to remove about half of its contents. Hydrogen fluoride was then distilled into the vessel containing the inorganic fluoride through the inlet pipe by keeping the vessel cold. Some of the earlier investigators prepared their own HF by decomposing $NaHF_2$. Most investigators, especially in later works, used commercial HF. Hydrogen fluoride placed in the vessel should have a purity of greater than 99.95 per cent HF with the main impurity being water. Composition of the mixture was determined by difference in weight with the addition of each compound.

Each mixture was raised to a temperature where only the liquid phase was present. The mixture was then cooled slowly with good agitation. Time-temperature data were recorded and used to construct the cooling curve.

The technique used for crystal growth and solubility studies by Ting and McCabe (29) may also be employed for freezing point determinations. The following gives their general procedure for crystal growth studies. A liquid mixture of known composition was placed in a batch crystallizer. The temperature of the mixture was high enough to prevent formation of the solid phase. The mixture was then cooled at a definite rate by controlling the temperature of the cooling medium circulating through the jacket on the crystallizer. The mixture was agitated continuously by means of a mixer. The first appearance of crystals was noted, as shown by the Tyndall effect developed by the crystals in a strong beam of light. Time-temperature data were used to construct cooling curves. These cooling curves gave indications of freezing point and heat effects caused by some type of phase change.

Solubility determinations were carried out in the following manner. The batch crystallizer was held at constant temperature for two to three hours with good agitation of an excess of solids. The mixer was turned off and the solids allowed to settle. A two milliliter sample of solution was sucked through a four millimeter tube filled with cotton and then into a seven millimeter tube. The cotton was to filter out any small crystals. Solubility was determined by chemical analysis.

The technique used in the present investigation was similar to the one used by Ting and McCabe. (29).

Stannous Fluoride

Most SnF_2 preparations have been made by the reaction of SnO and aqueous HF. (14, 17). Another method of preparation is the reaction of powdered tin and anhydrous HF. (12). Stannous fluoride has also been precipitated from a solution of NH_4F and $SnCl_2$. (30).

Stannous fluoride is a crystalline substance of rhomboidal prisms, generally slender needles, truncated on the edges so as to give many faces. (16). Melting point range of the compound is 210-215° C. (20). Its solubility in water is rather high, forming a 29.6 per cent solution at 18° C. and a 55 per cent solution at 95° C. The solution is clear, initially. After standing for an hour, it becomes cloudy due to hydrolysis; and a fine precipitate, probably $Sn(OH)_2$, begins to settle out. (20).

The Swedish chemist, Berzelius (3), in 1824 indicated SnF_2 decomposes to $SnOF_2$ when exposed to the atmosphere. However, in 1857, Marignac (16) reported SnF_2 as being stable in air. A possible explanation for the differences of the two authors could be that one had reference to only the surface of the crystals; whereas the other had reference to the whole crystal. Recent studies by Muhler (19) indicate oxidation of the surface does occur, but the inside of the crystal is not attacked.

Early preparations of fluorides for studies of their properties were made with hydrofluoric acid produced from the reaction of fluorspar (CaF_2) and H_2SO_4. Hydrofluoric acid prepared in this manner contains appreciable impurities such as H_2SiF_6, H_2SO_4, etc., which could have been partly responsible for early reports on the decomposition of SnF_2.

In 1856, Fremy (10) probably produced the first pure HF, and consequently, relatively pure fluorine compounds. He prepared a pure KHF_2 by recrystallization to free it from the fluorosilicate and heated this material to obtain pure HF.

The results of his work led him to classify fluorine compounds into three categories: (1) Anhydrous fluorides comparable to the chlorides and remarkably stable, (2) Hydrated fluorides usually unstable and decomposing to lose HF and leave an oxide or oxyfluoride, and (3) Hydrofluorides which are true acid salts. A stannous fluorine compound might appear in group three. According to Fremy (10), SnF_2 or $SnHF_3$ can be obtained, depending on the amount of acid employed.

Recent works of Nebergall, Day, and Muhler (20) failed to produce an acid fluoride when using up to 200 per cent excess aqueous HF.

Hydrogen Fluoride

Liquid HF resembles H_2O and HCN to a much greater extent than it does the other hydrogen halides. Its physical properties are quite abnormal when compared to the other hydrogen halides. X-ray diffraction studies show polymeric aggregates which explain the abnormal properties. (28).

Those metal fluorides which are soluble in HF probably are so because of the formation of hydrofluorides. Solubility, boiling point, and particularly conductivity investigations indicate that dissolution of inorganic compounds in liquid HF is generally accompanied by reaction between solute and solvent. (2).

After the present work had been completed, a recent study of the NaF-HF system by Adamczak, Mattern, and Tieckelmann (1) was noted. Their procedure was essentially the same as described earlier in the literature survey. Their investigation concentrated between a NaF mole fraction of 0.298 to 0.130. No freezing points were obtained below a NaF mole fraction of 0.25 even when the system was heated to 200° C. under 15 atmospheres. Thermal data showed a freezing point curve with about the same shape as the one developed for the SnF_2-HF system. A congruent melting point at 39.8° C. was reported for $NaF \cdot 4HF$. An incongruent melting point at 60.5° C. was reported for $NaF \cdot 3HF$. It existed in two forms. The form stable below 43.1° C. was called $\alpha NaF \cdot 3HF$ and the form stable above that temperature was called $\beta NaF \cdot 3HF$.

CHAPTER III

MATERIALS AND EQUIPMENT

Materials

The HF used in all the experiments came from a 200 pound cylinder purchased from Pennsalt Chemicals Corporation. Chemical analysis of the impurities in the HF is presented in Table V, Appendix A. Subtracting these impurities from the whole, a purity of 99.983 per cent HF on a wet basis and 99.990 per cent HF on a dry basis is obtained.

The SnF_2 was prepared in a semi-commercial plant by the Ozark-Mahoning Company. Chemical analysis of stannous and total tin were 74.86 per cent and 75.56 per cent, respectively. Fluorine analysis was 24.2 per cent F. Based on stannous tin analysis, the purity of the SnF_2 was calculated to be 98.8 per cent. The principal impurity was assumed to be $SnOF_2$. Complete analysis of the SnF_2 used in this investigation is given in Table VI, Appendix A.

The later experiments were conducted with SnF_2 prepared on a laboratory scale. Preparation was carried out by dissolving finely powdered tin in liquid HF to obtain a SnF_2-HF solution. The powdered tin was purchased from McGean Chemical Company. It was reported as being 99.975 per cent pure. Complete analysis of the tin is given in Table VII, Appendix A. Based on analysis of the SnF_2-HF solution, stannous tin was calculated to be 75.4 per cent and the total tin 75.9 per cent. Using 75.4 per cent stannous tin, the SnF_2 was calculated to be 99.6 per cent pure.

Equipment

Exploratory tests were conducted in a 180 milliliter polyethylene cylindrical vessel. The vessel was placed in a 800 milliliter beaker with the top section cut off. This equipment is shown in Figure 1. The polyethylene top was equipped with a silver thermal well for a thermometer, a stoppered vent hole for removing HF vapor, and a polyethylene-coated stiff wire in the shape of a dasher. A thin polyethylene bellows was fastened to the dasher shaft and the top of the vessel. This allowed the dasher to be moved up and down without losing HF vapor.

The polyethylene vessel was held in position in the glass cooling jacket by means of a rubber ring. Annular space between the polyethylene and glass vessels was one inch at the side and one and one-half inches at the bottom. A thermometer was inserted through a hole in the rubber spacer ring to obtain the temperature of the coolant.

An Eastern Industries Model B-1 centrifugal pump using one-quarter inch rubber tubing and eight millimeter glass tubing was used to circulate methanol through the cooling jacket. The methanol was cooled by being circulated through a three-eighths inch copper coil 20 feet long placed in a three-gallon stainless steel bucket containing a dry ice-methanol mixture.

After exploratory tests were completed, more elaborate equipment was built. Detailed drawings of the more elaborate equipment are shown in Figures 2 and 3.

The silver vessel was constructed of one-eighth inch silver plate, 99.9+ per cent pure, purchased from Handy and Harman Company. The vessel was two and three-quarters inches in diameter and three and seven-eighths inches high. The top was flanged and drilled for a standard three-inch flange.

A one-sixteenth inch clear Kel-F sheet was used for the top cover.

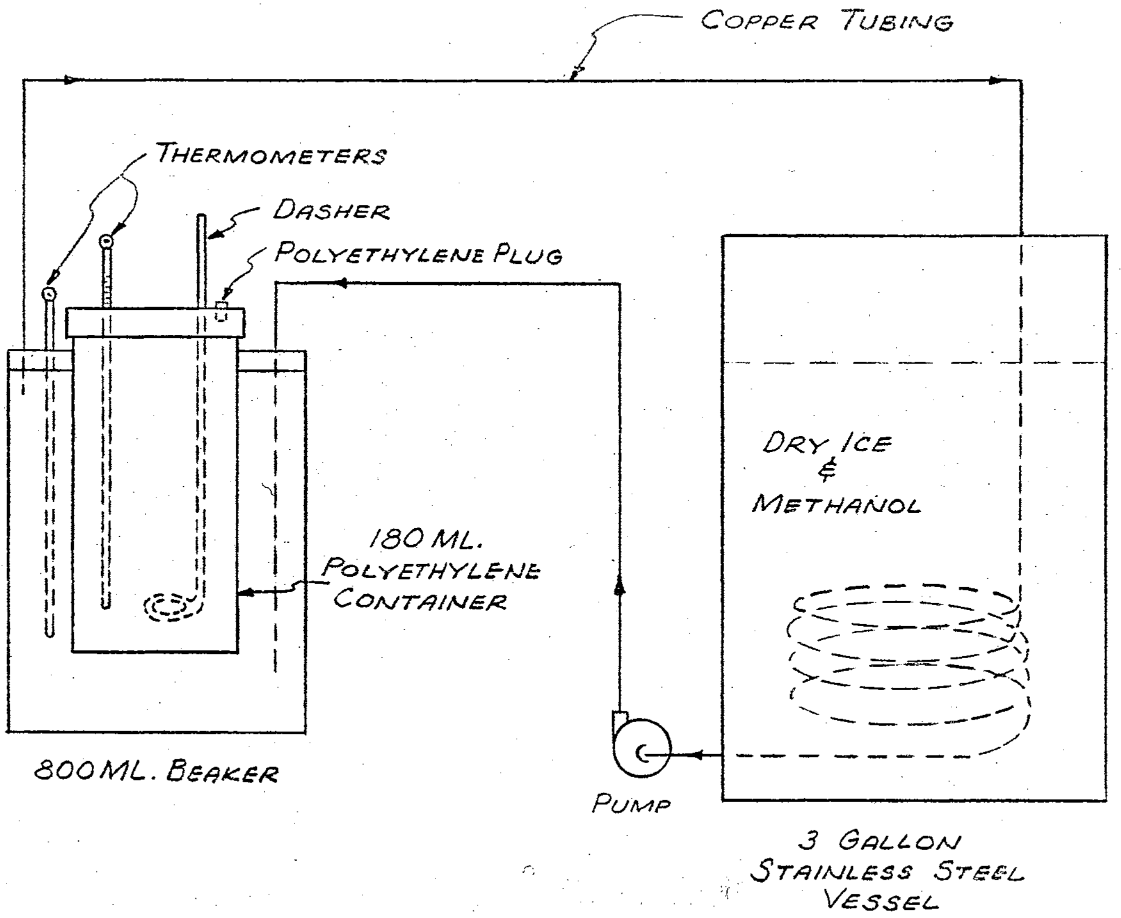

FIGURE 1

SCHEMATIC DIAGRAM OF
EQUIPMENT FOR PRELIMINARY INVESTIGATION

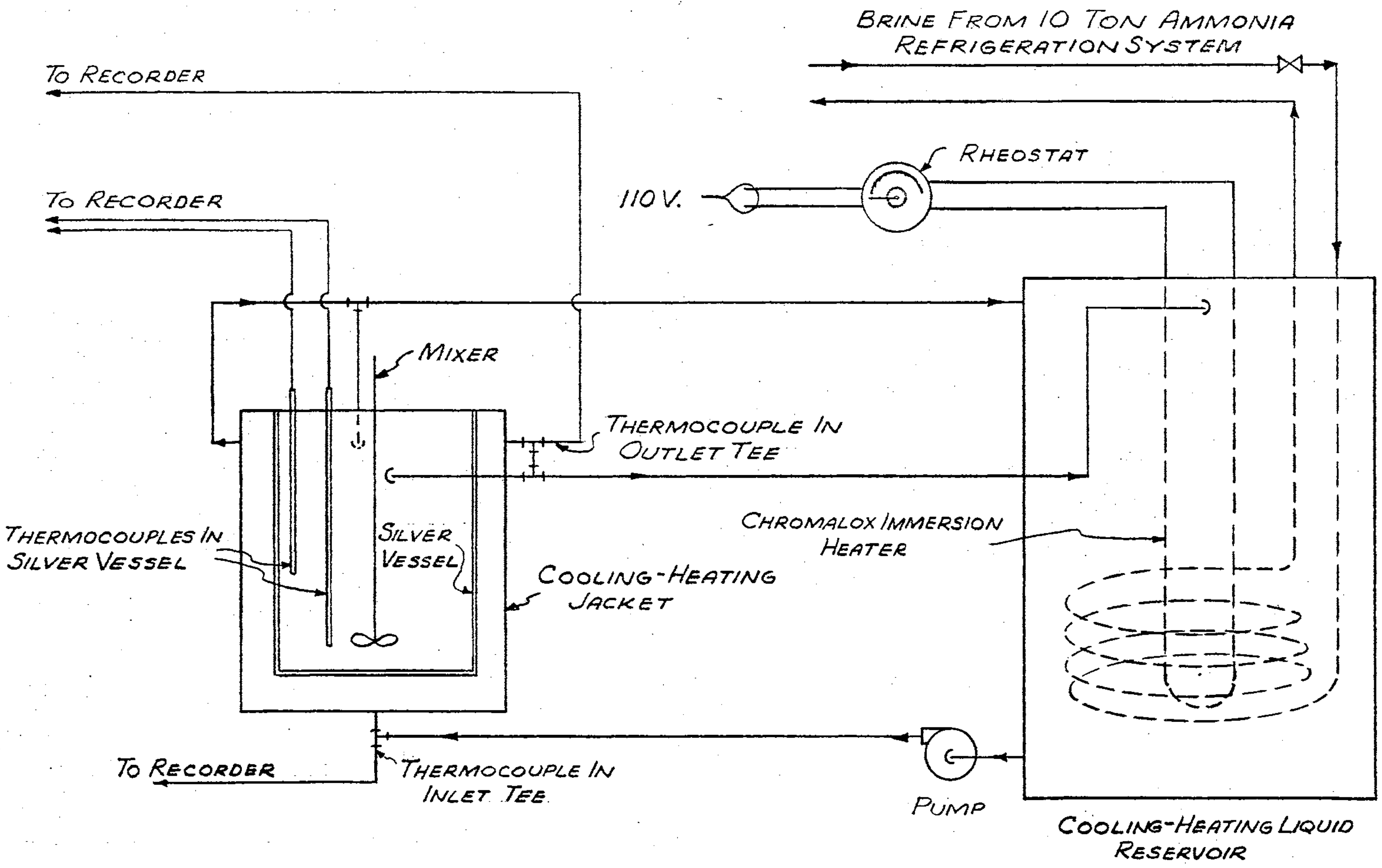

Figure 2

Schematic Diagram Of Equipment

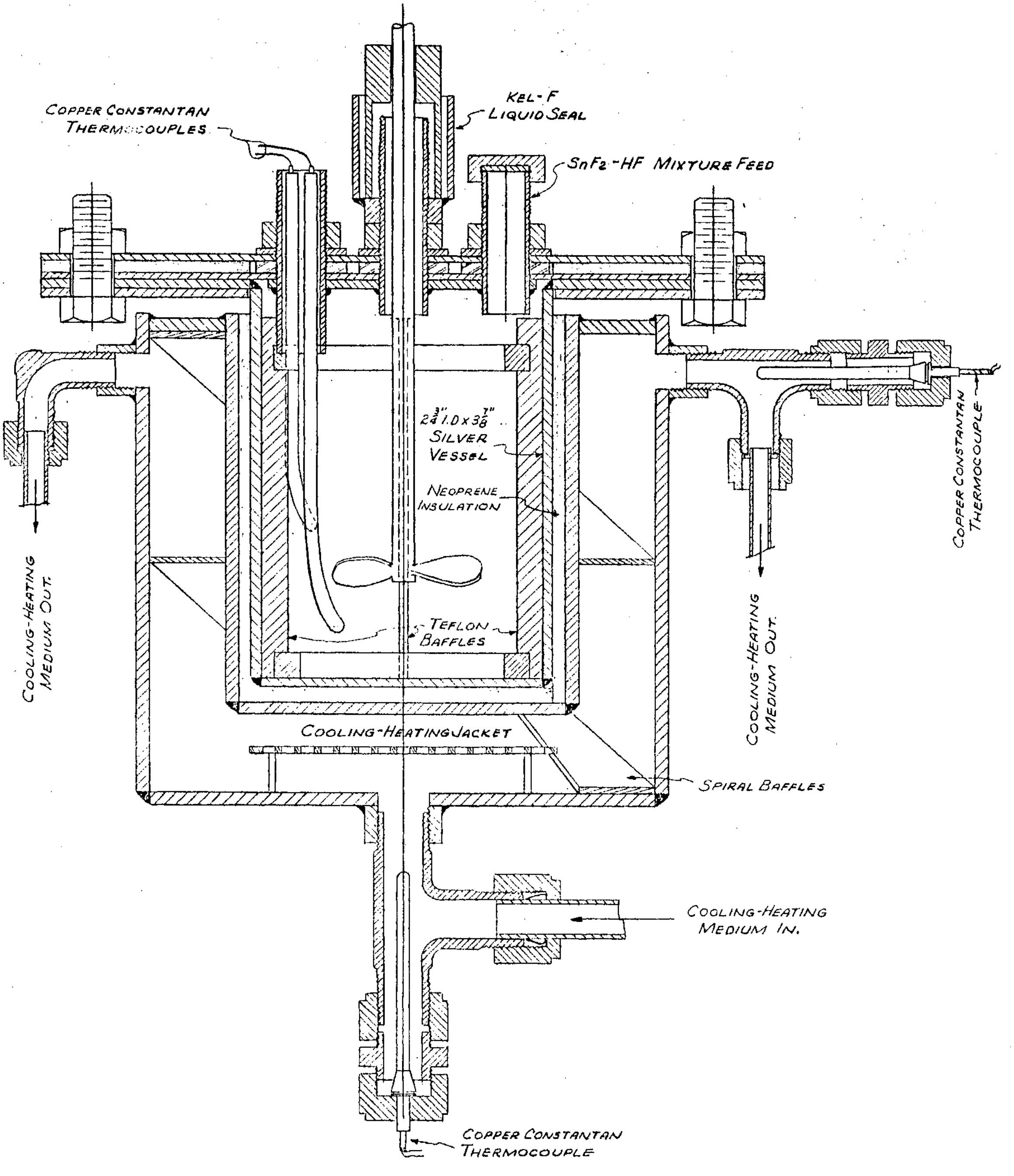

Figure 3

Detail Drawing Of Crystallizer

Steel back-up flanges were used to insure good sealing. After the initial run, the top was changed to a double sheet to prevent fogging by HF on the top of the vessel. This was accomplished by using a double Kel-F top with a one-eighth inch rubber gasket as a spacer between the two sheets and purging this space with nitrogen.

