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THE SYSTEMS $\text{UF}_4\text{-SnF}_2$ AND $\text{PuF}_3\text{-SnF}_2$

By

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ABSTRACT

The salt SnF_2 melts at $213 \pm 1^\circ\text{C}$ and boils at $850 \pm 5^\circ\text{C}$. It is potentially feasible for use in a fuel for a power reactor. Studies of the phase diagram of the system UF_4 - SnF_2 have been made by the techniques of filtration, differential thermal analysis, visual observation, and quenching, with identification of the solid phases through chemical analysis and by physical means. Three uranium-containing solid phases are observed, namely, UF_4 and the two secondary compounds, $\text{UF}_4 \cdot \text{SnF}_2$ and $\text{UF}_4 \cdot 2\text{SnF}_2$. Each of the two secondary compounds melts incongruently. The eutectic composition and temperature are 0.5 mole % UF_4 and 212°C . The peritectic point at which the compound $\text{UF}_4 \cdot 2\text{SnF}_2$ melts is at 4.5 mole % UF_4 and 340°C . That for the compound $\text{UF}_4 \cdot \text{SnF}_2$ is at 7.8 mole % UF_4 and 371°C . The solubility of PuF_3 in SnF_2 , which was also investigated, varies from 0.41 mole % at 350°C to 0.63 mole % at 550°C .

ACKNOWLEDGEMENTS

R. M. Douglass and the late Eugene Staritzky identified the solid phases with the polarizing microscope and x-ray diffraction. In addition to those mentioned in the text in various connections, thanks are due to Clayton D. Ross and Kenneth J. Schowalter and their co-workers for expert help in designing and machining the equipment.

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Chapter 1

PHYSICAL CHEMICAL PROPERTIES

Table 1.1 gives information on the individual components of the systems $\text{UF}_4\text{-SnF}_2$ and $\text{PuF}_3\text{-SnF}_2$. The figure of $213 \pm 1^\circ\text{C}$ for the melting point of SnF_2 , which agrees with a melting point of $210\text{-}5^\circ\text{C}$ reported by W. H. Nebergall et al.,¹ was obtained by the technique of differential thermal analysis described in Section 2.2. The boiling point of SnF_2 was determined in a copper still consisting of a pot and a long, thin condenser tube. The temperature was measured by means of a thermocouple located in a thermocouple well in the bottom of the pot. The middle 50% of distillate was obtained at $823 \pm 3^\circ\text{C}$ and 588 mm Hg. The distillate had undergone 3% oxidation to SnOF_2 , principally in dropping from the condenser to the receiver. One estimates the boiling point to be $850 \pm 5^\circ\text{C}$ at 760 mm Hg with the assumption of Trouton's rule, namely, that the entropy of vaporization is approximately 21 calories/mole $^\circ\text{C}$.² Thus mixtures of the components of Table 1.1 should not require pressure equipment for their containment up to a temperature of at least 800°C .

Table 1.1

PHYSICAL CHEMICAL DATA

Component	Melting Point, $^\circ\text{C}$	Normal Boiling Point, $^\circ\text{C}$	Density (g/cm^3) at 25°C	ΔF° of Formation (kcal/mole) at 25°C
SnF_2	213 ± 1	850 ± 5	4.68 ³	-147. ^{4,5}
UF_4	1036. ⁶	1417. ⁶	6.7 ⁷	-421. ⁶
PuF_3	1407. ⁸	2277. ⁹	9.32 ⁸	-357.2 ⁵

Although the stock of SnF_2 was stored in sealed polyethylene bottles, the material was found to be stable in an open atmosphere for long periods. For example, SnF_2 that was spread on a watch glass and exposed for 4 months to the forced draft of air in a laboratory hood at a relative humidity of 40% and a temperature of 23°C suffered less than 0.01% weight change. In agreement with its believed stability,^{4,5} molten SnF_2 has been found to undergo no decomposition upon being rocked at 650°C for 3 weeks in a platinum-clad bomb. There was a slight corrosive attack on the liner, but any disproportionation of SnF_2 to metallic tin and SnF_4 was immeasurably small. In a test of the reverse reaction, metallic tin and commercially available impure SnF_4 were rocked for 2 hours at 700°C in a molybdenum bomb. Subsequent analysis showed most of the tin salt to be SnF_2 , there probably having been insufficient time for complete reaction. In the phase studies to be described shortly, there was no evidence of decomposition of the SnF_2 at even the highest temperature (850°C) unless there was a source of oxygen, as in a leak in the container.

