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THE DISTILLATION OF URANIUM HEXAFLUORIDE AND
BROMINE PENTAFLUORIDE IN A 0.5-INCH-DIAMETER
PACKED COLUMN

by

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	iii
LIST OF TABLES.	vi
NOMENCLATURE	1
SUMMARY	3
INTRODUCTION.	4
LITERATURE REVIEW.	6
DESCRIPTION OF APPARATUS	31
EXPERIMENTAL PROCEDURES.	48
EXPERIMENTAL RESULTS.	65
DISCUSSION OF RESULTS.	73
CONCLUSIONS.	81
ACKNOWLEDGEMENTS	82
APPENDICES	83
I. CALCULATION OF H_{tu_g}	83
II. SOME PHYSICAL PROPERTIES OF UF_6 AND BrF_5	93
BIBLIOGRAPHY.	95

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Uranium Hexafluoride - Bromine Pentafluoride System as Determined by Ellis and Johnson ⁽⁴⁾	7
2.	Pressure-Composition Diagram, Bromine Pentafluoride - Uranium Hexafluoride as Determined by Liimatainen ⁽³⁾ . . .	8
3.	Vapor-Liquid Equilibrium for the System Bromine Pentafluoride - Uranium Hexafluoride as Determined by Liimatainen. ⁽³⁾ 70°C Isotherm.	9
4.	Vapor-Liquid Equilibrium for the System Bromine Pentafluoride - Uranium Hexafluoride as Determined by Liimatainen. ⁽³⁾ 90°C Isotherm.	10
5.	Distillation of Bromine Pentafluoride - Uranium Hexafluoride Mixture: Variation of Overhead Composition with Pressure	11
6.	Temperature - Composition Diagram-3 Atmosphere Isobar UF ₆ -BrF ₅	13
7.	Vapor-Liquid Equilibrium for the System Bromine Pentafluoride - Uranium Hexafluoride as Calculated by Liimatainen ⁽³⁾	14
8.	Flooding Rates in Packed Columns	17
9.	Column Pressure Drop vs Boilup Rate for BrF ₃ in 2-in. Diameter Column Packed with $\frac{5}{32}$ -in. Helices, Data of Page, et al.	18
10.	Column Pressure Drop vs Boilup in Batch Distillation of a Uranium Hexafluoride - Bromine Pentafluoride Mixture	19
11.	Pressure Drop in a Packed Column Distilling BrF ₃ , Holdup Neglected	21
12.	Evaluation of Surface Tension Exponent in Jesser-Elgin Equation, Data of McGill ⁽¹⁰⁾	23

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
13.	Uranium Hexafluoride - Bromine Pentafluoride Distillation Data of Mecham, <u>et al.</u>	26
14.	Schematic Diagram of Equipment for Continuous Stripping Column Test.	28
15.	Bromide Content in Column - Distillation of Bromine Pentafluoride Uranium Hexafluoride System	30
16.	0.5 Inch I.D. Interhalogen Still	32
17.	Interhalogen Still Sample Ports and Stillpot.	33
18.	Interhalogen Still Condenser Section	34
19.	Lapp Pulsefeeder Pump for Recirculating Side Stream . . .	38
20.	Thermal Flowmeter ORNL - Mark I	39
21.	Mark II Thermal Flowmeter and Differential Thermocouple	40
22.	Thermal Flowmeter Circuit.	42
23.	Control Panels for Interhalogen Still	44
24.	Calibration of Flowmeter - Interhalogen Still with n-Heptane and Methylcyclohexane. Change in Millivolts from Vacuum vs Rate Flow [lbs/(hr)(sq ft)].	50
25.	Calibration of Flowmeter with BrF ₅ - Change in Millivolts from Vacuum.	51
26.	Column Pressure Drop vs Boilup for Methylcyclohexane and n-Heptane	52
27.	Abbè Refractometer	54
28.	Equilibrating Time Experiment n-Refractive Index of Stillpot and Condenser vs Time from Startup.	55
29.	Htu _g vs Boilup - Methylcyclohexane and n-Heptane.	56

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
30.	Hydrolysis Bottle Assembly	58
31.	Pressure Drop vs Boilup ($L/V = 1$) for UF_6 in a 0.5-in. Column Packed with $\frac{1}{16}$ -in. Nickel Helices.	66
32.	Pressure Drop vs Boilup ($L/V = 1$) for BrF_5 in a 0.5-in. Column Packed with $\frac{1}{16}$ -in. Nickel Helices.	67
33.	Equilibrating Time Experiment - Mol Fraction BrF_5 vs Time	68
34.	Separation Efficiency for $UF_6 - BrF_5$ in a 0.5-in. Column Packed with $\frac{1}{16}$ -in. Helices - $L/V = 1$	70
35.	Comparison of Flooding Rates in Packed Columns	74
36.	Pressure Drop vs Vapor Flow to Determine the Exponent in the Equation $\Delta \bar{P} = KG^n$	75
37.	Relative Volatility for $UF_6 - BrF_5$ Vapor-Liquid Equilibrium Data of Liimatainen ⁽³⁾	78
38.	Refractive Index of Mixtures of n-Heptane and Methylcyclohexane	84
39.	Vapor Liquid Equilibrium for n-Heptane and Methylcyclohexane	85
40.	Calculations of Ntu_g for n-Heptane Methylcyclohexane Batch Distillation.	86
41.	Ntu_g vs Composition for n-Heptane and Methylcyclohexane Batch Distillation.	87
42.	Calculation of Ntu_g for $UF_6 - BrF_5$ Batch Distillation	89
43.	Ntu_g vs Composition for $UF_6 - BrF_5$ Batch Distillation . . .	90
44.	Ntu_g vs Composition at BrF_5 Rich End for Batch Distillation UF_6 and BrF_5	91
45.	Ntu_g vs Composition at UF_6 Rich End for Batch Distillation of UF_6 and BrF_5	92

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Summary of Calculations on 3 Atmosphere Isobar	12
II.	Flooding Rates for Dense Substances	16
III.	Separation Parameters in Distillation of a Uranium Hexafluoride - Bromine Pentafluoride Mixture	27
IV.	Column Operating Conditions	29
V.	Separation Results	29
VI.	Summary of Analytical Standards	61
VII.	Equilibrium Time Data	69
VIII.	Distillation of UF_6 and BrF_5 at Total Reflux with Low Concentrations of BrF_5	72
IX.	Distillation of UF_6 and BrF_5 at Total Reflux	72
X.	Comparison of Separations of Organic and Inorganic Materials	77
XI.	Comparison of Ntu_g Calculated from the x,y Data of Liimatainen ⁽³⁾ and the Assumption of a Constant α of 1.41 UF_6 - BrF_5	79

NOMENCLATURE

- C - proportionality constant
- E - separation factor = $x(1 - y)/y(1 - x)$
- f - fractional free space of dry packing
- G - vapor flow rate lb/(hr)(sq ft)
- H - volume of liquid per unit packed volume
- h - height of packing, ft
- HETP - height equivalent to theoretical plate
- Htu_g - overall height of a transfer unit based on vapor, in.
- k - dimensionless proportionality constant
- L - liquid flow rate - lb/(hr)(sq ft)
- M - molecular weight
- N - number of theoretical plates
- n - exponent
- Ntu_g - number of overall transfer units
- P - total pressure, atm
- P_c - critical pressure, atm
- P₀ - vapor pressure of a pure substance, atm
- $\overline{\Delta P}$ - pressure drop, in. of water/ft
- S - surface of dry packing per unit packed volume, ft⁻¹
- t - temperature, °C
- T_c - critical temperature, °K
- W - removal rate, lb/(hr)(sq ft)

x - concentration of the more volatile component of a binary mixture in the liquid, mole fraction

y - concentration of the more volatile component of a binary mixture in the vapor, mole fraction

α - relative volatility or separation factor

γ_1 - activity coefficient defined as $\gamma_1 = (Py/P_{01}x)$; $\lim \gamma \rightarrow 1$ as $x \rightarrow 1$

γ_2 - activity coefficient defined as $\gamma_2 = P(1-y)/P_{02}(1-x)$; $\lim V_2 \rightarrow 1$ as $x \rightarrow 0$

μ_g - absolute viscosity of vapor

μ_l - absolute viscosity of liquid

ν - kinematic viscosity of liquid, centistokes

ρ_g - density of gas, gm/ml

ρ_l - density of liquid, gm/ml

σ - surface tension

$\Phi = (\rho_g/0.075)^{1/2}$

SUMMARY

The purpose of this study was to investigate the separation efficiency of a packed column with the binary system uranium hexafluoride and bromine pentafluoride.

A one-half-inch-diameter column packed with one-sixteenth-inch nickel helices was constructed in a system designed to contain these corrosive materials. Several distillations were performed with the system methylcyclohexane and n-heptane for purposes of calibration. For both systems, pressure-drop measurements at various flow rates were determined and the flooding rates determined from these. Experiments to determine the equilibrium time were also conducted with both the organic system used for calibration and with inorganic system. Several batch distillations were performed for both systems. The organic system was distilled at one atmosphere whereas the inorganic systems were distilled at a pressure of three atmospheres. The separation efficiency was calculated as H_{tu_g} with the aid of the best equilibrium data available in the literature.

The flooding rates determined were 570 lb/(hr)(sq ft) for methylcyclohexane, 2680 lb/(hr)(sq ft) for uranium hexafluoride, and 2200 lb/(hr)(sq ft) for bromine pentafluoride. Equilibrium times of 34 hr and 24 hr were found for the organic and inorganic systems, respectively. The H_{tu_g} was found to be 1.2 in. for flows of 50 to 450 lb/(hr)(sq ft) for the n-heptane-methylcyclohexane system. The H_{tu_g} for the uranium hexafluoride-bromine pentafluoride system was 1.3 in. at flow rates above 285 lb/(hr)(sq ft) and was found to increase to almost 3 in. at flow rates below this. In distillations with very low concentrations of bromine pentafluoride, the corrosion of the column and packing interfered with the separation performance as a result of formation of bromine trifluoride, which remained in the stillpot.