The Kel-F top was used to support three one-quarter inch silver pipes, assembled to a silver back-up plate. The back-up plate was placed flush with the inside surface of the bottom Kel-F sheet. The top sections were threaded, and SAE jam nuts were used to tighten the pipes against the Kel-F top. Teflon washers were used around the three pipes to keep the Kel-F sheets divided. One pipe was used as a feed line, another was used to insert two silver thermocouples, and the third was for the mixer.

The two thermocouples in the silver vessel, as well as the two placed in the cooling jacket, were constructed in the same manner. Leeds and Northrup Catalog No. 24-55-11 B & S No. 24 gauge copper-constantan premium grade thermocouple wire was used for all thermocouples. The thermocouple wires were threaded through one-eighth inch silver tubes. Each junction was silver soldered to the tube resulting in a thermocouple with all exposed surfaces made of silver. The two thermocouples in the silver vessel were silver soldered in the silver pipe through which they entered. One thermocouple was located one-half inch from the bottom and three-quarters inch from the nearest wall. The other thermocouple was located one and one-half inches from the bottom and one-half inch from the nearest wall.

The mixer was a marine type propeller one and one-half inches in diameter on a one-quarter inch shaft twelve inches long. It was constructed of stainless steel type 316 and purchased from E. H. Sargent

Company. The mixer was powered by a E. H. Sargent motor with a cone-drive variable speed output. To assure uniform mixing, four one-quarter inch by three and one-half inch Teflon baffles were positioned vertically in the vessel and spaced 90° apart. The mixer shaft was inserted through the middle silver pipe. A liquid seal was used to prevent HF vapor from escaping. The outer cup was a mild steel tube seven-eighths inch I. D. welded to the jam nut. The inverted cup, machined from Teflon, had a one-sixteenth inch clearance between the outside cup and between the silver pipe. The upper section of the Teflon cup was drilled to obtain a tight fit on the mixer shaft. A Kel-F oil, Alkane 695, purchased from M. W. Kellogg Company, was used for the liquid seal.

A one-half inch SAE nut was used to make a cap for the feed line. A Kel-F disc was inserted in the cap to assure good sealing.

The silver vessel was easily inserted or removed from a heating-cooling jacket. This jacket was constructed from pieces of standard three and five inch mild steel pipes. The annular space for the cooling-heating medium was three-quarters inch. The sidewall and bottom of the cooling jacket were lined with one-eighth inch neoprene rubber. This rubber lining assured a tight fit of the silver vessel in the cooling-heating jacket and also reduced the heat transfer rate to give the desired rate of change in temperature of the SnF_2-HF mixture in the silver vessel. The cooling-heating medium entered the jacket in the center of the bottom. A perforated distributor plate located three-eighths inch off the bottom allowed the medium to flow evenly along the bottom of the jacket. Four spirals located in the annular space of the jacket gave a lateral motion combined with the vertical movement of the fluid. The liquid was discharged at the top of the jacket from four openings spaced equally. Then it traveled an equal distance to the liquid reservoir. A thermocouple was placed in the liquid inlet and discharge connections of the cooling jacket.

Circulation of the cooling-heating liquid was by means of an Eastern Industries centrifugal pump, model D-6. The cooling-heating liquid for all experiments was kerosene. Circulation rate of the cooling-heating liquid was three gallons per minute. A reservoir for the cooling-heating liquid was constructed of standard eight-inch mild steel pipe. A 500 watt, 110 volt Chromalox immersion heater was inserted in the middle of the reservoir. Three turns of three-eighths inch copper tubing were placed around the heater. The copper tubing served as a cooling coil with calcium chloride brine at -20° F. being circulated through the coil. The return lines from the cooling-heating jacket were placed to give good circulation of the liquid in the reservoir eliminating the use of a mixer. The entire equipment, except for the centrifugal pump motor, was placed in a 17-1/2 inch x 14 inch x 14 inch box. The void space in the box was filled with vermiculite insulation.

Cooling was effected by circulating -20° F. calcium chloride brine tapped off a main brine line. The main brine line was operated off a ten-ton Worthington self-contained ammonia refrigeration system. Heat supplied by the 500 watt heater was regulated by a Superior Electric 2KVA rheostat. Temperatures were recorded on a Leeds and Northrup Micromax series 4000 recorder with a range from -20° F. to 250° F.

The recorder was standardized before starting Series I by conducting cooling curve experiments on H_2O and 40 per cent aqueous Na_2SO_4 solution. The thermocouples were checked by determining the freezing point of H_2O before each series. Transition temperatures of Na_2SO_4 were not taken during the experimental work for fear of contamination. Cooling curves were conducted again at the end of the experimental work on H_2O and a 40 per cent aqueous Na_2SO_4 solution. The freezing point of H_2O never deviated enough from 32° F. that it could be observed on the recorder. The first transition temperature recorded for Na_2SO_4 to $Na_2SO_4 \cdot 10H_2O$ was 91° F. The transition temperature recorded after the work was completed was 90.5° F. The transition temperature for Na_2SO_4 to $Na_2SO_4 \cdot 10H_2O$ given in the literature is 90.4° F. (15). Cooling curves for H_2O and Na_2SO_4 conducted before experimental work was started are shown in Figures 20 and 21, respectively. Data for all cooling curves are given in Appendix B.

Cooling curve experiments performed above atmospheric pressure were conducted in the silver vessel used for the regular cooling curve experiments. The equipment for experiments performed above atmospheric pressure is shown in Figure 4. The silver vessel was modified by returning to the single Kel-F sheet top. The Kel-F liquid seal was removed, and the liquid seal connection was blanked off with a Kel-F gasketed cap. The silver vessel was placed in a eight-inch diameter by twelve-inch high cylindrical fiberboard container. A cylindrical fiberboard tube with a fiberboard disc was inserted in the bottom section of the container. This tube was positioned to give a one-half inch air space between the tube and the silver vessel. The disc was located three-quarters inch from the bottom of the fiberboard container. The space between the inserted tube and the wall of the container was filled with vermiculite insulation to one-quarter inch below the bottom of the silver flange. A similar fiberboard tube and disc were installed above the silver flange, and the space between the tube and the wall of the fiberboard container was filled with vermiculite insulation.

Small holes were perforated on the side and near the bottom of the

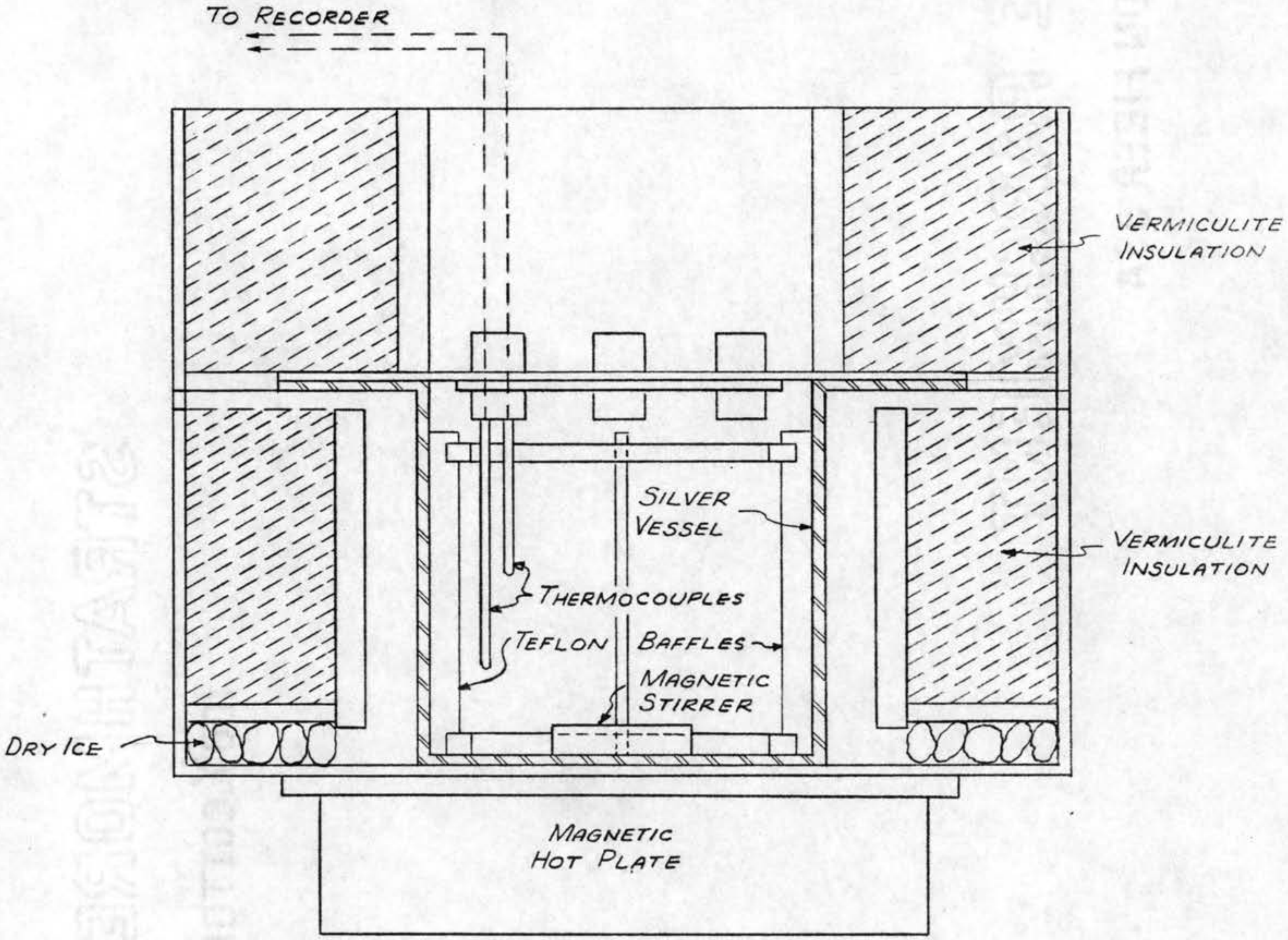

Figure 4

Equipment For System Under Pressure

fiberboard container to insert dry ice in the space between the bottom disc and the bottom of the fiberboard container. As the dry ice sublimed, the gas traveled up the annular space between the silver vessel and the fiberboard tube transferring heat away from the SnF_2-HF solution in the silver vessel. Mixing was accomplished by placing a Teflon covered magnetic bar in the silver vessel. The whole apparatus was placed on a magnetic hot plate.

The final cooling curve experiment was conducted in a 20 milliliter polyethylene cylindrical vessel. The cylindrical vessel was equipped with a pressure type top and a copper constantan thermocouple. The thermocouple, except for the junction, was covered with polyethylene tubing. The tubing was inserted through the top and welded to it. The 20 milliliter polyethylene vessel was placed in a small Dewar flask.

CHAPTER IV

EXPERIMENTAL WORK

The experimental work consisted, primarily, of cooling curve experiments on various SnF_2-HF mixtures. The time-temperature data were used to construct a partial freezing point diagram for the system SnF_2-HF. This diagram was used to determine the best method of crystallizing SnF_2 from its solution in HF.

Altogether, 45 cooling curve experiments were conducted over a SnF_2 concentration range of 10 mole per cent to 66.7 mole per cent. The validity of the interpretation of these cooling curves was substantiated by 14 solubility tests conducted over the same range. The boiling points for mixtures of seven different compositions were determined. These determinations were made on mixtures between SnF_2 molar concentrations of 47.6 per cent and 57.7 per cent. The latter was the maximum SnF_2 concentration obtainable in the liquid phase at atmospheric pressure. The total of 66 runs was divided into 15 different series of runs; each series represented the preparation of a new mixture of SnF_2 and HF.

The appearance of a fine white precipitate on the first experiment of each series in earlier work and after several experiments had been conducted in later work made it difficult to observe SnF_2 crystal formation. For this reason, SnF_2-HF mixtures were changed frequently. The white precipitate was assumed to be an impurity, probably $SnOF_2$, with very low solubility in HF.

Cooling Curves

Twelve of the fifteen series of experiments were composed of time versus temperature data of cooling SnF_2-HF mixtures of given compositions.

The first series, designated as Series A, consisted of seven runs with the HF:SnF_2 molar ratio ranging from 1.27 to 4.0. These runs were of an exploratory nature and conducted principally to determine the temperature and composition range which would be most suitable for studying the crystallization of SnF_2 from the liquid mixture.

The SnF_2-HF Mixture was prepared by placing 117.5 grams of SnF_2 in a weighed cylindrical polyethylene container. The container with the SnF_2 was placed on a pan balance and 62.3 grams of HF was added intermittently with vigorous movement of the dasher between additions. Composition of the mixture was changed for succeeding runs by vaporizing HF from the mixture. The new composition was determined by weighing the loss and calculating it as HF.

After the composition was determined, the container was placed in a larger beaker used to circulate the coolant, as shown in Figure 1. The mixture was heated to the temperature at which HF vapor was evolved from the container. Then, the cooling procedure was started by placing small pieces of dry ice in the methanol bath. Temperatures of the mixtures and cooling medium were recorded every three minutes. A constant temperature difference between the cooling medium and the mixture of 5° F., 10° F., or 20° F. (within ±1° F.) was maintained in each run. This was accomplished by periodically adding small pieces of dry ice to the alcohol bath. These temperature differences gave cooling rates from a maximum of 1.6° F. per minute to a minimum of 0.3° F. per minute. The mixture was agitated constantly except for observing temperatures and adding dry ice.

The mixtures were cooled until the concentration of solids was too high to allow good agitation of the mixture.

Representative cooling curves are shown in Figures 9 through 19. Significant breaks and arrests in the cooling curves are tabulated in Table I. No attempt was made to isolate and analyze the solid phase.

With the temperature and concentration range which appears to be most suitable for crystallizing SnF_2 from HF established, more elaborate equipment was designed and installed for use on the remaining cooling curve determinations. This equipment is shown in Figures 2 and 3.

Except for a few small modifications, the procedure for preparing the SnF_2-HF mixtures and conducting the experiments was the same for the next five series of cooling curve tests--Series I, II, III, V, and VII. Even though primary attention was given to conducting the cooling curve experiments, great concern was focused on the appearance, from time to time, of a trace amount of solids which would not readily dissolve. Obviously, the cooling curve experiments would have little significance if they were started with solid phase being present. Several techniques were employed in attempting to get clear, complete solutions. However, some runs were made with solid initially present for comparison with other runs.

In Series I, II, III, V, and VII, the SnF_2-HF mixture was prepared in the following manner: 313.4 grams of SnF_2 was placed in a pint polyethylene bottle and 350 milliliters of HF was added in three separate additions with vigorous shaking of the mixture between additions. Hydrogen fluoride was added by means of a polyethylene tube connecting the HF cylinder and the top of the bottle.

In Series I with the final addition of HF, 99 per cent of the solids was dissolved. The mixture was placed on a water bath at 130° F. When the temperature of the mixture had reached its boiling point, further dissolution of the solids had not occurred. The mixture was allowed to remain on the water bath for one hour at which time the solution had been concentrated to one-half its original volume. The amount of solids present in the mixture after concentration had not changed.

In the preparation of mixtures for the other four series, the mixtures were left on the water bath for varying lengths of time to evaporate the desired amount of HF.

The solids were allowed to settle, and as much clear solution as possible was decanted into another polyethylene bottle. The tube on top of this bottle was placed in the one-quarter inch pipe opening in the silver vessel, and the vessel was filled two-thirds full with SnF_2-HF mixture. The fit between the polyethylene tube and the silver pipe was relatively snug. The polyethylene tube was drawn to a small tip, and the flow was such that HF vapor was always coming out the tube and never air going in.

After each run had been completed, composition of the mixture was changed for the next run by vaporizing HF from or adding more HF to the mixture. As a rule, the first run in each series was the richest in HF. To vaporize HF and obtain a new composition for the next run, circulation of the heating medium was continued after the boiling point of the mixture was reached. This vaporized HF from the mixture and caused its temperature to rise. When the desired composition was reached, as indicated by temperature of the mixture, HF vaporization was stopped by turning off the heating medium pump. In the few cases where HF was added to the silver vessel, it was introduced from a polyethylene bottle in the same manner as the SnF_2-HF mixtures had been. After the composition of the mixture had been changed or a new mixture had been placed in the silver vessel, a sample was obtained and analyzed for tin and fluorine.

Samples were obtained with a one milliliter polyethylene pipet using a Tygon squeeze bulb. The sample and pipet were placed, as quickly as possible, in a weighed air-tight polyethylene bottle. The bottle with sample and pipet was placed in the freezing compartment of a refrigerator for eight hours to prevent HF loss when the sample was dissolved in water for analysis. All samples were taken at a temperature 5° F. below the boiling point of the mixture.