Solutions of UF_4 in fused SnF_2 retain the uranium entirely in the tetravalent state and even the presence of metallic tin does not reduce the uranium to the trivalent state. Hence it is likely that tetravalent uranium is its only stable state in fused SnF_2 . It is found that metallic tin is produced in stannous fluoride melts if an oxide is present. For example, a mixture of UO_2 with SnF_2 readily reacts at 550°C in the following manner:

Chapter 2

THE PHASE DIAGRAM OF THE SYSTEM $\text{UF}_4\text{-SnF}_2$

2.1 Solubilities Determined by Filtration

2.1.1 Purity of Materials

Commercially available SnF_2 (City Chemical Company, New York, N. Y.) was found to contain 75.4-75.6% Sn(II) as compared with the theoretical value of 75.75%. This and other determinations of Sn(II) were made iodometrically in an atmosphere of carbon dioxide. It was this SnF_2 which was used in about half the experiments involving filtration and on which the boiling point was determined. Evidence of a volatile impurity, possibly HF or H_2O , was shown by the evolution of white-appearing fumes between 200 and 500°C. However, there was no visible residue left in the pot of the distillation apparatus at the end of the distillation experiment, the highest temperature of which was 895°C. Values of solubility obtained with this material (see Table 2.1, Section 2.1.4) checked those obtained with further purified SnF_2 at representative temperatures, 225 and 300°C, at the lowest of which the effect of any volatile impurity should be near its maximum.

The further purified material was obtained by giving the commercial SnF_2 two consecutive treatments in a rocking copper bomb. It first was evacuated with a Cenco-Hyvac Vacuum Pump for 4-15 hours at 500°C. Between the bomb and the pump there was an absorption tube which contained Ascarite (a mixture of NaOH and asbestos) nearest the bomb and anhydrous $\text{Mg(ClO}_4)_2$ nearest the pump. The weight gain of the absorption tube during the operation was consistent with the difference between 75.75% and the Sn(II) content of the charge. Thus HF and/or H_2O appeared to be the main impurities if one could neglect a small amount of SnF_2 that probably was distilled into the tube. A weight of Baker's Analyzed tin mossy equal to 0.7% of the weight of the charge then was added to the bomb and the evacuation

was resumed at 225°C for 16 hours. Nobler metal fluorides and the last traces of HF were to be removed in this step. The tin was removed mechanically as unfused metal particles upon cooling. The product contained 75.7-75.8% Sn(II). A spectrographic analysis of the product showed 0.01-0.1% each of Ca and Cu, 0.001-0.01% each of Pb, Mg, Al, and Fe, and lesser amounts of other impurities.

The UF_4 , which was quite pure, was supplied by F. J. Hill, of this Laboratory. A spectrographic analysis showed the major impurities to be 35 ppm Ni, 15 ppm Fe, 15 ppm Cu, 10 ppm V, 10 ppm Ca, and 8 ppm Mg.