No azeotrope was found to exist in the inorganic system.

INTRODUCTION

The purification of uranium hexafluoride from systems containing fission product fluorides and interhalogens is required in various schemes for the processing of spent fuel elements. Distillation is thought to be a promising method of performing this separation.

Lawroski⁽¹⁾ has presented the relative merits of distillation of halogen systems for the recovery and purification of nuclear fuels. The various processes involve the dissolution of metallic fuels in bromine trifluoride, hydrofluoric acid, or molten salts, and further fluorination and purification steps resulting in a mixture of uranium hexafluoride, fission product fluorides, and bromine pentafluoride. A similar process described by Levitz⁽²⁾ involves a dissolution with an aqueous acid solution followed by drying and fluorination steps conducted in fluidized beds. The final purification could be effected by distillation with the use of bromine pentafluoride as the fluorinating agent.

A sizable amount of work has been done in proving that distillation techniques are applicable and in obtaining the data necessary to design plant-scale equipment and to further the study of the systems involved. An abundance of qualitative results exists. However, due largely to the lack of equilibrium data and some inconsistencies in the literature, only a small amount of reliable quantitative data are available.

In order to study the distillation of the various fluoride and interhalogen systems, a pilot-scale distillation column was constructed. The system was designed so that the column and packing are readily removable, thereby providing a flexible tool.

The objectives of the study performed were to evaluate the performance of a $\frac{1}{16}$ -in., nickel helix packing and to compare the

performance of the dense vapor system uranium hexafluoride-bromine pentafluoride with lighter component organic systems. The system n-heptane and methylcyclohexane was used as the organic reference. The uranium hexafluoride-bromine pentafluoride system was chosen because of the readily available vapor-liquid equilibrium data obtained by R. Liimatainen.⁽³⁾ The main factors examined in this study were:

1. pressure drop; 2. flooding rate; 3. equilibrating time; and
4. separation efficiency. Although simple modifications were designed for the study of holdup, none were performed in this study.

LITERATURE REVIEW

Equilibrium Data

Vapor-liquid equilibrium data for the bromine pentafluoride-uranium hexafluoride system have only recently appeared in the literature. Ellis et al.,^(4,5) published equilibrium data for the system, and reported an azeotrope at approximately 0.1 mol fraction uranium hexafluoride. Liimatainen,⁽³⁾ however, reported equilibrium data that gave no indication of an azeotrope, but found slight positive deviations from ideality. Liimatainen found that it was necessary to introduce fluorine into his equilibrium apparatus to inhibit the partial decomposition of bromine pentafluoride. Ellis et al., did not use this fluorine technique. Mecham⁽⁶⁾ also reported the use of fluorine to inhibit decomposition due to corrosion reactions in distilling the bromine pentafluoride-uranium hexafluoride system in a 1.75-in. packed column.

Figure 1 shows the data of Ellis as vapor pressure versus composition isotherms at 68 and 80°C. Figure 2 similarly presents the data of Liimatainen as 70°C and 90°C isotherms. Figures 3 and 4 present the data of Liimatainen as x-y composition plots for the 70°C and 90°C isotherms.

Ellis et al.,⁽⁴⁾ also reported the variation of the azeotrope composition with the operating pressure. These data are reproduced in Figure 5.

Liimatainen calculated a 3-atm isobar from his data. Table I is a summary of these calculations. Figure 6 is a temperature-composition plot of his results, and Figure 7 is an x-y plot of the same results for the 3-atm isobar. These data were used as a basis for calculating separation efficiencies.

Figure 1
System Uranium Hexafluoride-Bromine Pentafluoride
as Determined by Ellis and Johnson⁽⁴⁾

Figure 2

Pressure-Composition Diagram - Bromine Pentafluoride-Uranium Hexafluoride as Determined by Liimatainen⁽³⁾

Figure 3

Vapor-Liquid Equilibrium for the System Bromine Pentafluoride-Uranium Hexafluoride as Determined by Liimatainen⁽³⁾

Figure 4
Vapor-Liquid Equilibrium for the System Bromine
Pentafluoride-Uranium Hexafluoride
as Determined by Liimatainen(3)

Figure 5

Distillation of Bromine Pentafluoride-Uranium Hexafluoride Mixture: Variation of Overhead Composition with Pressure

Table I

SUMMARY OF CALCULATIONS ON 3-ATM ISOBAR
BY LIIMATAINEN(3)

Mole Fraction BrF ₅		Temperature, °C	Relative Volatility α
Liquid x	Vapor y		
0	0	87.7	lim = 1.80 x → 0
10	16.3	85.0	1.75
30	39.9	81.4	1.55
50	58.5	78.8	1.41
70	74.9	77.0	1.28
90	91.3	75.8	1.17
100	100	75.5	lim = 1.09 x → 1

Equations:

$$P = x_1 \gamma_1 P_{O_1} + x_2 (1-x) (P_{O_2})$$

$$\gamma_1 = 10C_1 x^2$$

$$\gamma_2 = 10C_2 (1-x)^2$$

	70°C	90°C
$C_1 =$	0.114	0.105
$C_2 =$	0.114	0.105

Distillation of Uranium Hexafluoride

Several columns have been built for distilling the interhalogen and metal fluoride systems. These have generally been packed columns with diameters from 0.5 to 5.0 in. A bubble cap tray column is reported by W. C. Ruch *et al.*,⁽⁷⁾ for the purification of uranium hexafluoride as a step in the production of the same from ore concentrates. J. T. Long^(8,9) has published the most complete collection of data available for the distillation of uranium hexafluoride and interhalogen systems. In the subsequent paragraphs, the data most applicable to the objectives of this work are reviewed, additional references to the original works and others not included in Long's publication are given.

Figure 6

Temperature-Composition Diagram - 3 Atmosphere Isobar UF_6 - BrF_5

Figure 7

Vapor-Liquid Equilibrium for the System Bromine
Pentafluoride-Uranium Hexafluoride
as Calculated by Liimatainen⁽³⁾

Flooding Rates

The liquid holdup increases markedly with the flooding of a packed column blocking the rising vapors. The factors affecting the holdup are the density, viscosity, and the surface tension of the liquid. An increase of the viscosity or surface tension and a decrease in the density would tend to increase the liquid holdup in the packing material. The metallic fluorides and interhalogens generally have extremely high densities and low surface tensions compared with organic systems. These characteristics should allow flooding rates to be obtained that are high in comparison with organic systems, even though the inorganics have somewhat higher viscosities. McGill⁽¹⁰⁾ has verified this experimentally, as have other investigators.

Table II presents a compilation of the flooding rate data in the literature. Unfortunately, most investigators actually have been unable to attain flooded conditions because of the requirements of high heat input necessary. Long has correlated the data of Page⁽¹¹⁾ and McGill⁽¹⁰⁾ by the method suggested by Sarchet⁽¹²⁾, together with the correction for variations in viscosity and density suggested by Pigford and Colburn.⁽¹³⁾ Figure 8 is a plot of

$$G/\Phi \nu^{1/2} (62.3/\rho_L)^{1/2}$$

as ordinate against

$$\frac{L}{G/\Phi \left(\frac{62.3}{\rho_L}\right)^{1/2}}$$

as abscissa, where

G = vapor flow rate at flooding lb/(hr)(sq ft)

L = liquid flow rate at flooding lb/(hr)(sq ft)

$\Phi = (\rho_G/0.075)^{1/2}$

ρ_G = density of the vapor lb/cu ft

ρ_L = density of the liquid lb/cu ft

ν = kinematic viscosity of liquid, centistokes.

This method was used to correlate the data rather than that of Sherwood, Shipley, and Holloway⁽¹⁶⁾ as modified by Lobo⁽¹⁷⁾ because of the lack of information concerning the packing surface area and the percentage of voids. The latter is probably the best method to date for flooding rate correlations.

Table II

FLOODING RATES FOR DENSE SUBSTANCES

(Most Laboratory Columns Provide too Little Heat Input to Reach Flooding.)

Compound	Boilup Rate at Total Reflux, lb/(sq ft)(hr)	Column Diameter, in.	Packing	Reference
Column Flooded				
UF ₆	1500-2000	0.5	$\frac{1}{16}$ -in. Ni Heli-Pak	(14)
UF ₆	4950 (calc)	0.87	$\frac{1}{8}$ -in. Ni Heli-Pak	(10)
BrF ₃	3900	2.0	$\frac{5}{32}$ -in. Ni helices	(8)
Column Not Flooded				
UF ₆	2380	0.75	$\frac{1}{8}$ -in. Ni Heli-Pak	(8)
UF ₆	3350	0.87	$\frac{1}{8}$ -in. Ni Heli-Pak	(10)
UF ₆ -C ₈ F ₁₆	5580	5.05	$\frac{5}{8}$ -in. Monel Raschig rings	(15)

Pressure Drop

Only two investigators have reported measurements of pressure drop with the interhalogen and metal fluoride systems. Page et al.,⁽¹¹⁾ reported pressure-drop data for BrF₃ in a 2-in.-diameter column packed with $\frac{5}{32}$ -in. helices. Figure 9 is a reproduction of their data.

Mecham et al.,⁽¹⁹⁾ reported pressure-drop data for a 16-ft, 1.75-in. column packed with Heli-Pak 2019. Figure 10 is a plot of the column pressure drop (in./ft column) versus boilup [lb mol/(hr)(sq ft)] for the UF₆-BrF₅ system studied.