After a sample was obtained, the mixture was cooled by starting the cooling medium circulating pump. The cooling medium was circulated at three gallons per minute. The cooling medium was in turn cooled by circulating a small flow of brine at -20° F. through the copper coils in the cooling medium reservoir bath. Rough temperature control of the cooling medium was accomplished with a three-eighths inch needle valve on the brine line. The 500 watt electric heater and rheostat were used for fine control. Above room temperature, the temperature difference between the mixture and cooling medium was maintained within ±1° F. of the desired temperature. The temperature difference for each run was changed to give different cooling rates; it ranged from 7° F. to 15° F. and gave cooling rates from 0.15° F. per minute to 1.3° F. per minute.

Below room temperature, heat losses to the outside were rather high, and the temperature difference was allowed to go to 20° F. to 30° F. Great care was not exercised in trying to maintain a constant temperature difference as was done above room temperature. The minimum cooling medium and composition temperatures obtainable were 0° F. and 28° F., respectively.

Temperatures were measured and recorded by the Leeds and Northrup Micromax Eight Point Recorder. All eight points were used, and the recorder was wired to give the temperature of the mixture and cooling medium alternately. Points one and five recorded the lower thermocouple in the SnF_2-HF mixture, and points three and seven recorded the higher thermocouple. Points two and six measured the temperature of the incoming coolant, and points four and eight recorded the outgoing coolant. The time required for recording each point was one minute. Consequently, the temperature of the mixture was recorded every two minutes.

The mixture was observed most of the time with a small powerful flash light shining against the highly polished silver wall and bottom of the vessel.

Cooling curve experiments were continued until the entire mixture was half frozen and the areas around the thermocouples were completely frozen.

After the cooling procedure had been completed, the brine was turned off and full power was supplied to the 500 watt heater.

In Series I, when heating the mixture, the temperature difference between the heating medium and the SnF_2-HF mixture was maintained at 10° F. $\pm$1° F. The data from the heating curves did not appear to be nearly as reliable as those of the cooling curve, and in the remaining tests, electrical input to the 500 watt heater was held constant with no attempt to maintain a constant temperature difference between heating medium and SnF_2-HF mixture.

In each of these five series, a different technique was employed in an attempt to eliminate the small trace of solids sometimes present. Initially, it was believed the solution was saturated with SnF_2. In Series I, HF was added until a molar ratio of $9HF:1SnF_2$ was reached. But even at this dilution, the solids were not completely dissolved.

Beginning with Series II, an alteration was made in the method of preparing the SnF_2-HF mixtures. The polyethylene bottle and silver vessel were purged with N_2 before placing any materials in them. This was done to prevent the air from oxidizing the SnF_2 which could cause formation of trace solids. Also, it was thought that possibly the water vapor in the air had a drastic effect on the solubility of SnF_2 in HF. This alteration did not eliminate but seemed to reduce the amount of trace solids.

The SnF_2-HF mixture for Series III was prepared to have a high molar ratio of $7HF:1SnF_2$. The mixture was placed in the silver vessel and maintained near its boiling point overnight with the mixer running. Attempts were made between runs to dissolve the trace solids by allowing the HF to vaporize slowly overnight with the mixer running.

In Series V, a silver reflux condenser was installed on the silver vessel. Before initiating each run, the mixture was maintained at its boiling point for six to eight hours with total reflux of the HF.

In the next two series of cooling curve experiments, Series VIII and IX, an attempt was made to dissolve the trace amount of solids by going to higher temperatures and pressures. To do this, the equipment, method of preparing SnF_2-HF mixtures, and cooling procedure were altered.

The silver vessel was removed from the cooling jacket and placed in a small insulated container shown in Figure 4. The openings in the Kel-F plastic top were blanked off. Agitation was effected by using a Teflon covered magnetic bar in the silver vessel and placing the equipment on a magnetic hot plate.

The SnF_2-HF mixtures for these two series were prepared by placing the silver vessel on a pan balance, adding 400 grams of SnF_2 to the vessel, and then the desired amount of HF. All composition determinations were made using the pan balance.

Since all experiments were conducted at elevated temperatures, cooling was accomplished by merely turning off the heat in the magnetic hot plate.

Before each run was started, the mixture was maintained at the maximum temperature for several hours in a final attempt to dissolve the trace amount of solids present. The temperature ranged from 150° F. to 200° F. and the time from four to forty-eight hours. At the end of each series, the fine solids were isolated and submitted for chemical analysis. The results are shown in Table IV, Appendix A. Analysis indicated these solids contained a large amount of Sn^{+4}. It was assumed the solids were $SnOF_2$.

To overcome the problem of $SnOF_2$ contamination, small amounts of SnF_2 were prepared on a laboratory scale for the remaining series of cooling curve experiments.

Stannous fluoride was prepared by adding 600 grams HF to 600 grams of finely divided tin powder in a gallon polyethylene container. After the tin was almost completely dissolved, activated carbon was placed in the mixture; and the liquid was filtered through a small porous carbon filter tube producing a clear SnF_2-HF solution. This solution was poured into the silver vessel which was placed in a small insulated container shown in Figure 4. Composition was determined by obtaining a sample and analyzing for tin and fluorine as before. Composition of the mixture was changed for succeeding runs by vaporizing HF from the mixture. The new composition was determined by weighing the loss and calculating it as HF. Cooling mixtures below room temperature for Series X and XI was accomplished by placing small pieces of dry ice in the insulated vessel. Care was taken to be sure the dry ice was not close to the silver vessel.

The liquid mixture remained free of the fine white precipitate until toward the end of the last run of each series. The fine white precipitate was separated and analyzed for Sn^{+2} and Sn^{+4}. The results show a high Sn^{+4} concentration and are given in Table IV, Appendix A.

The final cooling curve experiment was conducted in an attempt to determine if the thermal effects noted earlier were caused by changes to different forms of $SnF_2 \cdot HF$ or by transition to a different hydrofluoride not stable in the solid phase. Ten grams of HF and 78.35 grams of SnF_2 were weighed into a 20 milliliter polyethylene vessel under a blanket of N_2. The cap with the thermocouple was tightened on the vessel. The vessel and its contents were placed in a hot water bath and heated to 135° F. with intermittent shaking of the vessel to dissolve the SnF_2. After the SnF_2 was dissolved and the solution temperature was 135° F., the small vessel with the solution was placed in a small Dewar flask. The temperature was allowed to drop to 111° F. by natural cooling. Dry ice was added at this temperature for cooling during the rest of the experiment. Time and temperature data were recorded on the Leeds and Northrup recorder as in previous experiments.

Solubility Tests

Two series of solubility tests were conducted. The first series, designated as Series IV, consisted of five tests. These tests were conducted over a SnF_2:HF molar ratio of 1.287 to 0.988.

The silver vessel was placed in the cooling jacket equipment, shown in Figures 2 and 3, and a SnF_2-HF mixture with a composition of nine-tenths mole HF to one mole SnF_2 was placed in the silver vessel filling it three-fourths full. The mixture was cooled to 99° F. and maintained at that temperature for four hours. The mixer was turned off and the solids allowed to settle for 15 minutes. A sample was obtained with the polyethylene pipet and submitted for chemical analysis. Solubility determinations were made in the same manner for temperatures of 103.5° F., 122° F., 132° F., and 139° F.

Nine solubility determinations were made between a HF:SnF_2 molar ratio of 1.25 and 2.75 in Series XII and XIII. The solid phase in equilibrium with the liquid phase was isolated and analyzed to be approximately SnF_2:HF in every case.

Solubility tests were conducted by placing 400 grams of SnF_2 in weighed 500 milliliter polyethylene bottles. The bottles were placed on a pan balance and HF added as was done previously until the desired amount was obtained. The bottles were capped and placed in a water bath at 130° F. Each bottle was intermittently shaken to dissolve the SnF_2. After the SnF_2 was completely dissolved, the sample was placed in the refrigerator where it was cooled slowly and shaken frequently. Immediately after crystals began forming in the sample, the temperature was measured; a sample of the liquid was obtained with the one milliliter pipet; and the solids were isolated on a polypropylene Buchner funnel. By the time the liquid had been filtered from the solids, most of the liquid adhering to the solids had disappeared. The crystals were quickly blotted with a paper towel and placed in the freezing compartment of a refrigerator in polyethylene sample bottles.

Attempts were made to obtain solubility data and determine the solid phase in equilibrium with the liquid phase on mixtures having a HF:SnF_2 molar ratio of 0.85 and 0.5. The tests were conducted in the silver vessel used in previous tests and shown in Figure 2.

In each test, the silver vessel was placed on a pan balance and 1048.1 grams of SnF_2 were added. HF was then added to obtain the desired composition. A Teflon covered magnetic mixing bar was placed in the vessel, and it was then sealed with the Kel-F plastic top and placed on the magnetic hot plate. The mixture with a molar ratio of SnF_2:0.85HF was heated to 140° F. and maintained at that temperature for two hours with constant mixing. The SnF_2:0.5HF mixture was treated in the same manner only it was heated to 180° F. The mixture containing the smaller amount of SnF_2 was cooled to 112° F., and the higher SnF_2 mixture was cooled to 150° F. A preheated silver tube perforated on the bottom was inserted to the bottom of the silver vessel, and an attempt was made to isolate the solids from the liquid by pressure and gravity. The liquid was very viscous and the solids too small to obtain separation. Solubility results are shown in Table II and Figure 6.

Boiling Points

When Run No. 29 was completed, the SnF_2-HF mixture was reheated to vaporize HF and obtain a higher SnF_2 concentration. The temperature rose to the previous high of 144° F., but subsequent HF evaporation did not cause the temperature of the SnF_2-HF mixture to rise. Failure of the boiling point to rise indicated a SnF_2-HF solution which boils at 145° F. under one atmosphere is a saturated solution.

Runs Nos. 30 through 36 (Series VI and VII) were conducted to determine the SnF_2 concentration in SnF_2-HF solutions having boiling points between 130° F. and 145° F.

The SnF_2-HF mixtures in the two series of boiling point determinations were prepared and added to the silver vessel in the manner used in the preceding series of cooling curve experiments, Series V. The same equipment used in cooling curve experiments, Series V, was used for boiling point determinations. After the SnF_2-HF mixture was placed in the silver vessel and the mixer was turned on, the heating medium was started circulating. The rheostat was used to maintain the temperature of the heating medium 20° F. above the temperature of the SnF_2-HF mixture. After the boiling point of the mixture was reached, HF was evaporated by continued heating of the SnF_2-HF mixture until the boiling point had risen 2° F. to 3° F. The heating medium was stopped circulating, but the mixer was left running. The mixture continued to boil for one to two minutes after circulation of the heating medium was stopped, and the temperature rose about 0.5° F. One to two minutes after the mixture had stopped boiling, the temperature had dropped 0.5° F. to 1° F. below the maximum obtained. A sample of the SnF_2-HF solution was obtained and analyzed for tin and fluorine in the same manner as in the cooling curve experiments. After a sample was obtained, the heating medium was started circulating again, and the foregoing procedure repeated. The results are shown in Table III and Figure 19.

Analysis

The methods for determination of total tin and stannous tin were essentially those described by Farnsworth and Pekola. (11). The method for total tin involved: (1) Reduction of an acid solution with metallic iron, all of which must be reduced; (2) Holding the reduced state with nickel shot; (3) Preventing atmospheric oxidation by a blanket of CO_2; and (4) Titrating the reduced tin at about 32° F. with one-tenth Normal iodate solution using starch iodide indicator. The iodate solution containing atmospheric oxygen was standardized against tin metal.

Two minor deviations from the method cited above for total tin were used. Nickel metal was applied in the form of shot rather than a thin metal coil because the latter form prevented use of a magnetic stirrer in the titration, a device which, under the conditions of CO_2 blanketing, was quite desirable. Blanketing during digestion was maintained by setting a Liebig condenser with joint over the digestion flask and passing CO_2 gas down a three millimeter tube extending down through the condenser into the digestion flask but above the digesting liquid.

The method for stannous tin was the same except for the reduction of any stannic tin.

The error in determination of total tin is believed to be no greater than two-tenths per cent of the tin found in any given sample. The error in determination of stannous tin in solid samples was of about the same magnitude, but that in liquid SnF_2-HF mixtures was somewhat less accurate. This may be attributed to more handling of the sample during preparation which allowed oxidation. Because of this possibility regarding oxidation in preparation for analysis, most of the determinations of tin were made as total tin despite a presumption that the tin was present in the crystallizer as stannous tin.

The method for determination of fluoride involved a distillation from sulfuric or perchloric acid followed by titration at a pH of three with one-tenth Normal thorium nitrate using sodium alizarine sulfonate as an indicator. (34). This method required titration of a sample of five to fifteen milligrams of fluoride. The small size of sample coupled with an end point that could not be sharply read tended to lower the precision of the determination. The probable error of the determination of fluoride is believed to be of the order of two to three per cent of the fluoride content.

CHAPTER V

RESULTS AND DISCUSSION

Thermal arrest points and changes in slope in the cooling curves were interpreted as being phase transitions or freezing points. The freezing point and transition temperature data are tabulated in Table I and the solubility data in Table II. The data from Tables I and II were used to construct part of the phase diagram of the SnF_2-HF system shown in Figures 5, 6, and 7.

Between a mole fraction of 0.25 SnF_2 (which corresponds to the lowest freezing point temperature obtainable with the present equipment) and 0.5 SnF_2, temperature of the freezing point curve increases continuously except for inflections at 57° F. and 84° F. These inflections are in the vicinity of SnF_2:2HF and $2SnF_2$:3HF. It was assumed they were transition points of SnF_2:2HF and $2SnF_2$:3HF. However, analysis of the solid phase in equilibrium with the liquid phase between a molar ratio of SnF_2:1.63HF and SnF_2:3.05HF gave SnF_2:HF ratios from SnF_2:0.97HF to SnF_2:1.1HF. It was concluded the solid phase in equilibrium with a liquid phase molar ratio of SnF_2:1.63HF to SnF_2:3.05HF was $SnF_2 \cdot HF$.

Decided thermal effects were noted at 33° F., 57° F., 74° F., and 84° F. Representative cooling curves showing these thermal effects are presented in Figures 8 through 15. Except for the thermal effect at 74° F., these occur at definite SnF_2:HF ratios and give further evidence of transitions at these temperatures.

TABLE I

FREEZING POINTS AND PHASE TRANSITIONS OF THE SnF_2-HF SYSTEM

Run No.	Mole Fraction SnF_2	Freezing Point °F.	Phase Transition °F.	Final Temperature °F.
12	0.100	a	-	30
10	0.125	a	-	30
16	0.125	a	-	33
11	0.166	a	-	18
1	0.194	b	c	6
2	0.233	a	-	56
3	0.254	35	-	12
17	0.286	48	33	31
4	0.292	53	33	33
18	0.305	56	33	31
55	0.333	57	-	52
5	0.355	71	51	51
56	0.385	80	57	50
50	0.395	83	74	69
51	0.395	83	74	70
13	0.412	85	84, 74	60
19	0.416	87	74, 57	39
52	0.424	86	74	73
53	0.424	87	75	74
20	0.4425	100	84, 74, 57	55
8	0.445	103	84	80
9	0.445	103	84	82
54	0.459	b	84	84
21	0.462	107	84	80
37	0.4715	112	84	83
57	0.500	131	84, 74, 57, 30	31
27	0.513	123	105	99
14	0.535	109	84	66
28	0.541	116	105	104
29	0.571	105	105	105
41	0.588	>140	105	105
42	0.588	>150	-	115

TABLE I (Continued)

Run No.	Mole Fraction SnF_2	Freezing Point °F.	Phase Transition °F.	Final Temperature °F.
43	0.588	>157	105	103
44	0.588	>138	105, 84	83
47	0.612	>130	105	103
49	0.635	>220	-	186
45	0.625	>142	105	100
46	0.625	>160	105	104
38	0.667	>162	105	94
39	0.667	>160	105	90
40	0.667	>165	-	130
48	0.612	>192	104	104

a - Freezing point never reached.
b - Freezing point reached but not observed.
c - Phase transition never reached.

