MASTER

Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XIII. Condensed-phase Equilibria in the System

Molybdenum Hexafluoride-Uranium Hexafluoride

$\text{MoF}_6 - \text{UF}_6$

by

L. E. Trevorrow, M. J. Steindler,
D. V. Steidl, and J. T. Savage

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Chemical Engineering Division

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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XIII. Condensed-phase Equilibria in the System Molybdenum Hexafluoride-Uranium Hexafluoride

by

L. E. Trevorrow, M. J. Steindler,
D. V. Steidl, and J. T. Savage

ABSTRACT

Condensed-phase equilibria in the system MoF_6 - UF_6 have been studied by thermal analysis and X-ray diffraction. The temperature-composition phase diagram constructed from observed thermal arrests is characteristic of a binary system forming solid solutions, a minimum-melting mixture (22 m/o UF_6 at 13.7°C), and a solid-miscibility gap. The diagram shows that the maximum solid solubility of the smaller MoF_6 molecule in the UF_6 lattice is about 30 m/o MoF_6 , while the maximum solid solubility of the larger UF_6 molecule in the MoF_6 lattice is 12 to 18 m/o UF_6 . The temperature of the solid-state transformation of MoF_6 increases from $\sim -10^\circ\text{C}$ in pure MoF_6 to $\sim -5^\circ\text{C}$ in mixtures with UF_6 , indicating that the solid solubility of UF_6 is greater in the low-temperature form of MoF_6 than in the high-temperature form of MoF_6 . This solid-solubility relationship can be expected in view of the crystal structures of the pure components. The X-ray diffraction pattern of the high-temperature form of pure MoF_6 can be indexed as a body-centered-cubic structure; the X-ray pattern of the low-temperature form of pure MoF_6 can be indexed as an orthorhombic structure, similar to (but not necessarily identical to) the orthorhombic structure of UF_6 .

I. INTRODUCTION

Condensed-phase equilibria in several systems involving UF_6 and other components have been investigated. Among the systems studied are the binary systems BF_3 - UF_6 ,¹ ClF_3 - UF_6 ,² HF - UF_6 ,³ BrF_3 - UF_6 ,⁴ BrF_5 - UF_6 ,⁴ and Br_2 - UF_6 ,⁵ and the ternary system ClF_3 - HF - UF_6 .⁶ The phase diagrams for these binary systems show the formation of simple eutectic mixtures without solid solubility.

The only reported investigation of condensed-phase equilibria involving UF_6 and another hexafluoride as the second component is a recent

study of the system $\text{UF}_6\text{-PuF}_6$.⁷ Although it has been reported⁸ that the system $\text{NpF}_6\text{-UF}_6$ involves solid solutions, a phase-equilibrium diagram is not available.

This report describes the results of an experimental study of condensed-phase equilibria in the system $\text{MoF}_6\text{-UF}_6$ carried out by thermal analysis and X-ray diffraction analysis. A temperature-composition phase diagram was constructed from the temperatures of observed thermal arrests in $\text{MoF}_6\text{-UF}_6$ mixtures, and the basis for the formation of this type of diagram was established by knowledge of the physical properties of the pure components. The solid-solubility relations indicated by the diagram were traced to the crystal structures of the pure solids.

II. EXPERIMENTAL DETAILS

A. Materials

1. Uranium Hexafluoride

The UF_6 used in this work was a portion of a larger batch originally obtained from Oak Ridge National Laboratory. Almost two-thirds of the original batch had been distilled away in previous experimental work, contributing to the purification of the UF_6 from low-boiling impurities (e.g., HF , CF_4 , F_2).

Emission-spectrographic analysis of the material indicated that the predominant impurities were P, <400 ppm, and As, B, Cs, Pd, Re, Sb, Sn, and Th, each present at concentrations of <100 ppm. Two determinations of the triple point of a sample of the UF_6 yielded values of 64.1 and 64.2°C. The best literature value⁹ for the triple point of UF_6 is 64.05°C.