2.1.2 The Apparatus

The technique of sampling a liquid phase via a filter has been described by R. M. Bidwell et al. for phase studies at high temperature and pressure.¹⁰ In the present investigation, the sampling operation was complicated by the facts that the chemical components had inappreciable vapor pressures and the filtrates could not be handled as liquids below 200°C. Filtration was made under only the force of gravity, high-pressure equipment not being required. The filtered liquid was retained in the same compact container and at the same temperature in a compartment that was a twin of the equilibrium compartment. Figure 2.1 is a side vertical view of the filtration apparatus in its setup for rocking in the furnace. Although either copper or molybdenum undergoes inappreciable corrosion from UF_4 - SnF_2 mixtures under isothermal conditions, the internal surfaces of the filtration apparatus were composed entirely of copper. The filter was cut from 1/4 inch thick fritted copper stock and pressed into place. The filter stock, which was 40-45% as dense as solid copper, had been prepared from -50 to +170 mesh powder by D. H. Schell of this Laboratory. Each installed filter was tested before use with a water slurry of UF_4 in which the UF_4 was finer than 200 mesh. Initially a milligram or less of UF_4 appeared in the filtrate, after which the issuing water was perfectly clear. The cap was composed of non-porous Phosphor Bronze No. 354, Grade D (89.5% Cu, 10.5% Sn, minimum P), obtained from the American Brass and Copper Company, Oakland, California. Compared with copper, this material was stronger, more resistant to air oxidation, and less prone to give galling at the threads. Such galling as did occur was minimized by coating them with graphite before each use. The sealing edge, 0.025 inch wide and 0.010 inch high, occasionally had to be remachined between equilibrations. The copper gasket was 0.032 inch thick. Each thermocouple was made from calibrated Chromel-Alumel 20 mil wire which was insulated with ceramic in the form of beads and two-hole tubing. The tip was covered with Sauereisen Cement and was located within 1/4 inch of the filter

Fig. 2.1 The Filtration Apparatus (Full Scale)

A	Stainless steel key	H	Bronze screw cap
B	Brass bushing	J	Sealing edge
C	Furnace door	K	Copper gasket
D	Key well	L	Cap flats
E	Stainless steel collar	M	Thermocouple tip
F	Copper body	N	Inner wall of furnace
G	Fritted copper filter	P	Ground wire
		R	Stainless steel cradle

in the body of the copper. The mounting of the thermocouple exactly on the rocking axis gave a freedom from spurious effects and a minimum of mechanical wear.

Figure 2.2 is a photograph of the rocking mechanism. The furnace was a Model GTP Temco Electric Furnace of the Thermo Electric Manufacturing Company, Dubuque, Iowa, with internal dimensions of $4 \times 4 \times 3\text{-}3/4$ inches. However, the thermocouple and control unit were removed in favor of the noted installations. A rocking of the filtration apparatus through an arc of $10\text{-}50^\circ$ was obtainable with the setup as shown. The retaining spring on the bushing kept the key securely engaged with the filtration apparatus. The ratings of the electric motors were in the range of 2-90 RPM and 2-18 inch-pounds of torque. There was no excessive strain on the apparatus at 90 RPM, and this rocking rate was used in all but the earliest equilibrations. The thermocouple emf was bucked against that of a similar thermocouple in an ice bath and fed to a Brown recorder which could control the temperature to $1\text{-}3^\circ\text{C}$, the better control being obtainable at the lower temperatures.

2.1.3 Method of Operation

The clean filtration apparatus was charged about two-thirds full in one end with 15-25 grams of a $\text{SnF}_2\text{-UF}_4$ mixture having a higher uranium content than the expected solubility. The caps were screwed in place with the gaskets coated with graphite next to the caps in order to facilitate their separation after the equilibration. In the bomb there was therefore a molar ratio of oxygen from the air to Sn(II) ranging from 0.1% for a charge containing less than 10 mole % UF_4 to 1% for 80 mole % UF_4 . Values of solubility so obtained did not differ significantly from those obtained when both ends were flushed with argon prior to sealing. Nevertheless, flushing with argon was used in the later, more important equilibrations. The sealed bomb was installed in the furnace with the charge end down and set to rocking through an arc of $30\text{-}50^\circ$ for 1-3 hours. A temperature 100°C or so above the liquidus point was maintained provided it was less than 750°C . This top limit was necessary in order not to hazard a leak in the apparatus. After the uranium had thus dissolved, the apparatus was brought to the desired temperature of equilibration thereby producing what was presumably the thermodynamically stable solid phase. The rocking was continued at the control temperature for 15-75 hours, usually 25-50 hours. Such equilibrative times were sufficient to yield thermodynamic equilibria except for equilibrations at temperatures only slightly below an incongruent melting point. In the latter case having the composition of the charge closer to the solubility was helpful, as were more successive equilibrations. At the end of the equilibrative period