TABLE II

SOLUBILITY OF STANNOUS FLUORIDE IN HYDROGEN FLUORIDE

Run No.	SnF_2 Wt. %	HF Wt. %	Mole Fraction SnF_2	Mole Ratio $HF:SnF_2$	Solid Phase in Equilibrium	Temperature °F.
57	72.15	27.85	.247	3.05	$SnF_2 \cdot HF$	28
58	73.2	26.8	.258	2.87	$SnF_2 \cdot HF$	38
63	74.8	25.2	.275	2.64	-	47
59	75.7	24.3	.289	2.52	$SnF_2 \cdot HF$	52
64	78.3	21.7	.316	2.165	-	57
62	80.8	19.2	.345	1.895	$SnF_2 \cdot HF$	76
60	81.0	19.0	.353	1.840	$SnF_2 \cdot HF$	55
61	82.8	17.2	.381	1.630	$SnF_2 \cdot HF$	70
65	82.9	17.1	.380	1.630	-	79
22	85.9	14.1	.437	1.287	-	99
23	86.8	13.2	.456	1.190	-	103.5
24	87.8	12.2	.479	1.087	-	122
25	88.8	11.2	.503	0.988	-	132
26	88.3	11.7	.490	1.040	-	139

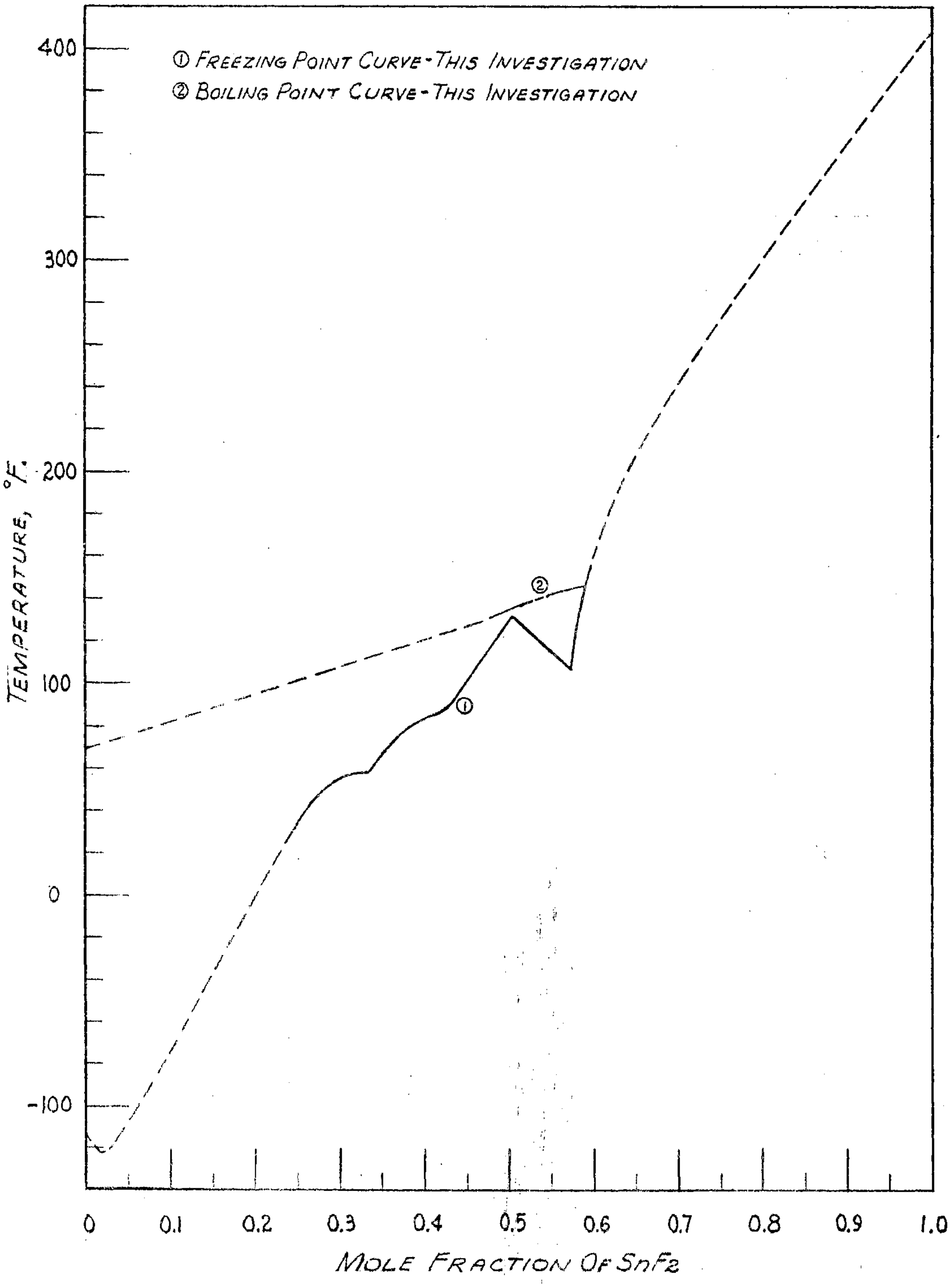

FIGURE 5 BOILING AND FREEZING POINT CURVES FOR THE SnF_2-HF SYSTEM

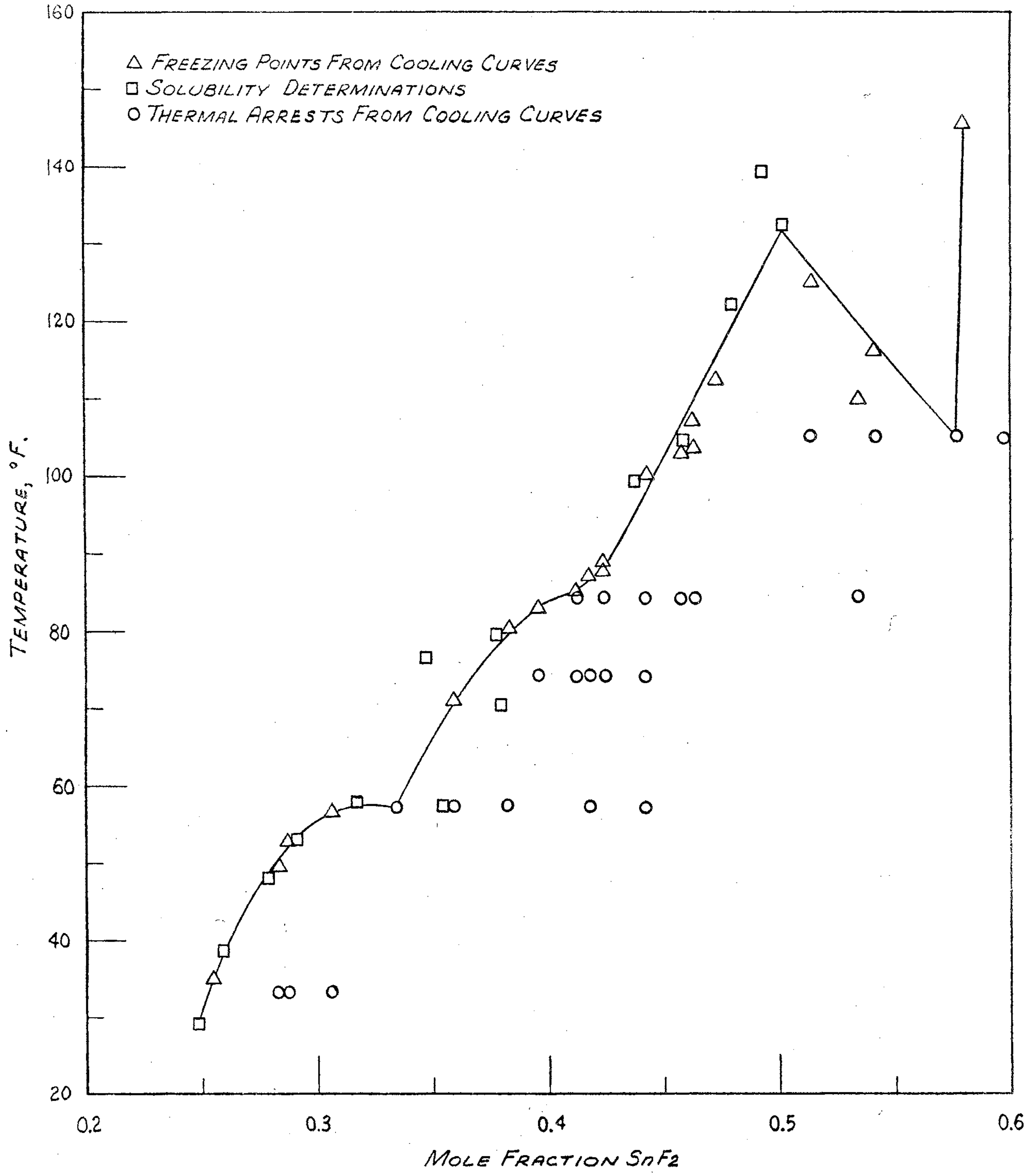

FIGURE 6 PARTIAL FREEZING POINT DIAGRAM FOR THE SnF_2-HF SYSTEM

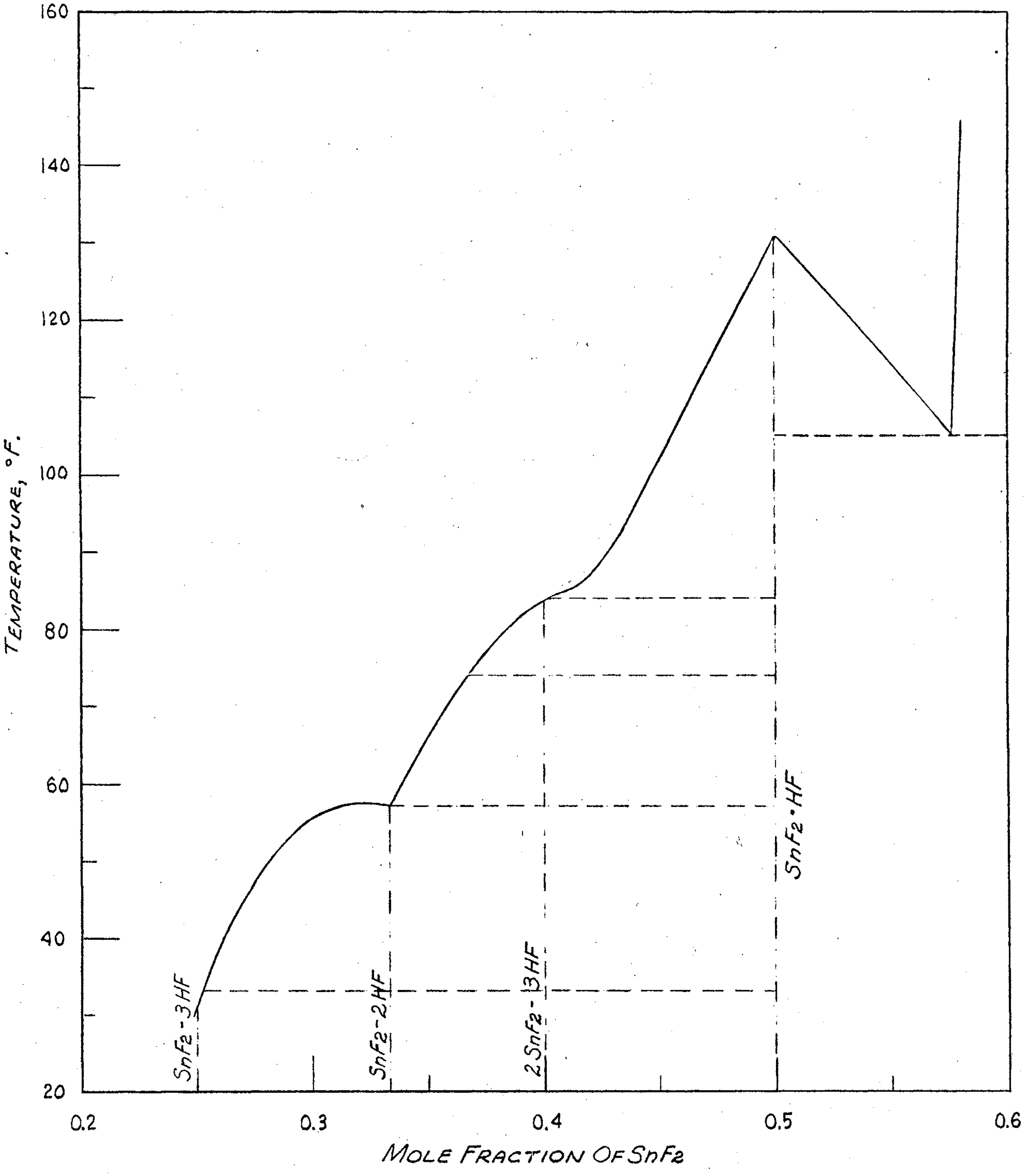

Figure 7 The System SnF_2-HF

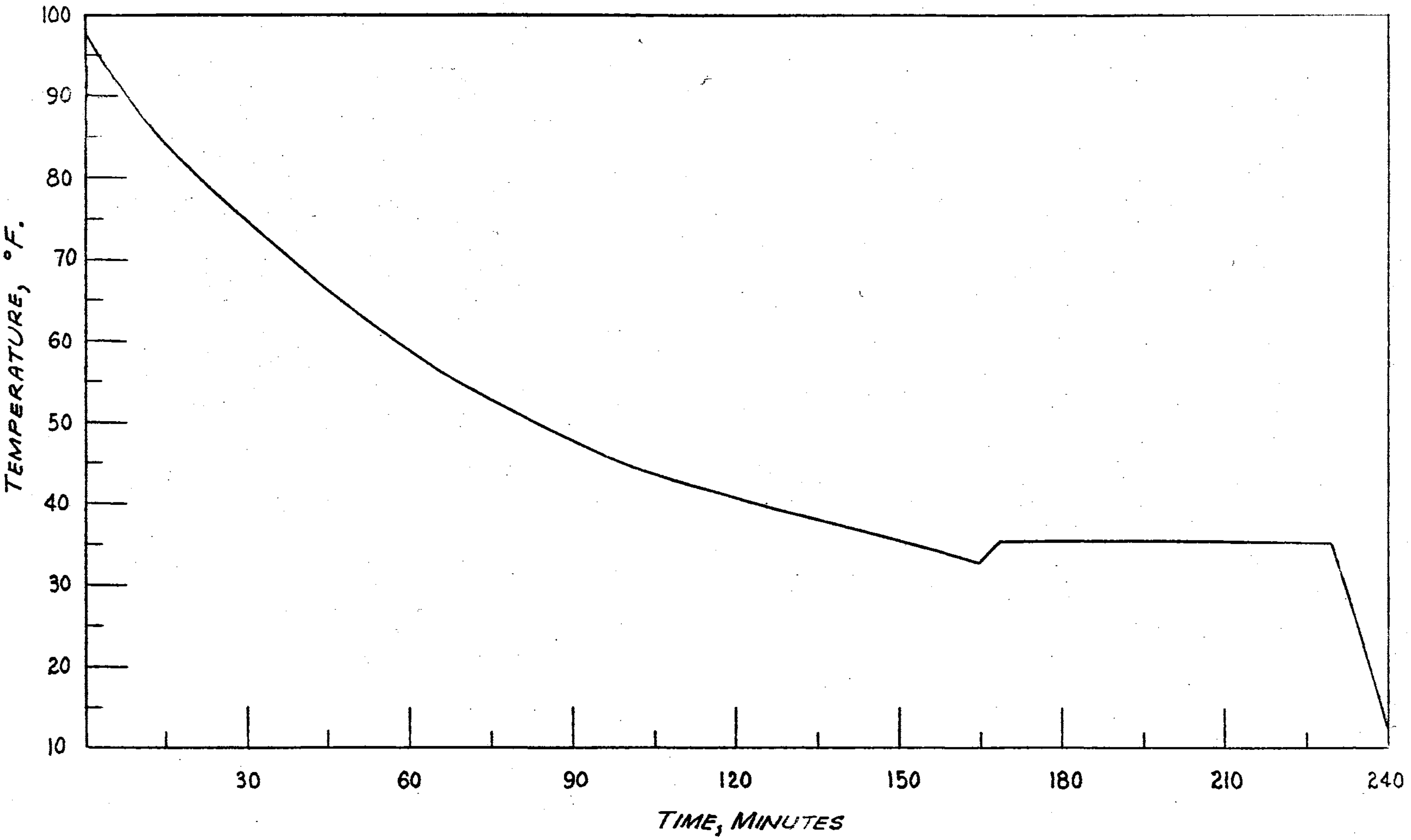

FIGURE 8 COOLING CURVE FOR 25.4 MOLE PER CENT SnF_2 - 74.6 MOLE PER CENT HF

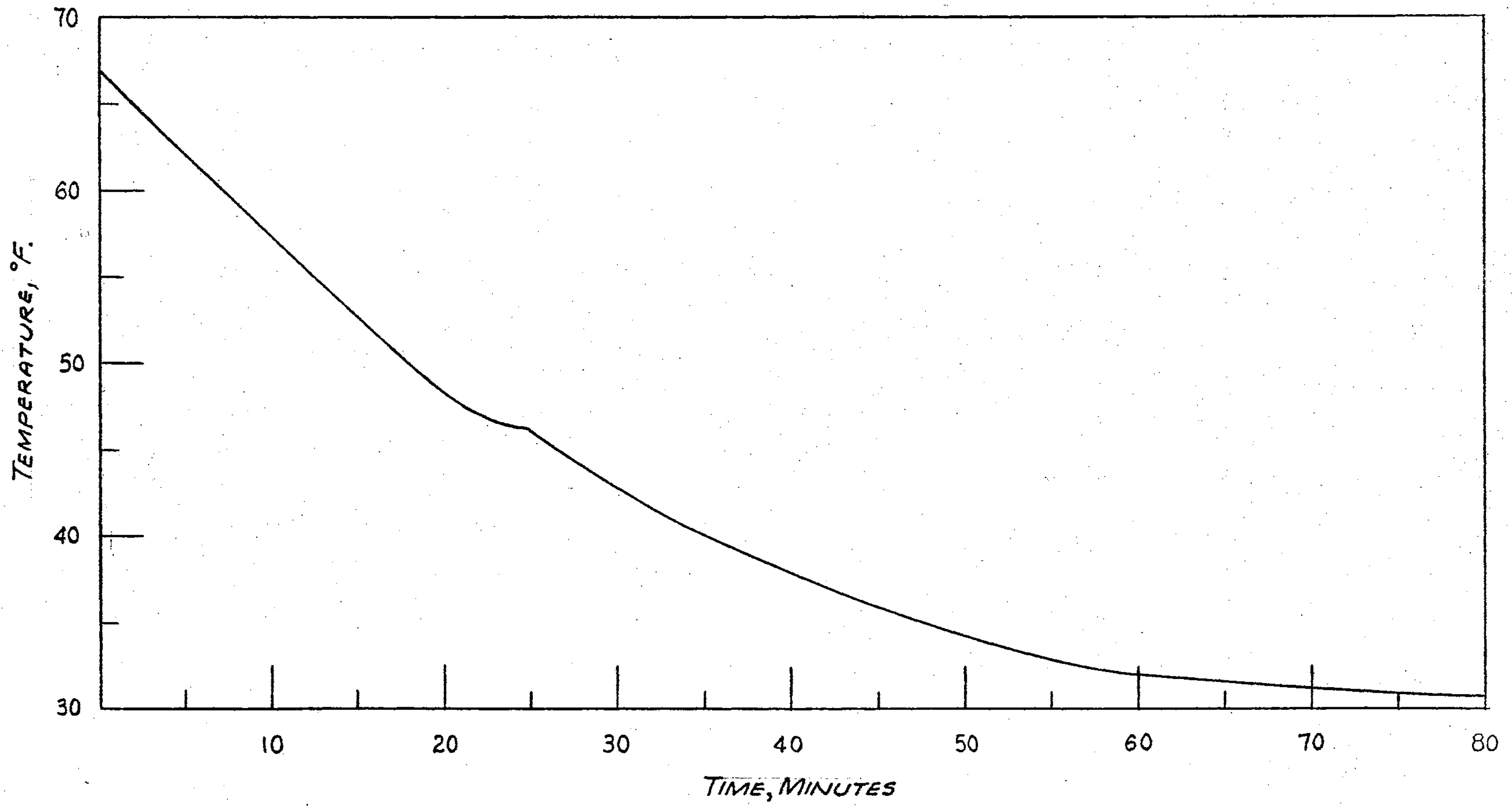

Figure 9 Cooling Curve For 28.6 Mole Per Cent SnF_2 - 71.4 Mole Per Cent HF

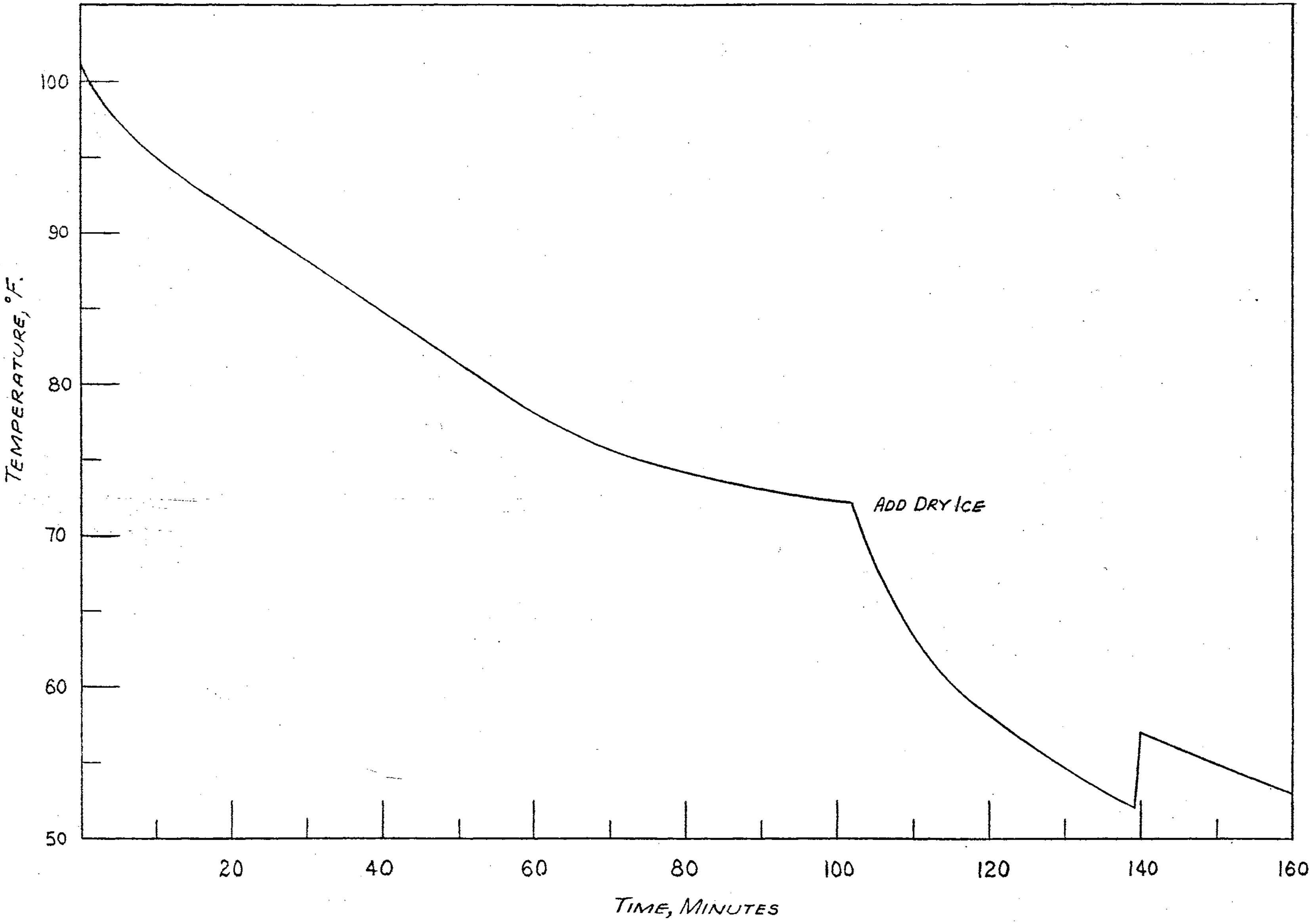

Figure 10 Cooling Curve For 33.3 Mole Per Cent SnF_2-66.7 Mole Per Cent HF

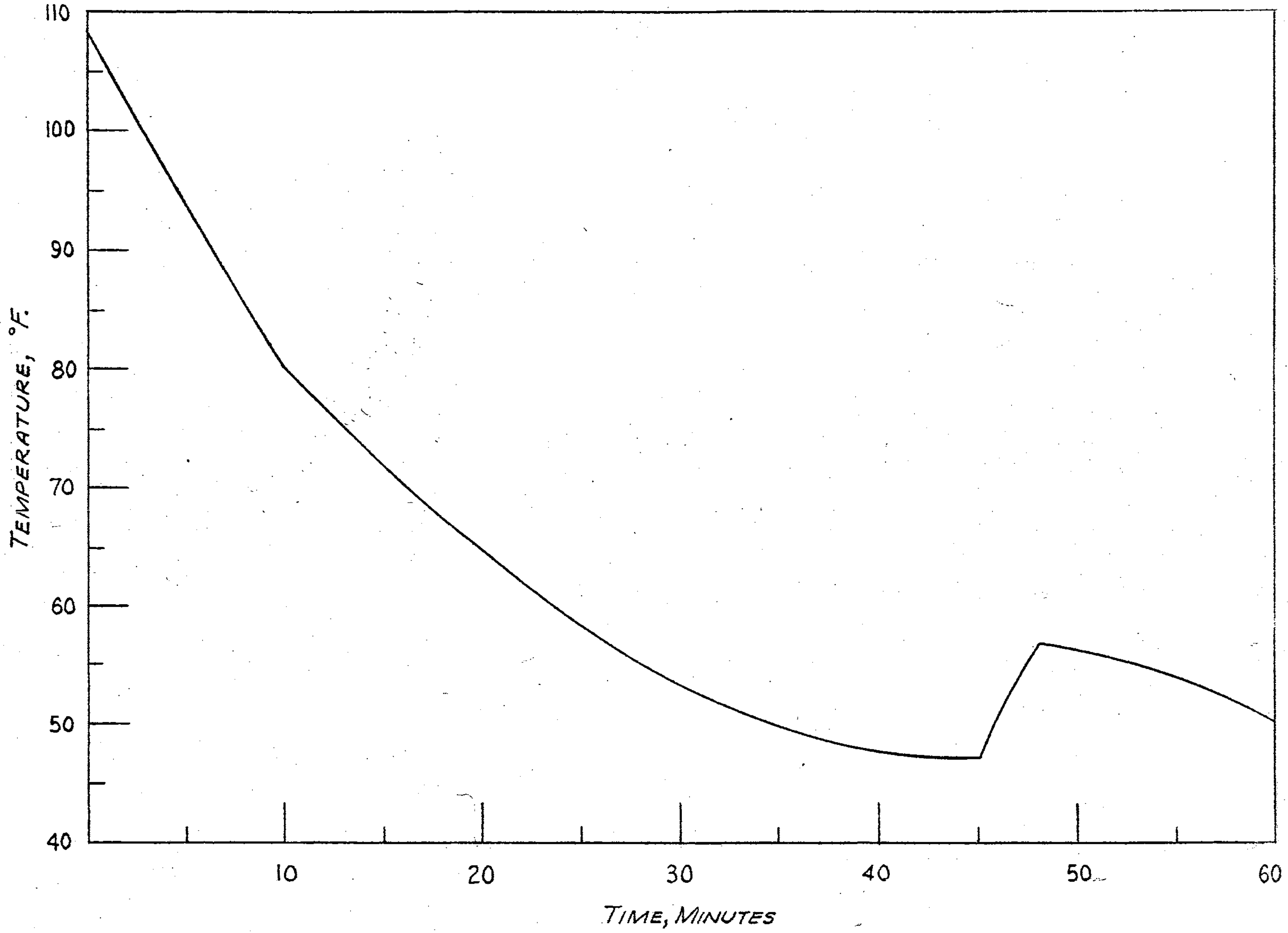

Figure 11 Cooling Curve for 38.5 Mole Per Cent SnF_2 - 61.5 Mole Per Cent HF

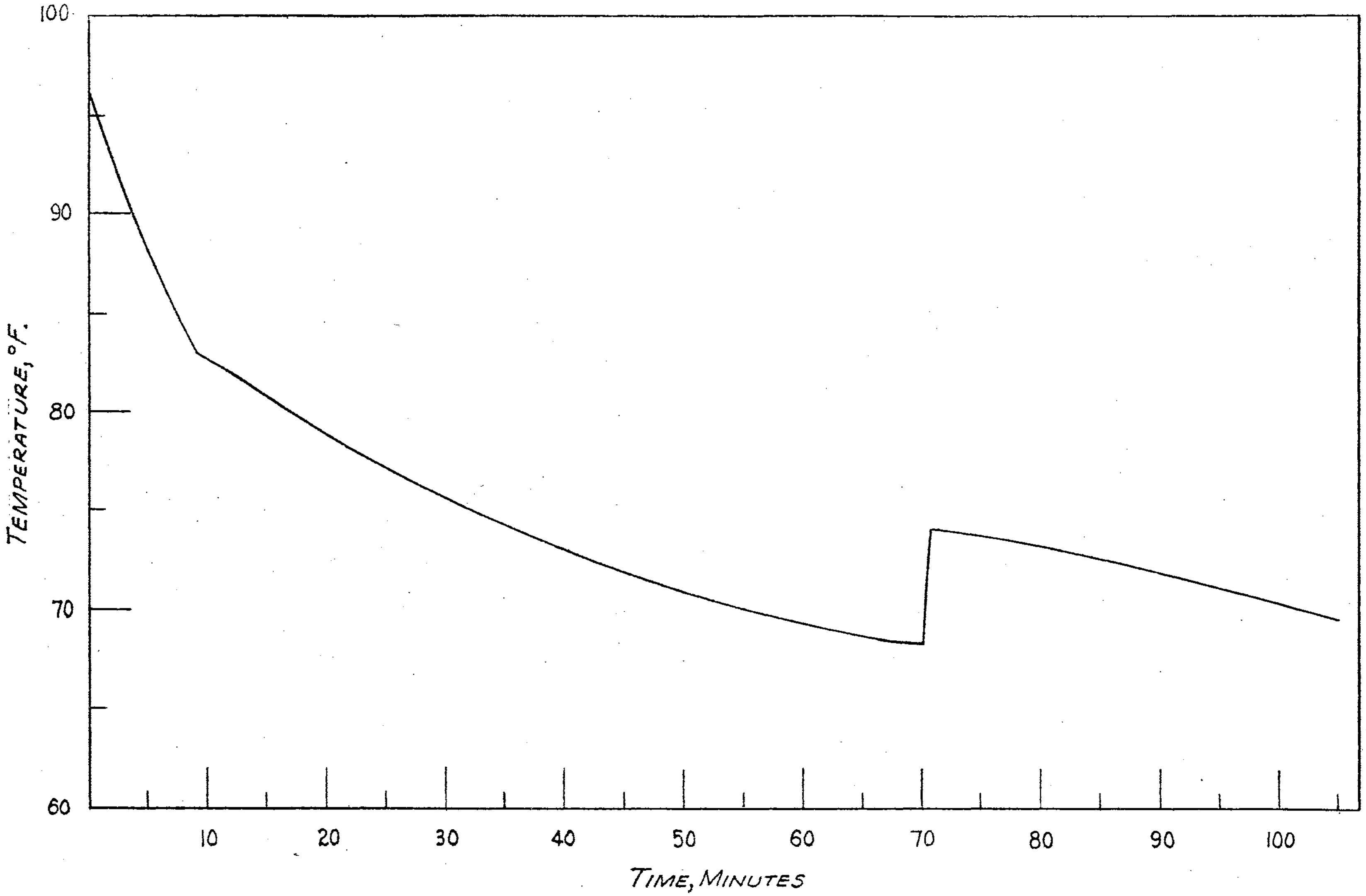

FIGURE 12 COOLING CURVE FOR 39.5 MOLE PER CENT SnF_2-60.5 MOLE PER CENT HF

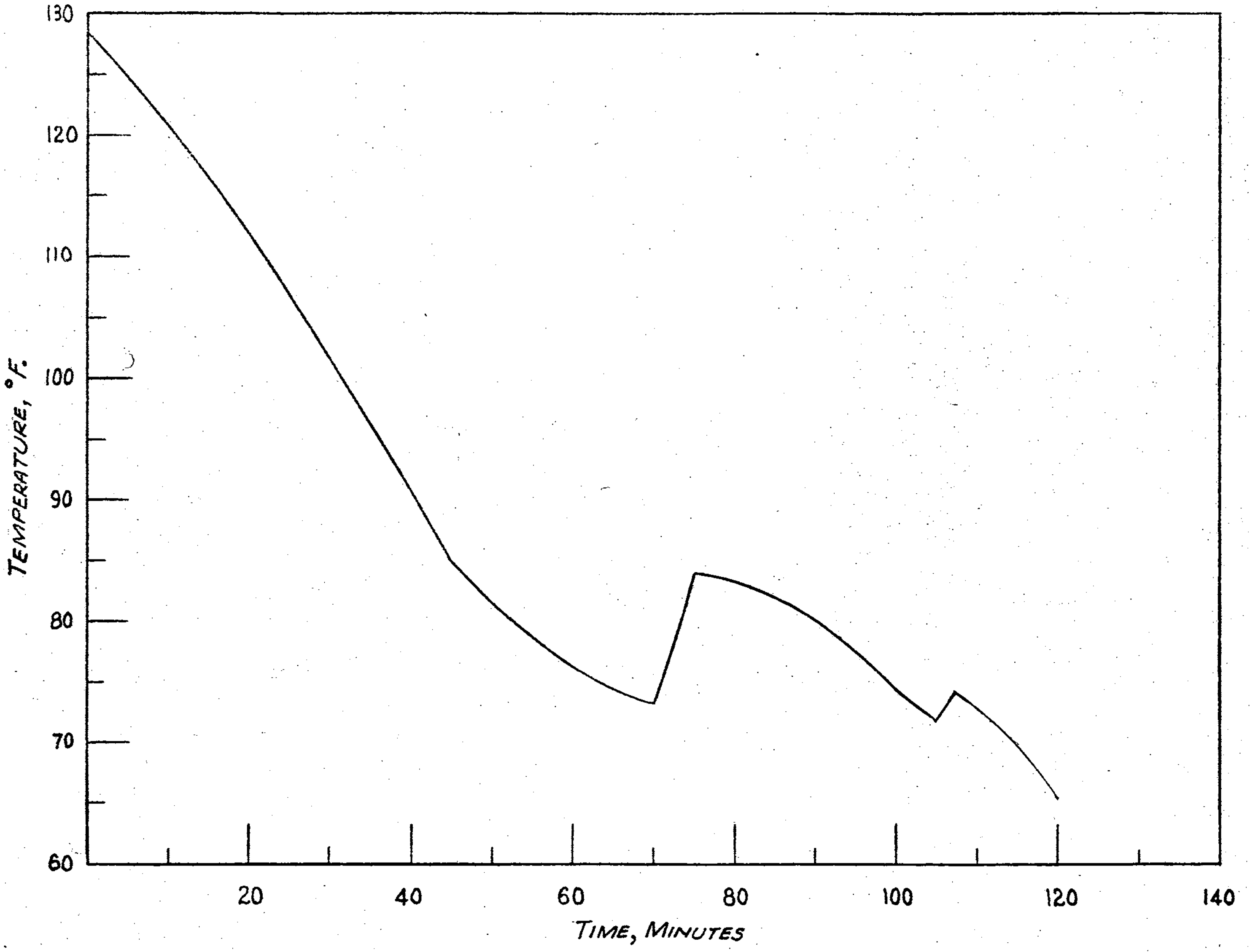

Figure 13 Cooling Curve For 41.2 Mole Per Cent SnF_2 - 58.8 Mole Per Cent HF

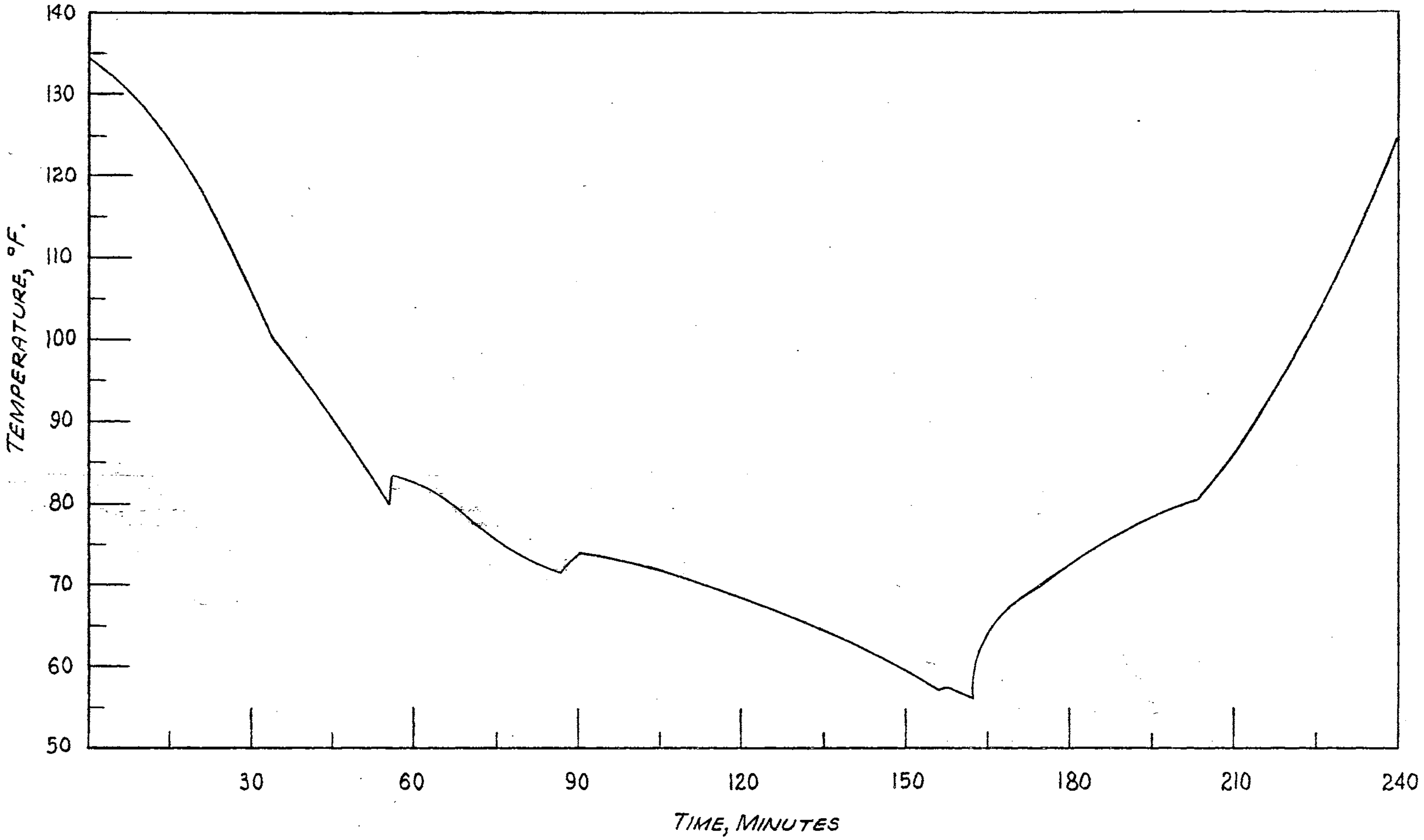

FIGURE 14 COOLING AND HEATING CURVE FOR 44.25 MOLE PER CENT SnF_2-55.75 MOLE PER CENT HF

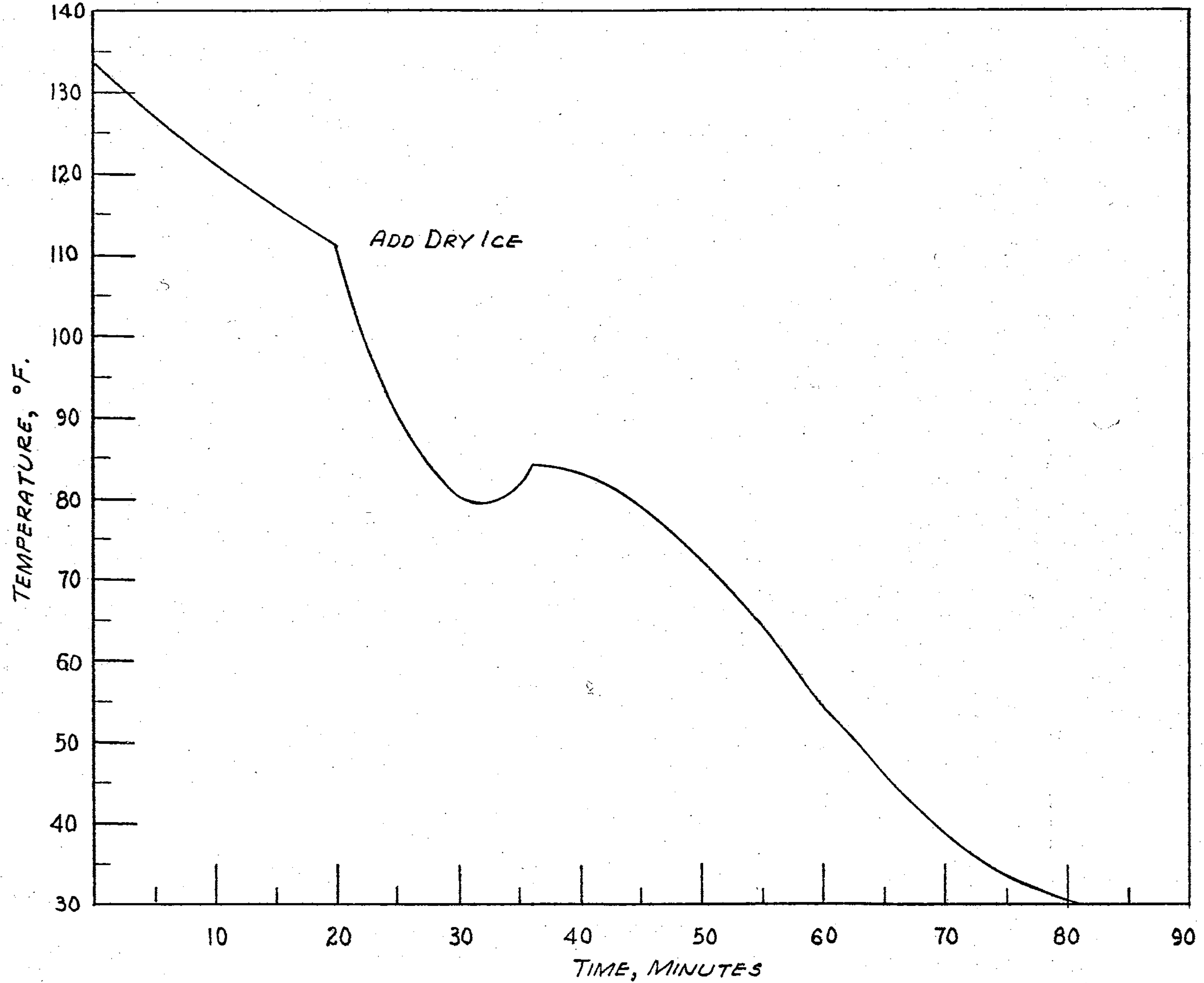

FIGURE 15 COOLING CURVE FOR 50.0 MOLE PER CENT SnF_2-50.0 MOLE PER CENT HF