Figure 8

Flooding Rates in Packed Columns

Figure 9
Column Pressure Drop vs. Boilup
Rate for BrF₃ in 2-in. Diameter
Column Packed with $\frac{5}{32}$ -in. Helices
Data of Page, et al.

Figure 10

Column Pressure Drop vs. Boilup in Batch Distillation of a Uranium Hexafluoride-Bromine Pentafluoride Mixture

Long correlated the data of Page et al.⁽¹¹⁾ He used the correlation of Reed and Fenske.⁽¹⁸⁾ The pressure drop varies with vapor rate according to the dimensionless equation

$$\rho_g \frac{\overline{\Delta P} (f - H)^3}{h \mu_g^2 S^3} = k \left(\frac{G}{\mu_g S} \right) \quad , \quad (1)$$

where

f = fractional free space of the dry packing

G = mass rate of throughput per unit of total cross section

H = volume of liquid holdup at boiling point per unit packed volume

k = dimensionless proportionality constant

h = height of packing

S = surface of dry packing per unit packed volume

$\overline{\Delta P}$ = pressure drop

μ_g = absolute viscosity of vapor at arithmetic average temperature of column

ρ_g = density of vapor at arithmetic average pressure and temperature of column

The results are presented in Figure 11. The expression

$\rho_g \frac{\overline{\Delta P} f^3}{h \mu_L^2 S^3}$ is plotted against $\frac{G}{\mu_L S}$ on a log-log scale; the slope is 1.88.

This agrees with the expected value of 1.7 to 1.8 reported by Page et al.⁽¹⁰⁾ for Fenske helices. It is apparent that the liquid viscosity was used in these calculations rather than the vapor viscosity. This is probably the reason for the slight difference, since correction for a lower viscosity would lower the slope of the plot.

Figure 11

Pressure Drop in a Packed Column Distilling BrF_3 , Holdup Neglected

Holdup

Only one experimenter has obtained data of holdup for the dense metallic fluorides or interhalogens. McGill⁽¹⁰⁾ has obtained holdup data for n-heptane, C-816, and uranium hexafluoride in an 0.87-in. column packed with $\frac{1}{8}$ -in. Heli-Pak.

Long attempted to correlate the data of McGill with that of Jesser and Elgin⁽²⁰⁾ for organic systems and water. Their equation is

$$H = H_w \mu_s^{0.1} / \rho_s^{0.78} \sigma_s^n \quad (2)$$

where

H = liquid holdup, cu ft/cu ft

H_w = liquid holdup of reference substance (water), cu ft/cu ft

σ_s = ratio of surface tension of liquid to that of reference (water at 20°C)

ρ_s = ratio of density of liquid to that of reference (water at 20°C)

μ_s = ratio of viscosity of liquid to that of reference (water at 20°C).

McGill calculated the surface-tension exponent for the UF_6 with the C-816 as a reference material, and also for the n-heptane, C-816, and UF_6 with water as a reference. Long also assumed that water holdup for the Heli-Pak was identical with that for 0.39-in. ceramic rings. Figure 12 is a reproduction of the correlation of the exponent versus vapor flow rate calculated by Long. An extrapolation of the data of Jesser and Elgin is also presented in the figure. Long states that "Disregarding the n-heptane data, the most logical conclusion that can be reached is that the Jesser-Elgin equation simply does not apply to these dense substances." A further possibility for the discrepancies of the data might be the comparison of the packing materials used in the two studies.

Figure 12

Evaluation of Surface-tension Exponent in Jesser-Elgin Equation; Data of McGill

Jesser and Elgin compiled data for $\frac{1}{4}$ -in. to 1-in. Berl Saddles, spheres, and rings, whereas the data of McGill was obtained for a $\frac{1}{8}$ -in. metal Heli-Pak, which is a noninterlocking packing designed for analytical columns and has been shown not to be particularly consistent in performance. The data of Tijunelis⁽²¹⁾ showed nonreproducibility with this packing.

Column Efficiency

Many investigators have reported values for HETP or Htu for distillations of systems containing metallic fluorides and interhalogens. All of these experimenters have used the assumption of a constant α equal to 1.41. Long reported the following distillation efficiencies:

1. A 2-in. column packed with $\frac{5}{32}$ -in. aluminum helices gave values of HETP from 4.5 to 6.3 in. for a uranium hexafluoride-bromine trifluoride mixture at Brookhaven.⁽¹¹⁾ The same column produced an HETP of 3.2 in. or more for a mixture of n-heptane and methylcyclohexane.

2. At K-25,⁽¹⁵⁾ a pilot-plant separation with $\frac{5}{8}$ -in. metal rings gave values of a 14.4-in. HETP in separating uranium hexafluoride from C-816. For comparison, $\frac{1}{2}$ -in. ceramic rings in a 2-in. column⁽²²⁾ showed values of 6.0 to 8.4 in. for HETP in separating n-heptane and methylcyclohexane, and in the tabulation of Perry's handbook, p. 620⁽¹³⁾ a HETP of 1.2 ft is cited for one-inch ceramic rings for the ethyl alcohol-water system.

3. Nimo⁽²³⁾ reported HETP data for the uranium hexafluoride-C-816 system that were somewhat uncertain because of partial decomposition of the fluorocarbon. However, it appeared that the HETP values were about twice those obtained with hydrocarbons.

4. Tests at Argonne National Laboratory⁽⁶⁾ on a 1.75-in. column packed with Heli-Pak 3019 gave a HETP of about 8 in. with a bromine pentafluoride-uranium hexafluoride mixture and only 2.0 in. with a n-heptane-methylcyclohexane mixture.

Based on this data, Long makes the statement that "It is concluded that at present the values of HETP for systems involving UF_6 or other dense substances may best be found by doubling the value obtained for hydrocarbon systems. Work reported to date has been carried out well below flooding; at higher boilup rates lower values of HETP may be found."

Mecham and his co-workers have published the largest amount of data for separation of the metallic fluorides and interhalogens by distillation.^(6,19,24-27) They reported an HETP of 15 in. for the system molybdenum hexafluoride-uranium hexafluoride.⁽²⁴⁾ All of their data were taken in a 1.75-in.-diameter column packed to a height of 16 ft with Heli-Pak 3019. They mainly investigated the uranium hexafluoride-bromine pentafluoride system because of the apparent difficulties involving side reactions occurring with the bromine trifluoride system. The bromine pentafluoride system offers the advantage of compatibility with fluorine in that it is the final fluorination product.

They performed four runs to demonstrate reduction of the bromine content and reported that it was necessary to sparge the column continuously with fluorine to eliminate discoloration of samples. It was apparent that the corrosion of nickel was producing elemental bromine and bromine trifluoride. The data from these runs, in which a concentration of <1 ppm bromine pentafluoride was reported in the fourth distillation performed, is presented in Figure 13.

Run 1

Run 2

Run 3

Run 4

Figure 13

Uranium Hexafluoride-Bromine Pentafluoride Distillation.
Data of Mecham, et al.⁽⁶⁾

A subsequent distillation was performed⁽¹⁹⁾ with the column acting as a stripping section, and the HETP calculated for each sampling period. Figure 14 is a schematic diagram of the column and shows the operation technique used. Table III gives the sampling data, the calculated Fenske separation factor E , and values of HETP calculated with a constant α (1.41).

Table III

SEPARATION PARAMETERS IN DISTILLATION OF A URANIUM
HEXAFLUORIDE-BROMINE PENTAFLUORIDE MIXTURE

Run Time (hr)	Composition, Mol Fraction BrF_5		Separation Factor E^a	Number of Theoretical Plates N^b	HETP ^c (in.)
	Overhead (x_d)	Still (y_s)			
0.2	0.816	0.252	13	-	-
2.2	0.934	0.250	42	-	-
4.6	0.998	0.247	1270	21.2	9.1
9.9	1.00	0.242	18000	29.2	6.6
13.5	1.00	0.238	7120	25.4	7.6
21.2	0.993	0.0277	4730	25.2	7.7
23.9	0.995	0.00937	20500	29.4	6.5
27.0	0.992	0.00297	41200	31.6	6.1
29.8	0.993	0.001545	88300	33.8	5.7
32.3	0.993	0.001170	123000	34.9	5.5
34.2	0.988	0.001540	29000	30.6	6.3
36.2	0.954	0.000721	28700	30.5	6.3
38.2	0.974	0.001960	19000	29.3	6.6
40.2	0.905	0.002760	3460	24.0	8.0
42.5	0.0666	0.000247	290	16.8	11.4
44.8	0.0970	0.000290	370	17.6	10.9
47.8	0.0470	0.000255	193	15.6	12.3
57.0	0.00348	0.000392	8.9		
59.0	0.00188	0.000290	6.5		
61.2	0.0245	0.000202	124		
63.0	0.00521	0.000220	24		
66.0	0.00865	0.000127	68		
82.7	0.00279	0.000216	13		
86.0	0.000646	0.000278	2.3		

$$aE = \frac{x_d(1 - y_s)}{y_s(1 - x_d)}$$

^bCalculated for total reflux by $N = \log_{\alpha} E$, where $\alpha = 1.40$

^cCalculated from above N for 16.0-ft column

Figure 14

Schematic Diagram of Equipment for
Continuous Stripping Column Test

The final distillation reported was also achieved with the column operating as a steady-state stripping section. Figure 15 is a semilog plot of the bromine content versus the operating time. Tables IV and V tabulate the operating conditions and results of this run. They report a H_{tu_g} of 2.0 in. for the n-heptane-methylcyclohexane system with this 1.75-in. column.