2. Molybdenum Hexafluoride

The MoF_6 used in this work was a high-purity material obtained commercially.* Analysis of the material by emission spectrography indicated that the concentrations of the predominant impurities were P, <20 ppm; Cs, Re, and Sb, each <10 ppm; U, <5 ppm; Sn, W, Zn, each <4 ppm; and all other impurities <2 ppm. The triple point of the material was $17.4 \pm 0.5^\circ\text{C}$. Literature values for the triple point are 17.4°C ,¹⁰ 17.5°C ,¹¹ and 17.57°C .¹²

*A. D. Mackay, Inc., New York, material prepared by General Chemical Division of Allied Chemical Co., Baton Rouge, La.

B. Apparatus

1. Containment of Materials

All experimental work with hexafluorides was performed in a metal manifold constructed of nickel tubing and fittings. The manifold incorporated Monel diaphragm valves* and several 1-in.-diam valves** with brass bodico, Monel bellows, and Teflon seats. Hexafluorides were transferred from one vessel to another in the manifold by vacuum distillation at room temperature.

2. Thermal-analysis Apparatus

Since the thermal-analysis apparatus was described in detail in a previous report,⁷ it will be only briefly summarized here. Mixtures to be examined by thermal analysis were contained in a nickel sample tube with a bottom well to admit the tip of a thermocouple. The sample tube was bolted through a Teflon-gasketed flange to a bellows-valve, which could be attached to a vacuum manifold by a flare fitting. The volume of the sample tube was about 4.9 ml when the valve was closed.

A mixture contained in the sample tube was subjected to thermal analysis while positioned in a cavity of a cylindrical nickel block, which was heated or cooled as a linear function of time with the aid of a programmed controller,[†] a control unit,^{††} and a silicon-controlled rectifier.

Iron-constantan thermocouples, calibrated against an NBS-standardized platinum resistance-thermometer, measured both the sample temperature and the difference in temperature between sample and reference tubes. The thermocouple wires were embedded in magnesia and electrically insulated from their Inconel sheaths. The signal of the thermocouple in the sample tube could be determined either by a recording potentiometer[‡] or by a manual potentiometer and a null meter.^{‡‡} The recording potentiometer, which recorded the sample temperature, was calibrated against the manual potentiometer before each experiment, and it was also calibrated during an experiment whenever the suppression of the recording potentiometer was reset.

* Valves No. 411 and 413, Hoke Incorporated, Cresskill, New Jersey.

** Vactronic Lab. Equipment, Inc., East Northport, Long Island, N. Y.

† Minneapolis-Honeywell Regulator Co., Philadelphia, Pa., Electronik Strip Chart Proportioning Program Controller.

†† Minneapolis-Honeywell, Electro-Volt Control Unit.

‡ Minneapolis-Honeywell, Recording Potentiometer, 1-mV span, 0- to 50-mV suppression.

‡‡ Leeds and Northrup Co., Type K-3 Potentiometer; Null Meter Model No. 9834.

For differential thermal-analysis measurements, two tubes were positioned side by side in the nickel block. One tube contained the mixture to be examined by thermal analysis; the other was used as a reference. Satisfactory baseline behavior in the record of the differential thermocouple was obtained by operating with the reference tube filled with air at 1 atm. The voltage indicating the difference between the sample and reference thermocouples was fed into a d.c. amplifier* capable of multiplying the difference signal by factors varying from 2.5 to 100. The amplified signal was displayed by a strip-chart recorder** with a zero center and a span of -5 to +5 mV.

C. Procedures

1. Sample-tube Conditioning

A new or reassembled sample tube received the following conditioning treatment: The tube was evacuated, then filled with fluorine gas to about 1 atm, and warmed periodically with a hot-air blower. After 1 to 15 hr, the fluorine was removed, and the tube was evacuated and weighed to obtain a tare.

2. Preparation of Mixtures

A sample tube was loaded as follows: A sample of UF_6 was vaporized at 25°C into a calibrated ballast tank, and the pressure was observed by a Bourdon gage.[†] The UF_6 sample was then condensed into a sample tube by cooling the bottom of the tube with liquid nitrogen or dry ice. The sample tube was removed from the vacuum manifold and weighed on a 1-kg capacity balance^{††} to determine the weight of the UF_6 sample. The sample tube was then reattached to the vacuum manifold, and a sample of MoF_6 was measured and condensed into the sample tube in a manner similar to that for the UF_6 . The sample tube was again weighed to determine, by difference, the weight of the MoF_6 sample. The total weight of a mixture was usually about 3.5 g.