After initial crystallization, further cooling produced more crystals and an apparent increase in viscosity of the solution. This continued until the mixture was cooled 5° F. to 10° F. below the initial thermal effect temperature. Spontaneous crystallization would then take place with the temperature rising to the thermal effect temperature. Decided changes to slower cooling rates were observed after spontaneous crystallization at the first thermal effect temperature. In some tests, the SnF_2-HF mixture was cooled below the second or third thermal effect temperature. Only occasionally were super-cooling or thermal arrests observed at the lower thermal effect temperatures. When arrests did occur, they were of short duration. There were, however, decided changes to slower cooling rates at these temperatures. Cooling rates of the mixtures were varied from 0.15° F. per minute to 1.6° F. per minute. The rate of cooling did not seem to be a factor in amount of super-cooling.

Thermal effects, where the monohydrofluoride was present and similar to the ones observed in the present study, were also observed by Cady (5) in his study of the KF-HF system, and Winsor and Cady (33) in their study of the CsF-HF system. They explained the thermal effects as changes in the crystal form of the monohydrofluorides. About the time the experimental work of this investigation had been completed, a study of the NaF-HF system was published. (1). The study consisted of cooling curve experiments and showed three thermal arrests between NaF:3HF and NaF:4HF. The authors indicated one arrest was the eutectic between NaF·3HF and NaF·4HF. Another arrest was the transition between αNaF·3HF and βNaF·3HF, and the third was the peritectic between αNaF·3HF and NaF·2HF. No mention was made of analyzing the solid phase.

Thermal effects observed in the present investigation might be explained by several changes in crystal form of $SnF_2 \cdot HF$. It is doubtful if the effects are peritectic points because the solid isolated at 30° F. from a solution with a molar ratio of SnF_2:3HF was $SnF_2 \cdot HF$. Another explanation might be the formation in the liquid phase of complexes which are not stable in the solid phase.