One facility has reported the use of a bubble plate column for the distillation of UF_6 from fluorinated ore concentrates.(7) They reported tray efficiencies of 50 to 60 percent compared with 75 percent with hydrocarbons.

Table IV
COLUMN OPERATING CONDITIONS

Operation	Startup Period	Steady-state Period
Run Time	0 to 20 hr	20 to 70 hr
Column Liquid Rate (L)	30 to 35 lb/hr	33.9 lb/hr
Still-pot Product Removal Rate (W)	0 to 6 lb/hr	3.9 lb/hr
Reflux Ratio (L/W, Stripping Section)	6 to infinity	8.7
Column Pressure Drop	5 to 60 in. water	13 in. water
F_2 Addition Rate (Standard Conditions)	190 ml/min	5 to 10 ml/min
Overhead Removal Rate	0.61 lb/hr (avg)	0.025 lb/hr
Vapor Velocity	-	~0.25 ft/sec

Table V
SEPARATION RESULTS
(Reflux Ratio: $L/W = 8.7$, see Table 4)

Run Time (hr)	ppm Bromide		Bromide Separation Factor	Number of Stages	Htu (in.)
	Overhead	Still Pot			
24	1580	15	105	17.9	10.7
31	344	11	30	12.7	15.1
44	425	1.8	236	21.2	9.06
49	240	0.65	370	>23.1	8.32
57	76	0.45	170	>19.9	9.65
63	58	0.70	> 85	>17.5	11.0
69	33	0.51	> 65	>15.9	12.1

Figure 15

Bromide Content in Column Distillation of Bromine
Pentafluoride-Uranium Hexafluoride System

DESCRIPTION OF APPARATUS

Column Design

Figure 16 is a diagrammatic flowsheet of the column and associated equipment. The column was operated as a batch still, but could also be operated as an enriching or an exhausting section. The operation as an exhausting section could be accomplished by recirculating a side stream by means of a Lapp Pulsafeeder Pump which could pump vapor from the condenser to the stillpot. The vapor flow between the column and the condenser and in the recirculating stream was indicated by a thermal flowmeter. The energy input to the stillpot was measured by recording readings on a voltmeter and an ammeter in the electrical circuit supplying the heater.

Sampling was accomplished from the following points:

1. condenser (vapor);
2. recirculating stream (vapor);
3. stillpot (vapor);
4. stillpot (liquid);
5. vapor line rising from the top of the column to the condenser (vapor).

The entire apparatus was installed in an insulated aluminum jacket. The air inside the jacket was heated and recirculated by a blower. A relatively constant-temperature environment was thus maintained for the entire system. Figures 17 and 18 are photographs of the apparatus. The entire apparatus with the exception of the controlling and recording instrumentation was located in a concrete cell with 18-in. walls.

Column

The column was a 7.5-ft length of nominal $\frac{3}{8}$ -in. nickel pipe (0.493-in. ID). The column was packed with $\frac{1}{16}$ -in. nickel helices.

Figure 16
0.5-in.-I D Interhalogen Still

Figure 17

Interhalogen Still Sample Ports and Stillpot

Figure 18
Interhalogen Still Condenser Section

Cone-shaped packing retainers of $\frac{1}{64}$ -in. nickel sheet drilled with $\frac{3}{64}$ -in.-diameter holes held the packing in place and acted as liquid distributors.

Top Flange Assembly (Column)

A modified, nominal 2-in. nickel flange served as a top assembly for the column. A partially hollowed, 3-in.-diameter rod with $\frac{3}{8}$ -in. tubing taps welded to the flange allowed entry to and exit from the top of the column. Three taps were provided, two for vapor exit and liquid return to and from the condenser, and one to allow for pressure measurement. The line for liquid return was welded directly to the down-line from the condenser. A thermal flowmeter was placed in the vapor line with $\frac{3}{8}$ -in. flare couplings. This line was welded to a side tap in the bottom of the condenser.

Condenser

The condenser consisted of six, nominal $\frac{1}{8}$ -in. nickel tubes wrapped with $\frac{1}{4}$ -in. copper tubing held in place with a sprayed copper jacket. The top was flanged to allow inspection. A vent in the top flange allowed for a noncondensables exit and pressure tap. Three $\frac{3}{8}$ -in. nickel tubes were welded to the bottom of the condenser. A tubing tap from the bottom of the condenser (see Figure 16) allowed for liquid return and was welded directly to the top flange assembly of the column. A U-shaped bend in this line maintained a liquid block to the vapor rising from the column. A side tap admitted vapor rising from the top of the column. A second side tap allowed exit or admittance of vapors to or from the recirculation line.

The $\frac{1}{4}$ -in. copper tubing was connected to a constant-temperature bath located outside the cell.

Stillpot

The stillpot was constructed of 3-in., schedule 40 nickel pipe, $7\frac{1}{4}$ in. in length, welded at both ends to $\frac{1}{4}$ -in. nickel plate. The top of the pot had a $\frac{3}{8}$ -in., schedule 40 nickel pipe extending $2\frac{7}{8}$ -in. to a nominal $\frac{1}{2}$ -in. flange. A $\frac{3}{8}$ -in. nickel tubing tap was placed in the pipe midway between the stillpot and flange to allow for pressure measurement. A liquid down leg and a vapor tap were located in the top of the pot along with two thermocouple wells. These were all constructed of $\frac{3}{8}$ -in., heavy-walled nickel tubing. The bottom of the stillpot had a centrally located $\frac{1}{2}$ -in.-diameter well, $2\frac{1}{2}$ in. long, to hold a cartridge heater. A 100-w cartridge heater operated from a Variac supplied energy to the contents of the stillpot.

A copper coil of $\frac{1}{4}$ -in. tubing was wrapped around the pot, and soft soldered to it, to allow rapid cooling of the stillpot. This was connected to a laboratory water supply and drain.

Valves and Piping

The sample, recirculating, and pressure tap lines were heavy-walled, $\frac{3}{8}$ -in. nickel tubing. The valves were Hoke packless-bellows type TM440, constructed of Monel and using Teflon gaskets and a Monel bellows for sealing. Teflon gaskets were used with flare connectors for the "breakable" connections; all other connections were welded.

Sample Tubes

The sample tubes were made either of nickel or fluoroethene. They were $\frac{3}{4}$ -in. OD and fitted with $\frac{3}{4}$ -in. copper female flare connectors which sealed to nickel male flare connectors welded to the sample lines. The valving was arranged so that the tube could be evacuated, filled with helium, or opened to appropriate points in the system for sampling.

Recirculating Pump

A Lapp Pulsafeeder pump with remote head provided the driving force in the recirculation system. The pump had a capacity of 1.5 CFH. The remote head was constructed of Monel with Monel diaphragm and Teflon gaskets. The intermediate head was constructed of stainless steel. A pre-treated fluorocarbon oil was used as a hydraulic medium between the intermediate and remote heads. Figure 19 is a photograph of the pump.

Flow Measurements

The thermal flowmeters measured the small change in temperature of the vapor stream as it passed through a heated section of tubing. Figure 20 is a sketch of a low-range meter (10 to 150 cc/min) developed at the Oak Ridge National Laboratory. About one watt of electrical energy was put through the nichrome heating wire. The temperature differential indicated by the electrical signal from the thermocouple was indicated on a recording potentiometer.

Two thermal flowmeters, one placed in the recirculating line and one in the vapor line rising from the column to the condenser, metered the vapor flow in the system. The recirculating stream meter had a low range and was of the one-block design (see Figure 20) whereas the column vapor meter had the two-block design, allowing greater range for boilup measurements (see Figure 21). Their signals were recorded on a Honeywell multipoint potentiometer with an adjustable span of 0-1.0 mv to 0-50 mv. Calibration points were continuously recorded from a constant-voltage transformer (115 vac to 5 vdc). The points 0.25, 0.50, and 0.75 mv were recorded by means of the appropriate voltage-divider circuit.

Figure 21 is a drawing of a high-range (1000 to 10,000 cc/min) thermal flowmeter developed at Argonne National Laboratory.⁽⁴¹⁾

Figure 19

Lapp Pulsafeeder Pump for Recirculating Side Stream

Figure 20
Thermal Flowmeter - ORNL Mark I

Figure 21

Mark II Thermal Flowmeter and
Differential Thermocouple

Figure 22 is a sketch of this type of flowmeter and of its associated control and recording circuit. A temperature difference of approximately 50° C was maintained between the two blocks. The electrical signal developed in the thermopile between the two legs of the meter was recorded by a recording potentiometer. The vapor-line flowmeter was directly calibrated with both the organic test mixture and bromine pentafluoride.

Temperature Control

Power to the column was supplied from three Sola constant-voltage transformers, rated at 1 KVA each. Originally Glasscol heating mantles supplied power directly to the column, stillpot, and condenser. The column had five $1\frac{1}{2}$ -ft mantles rated at 230 w each. The mantles were controlled from a panel of Variacs, which allowed individual control of each heater. Adiabatic operation was achieved by adjusting the Variac setting of each heater, with the column under a vacuum, until uniform temperatures were attained. Then, with the column at operating conditions, final adjustments were made by noting the temperature difference across a layer of felted glass insulation measured with iron-constantan differential thermocouples. The signals from these were recorded on the same multipoint recording potentiometer as the output of the flowmeters. This technique, however, proved to be a difficult and time-consuming operation. For these reasons, the aluminum jacket was insulated and fin-type heaters, a blower, and duct were installed to recirculate the air from the top of the system (condenser area) to the bottom (stillpot area), where it was heated. The air temperature was controlled by a Capacitrol unit, sensing the air temperature in the box with a shielded iron-constantan thermocouple. The differential temperatures along the column were still used as the criteria for setting the ambient air temperature in the box

Figure 22

Thermal Flowmeter Circuit

The recirculating and sampling vapor lines were superheated with asbestos-insulated nichrome heating wires. These were controlled from the main panel of Variacs. Figure 23 is a photograph of the control panels. The temperatures were measured at several points along a heated section and used as criteria for setting the Variacs. A positive temperature differential of 25°C was maintained on all superheated lines. The vapor line from the column to the condenser was also superheated.