3. Thermal-analysis Procedures

After the mixture had been prepared, the tube was heated to 70°C to melt both components. The tip of the tube was then placed against a block of dry ice. Contact with the dry ice vibrated the tube, mixing the components. This procedure also helped to condense the hexafluorides into the bottom of the tube. The sample-block assembly was then heated or

* Leeds and Northrup Co., Philadelphia, Pa., Model No. 9835-B.

** Minneapolis-Honeywell, Electronik 18 Recorder.

[†] Helicoid gage, 0-1000 mm, 8-1/2-in. diam, American Chain and Cable Co.

^{††} Mettler Instrument Corp., Princeton, N. Y., Model B-5.

cooled at a programmed rate to obtain accurate values of thermal arrests from which solidus and liquidus temperatures were obtained. Programmed thermal analyses were performed two to five times on each mixture. Most of the thermal analyses were performed at $0.3^{\circ}\text{C}/\text{min}$; however, some were performed at $0.6^{\circ}\text{C}/\text{min}$.

4. X-ray Diffraction Procedures

X-ray diffraction patterns for the hexafluorides were obtained from samples sealed into quartz capillary tubes of 0.15 to 0.25 mm ID, with wall thicknesses of 0.02 to 0.05 mm. The large end (9 mm OD) of each length of quartz tubing was attached to the nickel vacuum manifold (shown in Fig. 1) by a vacuum coupling using a neoprene O-ring, coated with a grease* resistant to fluorinating agents. After the manifold and capillary tubing were evacuated to 3×10^{-4} Torr, the capillary was baked either by a hot-air blower or a brush flame. The hexafluoride was transferred by vacuum distillation at room temperature through the vacuum line, and then condensed into the tip of the capillary. The capillary was sealed with a gas-oxygen flame while the tip of the capillary was immersed in liquid nitrogen.

Fig. 1. Vacuum Manifold Used to Prepare Samples for X-ray Diffraction Analysis

Mixtures of MoF_6 and UF_6 were prepared for X-ray diffraction analysis as follows: Molybdenum hexafluoride was measured tensiometrically using a ballast tank and Bourdon gage (see Fig. 1). The MoF_6 vapor was then removed from the ballast tank and condensed into the 3/4-in.-OD nickel test tube, where it was isolated by a valve. After excess MoF_6 vapor was evacuated from other sections of the vacuum line, the ballast tank was filled with a sample of UF_6 vapor, which was subsequently condensed into the same nickel tube. With valves 1 and 2 closed, valves 3 and 4 were opened, and the MoF_6 - UF_6 mixture was allowed to expand so that it filled both the ballast tank and the nickel tube. The MoF_6 - UF_6 vapors were allowed to mix at ambient temperature for 15 to 48 hr. Valve 1 was opened

*Kel-F No. 90 Grease, Minnesota Mining and Mfg. Co., St. Paul, Minn.

slightly and then closed so that a small amount of the mixed vapors was trapped in the capillary tube. This small sample was condensed into the tip of the capillary, and the capillary was sealed.

The capillaries were positioned in a 114.6-mm Debye-Scherrer camera, and X-ray diffraction photographs were obtained using filtered radiation from $\text{CuK}\alpha$ and $\text{CoK}\alpha$ sources. Subambient temperatures were maintained in the camera by providing a flow of cooled nitrogen within the camera. The camera temperature was controlled by regulating the flow rate of nitrogen gas. Both the camera and nitrogen-gas lines were insulated with a 1-in.-thick covering of Armaflex* foam.

5. Determination of Solid Density of High-temperature Form of MoF_6

The density of solid MoF_6 above its transformation point was determined from measurements of the volume and weight of a small sample. The volume of solid MoF_6 was measured by observing the height of a sample in a calibrated quartz tube. The quartz tube (9 mm OD) was joined by a brass vacuum coupling to a valve and flare fitting so that it could be attached to the vacuum line. The quartz tube was calibrated by filling the tube with various amounts of water, weighing the water, and measuring the height of the meniscus above the tip of the tube by a cathetometer.