Fig. 2.2 The Rocking Mechanism

the motor was stopped, the cotter pin was removed from the motor drive wheel, and the filtration apparatus was inverted by turning its key through 180°. The drive arm between the drive wheel and the key was then moved to the lower position of the key and the other end of the drive arm was connected to the drive wheel at the position of lowest pitch. The rocking was resumed. This gentle rocking was helpful in causing the liquid phase of mixtures high in UF_4 to flow to the filter. The filtration was continued at the control temperature for 15-75 hours (usually 40 hours), longer at lower temperatures. Then the filtration apparatus was removed from the furnace and cooled to room temperature in a fast stream of air. A maximum of 5 minutes was required to cool the bomb below 200°C in this manner. Cooling in a bed of powdered dry ice would not have been much more effective, and quenching in water might have allowed some inward seepage of water due to the seals loosening in the quenching.

A filtrate of the order of 1 gram usually was so obtained depending on the temperature and duration of the filtration. The filtrate was removed in its entirety and ground to a homogeneous powder before analysis. An aliquot taken for the uranium analysis was first digested in hot, concentrated HNO_3 , which brought the uranium into solution as U(VI) but left much of the tin as insoluble metastannic acid. The uranium was separated from the tin by extracting it from 4M HNO_3 + 2M $\text{Al}(\text{NO}_3)_3$ ¹¹ into 30% tributyl phosphate in Gulf BT solvent. Next, the uranium was extracted from the organic phase into 0.5M Na_2CO_3 , which was then acidified and assayed for uranium by the thiocyanate procedure.¹² The total tin content of an aliquot of the filtrate was determined iodometrically.¹³ A flowing CO_2 atmosphere was maintained during the titration. (The Sn(II) content could not be determined because aliquots could not be dissolved without oxidizing them.) Assuming the uranium to have been present as UF_4 and the tin as SnF_2 , one found that the material balance was $99 \pm 1\%$ for equilibrations below 400°C and within 5% of perfect for all equilibrations. The mole percentage of UF_4 in the filtrate was calculated from the analytical uranium/tin ratio with the assumption of a 100% material balance.

When there was leakage of material out of the equilibration apparatus or discernible air oxidation of the contents within, the results of the equilibration were discarded, as were the contents themselves. When it occurred, the air oxidation of the contents was manifested by a dark surface coloration of the normally green material. Oxidation often was accompanied by a decreased uranium concentration and sometimes a lower material balance in the filtrate. The material of the charge compartment was always examined for the phases present at the end of a series of equilibrations at a given temperature. A sampling of this material was also made after each equilibration when there was flushing with argon, and unanalyzed filtrate was

returned to the charge compartment. The sampled apparatus was always sealed with new gaskets before its return to the furnace for another equilibration.

2.1.4 Values of Solubility

Table 2.1 lists the experimental values of UF_4 solubility. The second column indicates the mole percentage of UF_4 that was in the charge as well as something of the purity of the contents. The third column gives the filtrate composition of successive filtrates, and the last column lists the solid phase with which the equilibrations had been made. It usually was determined by E. Staritzky and R. M. Douglass, of this Laboratory, in an optical examination of the contents remaining in the charge compartment. The percentages following the designation of UF_4 in the last column on the second page of the table are the mole percentages of UF_4 in the material remaining in the charge compartment. In spite of the effect of some unfiltered, adhering liquid phase, the figures show that the solid phase was UF_4 because they are significantly higher than the compositions of the charge and always above 50%.

Different series of equilibrations at the same temperature showed that the composition of the filtrate was not significantly influenced by the composition of the charge that was used. Hence there was no evidence of leakage of the solid phase through the filter. Similarly, there appeared to be no correlation between observed solubilities and either the purity of the initial charge or the removal of air by flushing with argon. Copper from the container appeared in filtrates to the extent of 0.1% or less by weight.

