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VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM BROMINE
PENTAFLUORIDE-URANIUM HEXAFLUORIDE

by

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NOMENCLATURE

a	= activity
ΔE	= energy of vaporization referred to zero pressure = calories/gram mole
e	= potential=volts
f	= fugacity
ΔH	= enthalpy change = calories/gram mole
$\bar{H}_1$	= partial molar enthalpy of component 1 in solution = cal./mole
H_1^0	= enthalpy of pure component at same temperature and pressure = cal./mole
M	= molecular weight = grams/gram mole
N	= gram moles
P	= total pressure = mm Hg
P_1^0	= vapor pressure of bromine pentafluoride = mm Hg
P_2^0	= vapor pressure of uranium hexafluoride = mm Hg
Pc	= critical pressure = mm Hg
R	= gas constant = 62.361 (liters)(mm Hg)/(°K)(gram mole)
r	= resistance = ohms
T	= absolute temperature = °K = t + 273.16
t	= temperature = °C
T_c	= critical temperature = °K
V	= volume of vapor bulb = liters
W	= weight of material in vapor sample bulb = grams
V_1	= liters of liquid BrF ₅ /gram mole
V_2	= liters of liquid UF ₆ /gram mole
X	= mole fraction bromine pentafluoride in liquid phase
Y	= mole fraction bromine pentafluoride in vapor phase

(continued)

Z = compressibility factor defined by $Z = \frac{MPV}{WRT}$

γ = fugacity coefficient = $\frac{f}{p}$

γ_1 = activity coefficient of bromine pentafluoride defined by

$$\gamma_1 = \frac{PY}{P_1^0 X} \text{ with } \lim \gamma_1 \rightarrow 1 \text{ as } x \rightarrow 1$$

γ_2 = activity coefficient of uranium hexafluoride defined by

$$\gamma_2 = \frac{P(1-Y)}{P_2^0(1-X)} \text{ with } \lim \gamma_2 \rightarrow 1 \text{ as } x \rightarrow 0$$

ϕ = volume fraction of component in liquid phase

α = relative volatility = $\frac{\frac{Y}{X}}{\frac{1-Y}{1-X}}$

μ = chemical potential

ρ = density of liquid = grams/ml

σ = standard deviation

$\psi(x)$ = a function of x

θ = time = minutes

Subscripts

1 refers to bromine pentafluoride

2 refers to uranium hexafluoride

c refers to critical point

i refers to ith component

L refers to liquid

s refers to solid

v refers to vapor

Operators

d = differential

Δ = finite difference

(continued)

Superscripts

^o refers to standard state of pure component at the temperature and pressure of the solution.

Constants

A, B in Van Laar equation

C in activity coefficient equation

K in vapor density equation

m = slope in generalized compressibility plot

CHAPTER I INTRODUCTION

Importance of Problem

The purpose of this investigation was to determine the vapor-liquid equilibria in the binary system consisting of bromine pentafluoride and uranium hexafluoride. Data on vapor-liquid equilibria have both a fundamental and applied significance. From the standpoint of physical chemistry, the data give insight into molecular interactions in the solution as evidenced by the degree of non-ideal behavior. From the chemical engineering point of view, the data give rise to the x-y curves which form the basis for determining the number of theoretical plates or transfer units in the design of a distillation column to separate the components.

The class of compounds known as interhalogens, of which bromine pentafluoride is a member, has only quite recently begun to be investigated in a systematic manner. Likewise the study of the physical and chemical properties of uranium hexafluoride received impetus when its potential was realized in the production of fissionable material.

The bromine pentafluoride-uranium hexafluoride system is one which is of importance in the field of the chemical processing of nuclear reactor fuels. The relative merits of distillation of halogen systems for the recovery and purification of nuclear fuels are discussed by Lawroski¹.

The Fluoride Volatility Process for natural uranium is based on the following steps²:

¹Superscripts indicate references which are summarized in the bibliography.

Dissolution of uranium metal in liquid bromine trifluoride

Product Fluorides

Fluorination

Distillation

recovery and purification of UF_6 .

The uranium hexafluoride can then be reduced to metallic uranium via the intermediate uranium tetrafluoride. An alternative process for enriched reactor fuels² which cannot be dissolved in bromine trifluoride involves the following:

Dissolution of uranium-zirconium reactor fuel in a molten salt such as $\text{NaF} \cdot \text{ZrF}_4$ at 600°C

Fluorination and Collection of UF_6

followed by

Distillation

recovery and purification of uranium hexafluoride from fission product fluorides or from bromine pentafluoride

A somewhat similar process now being studied for enriched reactor fuels 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 of the bromine pentafluoride-uranium hexafluoride system if bromine pentafluoride were used for the fluorinating agent rather than elemental fluorine.