After a sample of MoF_6 had been condensed into the tube on the vacuum line, the valve was closed to isolate the sample, and the tube was removed from the vacuum line and weighed to obtain the weight of the MoF_6 . The tube was then clamped in an upright position, and the MoF_6 was solidified. Void formation was minimized by slowly immersing the tube in an ice bath. After the MoF_6 had completely solidified, the tube was immersed in a constant-temperature water bath, and the height of the solid surface was measured with the cathetometer. The volume of the solid was determined by interpolation from the calibration curve.

III. RESULTS

A. Thermal Analysis

1. Cooling Curves

The interpretation of cooling curves, especially those of UF_6 -rich mixtures, was difficult because of extensive supercooling. The extent of supercooling might have been controlled more easily in larger samples. Bullard *et al.*¹³ found that UF_6 samples of 1000 to 2500 g supercooled only

* Armstrong Cork Company, Lancaster, Pa.

a fraction of a degree. Priest and Priest¹⁴ controlled supercooling in 130 to 150 g samples by bumping. Wendolkowski and Barber² indicated that stirring controlled the supercooling of UF_6 . In the present work, however, the supercooling of the small MoF_6 - UF_6 samples (~3.5 g total) was not eliminated by the use of manual bumping or by an electric core-box vibrator.

Because of the sharp maximum temperature in the cooling curves, the freezing point of a mixture could not be obtained with accuracy by a simple extrapolation of each cooling curve. Therefore, the extrapolation procedure of Andrews *et al.*¹⁵ was used to obtain the freezing point.

2. Heating Curves

Although cooling curves indicated liquidus points and solid-state transformations, the supercooling effect obscured the indication of solidus points. Many of the thermal analyses were carried out by obtaining heating curves to determine both liquidus points and solidus points. The liquidus points agreed satisfactorily with those obtained from cooling curves.

3. Temperatures of Thermal Arrests

Voltages of the sample thermocouple corresponding to thermal arrests were converted to temperatures using NBS Circular No. 561.¹⁶ Table I lists the temperatures of thermal arrests for the entire range of composition between 0 and 100 m/o UF_6 . The values listed in Table I are averages of replicate measurements, and the uncertainty values are standard deviations of the averages. Several of the liquidus-point values derived from cooling curves were obtained by the extrapolation procedure. These values are not averages, and the uncertainties associated with them have not been estimated.

4. Temperature-Composition Phase Diagram

The temperatures of thermal arrests are plotted as a function of composition in Fig. 2. The lines have been drawn to suggest the location of equilibrium phase boundaries and the best interpretation of the thermal-analysis data. The resulting diagram is characteristic of a system exhibiting solid solubility with a minimum melting point and a solid-miscibility gap.

Changes in the compositions of the condensed phases caused by differential vaporization of UF_6 and MoF_6 were estimated. Although the location of points on the liquidus curve in UF_6 -rich mixtures would be influenced more than any others by vaporization effects, the compositions of these points differed from those calculated from the total weights of the components by less than 1%. Since changes of this size are not large compared to the uncertainty of locating the liquidus curve in this region, the

effects of vaporization on the composition were considered unimportant in constructing the phase diagram from the thermal-analysis data.