The solubility figures of Table 2.1 have been plotted in Fig. 2.3 and a smoothed curve has been drawn through them. The data below 10 mole % UF_4 have been replotted in Fig. 2.4 on an expanded scale. The solubility curve clearly shows a change of slope at 371°C . The curve itself and the ranges of stability of the solid phases in Table 2.1 are in agreement with the data presented on differential thermal analysis. Equilibrium solubility figures were difficult to obtain by filtration in the range of temperature in which $\text{UF}_4\cdot\text{SnF}_2$ was the thermodynamically stable solid phase. This compound sometimes was formed completely from $\text{UF}_4(\text{s})$ only under long, strong rocking. Hence one often observed a metastable extension of the $\text{UF}_4(\text{s})$ -liquid curve into the area of the $\text{UF}_4\cdot\text{SnF}_2(\text{s})$ -liquid equilibrium. When thermodynamic equilibrium was attained, it was evidenced by the appearance of a single solid phase in the charge compartment and the agreement in composition of successive filtrates.

Table 2.1

THE SOLUBILITY OF UF_4 IN SnF_2

Temperature, °C	Charge	Observed Mole % UF_4 in Filtrate	Av. $\pm$ Std. Dev. of Mole % UF_4 in Filtrate	Solid Phase
218	4*	0.56, 0.54, 0.56	0.55 ± 0.01	$\text{UF}_4 \cdot 2\text{SnF}_2$
225	4	0.82, 0.73, 0.88, 0.79	0.82 ± 0.05	$\text{UF}_4 \cdot 2\text{SnF}_2$
225	4**	0.85, 0.82		$\text{UF}_4 \cdot 2\text{SnF}_2$
260	4	0.97, 1.04, 1.06, 1.03, 1.03, 1.06	1.03 ± 0.03	$\text{UF}_4 \cdot 2\text{SnF}_2$
300	5	2.60	2.73 ± 0.09	$\text{UF}_4 \cdot 2\text{SnF}_2$
300	4**	2.85, 2.72, 2.73		$\text{UF}_4 \cdot 2\text{SnF}_2$
325	7*	3.56, 3.75, 3.63, 3.76	3.68 ± 0.08	$\text{UF}_4 \cdot 2\text{SnF}_2$
350	5*	4.51, 4.70, 4.76, 4.94, 4.78	4.74 ± 0.14	$\text{UF}_4 \cdot \text{SnF}_2$
360	8*	4.65, 4.97, 5.07, 5.73, 5.06	5.10 ± 0.35	$\text{UF}_4 \cdot \text{SnF}_2$
365	7.25*	5.86, 5.90, 5.94, 5.81	5.88 ± 0.05	$\text{UF}_4 \cdot \text{SnF}_2$
370	9*	7.22, 7.25, 7.28	7.25 ± 0.02	$\text{UF}_4 \cdot \text{SnF}_2$
375	13*	7.36, 8.05, 8.08, 8.13	7.91 ± 0.32	UF_4
400	13*	9.15, 9.05, 9.03, 9.02	9.06 ± 0.05	--
450	20**	11.9, 12.1, 12.0	12.0 ± 0.1	--
500	20*	15.4, 15.2	15.0 ± 0.4	UF_4
500	20**	15.0, 14.4		--

Table 2.1 (Continued)

Temperature, °C	Charge	Observed Mole % UF ₄ in Filtrate	Av. ± Std. Dev. of Mole % UF ₄ in Filtrate	Solid Phase
550	35	17.7, 17.4, 16.6	16.1 ± 1.4 at 550°C	UF ₄ (87.7%)
549	20	16.8, 14.8, 14.3, 16.9		--
548	20	14.8, 14.8, 13.9, 14.6		--
550	27	18.9, 16.9		--
600	35	19.9, 22.3, 22.5, 21.4, 22.2	21.7 ± 1.0	UF ₄ (55.3%)
650	70	25.4, 25.1, 25.0	25.2 ± 0.2	UF ₄ (72.7%)
700	60	33.0, 33.9	34.2 ± 0.8	UF ₄ (91.9%)
700	70	34.9, 34.8		UF ₄ (82.1%)
748	60	36.5	36.2 ± 0.8 at 749°C	UF ₄ (76.8%)
749	80	37.1, 35.0, 36.1		
798	60	49.7, 49.9, 49.3	49.6 ± 0.3	UF ₄ (78.5%)
850	80	54.6, 58.0	~56	UF ₄ (95.9%)

*The further purified SnF₂ was used and the container was flushed with argon.