Finally, the compound uranium hexafluoride is particularly important in the field of uranium ore processing since it can be put into the gaseous diffusion cascades for separation of the U-238 and U-235 isotopes.

Review of Literature

When this study of uranium hexafluoride and bromine pentafluoride was started, no vapor-liquid equilibrium data on the system was available in the published literature. However, considerable experience had been accumulated on the separation of the two components by distillation. It is instructive to examine the results of the fractionations of the bromine pentafluoride-uranium hexafluoride system to obtain information on the general characteristics of the equilibrium x-y diagram. For this purpose, the pertinent published results are summarized herein.

It was established by Mecham, Liimatainen, and Kessie at the Argonne National Laboratory that a charge of uranium hexafluoride and bromine pentafluoride could be separated giving overhead fractions which were substantially pure bromine pentafluoride³. Also, after a distillation an essentially pure uranium hexafluoride fraction was recovered from the still pot.

In the absence of vapor-liquid equilibrium data, it was necessary to assume that the binary system behaved ideally in computing the per-

formance of the distillation column; under the conditions of operation, this corresponded to a relative volatility of 1.41. The data obtained from some of the fractionations are shown in Tables 1 and 2. It is apparent from these distillations, that the uranium hexafluoride-bromine pentafluoride system probably does not have an azeotrope since fractions of either component were obtained with less than one per cent of the other present. It is particularly worth noting that on four separate runs, in two different columns, many consistent overhead fractions were obtained which showed from 0.5 to 5 mole per cent uranium hexafluoride.

Data obtained by Mertes and Liimatainen⁴ on a smaller fractionating column operating under essentially the same conditions as those given in Table 1 give the results shown in Table 3.

Additional pilot plant data on fractionation taken by Mecham et al. with emphasis on the very low bromine pentafluoride concentration range, are shown in Figures 1 and 2. These data were obtained in the same pilot plant distillation column described in Table 1. The data show that uranium hexafluoride can be purified by distillation to the extent of having only a few parts per million of bromine pentafluoride present in the final product. The starting material for this run consisted of 60 lbs. of uranium hexafluoride and 10 lbs. of bromine pentafluoride. The fractionation was performed at a pressure of 3 atmospheres.

In the distillation of these bromine pentafluoride-uranium hexafluoride mixtures, it was found necessary to bubble in a slow stream of fluorine continuously to keep all of the bromine as bromine pentafluoride. Otherwise, it was found that corrosion reactions produced lower fluorides and free bromine; evidently the refluxing action over

Table 1. Batch Distillation of Uranium Hexafluoride-Bromine
Pentafluoride Mixture in a Pilot Plant Column⁵

Description of Test

Charge to Still Pot

67.3 lbs. total
22.5 mole per cent UF_6
77.5 mole per cent BrF_5

Operating Conditions

Pressure: 50 psia
Still Pot Temperature: 90°C
Column Top Temperature: 80°C
Reflux ratio: $V/D = 27/1$
Four-hour start-up period before takeoff

Column Data

Height of packed section: 16 ft
Inside diameter: 1.75 inches
Packing: Helipak: 3019

Data Obtained

Separation Results During Batch Distillation

Composition - Mole Per Cent Bromine Pentafluoride

<u>Still Pot</u>	<u>Overhead</u>
75.2	98.1
54.3	97.0
44.8	95.2

Table 2. Batch Distillation of a Uranium Hexafluoride-Bromine Pentafluoride Mixture³

<u>Run Time, hours</u>	<u>Composition, mole per cent bromine pentafluoride</u>	
	<u>Still Pot</u>	<u>Overhead</u>
0.2	25.2	81.6
2.2	25.0	93.4
4.6	24.7	99.8
9.9	24.2	~100.0
13.5	23.8	~100.0
21.2	2.8	99.3
23.9	0.94	99.5
27.0	0.30	99.2
29.8	0.15	99.3
32.3	0.12	99.3
34.2	0.15	98.8
36.2	0.07	95.4
38.2	0.20	97.4
40.2	0.28	90.5
42.5	0.02	6.7
44.8	0.03	9.7
47.8	0.03	4.7

Table 3. Batch Distillation of a Uranium Hexafluoride-Bromine
Pentafluoride Mixture in a Laboratory Column⁴

Column Data

Height of packed section: 94 inches
Inside diameter: 1/2 inch
Packing: 1/8 inch nickel helices

Separation Results

Composition - mole per cent Bromine Pentafluoride

<u>Still Pot</u>	<u>Overhead</u>
42.4	94.6
33.8	98.3

Figure 1
Separation of Bromine Pentafluoride-Uranium Hexafluoride Binary
in a Packed Column³

Figure 2
Bromine Pentafluoride-Uranium Hexafluoride Distillation⁶

the high surface area packing in the column promoted removal of the protective nickel fluoride film thus continually exposing small amounts of fresh nickel.