TABLE I. Temperature of Thermal Arrests in MoF₆-UF₆ Mixtures

Mole Fraction UF ₆	Temperature, °C							
	Liquidus		Solidus		Solid Transformation		Solid Transformation	
	Cooling	Heating	Heating	Cooling	Cooling	Heating	Cooling	Heating
0.964		63.2 ± 0.6	58.0 ± 0.1		5.5 ± 2.6 ^s			
0.910		62.4 ± 1.9	49.1 ± 0.6	14.2 ± 0.0 ^s	6.3 ^s		-2.7 ^s	
0.880		59.4 ± 0.6	43.0 ± 5.0					
0.873	60.8		12.3 ± 0.1	13.2 ± 0.2 ^s				
0.853		60.4 ± 2.4	43.0 ± 3.3	14.3 ± 0.1 ^s	2.5 ± 0.4 ^s		-3.6 ± 0.3 ^s	
0.809		55.4 ± 0.4	29.0 ± 4.0	14.4 ± 0.3 ^s	3.6 ± 1.6 ^s		-2.0 ± 0.1 ^s	
0.769		55.5 ± 0.8	26.6 ± 5.5	14.4 ± 0.0 ^s	2.4 ± 0.2 ^s		-2.2 ± 0.3 ^s	
0.729	52.1		12.4	13.8 ± 0.2				
0.719		53.2 ± 2.3	22.7 ± 2.6	14.5 ± 0.1	4.0 ± 1.8 ^s		-2.1 ± 0.4 ^s	
0.599		49.5 ± 2.1	13.5 ± 0.2	14.2 ± 0.2	5.9 ± 0.6 ^s		-5.6 ± 2.1 ^s	
0.583	46.4			13.7 ± 0.2			-3.3 ± 2.1 ^s	
0.516		46.0 ± 0.7	13.6 ± 0.0	14.2	7.7 ^s		-4.3	-8.3 ^s
0.490	40.0			13.7 ± 0.2			-2.0 ± 2.1 ^s	
0.451		43.6 ± 1.8	13.7 ± 0.1	14.2 ± 0.2	8.0 ± 0.6 ^s		-3.2 ± 1.9 ^s	-7.9
0.404	31.4		14.2 ± 0.1	13.9 ± 0.1	7.4 ± 0.8 ^s		-3.5 ± 0.7	-7.0 ± 0.7
0.354		33.3 ± 2.2	13.6	14.2 ± 0.2	8.3 ± 0.3 ^s		-4.1 ± 0.6	-8.3 ± 0.6
0.337	27.0 ± 1.6			13.6 ± 0.6	4.9 ± 0.9 ^s		-5.1 ± 1.4	
0.331	29.2			13.8 ± 0.2	7.3 ± 0.6 ^s		-4.1 ± 1.7	
0.308	21.3 ± 4.1	23.8 ± 1.3	13.6 ± 0.0	14.5 ± 0.1	7.7 ^s			
0.282	19.3 ± 2.5			14.5 ± 0.2	7.3 ± 0.6 ^s		-3.7	
0.276	21.9 ± 0.4		12.5 ± 0.3	13.9 ± 0.4	5.1 ± 1.0 ^s		-8.0 ± 0.3	-6.8 ± 0.1
0.263	>16.8	14.2 ± 0.1	13.7 ± 0.1	14.4			-4.8 ± 0.5	-4.9
0.237	16.0	14.1 ± 0.5	13.6 ± 0.4	14.4 ± 0.1	6.8 ± 2.1 ^s		-5.1	
0.231	16.0			13.4 ± 0.3	7.9 ^s		-4.9 ± 0.6	
0.200				13.0 ± 0.5			-2.3 ± 1.5	
0.198		14.2 ± 0.4	13.0 ± 0.6		9.7 ± 0.7			
0.173		14.8 ± 0.4	13.4 ± 0.1		7.5 ± 3.0			
0.166		14.8 ± 0.4	13.2 ± 0.4		6.0 ± 1.6			
0.152		15.2 ± 0.0	13.8 ± 0.0		4.7 ± 0.7			
0.146					3.4 ± 0.4	5.1 ± 0.3	-3.1 ± 0.6	-7.6 ± 0.1
0.116		15.7	14.5		5.8 ± 1.3		-3.2 ± 1.2	
0.109		15.6 ± 0.0	14.7 ± 0.1		-0.5 ± 0.3	-2.1	-5.7 ± 0.6	-5.5
0.0972					-1.9 ± 0.0	-0.5 ± 1.4	-6.3 ± 0.3	-6.6 ± 0.4
0.0702		16.7 ± 0.3	14.7 ± 0.5		-2.5 ± 0.0		-6.1	
0.0661		16.8 ± 0.3	15.8 ± 0.2			-0.6 ± 0.4	-6.2 ± 0.4	-6.9
0.0554		17.2	16.0				-6.2 ± 0.1	-7.6 ± 0.4
0.0551		16.6 ± 0.6	15.7 ± 0.4				-7.4 ± 0.2	-8.5
0.0527		17.6 ± 0.5	16.1 ± 0.1				-6.7 ± 0.0	-8.1
0.0326		17.1 ± 0.2	16.4 ± 0.2				-7.0 ± 2.3	-7.3 ± 0.6
0.0296		17.7	16.2				-8.8 ± 0.2	-7.9 ± 0.2
0.0							-9.0 ± 0.2	
							-10.8 ± 0.1	-9.8 ± 0.05

^sIndicates small thermal arrest.