**The further purified SnF₂ was used but there was no flushing.

Fig. 2.3 The Phase Diagram of the System $\text{UF}_4\text{-SnF}_2$

- Solubilities by filtration
 - △ Liquidus points from DTA heating curves
 - ▽ Liquidus points from DTA cooling curves
 - Taken from Reference 6
- Numbers indicate maximum DTA displacements ($^{\circ}\text{C}$) of thermal arrests in heating curves

Fig. 2.4 The Phase Diagram of the System UF_4 - SnF_2 below 10 Mole % UF_4

- Solubilities by filtration
- △ Liquidus points from DTA heating curves
- ▽ Liquidus points from DTA cooling curves
- Numbers indicate maximum DTA displacements ($^{\circ}\text{C}$) of thermal arrests in heating curves

2.2 Studies by Differential Thermal Analysis, Quenching, and Visual Observations

2.2.1 The Apparatus

Figure 2.5 shows the sealed copper container that held the sample during experiments involving differential thermal analysis (DTA). In order to eliminate a need for welding, the body was machined from a single bar of copper, and in order to minimize the dissipation of the sample's thermal effects, the lower walls were made as thin as practically possible. A copper gasket of 0.015 inch thickness usually was used in effecting the seal. The reference was ignited Al_2O_3 of similar total heat capacity. It was placed in a copper container identical to the one used for the sample, and the same furnace and rocking mechanism as that of Fig. 2.2 were employed except that higher rocking rates were used. However, mounted on the cradle shown in Fig. 2.1 was the holder that Fig. 2.6 illustrates. This holder, in turn, was rocked by a tubular key, which was held in place at the key well by a collar and set screw (see Fig. 2.7) and externally, as in Fig. 2.2, by a spring. The thermocouples were made of 28 B. and S. gage Chromel-Alumel wire which was covered with glass insulation and further insulated from the holder and furnace by ceramic beads. One thermocouple was threaded through the key and front arm of the holder, the other through the rear arm. Their tips were cemented into their respective thermocouple wells with Sauereisen Cement. The containers were wrapped circumferentially with thin asbestos sheet and placed in the holder. Thus, both containers and thermocouples were insulated electrically from the holder and the furnace.

The wiring scheme was similar to that of W. Roberts-Austen as modified by G. K. Burgess.¹⁴ Figure 2.8 shows how the thermocouples were connected to a four-point Brown recorder in DTA experiments. The Brown recorder had a 10 millivolt span and internal bucking voltages available in multiples of 10 millivolts. Point No. 1 printed the temperature of the sample. The difference between point No. 3 and point No. 2 represented the difference in temperature between the sample and the Al_2O_3 . (Point No. 4 read the same as point No. 2.) The external bucking voltage was adjusted to bring points 2, 3 and 4 to a convenient region on the scale. Differential thermal effects of as little as $1/2^\circ\text{C}$ could be detected with this arrangement.

2.2.2 Method of Operation

Only SnF_2 that had been evacuated at 500°C and treated with tin at 225°C was used in obtaining the DTA results presented here. The previously

(Text continues on page 25.)

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Fig. 2.7 Steel Key and Collar

Fig. 2.8 Wiring to a Four-Point Brown Recorder for DTA Experiments

mentioned UF_4 was also used. The threads of the container were coated with graphite, as was the side of the gasket next to the cap, and the container was flushed with argon before sealing. The assembled apparatus was rocked 1-2 hours through an arc of $40-50^\circ$ at 100°C or so above the liquidus point, but not above 825°C in order to avoid the risk of a leak. During this period and during the subsequent heating and cooling curves the rocking rate was in the range of 90-300 RPM. The higher rate was near the limit of the apparatus without modification. Cooling curves were of comparatively little value because of the sluggishness of the transition $\text{UF}_4(\text{s}) + \text{liquid} \rightarrow \text{UF}_4 \cdot \text{SnF}_2(\text{s}) + \text{liquid}$. Instead, the clearest and most reproducible thermal effects were obtained with heating curves at a heating rate of $2-5^\circ\text{C}$ per minute after the cooled mixture had been allowed to rock a few days at $200-300^\circ\text{C}$, depending on the mixture. After the last such equilibrative period the container was opened and the contents removed for an examination of the phases present. Often it could be outfitted with a new gasket and used again with, however, new thermocouples for each sample. The insulation was good enough for several heating curves.