The most recent run performed by Kessie, et al.⁷ simulated the operation of continuous distillation column as contrasted to the previous batch-fractionations.

The column was set up to operate as a steady state stripping section. A diaphragm pump was used to circulate still pot product vapor through a sampler system and back into the column at the feed point at the top of the packed section. Vapor from just above the feed point was also circulated through a sampler system and back into the column at the feed point. The initial column charge consisted of 49.4 lb uranium hexafluoride and 5.0 lb bromine pentafluoride. Fluorine was added continuously during the run.

In the start-up period, material was collected overhead fairly rapidly to remove the bulk of the bromine pentafluoride. In the steady-state part of the run, very little material was taken overhead, and the column operated at finite reflux by re-cycling overhead and bottom vapor as described above. The column was operated at 45 psia throughout the run. The data are shown in Figure 3; the results show that the bromine impurity in the uranium hexafluoride product was less than 1 ppm.

Midway during the experimental part of this investigation on vapor liquid equilibria, two publications by Ellis, et al. from Harwell, England appeared in the literature^{8,9}. The interesting point in the papers of Ellis and co-workers is that they reported an azeotrope in the uranium hexafluoride-bromine pentafluoride system at about 90 mole

Figure 3

Bromide Content in Column Run C-8
Bromine Pentafluoride - Uranium Hexafluoride System⁷

per cent bromine pentafluoride. Also, Ellis, et al. reported values for the vapor pressure of bromine pentafluoride which were 6 to 14 per cent higher than the values obtained by R. Long¹⁰. A detailed comparison of vapor pressures is given in Table 4. Ellis found that his vapor pressure values for bromine pentafluoride agreed with the values computed from the equation obtained by Ruff¹¹. Ruff's data were obtained for pressures below one atmosphere. The equilibrium data published by Ellis and his co-workers is shown in Figure 4. Long's data⁸ agreed with Ruff's in the vicinity of one atmosphere.

Ellis, et al. also reported the results of a fractionation of a uranium hexafluoride-bromine pentafluoride mixture in a packed column⁹. The results were obtained in a packed distillation column one inch in diameter by five feet in length. One charge of 2300 grams of uranium hexafluoride and 90 grams of bromine pentafluoride was put into the boiler. A one-hour equilibrium period was allowed at 41 psig. Overhead vapor samples showed 0.9 mole fraction bromine pentafluoride. By changing the column pressure, the composition of the overhead was observed to change; these changes are shown in Figure 5 and were attributed to a shift in the azeotrope. It is worth mentioning that it is entirely possible that the degree of separation from an initial charge of 7.3 mole per cent bromine pentafluoride to an overhead of 90 per cent bromine pentafluoride was limited not by the presence of an azeotrope but rather by the number of plates in the five foot column.

The apparatus used by Ellis and Johnson⁸ in their determination of the phase equilibria, consisted of a 0.5-liter Monel vessel. A copper dip tube line was used to withdraw liquid samples. Pressures were

Table 4. A Comparison of Published Values for the Vapor Pressure of Bromine Pentafluoride

Temperature (°C)	Vapor Pressure P_1^0 mm Hg		Per Cent Difference
	Ellis, et al.*	Long**	
50	1078	1032	4.5
60	1527	1432	6.6
70	2120	1945	9.0
80	2888	2590	11.5
90	3869	3389	14.2
100	5103	4363	17.0

* Ellis and Johnson⁸ stated that their values of P_1^0 agreed with extrapolated values of Ruff¹⁰; hence, the above values were computed at 10 C intervals from Ruff's equation

$$\log_{10} P_1^0 = 8.0716 - \frac{1627.7}{t + 273}$$

** Computed from equation given by R. Long¹⁰

$$\log_{10} P_1^0 = 6.4545 + 0.001101 t - \frac{895}{t + 206}$$

Additional measurements on the vapor pressure of bromine pentafluoride in the range 400 to 760 mm Hg have been made by Rogers and Speirs¹². They give the equation

$$\log_{10} P_1^0 = 7.9727 - \frac{1598.2}{T}$$

where P_1^0 = mm Hg at 0°C and T = °K

Figure 4
System Uranium Hexafluoride - Bromine Pentafluoride
as Determined by Ellis and Johnson⁸

Figure 5
Distillation of Bromine Pentafluoride –
Uranium Hexafluoride Mixture:
Variation of Overhead Composition With Pressure⁹

measured with a 0 to 200 psig bourdon tube gauge. A spiral, copper tubing connected the vessel to the sampler system. The vessel, in a thermostat, was shaken by a rocking device for one hour and then allowed to settle for 15 minutes at which time samples were taken and analyzed by a sonic method. Temperatures were observed on a recorder; temperatures of the various vessels and sampler agreed to within $\pm 1^{\circ}\text{C}$.