Temperature Measurement

Iron-constantan thermocouples were placed throughout the system, and their signals were transmitted to either a Honeywell 48-point indicating potentiometer or a Honeywell 12-point recording potentiometer. Fifteen thermocouples, one every 6 in., were welded to the column. Two thermocouples were located in the stillpot, one in the vapor zone and the second in the liquid region. Two were located in thermowells in the condenser, one above and one below the cooling coils. Other thermocouples were welded in the following locations:

1. thermal flowmeter bodies;
2. liquid down leg (condenser to column);
3. various vapor lines;
4. each sample assembly;
5. remote head;
6. remote head inlet and outlet;
7. pressure transmitter;
8. differential pressure transmitter;
9. chemical traps;
10. vacuum pump;

Figure 23

Control Panels for Interhalogen Still

Column Pressure Recording and Control

The pressure in the column was sensed by a Taylor pressure transmitter with a Monel bourdon tube sensing element. It pneumatically transmitted a signal to a Taylor recorder-controller located outside of the cell. A 60-w, Acrowatt plate-type heater located next to the bourdon tube inside the transmitter prevents condensation. The transmitter was located outside of the insulated jacket and was connected through the top of the assembly to the top flange of the condenser. The constant-temperature condenser coolant reservoir was filled the ethylene glycol for operation with the organics and with distilled water for operation with inorganics. Energy was supplied by two 500-w, U-shaped calrod heaters. The temperature was controlled by a Capacitrol unit activated from a resistance bridge circuit with a thermistor as the temperature-sensing element. Variable resistance Helipots in opposing legs of the bridge circuit were used to determine the setpoint and to fix the sensitivity. An alternative method of control was installed but not used. A Foxboro control valve with a flow range of 0.1 to 1 gpm was installed with a bypass on the outlet of the cooling coil of the condenser. This was operated from the Taylor Recorder-Controller which recorded the column pressure.

Measurement of Differential Pressure

Originally, two Booth-Cromer pressure transmitters of Monel construction (see Figure 18), which used a balanced diaphragm to transmit helium pressure signals to a Taylor differential transmitter, translated the differential pressure to a 3- to 15-psi air signal. This signal operated a Taylor differential-pressure recorder.

The Booth-Cromer systems proved to be unreliable for continuous operation. Constant recalibration was necessary. The Booth-Cromers were replaced with a valving system and a Taylor

differential-pressure transmitter with a bronze bellows. The pressure transmitter was installed inside the insulated jacket and wrapped with insulated nichrome heating wire. The valving system was arranged so that the transmitter could be kept evacuated except during operation. The heating wires maintained a superheated condition in the transmitter to maintain a vapor phase for the interhalogen system.

Fluorine Supply

Fluorine was supplied to the column through a bubbler system from a central fluorine manifold. The use of Fluorolube in the fluorothene tubes allowed a visual control of the flow.

Helium Supply

Helium was supplied from a two-cylinder manifold located outside the cell.

Vacuum System

A Cenco Megavac pump was filled with fluorolube and operated with $\frac{1}{2}$ -hp motor. This supplied the vacuum for the system. Chemical traps with activated alumina were installed in the line before the pump. The pump was exhausted directly to a duct of the cell air system, which was scrubbed in a caustic scrubbing system.

Safety Features

The following safety devices were provided for the operation of the column:

1. A microswitch on the 12-point temperature recorder, which was set 25° above the operating temperature of the column, operated a relay that turned off the power to the stillpot and opened a valve in the cooling water line to the stillpot. A warning light on the panel was also lit.

2. A pneumatic switch was installed on the 3- to 15-psi air signal from the column pressure transmitter to the pressure recorder. This relay operated the stillpot relays when a pressure signal greater than 60 psia was recorded.

3. An emergency switch was provided for manual operation of the relay.

4. The jacket was operated at a negative pressure with a butterfly valve in a 6-in. circular duct connected to a caustic scrub system for the cell air supply. A $\frac{1}{4}$ -in. hole normally "bled" the air supply in the jacket. A fine nylon string supported the butterfly valve. This cord was strung throughout the column so that any interhalogen leak would break the nylon and open the valve.

5. An independent air-supply mask, leather gloves, and leather jacket were supplied for the operator.

EXPERIMENTAL PROCEDURES

Construction and Leak Testing

During construction of the column, each section was leak checked with a mass spectrograph leak detector. When construction was completed, the column was packed by dropping single turns of the $\frac{1}{16}$ -in. nickel helices into the top of the column, accompanied by a continuous gentle tapping along the pipe wall. The column was packed until further tapping caused no settling of the packing. The packing retainers were spot welded in place to insure no movement. The column was then assembled and leak checked, first with helium by a mass spectrograph leak detector, and then by evacuating the system and measuring the pressure with a McLeod gauge at intervals. A final leak rate of 42 cc per week or 2.46 g of UF_6 was calculated from the pressure measurements.

Equipment Calibrations

Calibrations of the temperature- and pressure-measuring instruments were performed before operation of the column with the organic systems, before interhalogens were introduced, and at several times during operation of the system. The temperature measurements were found always to be accurate to within 0.5°C within the 0 to 100°C range (ice and boiling water calibrations).

The pressure recorder was calibrated with a manometer; both recorded the pressure within the condenser. The calibration was performed several times, and there was always less than a one percent of the 60-psia range error. The differential-pressure recorder was calibrated before and after measurements were taken, and the measurements were corrected. However, the largest correction necessary was only 0.2 in. of water.

The millivolt recorder was continuously calibrated by recording precalibrated voltages from a dc source with a variable voltage-divider system made from a resistance bridge that allowed continuous recording of 0.25, 0.50, 0.75, and 1.00 mv.

Flowmeter Calibrations

The thermal flowmeter monitoring the flow of vapor from the top of the column to the condenser was directly calibrated with air, n-heptane, methylcyclohexane, and bromine pentafluoride. The flowmeter in the recirculating line was only calibrated for one flow with the methylcyclohexane and n-heptane mixture and for one flow with the inorganics. This was all that was necessary to check the operation of the column with reflux. Figure 24 is the calibration for the high-range thermal flowmeter with both organics. The calibration was accomplished by throttling a vapor flow from the column through the flowmeter to a collection pot placed on a scale. The rate of collection of the material was determined with a stop watch by unbalancing the scale with weights of a few grams and determining the time required to collect enough material to balance the scale. The calibration of the flowmeter with the bromine pentafluoride was accomplished in the same manner. Figure 25 is the calibration with the bromine pentafluoride.

The performance of the column was calibrated with n-heptane and methylcyclohexane. Initially, pressure-drop measurements were made with great care to maintain adiabatic conditions in the column. These measurements served as criteria for subsequent adiabatic operation, since the pressure drop was very sensitive to proper operation of the column. The pressure drop versus flow rate data for both the calibration and actual distillations are shown in Figure 26. Flooding occurred at 450 lb/(hr)(sq ft) for methylcyclohexane.

Figure 24

Calibration of Flowmeter - Interhalogen Still with n-heptane and Methylcyclohexane.
Change in Millivolts from Vacuum vs. Flow Rate [lb/(hr)(sq ft)]

Figure 25

Calibration of Flowmeter with BrF_5 - Change in Millivolts from Vacuum

Figure 26

Column Pressure Drop vs. Boilup for Methycyclohexane and n-heptane

Several distillations were performed and samples collected in the fluorothene tubes. They were analyzed with an Abbé refractometer (see Figure 27). The data of Bromiley⁽²⁵⁾ were used with calibrations of known mixtures of research-grade materials. The refractometer was accurate to an N_D of within ± 0.0002 ; with the test mixture, a $\pm 0.5\%$ variation was inherent in the analysis.

An equilibrating experiment was performed to determine the required operating time. In Figure 28 the compositions of condenser and stillpot samples are plotted against time. The final compositions corresponded to a separation efficiency, expressed as an Htu_g , of 1.23 in. of packed column.

Several distillations were performed at various vapor flow rates. Results are presented in Figure 29. Because the column was designed to perform efficient distillations with inorganic systems rather than to determine separation efficiencies, the analytical data with the organic system were always in the range of nearly pure substances. In these regions of the equilibrium diagram, a small change in concentration has a large effect on efficiency. The 0.5% variation in the analytical method translates itself to an accuracy of 10% in the efficiency if consideration is given the error at both ends.

Hydrolysis and Analysis

The uranium hexafluoride was obtained from Oak Ridge National Laboratory and was certified to be natural uranium hexafluoride with less than 0.01 weight percent hydrogen fluoride impurity. A small amount of the initial vapor coming from the container was discarded. The main impurity (hydrogen fluoride) is concentrated in the vapor phase. The uranium hexafluoride was a white solid at room temperature.

Figure 27
Abbé Refractometer

Figure 28

Equilibrating Time Experiment - Refractive Index of Stillpot and Condenser vs. Time from Startup

Figure 29

H_{tu_g} vs. Boilup - Methycyclohexane and n-heptane

The bromine pentafluoride was obtained from General Chemical Company. It was necessary to purify the material by taking a middle cut consisting of less than two-thirds of the initial charge to the column. The bromine pentafluoride was a colorless liquid at room temperature.