The container of Fig. 2.5 was also used in the quenching experiments. For these experiments the container was filled with a previously heated charge and a thermocouple was cemented into the thermocouple well. The container was controlled within 3°C of the desired temperature for a day or so and was then quickly removed and dropped into water. Quenching from the temperature of equilibration to less than 100°C took place in about 5 seconds. Although the seal sometimes loosened sufficiently during the quenching to produce a slight wetting of the charge, the effect was only superficial.

2.2.3 Experimental Results

The results have already been included in Figs. 2.3 and 2.4. An illustration of the experimental data is found in Fig. 2.9, which shows one of the heating curves obtained with 5.0 mole % UF_4 at a rocking rate of 90 RPM. The maximum cooling effect in a thermal arrest was read from the maximum difference between the No. 3 curve and the No. 2 and No. 4 curve and plotted in the phase diagrams at the temperature of the transition. This indication of the strength of the arrest was only approximate because the heating rates varied somewhat. It showed that the arrest at 212°C was the eutectic arrest. The heat of the reaction at the incongruent melting point of the compound $\text{UF}_4 \cdot 2\text{SnF}_2$ was quite small. Less reliance was placed on thermal arrests for 40, 50, and 60 mole % UF_4 because of the difficulty in getting the reaction $\text{UF}_4 \cdot 2\text{SnF}_2(\text{s}) + \text{UF}_4(\text{s}) \rightarrow 2\text{UF}_4 \cdot \text{SnF}_2(\text{s})$ or $\text{SnF}_2(\text{l}) + \text{UF}_4(\text{s}) \rightarrow \text{UF}_4 \cdot \text{SnF}_2(\text{s})$ to go to completion before heating curves were made. There was this lack of

Fig. 2.9 Representative Heating Curve

equilibrium for these mixtures even though they had been previously heated above 500°C, ground up, mixed,* and equilibrated at 350°C (40% and 50%) or 300°C (60%) prior to the taking of the heating curve. A liquidus point was obtained from a heating curve as the temperature at which a sustained thermal effect disappeared, as in Fig. 2.9. This effect was 1° or less in strength and its disappearance usually was gradual enough to make the liquidus temperature uncertain by 5° or more. A liquidus point observed on cooling often was accompanied by a slight supercooling even at a rocking rate of 300 RPM. For this reason a little more confidence is placed in liquidus points observed in heating.

Material remaining in the charge compartment of the filtration apparatus occasionally was equilibrated again at the same or higher temperature in the container of Fig. 2.5, then quenched. Thus material from a filtration run at 500°C, again equilibrated at 500°C and quenched, revealed large crystals of UF_4 only. The material from the filtration run at 325°C, equilibrated at 350°C before quenching, indicated the solid phase to have been $\text{UF}\cdot\text{SnF}_2$ at 350°C.

Visual observations were made on some mixtures in auxiliary experiments at 300–400°C. Observations of a few seconds duration were made on 8 mole % UF_4 + 92 mole % SnF_2 by means of a melting point block. Others were made over a period of several days on mixtures of 20 and 27 mole % UF_4 in SnF_2 . The mixtures were contained in a copper receptacle having a synthetic sapphire window for observations and a thermocouple well to enable a reliable measurement of the temperature. No coexistence of immiscible liquids was apparent in any of the experiments. The observations were qualitatively consistent with the phase diagram presented in Figs. 2.3 and 2.4.

*Cf. H. Rheinboldt, J. prakt. Chem., 111 (2), 242 (1925).

Chapter 3

THE SOLUBILITY OF PuF_3

Experiments had shown that the fusing of mixtures of PuF_4 and SnF_2 resulted in the reduction of the plutonium to the trivalent state no matter whether the container was copper, molybdenum, or gold. The corrosion so produced was appreciable in copper, inappreciable in molybdenum, and sensibly zero in gold. As a result of the experiments in the latter two containers it was decided that the following reaction lay mostly to the right:

(Glassner's estimates indicate that the equilibrium constant should be of the order of unity.⁵) Subsequent studies of plutonium were made with the plutonium added as PuF_3 .