It is apparent that the published results of Ellis, et al.^{8,9} are not in agreement with the work of Mecham, et al.^{3,4,5,6,7}. In one case an azeotrope is reported and in the other there is no evidence for an azeotrope. Also, in the pressure range of interest (2 to 5 atmospheres) there is marked disagreement between the values of the vapor pressure for pure bromine pentafluoride as reported by Ellis and Johnson⁸, and those of Long¹⁰. Therefore, one of the main objectives of any investigation of the bromine pentafluoride-uranium hexafluoride system should be to clear up these discrepancies.

The high values for the vapor pressure values of bromine pentafluoride⁸ might possibly be explained by the presence of an inert gas or by a small amount of a highly volatile component such as hydrogen fluoride. Similarly, any marked changes in the phase equilibrium data could be due to the presence of such impurities as free bromine, bromine trifluoride, and bromine monofluoride. By chemical analysis it would be quite difficult to detect, say 0.2 per cent bromine or bromine trifluoride in the pentafluoride. However, the presence of color in the normally colorless solutions of uranium hexafluoride and bromine pentafluoride furnishes a very sensitive test for impurities such as bromine.

The only other report which could be found on the distillation of uranium hexafluoride-bromine pentafluoride binary mixtures, was one which described total reflux fractionations performed at the Brookhaven National Laboratory¹³. Three runs were made on a packed column made of aluminum with 5/32 inch aluminum helices as packing. The column was two inch ID by 100 inches long. No details of the composition were given; however, it was stated that the general range of operation was from 10 per cent bromine pentafluoride in the still pot to 90 per cent in the overhead at pressures of 1935 to 2230 mm Hg and vapor velocities of from 0.2 to 0.4 ft/sec. HETP's of 7.0 to 8.5 inches were reported; these values were computed from the Fenske equation based apparently on an ideal relative volatility of about 1.4. These HETP's are in agreement with results obtained at ANL which were also based on an ideal α ^{5,7}. Using an $\alpha = 1.40$ and an HETP of seven inches in a 100-inch column, the overhead composition corresponding $X_s = 10$ per cent would be $X_d = 93$ per cent bromine pentafluoride.

The condensed phase equilibrium diagram for the bromine pentafluoride-uranium hexafluoride system has been published¹⁴. The results, as shown in Figure 6, indicate a simple eutectic at 3.2 mole per cent uranium hexafluoride at a temperature of -63.5°C . The solubility of uranium hexafluoride in the liquid bromine pentafluoride was stated to be essentially ideal.

Also, as part of the literature survey, the properties of bromine pentafluoride and uranium hexafluoride which were needed for the calculations and which were otherwise of interest to the interpretation of the equilibrium data, were compiled.

Figure 6
The Condensed System
Bromine Pentafluoride-Uranium Hexafluoride¹⁴

Properties of Bromine Pentafluoride

Formula weight: 174.916

Vapor pressure¹⁰

$$\log_{10} P_1^0 \text{ (mm Hg)} = 6.4545 + 0.001101 t - \frac{895}{t + 206}$$

for the range 50 to 150 C. $t = ^\circ\text{C}$

Estimated critical constants¹⁰

Critical temperature = $213 \pm 20^\circ\text{C}$

Critical pressure = $47 \pm 10 \text{ atm}$

Ideality of vapor¹⁰

One determination at 29°C and 330 mm showed normal vapor density

Structure of the molecule

One F atom is in a different environment from the other four on the basis of nuclear resonance spectra¹⁵. A square pyramidal configuration best explains the spectra and also the dipole moment¹⁶. The dipole moment of BrF_5 vapor is $= 1.51 \pm 0.10 \text{ D}$. The dielectric constant of liquid BrF_5 is given by¹⁶

$$E = 8.20 - 0.0177 t$$

From these data it is concluded that BrF_5 liquid is not appreciably associated¹⁶.