The sharpness of the freezing point curve maximum at a temperature of 132° F. and a SnF_2-HF molar ratio of one to one would indicate this to be a very definite congruent melting point and $SnF_2 \cdot HF$ to be stable. $SnF_2 \cdot HF$ was isolated and proved to be fairly stable. However, its HF vapor pressure appears to be fairly high, at room temperature, and the salt decomposed to SnF_2 and HF over a 48 hour period when exposed to the atmosphere.

Cooling curves with a SnF_2 concentration greater than 50 mole per cent gave a eutectic temperature of 105° F. Representative cooling curves for mixtures with compositions in this range are shown in Figures 16, 17, and 18. The freezing point curve appears to drop from the 132° F. maximum to the eutectic temperature of 105° F. at a ratio of approximately SnF_2:0.75HF. From the eutectic, the freezing curve appears to rise very rapidly to 145° F. at a SnF_2 composition slightly more than SnF_2:0.75HF. From this point, presumably, it continues to rise to the melting point of SnF_2 at 410° F.

Boiling point data given in Table III were used to construct the boiling point curve given in Figure 19. The boiling point of the mixture rose continuously with increased SnF_2 concentration until a temperature of 145° F. was reached. At this temperature, in most runs, further vaporization of HF resulted in crystallization of SnF_2 with the temperature and

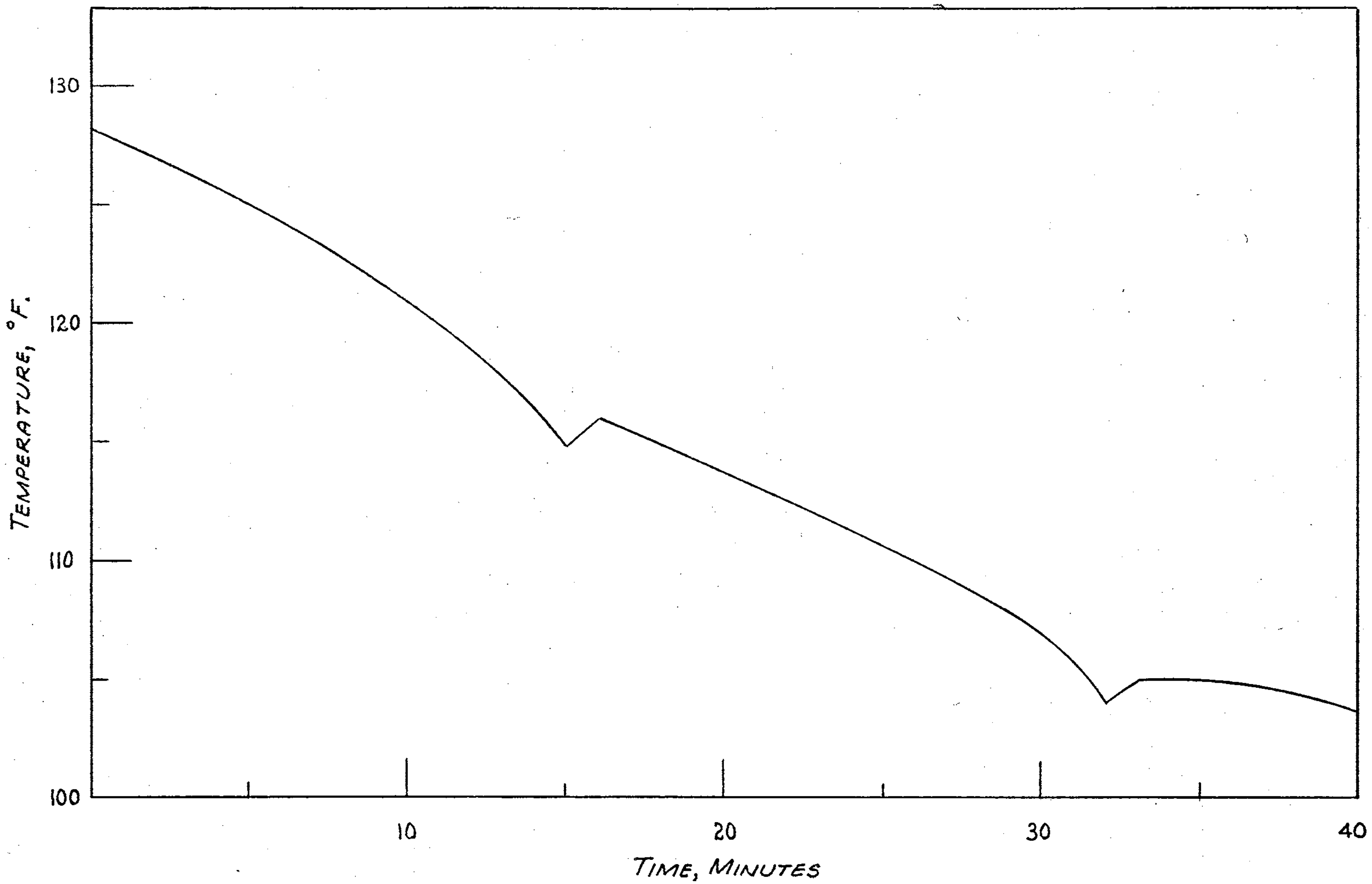

Figure 16 Cooling Curve For 54.1 Mole Per Cent SnF_2 -45.9 Mole Per Cent HF

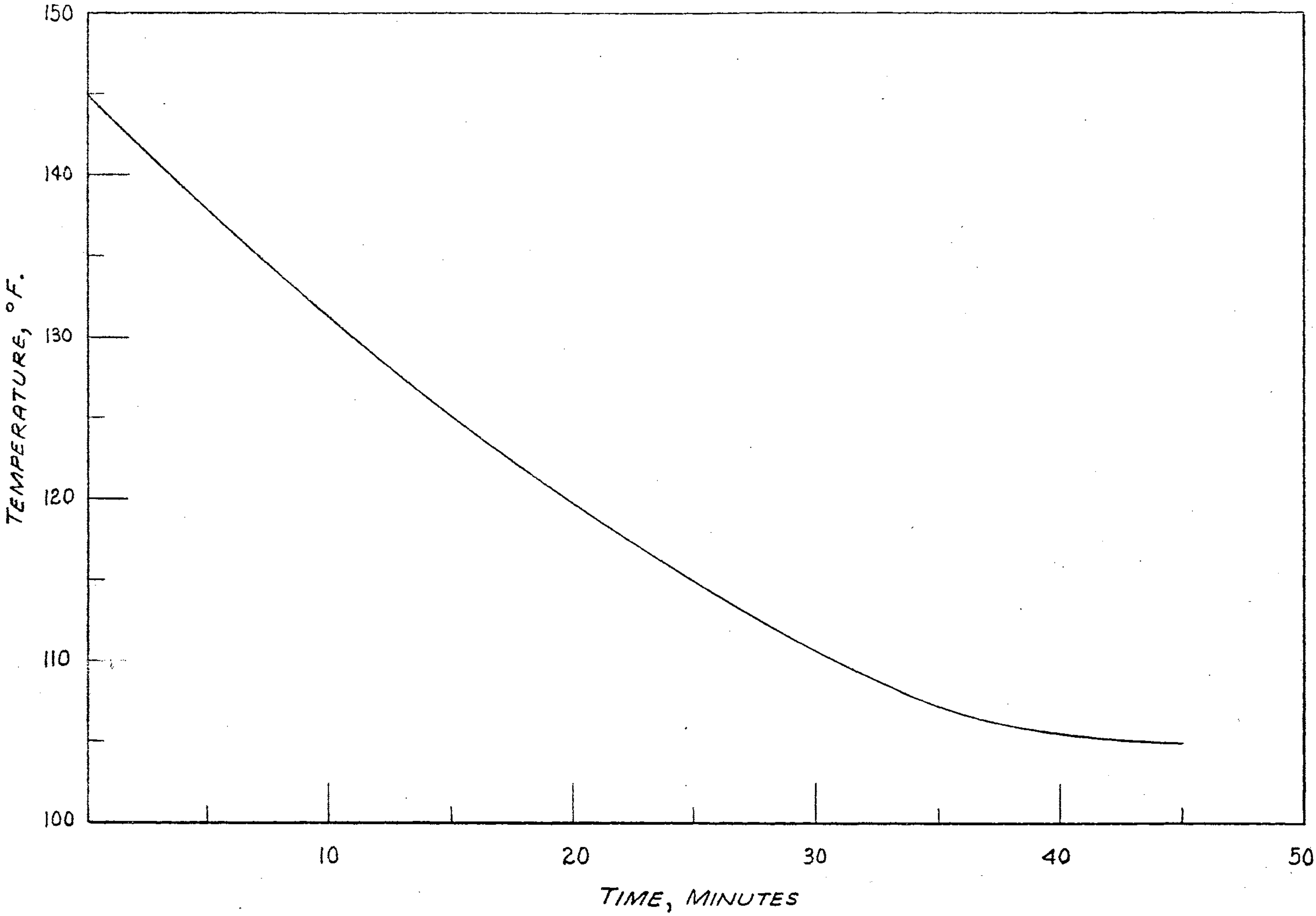

FIGURE 17 COOLING CURVE FOR 57.14 MOLE PER CENT SnF_2-42.86 MOLE PER CENT HF

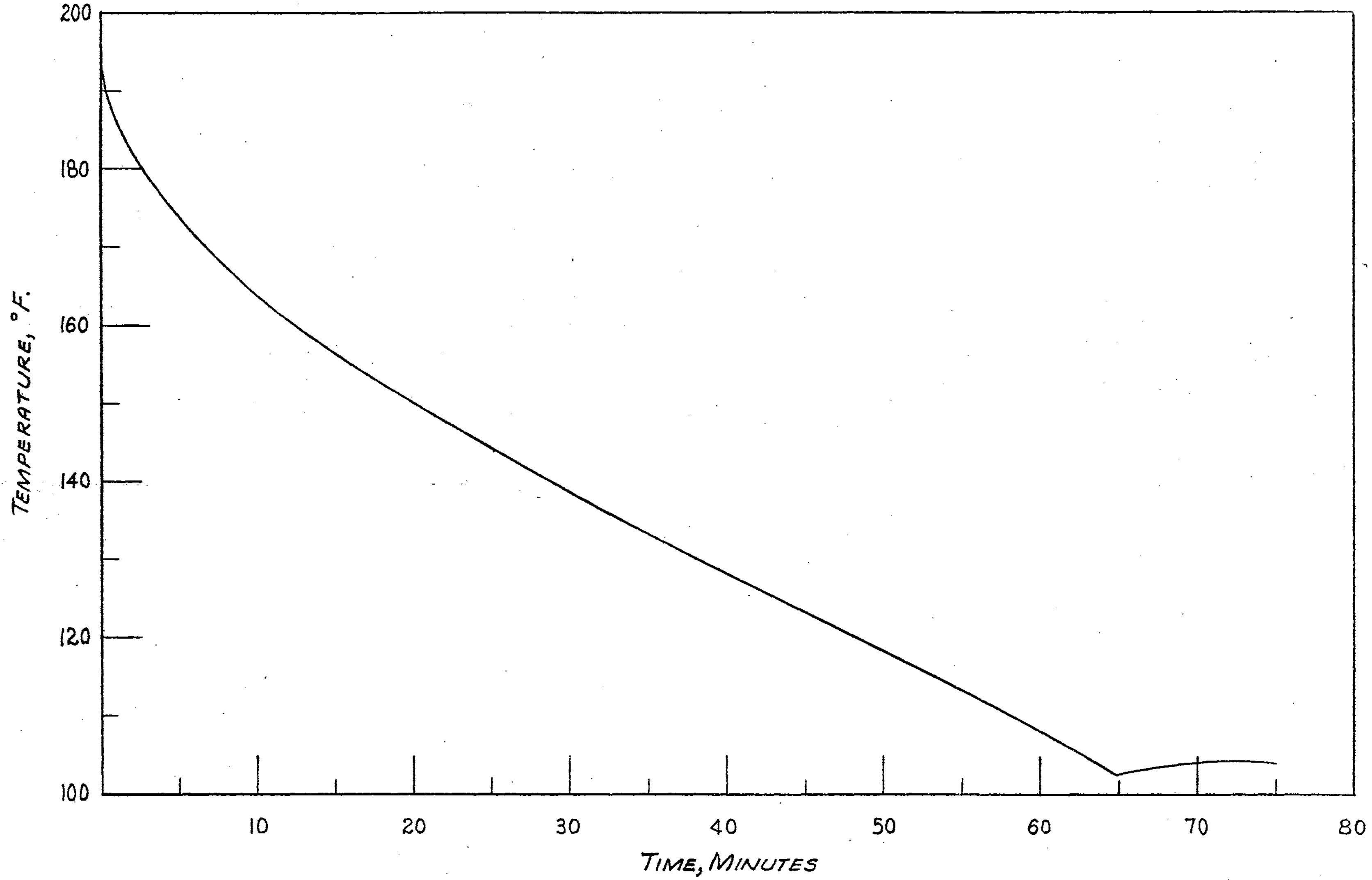

FIGURE 18 COOLING CURVE FOR 66.7 MOLE PER CENT SnF_2 - 33.3 MOLE PER CENT HF

TABLE III

BOILING POINTS OF SnF_2-HF SOLUTIONS

Run No.	SnF_2 %	HF Wt. %	Mole Fraction SnF_2	Mole Ratio HF:SnF_2	Boiling Point °F. at 760 mm.
30	87.8	12.2	0.476	1.1	131.4
31	88.8	11.2	0.504	1.01	136.2
34	89.5	10.5	0.517	0.933	136.8
35	90.0	10.0	0.531	0.882	140.2
32	90.2	9.8	0.537	0.862	141.2
36	91.3	8.7	0.575	0.738	145.0
33	91.4	8.6	0.577	0.736	145.0