Fig. 2. Phase Equilibria in the Condensed System UF₆-MoF₆

B. X-ray Diffraction Analysis

1. Pure MoF₆, High-temperature Form

X-ray diffraction photographs of MoF₆ powder taken at 10°C can be indexed on the basis of a body-centered-cubic unit cell with a lattice constant, $a = 6.23 \pm 0.01 \text{ \AA}$. The similarity of the MoF₆ diffraction pattern to that of molybdenum metal indicates that the molybdenum atoms in the hexafluoride, as in the metal, are located at the body center and corners of a cube.

2. Pure MoF₆, Low-temperature Form

X-ray diffraction photographs of MoF₆ powder taken below -10°C are indexable on the basis of an orthorhombic unit cell. Lattice constants from a pattern obtained at -20°C are $a = 9.65 \pm 0.02$ Å, $b = 8.68 \pm 0.03$ Å, and $c = 5.05 \pm 0.02$ Å. An orthorhombic MoF₆ diffraction pattern was therefore calculated using the atomic coordinates derived by Hoard and Stroupe for UF₆.¹⁷ The agreement of calculated and observed values for MoF₆ listed in Table II indicate that the low-temperature structure of MoF₆ is similar to, but not necessarily identical to, the orthorhombic structure of UF₆.

TABLE II. X-ray Diffraction Data^(a) Obtained from MoF₆ Powder
(Low-temperature Form)

hkl	$d(\text{Å})_{\text{obs}}$	$d(\text{Å})_{\text{calc}}^{(b)}$	$I_{\text{obs}}^{(c)}$	I_{calc}
101	4.48	4.47	W	38
011	{ 4.36	4.36	{ W }	24
020		4.34		57
210	4.19	4.22	S	100
111	3.98	3.98	M	66
201	3.48	3.49	W	16
121	3.11	3.11	F	29
221	{ 2.708	2.719	{ M }	11
301		2.713		13
311	2.580	2.589	F	14
230	2.473	2.481	F	18
112	2.349	2.351	F	12
321	2.298	2.300	F	14
202	{ 2.234	2.237	{ W }	12
231		2.227		23

(a) Obtained with cobalt K α radiation.

(b) Calculated for MoF₆ using atomic coordinates derived by Hoard and Stroupe¹⁷ for UF₆.

(c) S = strong, M = medium, W = weak, F = faint.

The crystal-structure change associated with the solid-state transformation of pure MoF₆ (i.e., body-centered cubic above the transformation, to orthorhombic below it) is analogous to the cubic-to-orthorhombic transformation reported¹⁸ for the 5d hexafluorides, WF₆, ReF₆, OsF₆, IrF₆, and PtF₆.

3. MoF₆-UF₆ Mixtures

X-ray diffraction patterns obtained from mixtures with 5 m/o UF₆ at 6°C and 14 m/o UF₆ at 0 to 7°C appeared to be the same as patterns obtained from the high-temperature form of pure MoF₆. X-ray diffraction patterns obtained from a mixture with 91 m/o UF₆ at 0 to 5°C appeared to be the same as a pattern obtained for pure UF₆.

C. Solid Density of High-temperature MoF₆

The density of solid MoF₆ was obtained from weight and volume measurements at two temperatures above the transformation point. At +8°C the density was 2.91 g/cc, and at 0°C the density was 2.88 g/cc. The density calculated from X-ray diffraction data obtained for pure MoF₆ at +10°C on the basis of a body-centered-cubic unit cell containing 14 atoms (2 x MoF₆) was 2.88 g/cc. The agreement between this calculated value and that obtained from weight and volume measurements appears to confirm the cubic structure for the high-temperature form of pure MoF₆.