The PuF_3 had been prepared by K. W. R. Johnson, of this Laboratory. Analysis showed it to contain 80.7% by weight plutonium compared with a theoretical value of 80.74%, and its ignition to PuO_2 gave exactly the theoretical weight ratio. Spectrographic analyses showed extremely small amounts of impurities although there may have been as much as 100 ppm of plutonium hydride.

The same apparatus was employed as in the preceding chapter. The copper filtration apparatus was inappreciably corroded by any of the mixtures not containing PuF_4 . The same method of operation was employed except that the filtrates were radioassayed for plutonium and a 100% material balance was assumed. Table 3.1 shows the results that were obtained with mixtures of PuF_3 in SnF_2 . The error estimated for the solubilities includes a 2% relative error in the radioassay. The solid phases were identified morphologically by R. M. Douglass as PuF_3 , i.e., there was no evidence of a PuF_3 - SnF_2 compound. The solubilities obtained are at least an order of magnitude less than those of the system UF_4 - SnF_2 at the same temperatures. The solubility of

PuF₃ in 10 mole % UF₄ + 90 mole % SnF₂ was determined similarly at 450°C. Two determinations averaged 0.22 ± 0.02 mole % PuF₃ in this mixture. Hence the presence of UF₄ appears to depress the solubility of the PuF₃.

Table 3.1

THE SOLUBILITY OF PuF₃ IN SnF₂

<u>Temperature, °C</u>	<u>Mole % PuF₃ in Filtrate/Charge</u>	<u>Av. ± Est. Error of Mole % PuF₃ in Filtrate</u>
350	0.41/10.0	0.41 ± 0.02
450	0.52/4.3*	0.52 ± 0.02
550	0.63/10.0	0.63 ± 0.02

*The SnF₂ from which this charge was made had been evacuated at 500°C and treated with Sn⁰ at 225°C.

Chapter 4

DISCUSSION

As a result of the present experiments, the solubility curve in the system $\text{UF}_4\text{-SnF}_2$ is thought to be fairly well established. That is the part of the studies of most practical importance. The relations below the liquidus are consistent with all the data but additions and refinements may be possible. The eutectic composition and temperature are 0.5 mole % UF_4 and 212°C . The peritectic point at which the compound $\text{UF}_4\cdot 2\text{SnF}_2$ melts is at 4.5 mole % UF_4 and 340°C . That for the compound $\text{UF}_4\cdot \text{SnF}_2$ is at 7.8 mole % UF_4 and 371°C . The information on the system $\text{PuF}_3\text{-SnF}_2$ is too sparse to enable the construction of a phase diagram; it is indicative of only the solubilities available.

The low melting points of the more dilute $\text{UF}_4\text{-SnF}_2$ mixtures and the 850°C boiling point of the solvent should allow operation without appreciable pressure at temperatures of interest for power reactors. The cross section for neutron capture in tin is 0.60 barn for thermal neutrons and about 0.03 barn for 1 Mev neutrons.¹⁵ Neutron capture in fluorine is nil. Hence SnF_2 is feasible pressure-wise and neutron-wise as a fuel solvent for either a thermal or a fast reactor.

Copper containers are useful in making studies such as those reported here. Molybdenum is considerably more resistant to corrosion, nickel less so. A container for a SnF_2 fuel may be developed from one of these materials or a combination of them.

Compositions of 1-7 mole % UF_4 , or 0.41 mole % PuF_3 , in SnF_2 give moderate critical masses with graphite moderation. The melting points of these mixtures are quite low ($212\text{-}375^\circ\text{C}$), thus facilitating handling and ease of start-up as well as probably minimizing the operating temperature for a given power output. One could obtain a specific power output well in excess of 1000 watts per gram of fissionable material. Because of the high dilution available in such fuels a high burnup might be obtainable before fission product

solids would become objectionable and reprocessing would be necessary. The large temperature coefficient of solubility of the UF_4 could be useful in reprocessing. Thus SnF_2 fuels appear favorable for a simple "burner" of fissionable material. Elementary considerations indicate that a considerable conversion of fertile to fissionable material could be obtained, but it would have to be achieved mainly in a blanket.

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