The purities of these materials were checked by wet chemical analysis, spectrographic analysis, and by their vapor pressures. Their purities were greater than 99.5 percent. The main impurities were nickel, copper, aluminum, and iron.

In order to use conventional analytical techniques with a system of bromine pentafluoride and uranium hexafluoride, it was first necessary to prepare the sample as an aqueous solution. This was done for safety and convenience. The required hydrolysis was carried out in a closed system. The reaction vessel (a glass bottle) is shown in Figure 30.

The reactions proceeded very vigorously. Liimatainen⁽³⁾ has discussed the reactions involved.

The reaction of bromine pentafluoride with water is thought to be

Enough hydrazine was added when a bromine analysis was required to reduce the bromine by the reaction

The reaction of uranium hexafluoride with water is

The result is a yellow solution. The solubility of UO_2F_2 in water at 25°C is 67.3 weight percent.

Figure 30
Hydrolysis Bottle Assembly

Since relatively large amounts of gas were produced, the gas bottles were large compared with the sample size. A 500-ml bottle was used for samples under 10 g with 200 ml of water. Fluorothene grease was used on the stopper to improve the seal. Tape was put on the bottle for safety.

The fluorothene (monochloro-trifluoroethylene polymer) tube containing the interhalogen sample was kept in a Dewar flask with liquid nitrogen for 10 min to freeze the sample. The tube was then uncapped and placed in the hydrolysis bottle. The sample was then allowed to melt and drip into the water. After the tube was allowed to stand for at least an hour, the assembly was shaken for a few minutes. When the hydrolysis was completed, the solution was poured into a volumetric flask. The assembly and tube were rinsed with distilled water and the final volume brought to either 500 or 1000 ml.

The analyses were performed by the Analytical Laboratory of the Chemical Engineering Division. The uranium was determined by either a volumetric analysis or a fluorometric analysis, depending on the range of concentration. The volumetric determination consisted of reducing the uranium in UO_2F_2 from the +6 valence state to a mixture of +3 and +4. An aeration then converted all the uranium to the +4. The U^{+4} is then titrated with excess ceric ion; the following reaction takes place:

The excess ceric ion was back titrated with ferrous ion:

with an automatic titrator. Fluoride ion is known to interfere with the analysis; hence the HF was removed by fuming with H_2SO_4 .

The fluorometric analysis consisted of extracting the uranium with hexone from an acid-deficient solution of aluminum nitrate. An aliquot was pipetted onto a NaF-1% LiF tablet. The tablet was fused and the uranium content determined with a fluorophotometer.

The bromide analyses were done either by an amphoteric or an activation analysis. The amphoteric technique⁽²⁹⁾ consisted of a titration as follows:

A plot of the current versus milliliters of thiocyanate ion indicated the endpoint.

The activation analysis which was used for samples with low bromine concentrations (10^{-3} to 10^{-5} mg/ml) consisted of the following steps. Elemental bromine was distilled from a dichromate-sulfuric acid medium and collected in an ammoniacal solution.⁽³⁰⁾ This solution was irradiated for one bromine-80 half-life (18 min) at a nominal flux of 2×10^{13} n/(sq cm)(sec) and counted⁽³¹⁾

A sample of the demineralized water was also analyzed for bromine and less than 0.001 ppm was found.

In order to obtain estimates of the accuracy and precision of the sampling, hydrolysis, and analytical techniques, duplicate samples were taken from the column and standard solutions were prepared. The standards were made from hydrolyzed samples of the pure components. Mixtures were made to cover the range of analysis used. The standards were analyzed both before and during the period of time when the distillation runs were made. Standards with only BrF_5 or UF_6 and mixtures of the two were submitted. The results of analysis on the prepared standards are shown in Table VI.

Table VI

SUMMARY OF ANALYTICAL STANDARDS

Analyzed for	Kind of Analysis	Number of Analyses	C_{χ} Standard* Deviation as Percent of Mean	Percent** Deviation of Mean from Calculated
U	Volumetric	6	0.65%	0.35%
U	Fluorometric	6	3.0%	1.0%
Br	Amphoteric	6	3.7%	1.5%
Br	Activation	6	21.0%	7.1%

$$\text{*Standard deviation, } s = \sqrt{\frac{\sum_{i=1}^N (x - \bar{x})^2}{N - 1}}$$

and

$$C_{\chi} = \frac{s}{\bar{x}} (100)$$

**Calculated value determined from weight of initial sample and dilution factors.

The results showed that

1. The sampling technique was good since duplicate samples taken in each range of analysis showed no significant variations.
2. The bromide did not interfere with the uranium analysis and, conversely, the uranium did not interfere with the bromide analysis.
3. There was no significant addition of bromine to the samples through detection with demineralized water.

The uranium analyses were made for samples with low UF_6 concentrations and bromide analyses were made for samples with low BrF_5 concentrations to avoid the uncertainty inherent in subtracting

two large numbers to obtain a lesser number. Both the bromide and uranium were analyzed for in the middle composition range and allowed a further check of accuracy when compared with the total weight of the sample.

Operation

The operating techniques which were necessary for the inorganics were developed with the organic system rather than using simpler possible methods, because of their less hazardous nature. The following descriptions apply to both systems.

Charging Material

The feed materials were boiled from the original containers into transfer pots, made of nickel, which were fitted with valves and flare tubing fittings. The pots were weighed. Continuous weighing of the collection pots was possible by the use of flexible nickel tubing which connected the column to the pot. The column was first evacuated and then filled with helium or fluorine, depending on which system was being used. The desired amount of material was charged to the column by heating the transfer pot. The entire system was brought to operating temperatures, and cooling water was supplied to the stillpot.

Between each inorganic distillation, fluorine was bubbled through the system from the line extending to the bottom of the stillpot to inhibit the formation of bromine trifluoride.

Distillation

The pressure in the column was brought to the vapor pressure of the feed materials by evacuating the gas (He or F₂) from the system, through the cold traps and chemical traps, with the vacuum system. The still could be readily evacuated to a pressure of 10 μ as indicated on a McLeod gauge.

The cooling water to the stillpot was turned off and the coil cleared with high-pressure air. The power to the cartridge heater in the stillpot was turned on. At this point, the column was operated with the recirculating line open, thereby allowing a direct path (not through the pump) from the stillpot to the condenser. Preflooding of the packing was accomplished in this manner.

The temperature of the recirculated air in the jacket was set so that the various differential temperatures measured across the column insulation, stillpot, and condenser were at a minimum. The maximum deflection was 0.02 mv. This corresponded to a temperature drop across the insulation of less than 0.5°C. The maximum estimated heat loss or gain from the column, based on a uniform temperature differential in the same direction, was less than 0.1 lb/(hr)(sq ft) in terms of boilup of bromine pentafluoride. This estimate is conservative since the temperature gradients were not all in the same direction. The differential temperatures, pressure drop, and agreement between the calculated boilup from the stillpot and measured vapor flow to the condenser were very sensitive. When any of these were adjusted properly, the others would agree. This made the operation of the column fairly simple. The only difficulty encountered was the occasional cooling of the recirculating line or a pressure tap due to an electrical failure, which would in effect add an additional condenser to the system. With these lines superheated a few degrees above the box temperature, the column operated properly.

When the column was operating at the proper pressure (45 psia for inorganics and 15 psia for organics), the recirculating line was closed and the distillation begun. Minor adjustments were necessary since a temperature differential appeared along the column as the separation commenced.

Sampling

After the column was operated for a sufficient length of time (48 hr for organics and 24 hr for the inorganics), the condenser and stillpot were sampled. This was accomplished in the following manner.

1. The sample tubes were placed on the column and evacuated. A leak check was made at this point by isolating the sample tubes and the pressure gauge from the rest of the system and vacuum. A pressure rise indicated a leak.

2. With the tubes leak tight, a small amount of interhalogen was used to insure a prefluorination. (Ignition of the tubes sometimes occurred.) The tube and sample line, which were separated from the system and other sample tubes by valves, were evacuated. The sample was then taken by filling the sample line from the system while it was isolated from the sample tube by a closed valve. The sample tube was opened to the line after it had in turn been isolated from the system. This limited the size of the sample and insured against a continuing leak from the system if the tube failed.

3. A Dewar flask containing liquid nitrogen was placed around the sample tube and left for 10 min to insure freezing of the sample. Helium was then allowed to fill the line and tube. Then the tube was taken off and capped.

4. The appearance of the sample was noted. The samples were then analyzed or hydrolyzed depending on the system being used.

EXPERIMENTAL RESULTS

Pressure Drop

The pressure drop was determined as a function of the vapor flow rate for both uranium hexafluoride and bromine pentafluoride. The column was operated at total reflux for these measurements. The pressure drop data for uranium hexafluoride is presented in Figure 31. The flooding point was determined as 2680 lb/(hr)(sq ft). Above this flow, the pressure drop across the column would slowly rise, suddenly decrease, and then rise again.

The pressure-drop data for bromine pentafluoride are shown in Figure 32. Above a flow of 2200 lb/(hr)(sq ft) the column flooded.

Equilibrating Time

In order to determine the necessary operating time, an experiment to find the equilibrating time was conducted. The compositions of the stillpot and condenser were determined at various intervals over a 48-hr period. Figure 33 shows the results of this experiment. The equilibrating time was determined to be approximately 22 hours with the column operating at a boilup of 760 lb/(hr)(sq ft). The data are tabulated in Table VII.