IV. DISCUSSION

A. Nonequilibrium Thermal Arrests

A number of small thermal arrests are located in the region labelled S₂ on the diagram in Fig. 2 where, according to the interpretation suggested, only the primary solid solution S₂ is stable. These thermal arrests are attributed to fractional crystallization,¹⁹ which occurs if diffusion in the solid phase is not fast enough to allow the establishment of equilibrium between solid and liquid phases during crystallization. In the extreme case of no solid-state diffusion, the first nucleus (or nuclei) of solid formed when the mixture is cooled is completely removed from the reaction. As cooling proceeds, the crystal nucleus becomes the core of a layered structure, each succeeding layer being poorer in the higher-melting component (UF₆). With the removal of UF₆-rich liquid from the reaction, the composition of the remaining liquid proceeds along the liquidus curve and approaches the composition of the minimum-freezing mixture as a limit, while the freezing point of remaining liquid approaches the eutectic point as a limit. Thus, for a mixture with a total composition of 80 or 90 m/o UF₆, the last bit of liquid to freeze may have the composition of the eutectic mixture (~22 m/o UF₆).

If the solid phase has not annealed before the mixture is heated to obtain a melting curve, the first bit of solid to melt will be the outer layer with the composition and melting point of the eutectic mixture. Thus, when UF₆-rich mixtures were heated, the first slight absorption of thermal

energy was observed at the eutectic point, but the major and definite thermal arrests occurred at higher temperatures; these latter points were assumed to indicate the location of the solidus curve.

Very small heat effects yielding thermal arrests at $+5^{\circ}\text{C}$ have been observed over a wide range of composition. These heat effects are so small as to be observed only by differential thermal analysis at high amplification of the thermocouple signal. All other arrests were easily observed at rates of $0.6^{\circ}\text{C}/\text{min}$, whereas the effects at $+5^{\circ}\text{C}$ were observed only for faster cooling rates (3 to $6^{\circ}\text{C}/\text{min}$), suggesting a nonequilibrium situation. The arrests at $+5^{\circ}\text{C}$ are interpreted as the result of a combination of fractional crystallization and supercooling of the liquid of eutectic composition. In nonequilibrium cooling of any mixture of the UF_6 -rich side of the eutectic, the composition of the last-remaining portions of liquid would decrease in UF_6 until the eutectic point is reached. The composition of mixtures that supercool past the eutectic follows an extension of the liquidus curve.²⁰ Thus, a small, last-remaining portion of liquid could cool below the eutectic temperature to about 5°C , at which point the composition of the liquid becomes equal to the composition at the boundary of the solid-state miscibility gap, and, upon freezing of the liquid, a small heat effect is generated.

B. The Effect of UF_6 on the MoF_6 Solid-state Transformation

The temperature of the solid-state transformation of pure MoF_6 obtained by thermal analysis is $-10.8 \pm 0.1^{\circ}\text{C}$ from cooling curves and $-9.8 \pm 0.05^{\circ}\text{C}$ from heating curves. The value of -9.8°C is considered to be better since supercooling occurred during the determination of cooling curves. Literature values for this solid-state transformation are: -8.7°C , obtained from the intersection of vapor pressure curves;¹⁰ -9.6°C , obtained in calorimetric measurements;¹¹ and -9.68°C , also obtained in calorimetric measurements.¹²

The results of thermal analysis show that the temperature of the solid-state transformation in MoF_6 is higher ($\sim -5^{\circ}\text{C}$) in UF_6 mixtures than it is in pure MoF_6 . This behavior creates a peritectoid on the lower MoF_6 -rich side of the diagram in Fig. 2. An increase of the transformation temperature of a component A in mixture with another component B indicates that component B is more soluble in the low-temperature form of component A.¹⁹ It is therefore concluded, on the basis of the observed increase in the transformation temperature (not on the basis of a chemical analysis of solids S_1 and S_3), that UF_6 is more soluble in the low-temperature form of MoF_6 than in the high-temperature form.