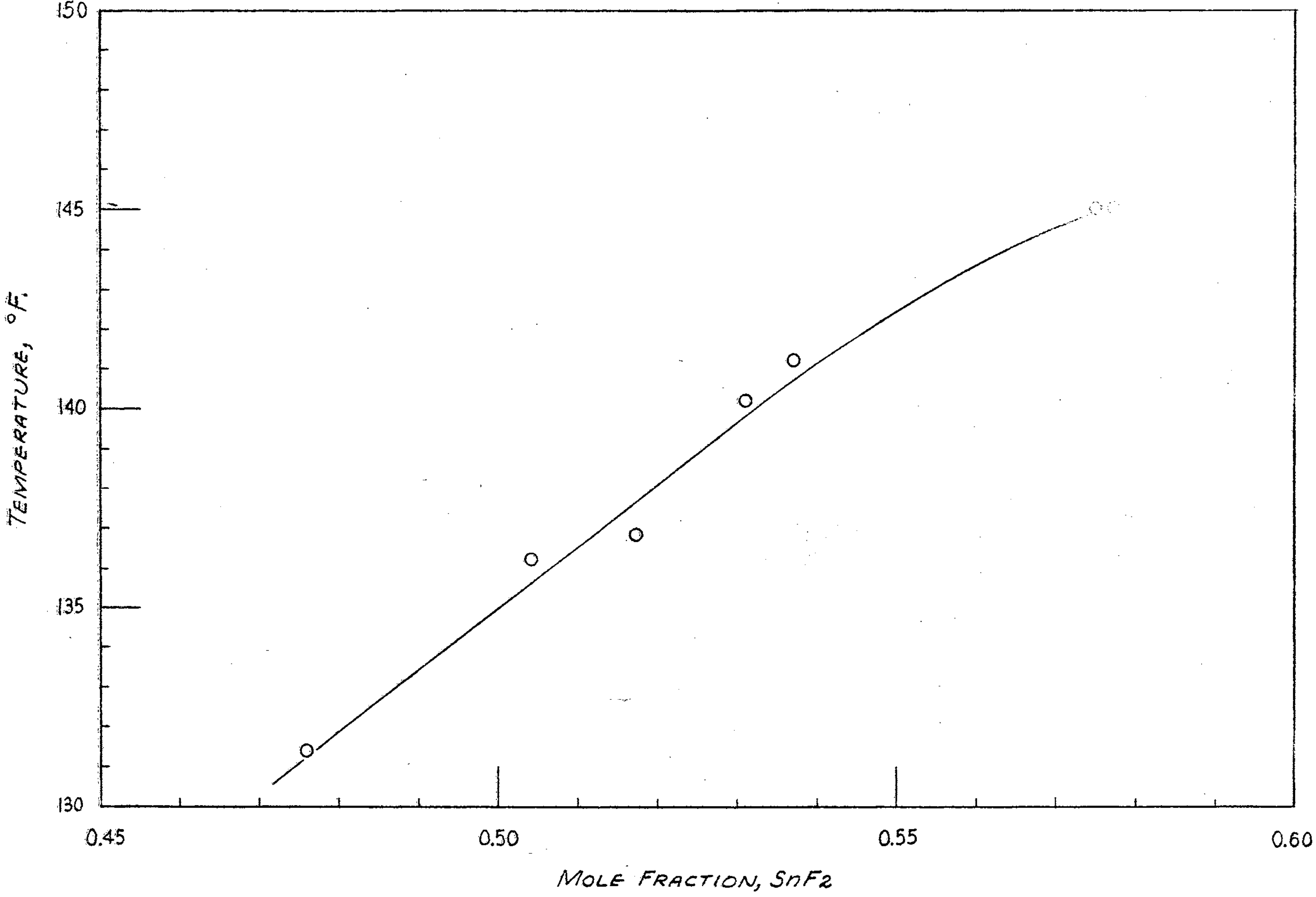

FIGURE 19 BOILING POINTS OF SnF_2-HF SOLUTIONS CORRECTED TO 760 MM. PRESSURE

composition of the liquid phase remaining constant. In a few runs the temperature rose above 145° F. It is believed the temperature recorded was not that of the solution but the solids. With continued vaporization of HF, the mixture became more and more viscous and highly concentrated with solids. Eventually, the mixture was of a pasty consistency which then transformed into SnF_2 crystals. The crystals were relatively free of clusters and most of them between 30 and 60 mesh in size. After the HF was removed, the SnF_2 crystals were free-flowing.

One of the most difficult problems was to secure complete dissolution of all the solids present in the mixture. In the initial tests, about 99 per cent of the SnF_2 would dissolve in the HF; the one per cent remaining was left in the form of solids. These solids appeared as a fine white precipitate which did not have the appearance of SnF_2 crystals. In the initial test, successive additions of more HF were made in an attempt to dissolve the remaining trace of solids. In all cases, the amount of these fine solids appeared to remain about the same. Next, the mixtures were maintained at their boiling point for six to eight hours with constant refluxing of the vaporized HF. Again, the solids were never dissolved and their concentration appeared to remain constant. Maintaining the mixtures under pressure so as to obtain temperatures 30° F. to 40° F. above their boiling points at atmospheric pressure did not accomplish complete dissolution of the solids.

Isolation of the solids for visual observation and chemical analysis led to the belief that they were not SnF_2 or a stannous fluoride-hydrofluoride but were probably $SnOF_2$. Analyses of these solids are given in Table IV. The very low solubility of SnF_2 in HF as reported by Clifford (8) might be explained by the presence of this compound as a

TABLE IV

INSOLUBLE RESIDUE ANALYSIS

Series	Total Sn %	Sn^{+2} %	F %	SnF_2 % Sn^{+2} Basis	$SnOF_2$ % Sn^{+4} Basis	HF % Difference
VIII	70.63	62.11	-	82.00	12.40	5.6
IX	66.67	57.03	31.51	75.38	14.04	10.58
X	66.53	61.87	32.08	81.75	6.78	11.47

coating on SnF_2 crystals. Preparation of SnF_2 of higher purity from tin powder in HF in later tests gave much better results in observing the initial formation of solids and a break in the cooling curve.

The initial crystallization temperature was determined from the first change in slope of the cooling curve. With the change in slope, a spread of 0.5° F. to 1.0° F. in the curve was produced by the two thermocouples and continued for approximately 5° F. In later runs when essentially all the $SnOF_2$ had been removed from the system, visual observation of initial crystallization could be made with the use of a powerful flash light.

As the SnF_2 concentration increased, the reliability of sampling and analyzing, and interpretation of the cooling curve data became less. This may be attributed, mainly, to the increased viscosity of the mixture caused by the high concentration of SnF_2. This is especially true in SnF_2 concentrations greater than 50 mole per cent.

In the experiments where both cooling and heating curve determinations were made, comparison of the data revealed the heating curves showed thermal effects at slightly higher temperatures than the cooling curves and were not nearly as pronounced. Also, breaks where the solid phase disappeared were difficult to observe. Consequently, only data from the cooling curves were used to construct the phase diagram. Explanation for the thermal effects taking place at slightly higher temperatures on the heating curves might lie in the fact the mixer was not turned on until a good portion of the mixture had melted. When heating, the rate of heat input was probably greater than the rate of dissolution, and the liquid and solid were not in equilibrium. This would explain the absence of a sharp break in the heating curve.

The solubility tests were conducted, primarily, to strengthen the interpretation of the cooling curve data. Good correlation between the cooling curves and solubility data was obtained. Compositions of the SnF_2-HF mixtures were picked at random, and usually, tests with the same composition were conducted on different SnF_2-HF preparations. Solubility tests which did not give results within experimental error were those performed in polyethylene bottles with primary interest in determining the solid phase in equilibrium with the liquid phase.

The cooling curves on H_2O and Na_2SO_4 obtained at the beginning and end of this study were helpful in interpreting cooling curve data. Representative cooling curves for H_2O and Na_2SO_4 are shown in Figures 20 and 21, respectively.

Stannous fluoride may be isolated from a SnF_2-HF solution by crystallizing $SnF_2 \cdot HF$ and then decomposing it or by crystallizing SnF_2 directly. Between a SnF_2 molar concentration of 25 per cent and 57.14 per cent, $SnF_2 \cdot HF$ is crystallized from the solution. When this compound is isolated and allowed to stand at room temperature, it gradually decomposes leaving a fine powder of SnF_2. Faster decomposition of the $SnF_2 \cdot HF$ may be achieved by heating the crystals.

To obtain SnF_2 crystals rather than $SnF_2 \cdot HF$ crystals, crystallization must take place at a SnF_2 concentration higher than 57.14 mole per cent (91.85 weight per cent). Crystallization of SnF_2 in this range may be accomplished by HF evaporation or by cooling.

Stannous fluoride crystals may be filtered from a SnF_2-HF solution or the HF evaporation may continue until only solid SnF_2 remains. Due to the extremely hazardous nature of HF, the simplest method of separating the SnF_2 from HF should be utilized. Therefore, it was concluded the better method of isolating SnF_2 from a SnF_2-HF solution is to continue

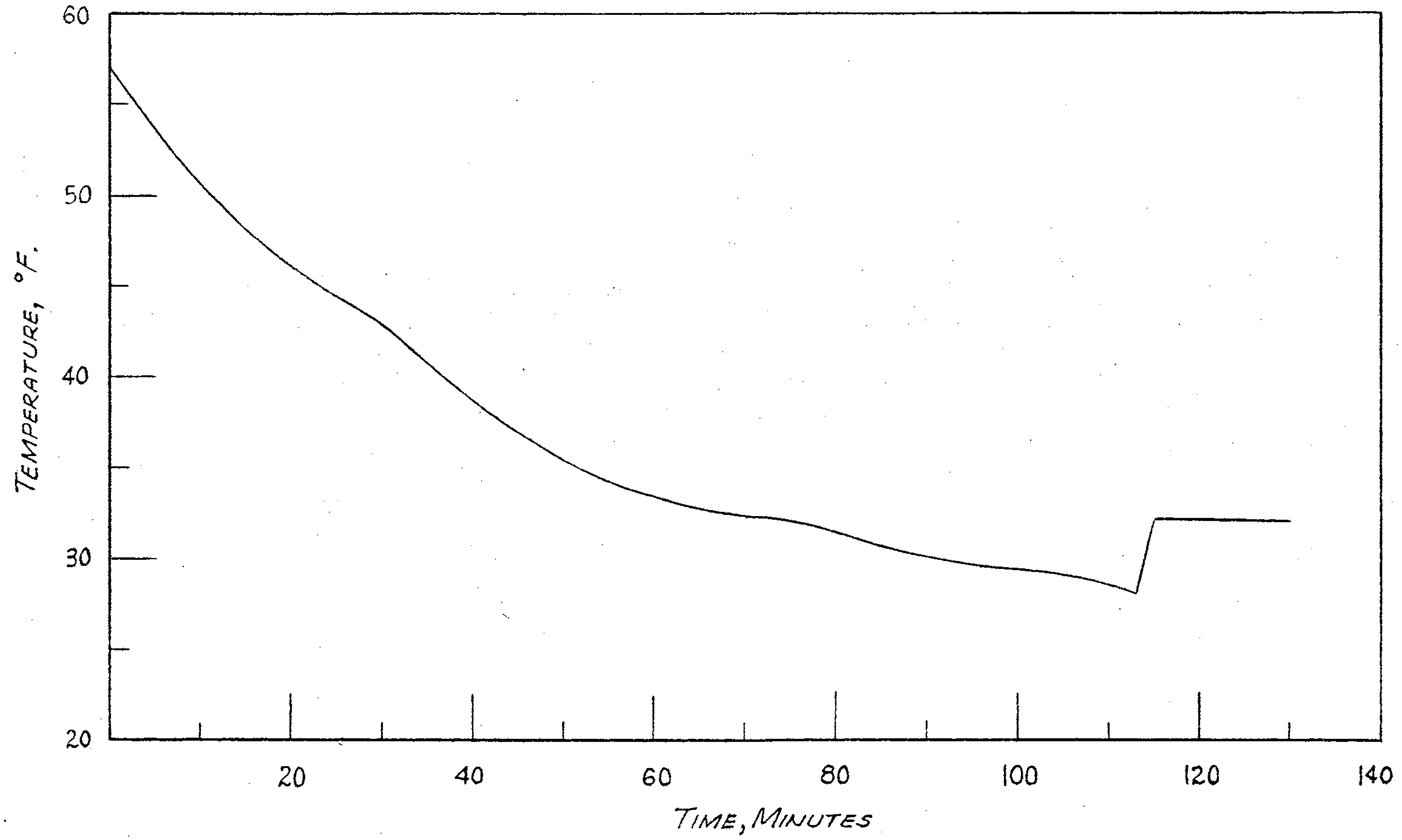

Figure 20 Cooling Curve For H_2O

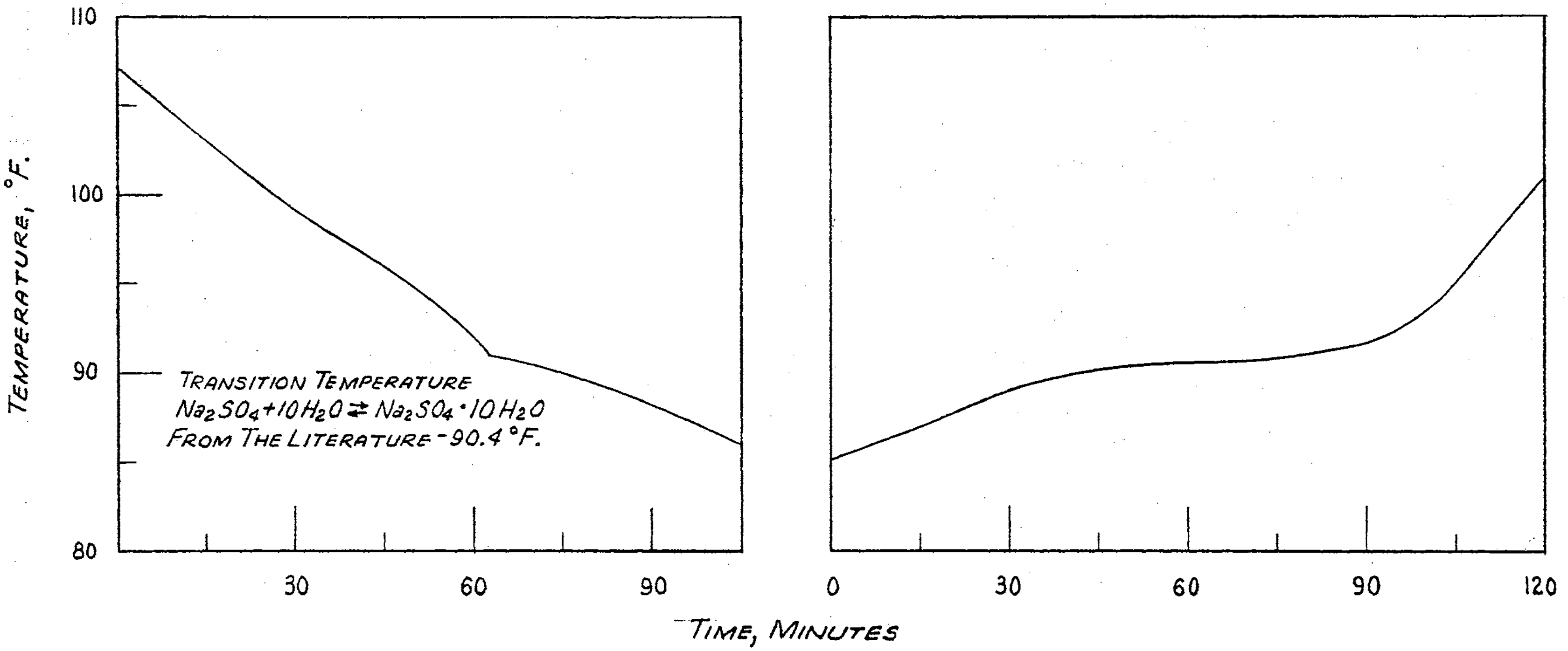

Figure 21 Cooling And Heating Curve For 40 Per Cent Na_2SO_4 - 60 Per Cent H_2O

evaporation of HF until the SnF_2 crystallized is virtually free of HF.