Column Efficiency

The separating efficiency of the column was determined as a function of the vapor flow rate and stillpot concentration for batch operation ($L/V = 1$). The efficiency was calculated as Htu_g from the expressions

$$Ntu_g = \int_{y_1}^{y_2} \frac{dy}{y^* - y} \quad (3)$$

and

Figure 31

Pressure Drop vs. Boilup ($L/V = 1$) for UF_6 in a 0.5-in. Column
Packed with $\frac{1}{16}$ -in. Nickel Helices

Figure 32

Pressure Drop vs. Boilup ($L/V = 1$) for BrF_5 in an 0.5-in. Column
Packed with $\frac{1}{16}$ -in. Nickel Helices

Figure 33

Equilibrating Time Experiment - Mol Fraction BrF_5 vs. Time -
 $V = 760 \text{ lb}/(\text{hr})(\text{sq ft})$

$$Htug = h/Ntug \quad , \quad (4)$$

where

$Ntug$ = number of transfer units (based on vapor)

$Htug$ = height of transfer units (based on vapor)

h = height of column (90 in.).

The calculation was done graphically. The method of calculation, presented in the Appendix, resulted in a graph of $Ntug$ versus composition with $Ntug$ equal to zero at 50 mole percent. To calculate the total $Ntug$, the individual values, which were taken from the graph for each of the two compositions (stillpot and condenser), were added. Then $Htug$ was calculated from equation 2. The results of the experiments are plotted in Figure 34. A sample calculation is presented on page 71.

Table VII

EQUILIBRIUM TIME DATA*

Time, hr	Stillpot Mol Fraction BrF_5	Condenser Mol Fraction BrF_5
0	0.792	0.792
4	0.786	0.9899
8	0.781	0.9983
8	-	0.9985
18	0.767	0.9997
22	0.760	0.9986
26	-	0.9997
30	0.762	0.9998
34	0.758	0.9998
44	0.760	0.9997
48	0.759	-
48	0.759	0.9996

* $Htug = 1.32$ in.

Figure 34

Separation Efficiency for $\text{UF}_6\text{-BrF}_5$ in a 0.5-in. Column
 Packed with $\frac{1}{16}$ -in. Helices - $L/V = 1$

For one distillation, a sample from the condenser was taken that weighed 3.5706 g. It was hydrolyzed and diluted to a final volume of 500 ml. This solution was analyzed for uranium and found to contain 0.0042 mg/ml.

The total amount of uranium was calculated as follows:

$$\frac{0.0042 \text{ mg/ml U} \times 500 \text{ ml}}{1000 \text{ mg/g}} = 0.0021 \text{ g U} .$$

The moles of UF_6 and BrF_5 were then calculated.

$$\frac{0.0021 \text{ g}}{238.07} = 0.0000088 \text{ mole } \text{UF}_6$$

$$0.0000088 \text{ mole } \text{UF}_6 \times 352.07 = 0.0031 \text{ g } \text{UF}_6$$

$$3.5706 \text{ g Sample}$$

$$0.0031 \text{ g } \text{UF}_6$$

$$3.5675 \text{ g } \text{BrF}_5$$

$$\frac{3.5675}{174.92} = 0.0204 \text{ mole } \text{BrF}_5$$

The total moles of sample was then,

$$0.0204 \text{ mole } \text{BrF}_5$$

$$0.000009 \text{ mole } \text{UF}_6$$

$$0.0204 \text{ mole of sample.}$$

The mole fraction of UF_6 was

$$\frac{0.0000088}{0.0204} = 0.00043$$

and the mole fraction of BrF_5 was

$$1 - 0.00043 = 0.99957 .$$

The stillpot sample was similarly determined to have a mole fraction of 0.200 for BrF_5 from the bromide analysis. The Ntug was

then determined (from Figures 40 and 41) as 70.4. The H_{tug} was calculated as

$$90.0/70.4 = 1.28 \text{ in.}$$

In addition to the runs shown in Figure 34, several runs were made at low stillpot concentrations in which very high and inconsistent H_{tug} 's were encountered. The data from these runs are presented in Table VIII. The system was limited in that the concentration of BrF_5 seemed to be relatively constant. In Table IX the separation data, which are presented graphically in Figure 34, are tabulated.

Table VIII

DISTILLATION OF UF_6 AND BrF_5 AT TOTAL REFLUX

Flow, lb/(hr)(sq ft)	Composition		H_{tug} , (in.)
	Condenser Mol Fraction BrF_5	Stillpot Mol Fraction BrF_5	
760	0.900	0.00015	3.3
285	0.760	0.00041	4.7
1100	0.575	0.00026	5.4
490	0.550	0.00072	6.5
1710	0.309	0.00086	8.2
1710	0.286	0.00012	5.9
285	0.120	0.00019	7.3

Table IX

DISTILLATION OF UF_6 AND BrF_5 AT TOTAL REFLUX

Run No.	Flow, lb/(hr)(sq ft)	Composition Mol Fraction BrF_5		H_{tug} , (in.)
		Condenser	Stillpot	
1	760	0.9999	0.951	1.31
2	1710	0.9997	0.770	1.32
3*	760	0.9996	0.759	1.32
4	285	0.9988	0.750	1.72
5	1460	0.9994	0.230	1.35
6	1100	0.9992	0.168	1.39
7	760	0.9996	0.200	1.28
8	490	0.9994	0.191	1.33
9	285	0.9924	0.230	2.64

*Equilibrium Distillation.

DISCUSSION OF RESULTS

The flooding rates observed with bromine pentafluoride, uranium hexafluoride, and methylcyclohexane are compared with the published data of other investigators in Figure 35. The function

$$\frac{G}{\Phi}(\nu)^{1/2} \left(\frac{62.3}{\rho_L} \right)^{1/2}$$

is plotted against the function

$$\frac{L}{\frac{G}{\Phi} \left(\frac{62.3}{\rho_L} \right)^{1/2}}$$

on a log-log scale. The data of McGill, Page, and Sarchet calculated by Long⁽¹⁰⁾ (presented in Figure 8) were included on the figure for comparison. The flooding rates are consistent with those shown in Figure 35, and they are also mutually consistent.

In order to compare the pressure-drop measurements with those from prior investigations, the exponent in the equation

$$\overline{\Delta P} = kG^n \tag{5}$$

was determined graphically. The graph is shown in Figure 36. The values of the exponent n were found to be 1.74 for methylcyclohexane, 1.78 for uranium hexafluoride, and 2.30 for bromine pentafluoride. Reed and Fenske⁽²²⁾ reported that, for several organic materials in columns packed with single-turn metal helices, the experimental value of the exponent n varied from about 1.7 to 2.2. The exponent for bromine pentafluoride was found to be only slightly higher than this range. The other values determined were in good agreement with those reported. The deviation of the bromine pentafluoride data is reasonable considering the difficulties involved in measuring pressure drop with this corrosive medium. The sensing element could be left in contact with the system for only very limited periods of time.

Figure 35

Comparison of Flooding Rates in Packed Columns

FIGURE 36
PRESSURE DROP VERSUS VAPOR FLOW TO DETERMINE
THE EXPONENT IN THE EQUATION- $\Delta P = kG^n$

The data for equilibrium time are difficult to compare with those in the literature, since very little data are reported as such and only rough estimates of the order of magnitude of the time required for a column to come to equilibrium are available. Coulson⁽³³⁾ has reported a method of making the estimate, which requires column holdup information which was not measured with this system. The equilibrium-time experiments, however, allowed greater confidence in the results, since the time required to reach equilibrium has been determined and the successive samples allowed a measure of the reproducibility of the sampling techniques and analyses.

Correlations of separation efficiency are limited to a few empirical equations that only include a small number of the variables involved in distillation. The variations in equipment and systems make these difficult to use. In order to compare the data with other investigators, a comparison of the ratios of the reported separation efficiencies as H_{TUG} or HETP for organic and inorganic systems is shown in Table X. There is obviously a large discrepancy in the data reported. Several reasons for these differences are apparent. All of the previous investigators have calculated their separation efficiencies assuming a constant α of 1.41. Figure 37 is a plot of the relative volatility, α , as a function of composition for the uranium hexafluoride-bromine pentafluoride system from the data of Liimatainen.⁽³⁾ In order to compare the calculation of separation efficiencies for packed columns, the N_{TUG} for various hypothetical separations have been calculated from the equilibrium data of Liimatainen⁽³⁾ and by assuming an α of 1.41. The results of these calculations are presented in Table XI. It is apparent from these results that for separations resulting in a condenser product rich in bromine pentafluoride, the resulting H_{TUG} calculated by assuming an α of 1.41 would be about twice as large as that calculated from the measured equilibrium data.

Table X
COMPARISON OF SEPARATIONS OF ORGANIC
AND INORGANIC MATERIALS

Systems Distilled	HETP, Htug or Tray Eff.	Ratio	Reference
<u>Literature</u>			
1. UF ₆ -BrF ₅ n-heptane- methylcyclohexane	4.5 to 6.3 3.2	1.4 to 2.0	(11)
2. UF ₆ -C-816 n-heptane- methylcyclohexane	14.4 6.4 to 14.4	2.2 to 1.0	(15,13,22)
3. UF ₆ -BrF ₅ n-heptane- methylcyclohexane	5.5 to 12.3 2.0	2.8 to 6.2	(6)
4. UF ₆ -various inorganic fluorides Hydrocarbons	50 to 60% 75%	1.3 to 1.5	(7)
<u>Measured</u>			
5. UF ₆ -BrF ₅ n-heptane methylcyclohexane	1.3 1.2	1.1	
6* UF ₆ -BrF ₅ n-heptane- methylcyclohexane	3.3 to 8.2 1.2	2.8 to 6.8	

* Data with stillpot concentrations less than 0.0008 mole fraction BrF₅.