This conclusion might be anticipated on the basis of the crystal structures: A solid of orthorhombic structure (UF_6) is expected to be more soluble in another solid of orthorhombic structure (low-temperature form of MoF_6) than in a solid of cubic structure (high-temperature form of MoF_6).

C. Comparison of Solid Solubilities

The limit of solid miscibility has been related to the energy of distortion of the crystal lattice when atoms of a second component are introduced into the lattice; Hildebrand and Scott²¹ and Lawson²² expressed the distortion energy as a function of the molal volumes of the two components. These authors recognized that the solubility of small atoms in a lattice of large atoms is greater than the solubility of large atoms in a lattice of small ones. The same relationship presumably holds for molecular lattices. The solid-solubility relations indicated in Fig. 2 are in accord with this thesis. The molal volumes²³ are 84 cm³ for MoF₆ and 96 cm³ for UF₆. Figure 2 indicates that the maximum solubility (~30 m/o MoF₆) of the smaller MoF₆ molecule in the primary solid solution S₂ (presumably the UF₆ lattice) is greater than the maximum solubility (~12 to 18 m/o UF₆) of the larger UF₆ molecule in either of the primary solid solutions, S₁ or S₃ (presumably MoF₆ lattices).

D. Correlation of X-ray Diffraction Patterns from MoF₆-UF₆ Mixtures with the Phase Diagram

X-ray diffraction patterns from mixtures with 5 m/o UF₆ at 6°C and 14 m/o UF₆ at 0 to 7°C appeared to be the same as those obtained from the high-temperature form of MoF₆, suggesting a cubic structure. According to Fig. 2, the stable phase in these mixtures is the primary solid solution S₁, which would be expected to have the lattice of the high-temperature form of pure MoF₆.

The X-ray scattering pattern from a mixture with 91 m/o UF₆ at 0 to 5°C appeared to be the same as that obtained for pure UF₆. Figure 2 shows that the stable phase in this mixture is the primary solid solution S₂, which would be expected to have the lattice of pure UF₆.

V. SUMMARY

Condensed-phase equilibria in the system MoF₆-UF₆ were studied by thermal analysis of hexafluoride mixtures varying in composition from 0 to 100 m/o UF₆. The temperature-composition phase diagram constructed from the thermal arrests reflects the formation of solid solutions in the mixtures, a minimum melting mixture at 22 m/o UF₆ and 13.7°C, and a solid-miscibility gap. The diagram indicates that the maximum solid solubility of MoF₆ (the smaller molecule) in the UF₆ lattice is about 30 m/o MoF₆, while the maximum solid solubility of UF₆ in the MoF₆ lattice is 12 to 18 m/o UF₆. This solid-solubility relation is analogous to other binary systems in which the solubility of small atoms in a lattice of large ones is greater than the solubility of large atoms in a lattice of small ones.^{21,22}

The solid-state transformation of MoF_6 was observed to increase from $\sim -10^\circ\text{C}$ in pure MoF_6 to $\sim -5^\circ\text{C}$ in UF_6 mixtures. This behavior is the basis for a peritectoid in the phase diagram; it also indicates that the solid solubility of UF_6 is greater in the low-temperature form of MoF_6 than in the high-temperature form of MoF_6 .

X-ray diffraction patterns for the high-temperature form of MoF_6 can be indexed as a cubic structure; the patterns for the low-temperature form of MoF_6 can be indexed as an orthorhombic structure, similar to, but not necessarily identical to, the orthorhombic structure of UF_6 . Since UF_6 and the low-temperature form of MoF_6 have similar structures, the solid-solubility of UF_6 would probably be greater in the low-temperature form of MoF_6 than in the high-temperature form.

The solid density of the high-temperature form of MoF_6 , determined from measurements of weight and volume, was 2.91 g/cc at 8°C and 2.88 g/cc at 0°C . The density calculated from X-ray diffraction patterns obtained at 10°C , assuming a body-centered-cubic unit cell containing 14 atoms ($2 \times \text{MoF}_6$), was 2.88 g/cc . The agreement between this calculated value and that obtained from weight and volume measurements confirms the cubic structure for the high-temperature form of MoF_6 .

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