Crystallization of SnF_2 may also be accomplished by cooling a SnF_2 solution. It would be necessary to maintain the SnF_2 concentration higher than 57.14 mole per cent, the eutectic composition which freezes at 105° F., to prevent formation of a eutectic mixture of SnF_2 and $SnF_2 \cdot HF$. The difference in concentration of SnF_2 between the eutectic point and boiling point is so very small; it would appear the process would be very difficult to control.

CHAPTER VI

SUMMARY AND CONCLUSIONS

To determine how SnF_2 may be crystallized and separated from a SnF_2-HF solution, a part of the freezing point-concentration diagram for the system SnF_2-HF was developed. The following conclusions were made from this study.

Stannous fluoride is highly soluble in anhydrous HF. The maximum concentration is 57.7 mole per cent (92.3 weight per cent SnF_2) at 145° F. and one atmosphere.

Stannous fluoride can be crystallized from a saturated SnF_2-HF solution by evaporating HF.

Stannous fluoride can be crystallized from a SnF_2-HF solution greater than 57.14 mole per cent SnF_2 by cooling, provided the temperature is maintained above the eutectic, 105° F.

In SnF_2-HF solutions with a SnF_2 concentration less than 57.14 mole per cent and to at least 25 mole per cent, $SnF_2 \cdot HF$ can be crystallized by cooling.

Stannous fluoride monohydrofluoride is not stable when removed from the SnF_2-HF solution and decomposes to form SnF_2 and HF.

In a SnF_2-HF solution between a SnF_2 concentration of 25 mole per cent and 57.14 mole per cent, no hydrofluoride other than $SnF_2 \cdot HF$ was isolated.

Thermal effects in the SnF_2-HF system occur at 33° F., 57° F., 74° F., and 84° F. indicating phase transitions. The exact nature of these effects is not known.

A eutectic is obtained at 105° F. between $SnF_2 \cdot HF$ and, presumably, SnF_2.

Future studies on the SnF_2-HF system might include:

1. Developing a better technique and conducting a more precise study on the SnF_2-HF system between a SnF_2 concentration of 50 mole per cent and 100 mole per cent. This would involve equipment designed to contain the system under more than two atmospheres pressure.

2. Further study of the whole SnF_2-HF system to determine the exact nature of the thermal effects noted in this study and also if any other stannous fluoride-hydrofluorides exist.

3. A study of the SnF_2-HF-H_2O system to determine the effect of different ratios of HF and H_2O on the solubility of SnF_2.

SELECTED BIBLIOGRAPHY

1. Adamzcak, R. L., Mattern, J. A., Tieckelmann, H., J. Phys. Chem. 63, 2063 (1959).

2. Audrieth, L. F., Kleinberg, J., *Non-Aqueous Solvents*, John Wiley, New York, 1953.

3. Berzelius, J. J., Pogg. Ann. 1, 34(1824).

4. Bowden, S. T., The Phase Rule and Phase Reactions, McMillan, London, 1938.

5. Cady, G. H., J. Am. Chem. Soc. 56, 1431-4(1934).

6. Cady, G. H., Private Communication, April, 1960.

7. Clibbins, D. A., *The Principles of the Phase Theory*, McMillan, London, 1920.

8. Clifford, A. F., Beachell, H. C., Jack, W. M., J. Inorg. Nucl. Chem. 5, 57(1957).

9. Daniels, F., Mathews, J. H., Williams, J. W., *Experimental Physical Chemistry*, McGraw-Hill, New York, 1941.

10. Fremy, E., Ann. Chim. Phys. 3, 47(1856).

11. Farnsworth, J., Pekola, J., Anal. Chem. 31, 410(1959).

12. Gilliland, J. E., Ray, R., White, W. E., U. S. Patent 2,924,508.

13. Jache, A. W., Cady, G. H., J. Phys. Chem. 56, 1106(1952).

14. Kirk, R. E., Othmer, D. F., *Encyclopedia of Chemical Technology*, Interscience, New York, 1955.

15. Lange, N. A., *Handbook of Chemistry*, Ninth Edition, Handbook, Sandusky, Ohio, 1956.

16. Marignac, C., Ann. Mines. 12, 1(1857).

17. Mellor, J. W., *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, Fourth Edition, Longmans-Green, New York, 1946.

18. Millard, E. B., *Physical Chemistry for Colleges*, McGraw-Hill, New York, 1946.

19. Muhler, J. C., Private Communication, June, 1958.

20. Nebergall, W. H., Day, H. G., Muhler, J. C., J. Am. Chem. Soc. 74, 1604(1952).

21. Ricci, J. E., The Phase Rule and Heterogeneous Equilibria, Van Nostrand, New York, 1951.

22. Reilly, J. Rae, W. N., Physico-Chemical Methods, Van Nostrand, New York, 1954.

23. Rogers, M. T., Speirs, J. L., Panish, M., J. Am. Chem. Soc. 78, 3288(1956).

24. Rogers, M. T., Speirs, J. L., Panish, M., Thompson, H. B., J. Am. Chem. Soc. 78, 936(1956).

25. Ruff, O., Staub, L., Z. anorg. allgem. Chem. 212, 399(1933).

26. Rutledge, G. P., Jarry, R. L., Davis, J. W., J. Phys. Chem. 57, 541(1953).

27. Scheele, C. W., Svenska Akad. Handl. 33, 120(1771).

28. Simons, J. H., Fluorine Chemistry, Academic Press, New York, 1954.

29. Ting, H. H., McCabe, W. L., Ind. Eng. Chem. 26, 1201(1934).

30. Unverdorben, O., Trommsdorff's Journ. Pharm. 9, 22(1824).

31. Webb, K. R., Prideaux, E. B. R., J. Chem. Soc., 24(1939).

32. Wetmore, F. E. W., LeRoy, D. J., Principles of Phase Equilibria, McGraw-Hill, New York, 1950.

33. Winsor, R. V., Cady, G. H., J. Am. Chem. Soc. 70, 1500(1948).

34. Willard, H. H., Winter, O. B., Ind. Eng. Chem., Anal. Ed. 5, 7(1933).

APPENDIX A

TABLE V

HYDROGEN FLUORIDE ANALYSIS

HF by difference	99.983 %
H_2SiF_6	Nil
H_2SO	Nil
H_2O	0.0064%
SO_2	0.0105%

TABLE VI

STANNOUS FLUORIDE ANALYSIS

SnF_2 (Sn^{++} Basis)		98.8 %
Total Tin as Sn		75.56 %
Stannous Tin as Sn		74.86 %
F		24.2 %
Loss at 105° C. (Atmospheric pressure, 2 hours)		0.002 %
Fe		0.0021%
Ni	Less than	0.002 %
Cu	Less than	0.002 %
Pb	Less than	0.002 %
Sb		None Determined
As		None Determined
Total Fe,Ni, Cu, Pb, Sb, and As	Less than	0.02 %

TABLE VII

POWDERED TIN ANALYSIS

Tin		99.975%
Antimony	Less than	0.02 %
Arsenic	Less than	0.001%
Lead	Less than	0.001%
Iron	Less than	0.002%

APPENDIX B

TABLE VIII

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	1		2		3		4		5		6	
Solution Composition Mole Fraction SnF_2	0.194		0.233		0.254		0.292		0.355		0.438	
Cooling Rate	1.0° F./min.		0.6° F./min.		0.5° F./min.		1.4° F./min.		0.8° F./min.		1.6° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	5	76	2	94.5	5	92	2.5	95	5	93	1	97
	10	69	5	91	10	88	5	90	10	83	3	88
	15	62	10	89	15	84	10	80	15	78	5	81
	20	57	15	87	20	81	15	70	20	71	7	73
	25	52	20	83	30	75	20	62	25	66	9	65
	30	47	25	80	40	69	25	55	30	62	12	62
	35	43	30	77	50	63	30	52	35	59	15	59
	40	41	35	74	60	59	35	45	40	57	20	57
	45	39	40	72	70	55	40	41	45	55	25	55
	50	37	45	70	80	51	45	37	50	52	30	53
	55	32	50	68	90	47	50	33	55	48	35	51
	60	29	55	66	100	45	55	32	58	46	37	48
	65	28	60	64	110	43	60	32	60	48	39	47
	70	28	65	62	120	41	65	32	61	50	40	47
	75	28	70	60	130	40	70	33	65	51	52	47
	80	28	75	58	140	37			70	51		
	85	25	80	56	150	35						
	90	23			160	33						
	95	20			165	32						
	100	18			167	33						
	105	15			168	34						
	110	15			169	35						
	125	15			230	35						
	135	9			235	20						
	140	6			240	12						

TABLE IX

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	7		8		9		10		11		12	
Solution Composition Mole Fraction SnF_2	0.444		0.445		0.445		0.125		0.166		0.10	
Cooling Rate	1.6° F./min.		0.8° F./min.		0.5° F./min.		0.4° F./min.		0.8° F./min.		0.2° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	3	126	2	137	0	136	0	87	0	102	0	75
	6	113	15	127	15	125.5	15	79	15	85	30	64
	9	102	30	115	20	114	20	68	30	73	60	59
	12	92	45	103	45	103	45	58	45	67	90	53
	15	84	53	99	49	102	60	51	60	60	120	49
	18	79	55	103	60	96	75	48	75	52	150	45
	21	76	60	97	75	88	90	45	90	46	180	41
	24	73	75	88.5	87	83	120	40	120	37	210	39
	27	71	90	83	90	84	180	35	150	27	240	37
	30	68	97	84	105	84	240	32	210	18	270	35
	33	66	100	84	120	83	300	30			300	34
	36	64	110	84	135	82.5					330	33
	39	62	120	84							360	32
	42	60	130	84	150	84*					390	31
	45	58	140	83.5	165	86					420	30
	48	57	150	80	180	88						
					195	91						
					198	92						
					203	95						
					207	102						
					210	110						
					225	123						
					240	134						
					255	140						

* Heating

TABLE X

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	13		14		15		16		17		18	
Solution Composition Mole Fraction SnF_2	0.412		0.535		1.0		0.125		0.286		0.305	
Cooling Rate	1.0° F./min.		0.8° F./min.		1.0° F./min.		0.5° F./min.		1.0° F./min.		1.0° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	0	128	0	143	0	90*	0	95	0	67	15	90
	15	117	10	132	15	97	30	85	5	62	30	76
	30	101	20	120	30	104.5	60	78	20	48	45	62
	45	85	30	107	45	112.5	90	73	22	47	52	56
	60	76	32	103	60	120.5	120	69	25	46	60	52.5
	70	73	34	107	66	124	180	64	35	40	70	48
	75	84	36	109	75	133	300	52	50	34	90	41
	90	80	38	109	82	143	360	46	65	31.5	100	39
	100	74	40	108	90	144	420	33	80	31	120	35
	105	72	50	100	120	144					135	32.5
	107	74	60	91	147	144					150	31
	120	65	72	82	150	145					155	52
	135	60	76	84	165	148					165	39
			80	84	174	161**					180	36
			90	84	180	158					190	34
			100	84	189	148					210	33
			110	82	213	133					225	32
			120	79	225	123					240	31
			140	72							265	40
			160	64							295	64
			180	66							300	76

* Heating
** Cooling

TABLE XI

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	19		20		21		27		28		29	
Solution Composition Mole Fraction SnF_2	0.416		0.4425		0.462		0.513		0.542		0.571	
Cooling Rate	1.2° F./min.		1.0° F./min.		1.2° F./min.		0.9° F./min.		0.7° F./min.		0.8° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	8	120	0	134	0	137	0	132.5	0	128	0	144
	15	110	15	125.5	8	137	20	128.5	12	119	15	125
	30	91	30	105.5	15	130	30	135	15	115	30	111
	34	87	35	100	20	123	35	124	16	116	35	107
	45	76	45	90	30	109	45	115	20	114	37	106
	50	72	55	80	32	107	55	110	30	107	40	105.5
	60	65	56	83.5	36	107	60	109.5	32	104	45	105
	75	63	59	83	38	105	66	108	33	105		
	50	62	60	82.5	45	98	70	104	40	104		
	100	58	75	75	60	86	72	104.5				
	105	74.5	87	71	66	82.5	74	105				
	120	65.5	90	74	70	84	90	99				
	133	59	105	72	80	84						
	135	58	120	67	90	83.5						
	140	57	135	65	120	80						
	150	55	150	60								
	165	52	156	57								
	180	50	158	57.5								
	210	47	160	56.5								
	240	42	162	56								
	270	39										

TABLE XII

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	37		38		39		40		41		42	
Solution Composition Mole Fraction SnF_2	0.4715		0.666		0.666		0.666		0.588		0.588	
Cooling Rate	0.4° F./min.		0.5° F./min.		0.4° F./min.		0.4° F./min.		0.3° F./min.		0.2° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	0	121.5	0	162	0	160	15	84*	0	140	0	150
	6	120	15	158	15	156	30	87	15	136	15	147
	18	112	30	152	30	151	45	94	30	132	30	143
	30	106	45	146	45	146	60	103	45	128	45	140
	45	100	60	139	60	140	70	108	60	124	60	137
	60	93	75	133	75	135	75	109	65	123	75	133
	70	80	90	127	90	130	90	112	75	121	90	130
	90	85	105	124	105	126	100	117	90	117	105	127
	105	83	120	121	120	122	105	120	105	114	120	124
	120	81	135	118	135	119	120	130	120	111	135	123
	135	80	150	114	150	115	135	140	135	109	150	121
	150	79.5	165	110	165	112	150	150	150	107	165	118
	154	79.5	180	106	180	110	165	160	165	106	180	115
	155	84	195	104	195	108	170	165**	180	105		
	165	84	210	103	210	106	185	162				
	180	83	225	102	225	105	200	157				
			240	100	240	105	215	151				
			255	97	255	104	220	149				
			270	94	270	103	230	147				
					285	101	245	144				
					300	98	300	130				
					315	96						
					330	94						
					345	92						
					360	90						

* Heating
** Cooling

TABLE XIII

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	43		44		45		46		47		48	
Solution Composition Mole Fraction SnF_2	0.588		0.588		0.625		0.625		0.612		0.612	
Cooling Rate	1.2° F./min.		0.7° F./min.		0.6° F./min.		1.0° F./min.		0.8° F./min.		0.9° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	0	157	0	138	0	142	0	160	0	130	0	192
	5	152	15	123	15	131	5	157	15	120.5	10	163
	20	132	20	120	25	123	15	150	20	117	25	144
	30	120	40	106	30	120	18	148	25	113	40	127
	35	115	45	105	45	110	20	145	30	110	55	114
	40	110	60	100	55	105	25	140	35	103	65	102
	45	105	75	95	60	105	30	138	37	105	70	104
	47	105	90	92	75	100	45	131	70	103	75	104
	50	103	105	88			60	126				
			120	85			75	113				
			135	84.5			85	105				
			150	84			90	105				
			165	83.5			95	105				
							100	104.5				
							105	104.5				

TABLE XIV

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	49		50		51		52		53		54	
Solution Composition Mole Fraction SnF_2	0.635		0.395		0.395		0.424		0.424		0.459	
Cooling Rate	0.6° F./min.		0.5° F./min.		0.5° F./min.		1.0° F./min.		0.5° F./min.		0.8° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	0	72*	0	96	0	105	0	108	0	106	0	120
	5	74	7	85	8	94	4	100	15	96	5	114
	10	75	9	83	16	82	10	86	20	93	20	99
	15	76	11	82.5	20	78	15	80	27	88	25	94
	20	82	13	81	25	74	21	75	30	87	35	86
	25	84	25	77	40	68	26	71	45	80	40	84
	30	85	30	75	42	74	38	68	60	75	50	80
	35	88	45	72	50	72	40	74	75	72	60	84
	45	100	60	69	55	74	50	73	85	69	65	84
	50	104	70	68	65	70			90	75		
	60	106	71	74					105	74		
	75	118	75	73								
	90	135	90	71								
	105	147	105	69								
	0	220**										
	5	212										
	10	209										
	15	201										
	20	194										
	25	186										

* Heating
** Cooling

TABLE XV

COOLING AND HEATING CURVE--EXPERIMENTAL DATA

Run No.	55		56		57	
Solution Composition Mole Fraction SnF_2	0.333		0.385		0.50	
Cooling Rate	0.3° F./min.		0.4° F./min.		1.1° F./min.	
	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
	0	101	0	110	0	134
	15	93	10	80	2	131
	30	88	15	72	10	121
	45	83	30	53	20	111*
	60	78	45	47	24	93
	75	75	48	57	26	87
	90	73	60	50	31	79
	102	72*			34	80
	105	68			36	84
	120	58			40	83
	135	53			44	80
	139	52			50	73
	140	57			55	64
	150	55			59	57
	165	52			65	45
					70	39
					75	33
					80	31

* Add Dry Ice

TABLE XVI

COOLING AND HEATING CURVE--STANDARDIZING RECORDER

Water		Water		Sodium Sulfate		Sodium Sulfate	
Cooling Rate 0.3° F./min.		Cooling Rate 0.6° F./min.		Cooling Rate 0.3° F./min.		Cooling Rate 0.6° F./min.	
Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.	Time Min.	Temp. °F.
0	57	0	85	0	107*	0	108
15	48	3	80	15	103	4	105
30	43	7	70	30	99	8	102
45	37	12	60	45	96	12	100
60	33	20	50	60	92	16	98
75	32	27	40	62	91	20	96
90	30	38	30	75	90	23	94
105	29	43	28	90	88	27	91.5
113	28	44	30	105	86	30	90.8
115	32	45	32	0	85**	32	90.5
120	32	60	32	15	87	34	90
130	32	75	32	30	89	38	89
				45	90	42	88
				60	90.5	45	86
				75	91		
				90	91.5		
				100	93		
				105	95		
				120	101		

*Cooling
**Heating

VITA

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Master of Science

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