Figure 37

Relative Volatility for UF_6 - BrF_5 Vapor-Liquid Equilibrium Data
of Liimatainen⁽³⁾

Table XI

COMPARISON OF Nt_{ug} CALCULATED FROM THE x, y DATA OF LIIMATAINEN⁽³⁾ AND THE ASSUMPTION OF A CONSTANT α OF 1.41 FOR UF_6 - BrF_5

Separation		Nt_{ug}^* $\alpha = 1.41$	Nt_{ug} x, y Plot	Ratio
Stillpot Mole Frac. BrF_5 y_1	Condenser Mole Frac. BrF_5 y_2			
0.80	0.9999	37.8	79.7	2.1
0.80	0.9990	26.4	53.0	2.0
0.10	0.9999	50.0	95.9	1.9
0.10	0.80	12.4	15.2	1.2
0.001	0.80	24.2	18.4	0.8
0.0001	0.80	29.8	23.6	0.8
0.0001	0.9999	56.2	103.3	1.8

*Calculated from

$$Nt_{ug} = \frac{1}{\alpha - 1} \ln \frac{y_2(1 - y_1)}{y_1(1 - y_2)} + \ln \frac{1 - y_1}{1 - y_2}$$

These results explain some of the discrepancies between those of previous investigators and of this study. However, separations performed when stillpot products had very low concentrations of bromine pentafluoride should have separation efficiencies of about the same magnitude by either method of calculation. By comparing the results of the several investigators and those reported in this study, it is apparent that the reported separations are very poor and inconsistent for those yielding the stillpot products with low bromine pentafluoride. Most of the work has been done in this region, since the desired product of the separations processes has been a pure uranium hexafluoride.

These discrepancies can be explained by taking note of the measures which were necessary to obtain clear-appearing samples. Both Liimatainen⁽³⁾ and Mecham⁽⁶⁾ reported that it was necessary to keep fluorine in contact with the system to inhibit the accumulation of bromine and bromine trifluoride from the corrosion reactions taking place. It was necessary in this study to purge the system with fluorine between each distillation.

A calculation of the total corrosion occurring in the column from the data of Seefeldt⁽⁴⁰⁾ for a 24-hr period would give a buildup of bromine trifluoride equivalent to a mole fraction of 0.0004. This calculation was based on a corrosion rate of 10 mils/year and a column and packing surface area of 9,960 sq cm. This compares extremely well with the amounts found in stillpot samples with low bromine content (reported in Table V). They range from 0.0001 to 0.0008 mole fraction.

Finally, the data shown in Table IV report condenser concentrations as great as 0.9999 mole fraction bromine pentafluoride. The concentrations were below the reported⁽⁵⁾ azeotrope at 0.90 mole fraction bromine pentafluoride. There was no azeotrope found in these experiments.

CONCLUSIONS

From these experiments it is concluded that:

1. The flooding rate for uranium hexafluoride in a 0.5-in.-diameter column packed with $\frac{1}{16}$ -in. nickel helices is 2680 lb/(hr)(sq ft).
2. The flooding rate for bromine pentafluoride in the same column is 2200 lb/(hr)(sq ft).
3. The time required for the uranium hexafluoride-bromine pentafluoride system to come to equilibrium in the same column at a flow rate of 760 lb/(hr)(sq ft) is 22 hr.
4. There is no azeotrope in the uranium hexafluoride-bromine pentafluoride system below a mole fraction of 0.9999 for bromine pentafluoride.
5. The H_{tu_g} for this column is 1.3 in. above a flow of 285 lb/(hr)(sq ft) and below flooding conditions.
6. The ratio of efficiencies for the inorganic system uranium hexafluoride and bromine pentafluoride to the organic system n-heptane-methylcyclohexane is 1.1.
7. Separations which would give pure uranium hexafluoride products (concentrations below about 0.001 mole fraction bromine pentafluoride) are complicated by the formation of bromine trifluoride through corrosion reactions. The addition of fluorine inhibits this formation.

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APPENDIX I

CALCULATION OF H_{tu_g}

A. Organic Reference - n-heptane, methlycyclohexane

1. Analysis of Samples

The organic samples were analyzed for composition with an Abbé refractometer. The data of Bromiley and Quiggle⁽²⁸⁾ were used along with data taken from mixtures of known composition made from the materials used in this study. Both sets of data are plotted in Figure 38. This graph was used to determine the composition of the samples.

2. Calculation of Batch-distillation Efficiencies

The equation

$$N_{tu_g} = \int_{y_1}^{y_2} \frac{dy}{y^* - y} \quad (3)$$

was integrated graphically with the use of the equilibrium data from Ju Chin Chu.⁽³²⁾ Figure 39 is the xy diagram for this system. Figure 40 is the graphical solution of equation 3. The quantity $\frac{1}{y^* - y}$ is plotted versus the mole fraction of n-heptane in the vapor.

Figure 41 is a plot of the value of N_{tu_g} versus the composition with the 0.50 mole fraction at a reference equal to zero. In order to calculate the total value of N_{tu_g} , the values from this reference to the composition of the still pot and condenser samples were added or subtracted depending on whether the samples had compositions on either side of the reference or on the same side.

The value of H_{tu_g} was then calculated from

$$H_{tu_g} = \frac{90}{N_{tu_g}} \quad .$$

Figure 38

Refractive Index of Mixtures of n-heptane and Methylcyclohexane

Figure 39

Vapor Liquid Equilibrium for n-heptane and Methylcyclohexane

Figure 40

Calculation of Ntu_g for n-heptane-methylcyclohexane Batch Distillation

Figure 41

N_{tug} vs. Composition for n-heptane-methylcyclohexane
Batch Distillation

B. Inorganic System - UF₆ and BrF₅

1. Calculation of the Ntu_g for Batch Distillation

The data of Liimatainen⁽³⁾ for the 3-atm isobar were used to calculate the Ntu_g graphically. Figure 6 is the x, y diagram for this system. Figure 42 was used to graphically integrate equation 1.

It is a plot of $\frac{1}{y^* - y}$ versus y for the bromine pentafluoride-uranium

hexafluoride system. Figure 43 is the resulting plot of Ntu_g as a function of the mole fraction of bromine pentafluoride in the sample with a zero reference at 50 mole percent.

In the composition regions below 0.01 mole percent and above 0.99 mole percent, the additional Ntu_g was calculated by assuming a constant value of α by means of the relation $y = \alpha x$. The values of α were taken from the data of Liimatainen.⁽³⁾

Figure 37 is a plot of the value of α for the 3-atm isobar as a function of composition. Figures 44 and 45 are semilog plots of composition versus Ntu_g in these dilute ranges. The Ntu_g is referenced as zero at 0.01 and 0.99 mole percent, so that this value of Ntu_g only has to be added to that already calculated for the particular separation performed.

Figure 42

Calculation of Nt_{ug} for UF_6 - BrF_5 Batch Distillation

Figure 43

N_{tug} vs. Composition for UF_6 - BrF_5 Batch Distillation

Figure 44

$Ntug$ vs. Composition at BrF_5 Rich End for
Batch Distillation of UF_6 and BrF_5

Figure 45

Ntu_g vs. Composition at UF_6 Rich End for
Batch Distillation of UF_6 and BrF_5

APPENDIX II

SOME PHYSICAL PROPERTIES OF UF₆ AND BrF₅

<u>UF₆</u>	<u>Reference</u>
Molecular Weight	352.07 g/g-mol
Triple Point	64.02 ± 0.05°C, 1137 mm Hg (34)
Sublimation Point	56.4 ± 0.2°C (35)
Appearance	
Gas: colorless	
Liquid: colorless	
Solid: white	(35)
Density, g/ml	
Solid, ρ = 4.92 (64°C)	
Liquid, ρ = 3.674 (64°C)	(35)
Vapor Pressure, mm Hg	
Solid (0 to 64°C)	
$\log_{10} p = 6.38363 + 0.0075377t - \frac{942.76}{(t + 183.416)}$	(34)
Liquid (64°C to t _c)	
$\log_{10} p = 6.93718 - \frac{1091.537}{(t + 217.32)}$	(35)
Critical Properties	
t _c = 230.0 ± 0.2°C	
P _c = 45.5 ± 0.5 atm	(34)
ΔH (Vaporization), kcal/g-mol	
ΔH _v = 6.82 (64.02°C)	
Viscosity, centipoise	
Gas, μ = (1.67 + 0.0044t)(10 ⁻²)(t = °K)	
Liquid, μ = 0.663 (75°)	
Thermal Conductivity, cal/(cm)(sec)(°C)	
Gas, k = (1.459 + 0.00614t)(10 ⁻⁵)	
Liquid, k = 3.3 × 10 ⁻⁴ ± 3% (72°C)	

<u>UF₆</u>	<u>Reference</u>	
Surface Tension, dynes/cm		
	Temperature (°C)	Surface Tension
	70	16.8 ± 0.3
	80	15.6 ± 0.3
	90	14.3 ± 0.3
	100	13.1 ± 0.3
<u>BrF₅</u>		
Molecular Weight	174.92 g/g-mol	
Boiling Point	42.2°C	(36)
Melting Point	-61.3°C	(37)
Appearance		
Gas:	colorless	
Liquid:	colorless	
Solid:	white	
Density, g/ml		
Solid, ρ =	3.09 (-61°C)	
Liquid, ρ =	2.4604 (25°C)	(38)
Vapor Pressure, mm Hg		
Liquid (-60 to 25°C)		
$\log_{10} p = 8.0716 - \frac{895}{(t+273)}$		
Liquid (25 to 146°)		
$\log_{10} p = 6.4545 + 0.001101t = \frac{895}{(t+206)}$		
Critical Properties		
$t_c = 213 \pm 20^\circ\text{C}$		
$P_c = 47 \pm 10 \text{ atm}$		
ΔH (Vaporization)	6.388 kcal/g-mole (75°C)	(39)

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