Liquid density

$$\rho = 2.5509 - 3.484 \times 10^{-3}t - 3.45 \times 10^{-6}t^2$$

Data taken with a dilatometer over the range -15 to 76°C ¹⁷.

Independent determinations of the liquid density gave a value of 2.4604 g/ml at 25°C ¹⁸.

This value differs by 0.06 per cent from the value computed at 25°C from the above equation.

Electrical resistivity of liquid = 1.1×10^7 ohm-cm¹⁹.

Properties of Uranium Hexafluoride

Formula weight: 352.07

Vapor pressure²⁰:

$$\log_{10} P_2^0 \text{ (mm Hg)} = 6.99464 - \frac{1126.288}{t + 221.963}$$

for the range 64 to 116°C, $t = ^\circ\text{C}$

Critical constants²⁰

Critical temperature = $230.2 \pm 0.2^\circ\text{C}$

Critical pressure = 45.5 ± 0.5 atm

Ideality of vapor

From vapor density data²¹

molecular weight of UF_6 = 353 ± 1 as computed from vapor density at 50°C using ideal gas law. Independent measurements of gas density gave the molecular weight as 352 ± 1 ²² in the range 18 to 96°C and 0.03 to 1090 mm Hg.

From PVT²³ and molar polarization data²⁴ the non-ideality factor in the empirical equation of state $P(1 + AP)V = RT$ is given by $A \text{ (atm}^{-1}\text{)} = 1.2328 \times 10^6 T^{-3}$. The above data were obtained at temperatures of 44, 60 and 94°C and for pressures up to 1 atm.

Liquid density

Dilatometer method²² and floating bobbin method²⁶ give data which agree with each other to ± 0.5 per cent.

$$\rho = 3.630 - 5.805 \times 10^{-3} (t - t_f) - 1.36 \times 10^{-5} (t - t_f)^2$$

where $t_f = 64.052^\circ\text{C}$

ρ = density of saturated UF_6 liquid = grams/cm³

Above equation for $\rho = \rho(t)$ applies up to 162°C .

Triple point

$64.02 \pm 0.05^\circ\text{C}$ at 1137 mm Hg²⁰.

Structure of molecule

UF_6 is a nonpolar molecule as indicated by a zero dipole moment²⁴. The molecule is a symmetrical octahedron as determined by diffraction and spectral data²⁵.

A brief review was also conducted on the methods used to obtain vapor-liquid equilibrium data. Considerable work has been reported in the literature on the development of suitable equipment. Critical reviews of various designs have been made by Gilliland²⁷, Fowler²⁸, and Hala, et al.²⁹ The techniques commonly used are as follows^{27,29}:

1. Static apparatus
2. Flow method
3. Dew point and bubble point determination
4. Distillation method
5. Dynamic circulation still
6. Mechanical circulation still

In the static type, the liquid is placed in a closed vessel under its own vapor pressure. The vessel is shaken or rocked to provide contact between the vapor and liquid phases. This static type was used by Ellis and Johnson in their work on the bromine pentafluoride-uranium hexafluoride

system⁸. In the flow type, usually an inert carrier gas is bubbled through a series of liquid contactors of known composition until the gas is saturated.

The dew point and bubble point method involves having an isothermal enclosure of variable volume. Discontinuities in the pressure-volume isotherms are observed. The distillation method is essentially a one plate, batch still. The most common example of the dynamic circulation still is the Othmer type, and its many modifications, in which the liquid is boiled and then condensed. The condensate is then returned to boiler. This type, where recirculation of the vapors is achieved thermally seems to have been the most widely used. Finally, in the mechanical circulation still, the vapor is recycled through the liquid by a pump. The first investigator to use the mechanical circulation still was B. F. Dodge³⁰; his study involved determining the vapor-liquid equilibrium in the system oxygen-nitrogen. Dodge used a mercury piston pump.

Since the work of Dodge, other investigators including Fischer³¹ et al., and Jarry³² et al. have also used the mechanical recirculation method. In the design and operation of an equilibrium still there are several criteria which must be kept in mind^{27,29}.

The system must not leak, since then the compositions would not reach a steady state,

System must be isothermal to avoid condensation of vapor,

There should be no entrainment of the liquid into the vapor leaving the equilibrium cell,

The liquid in the cell should not have concentration gradients.

From these factors, together with such considerations as simplicity of operation, adaptability to handle interhalogens^{31,32}, and the fact it seemed desirable to be able to bubble the vapor through the liquid continuously to insure intimate contact of the two phases, the isothermal, mechanical recirculation design was chosen for use in this investigation.

Once an equilibrium still has been built, there are two methods of evaluating its performance. The first is to determine the vapor-liquid equilibrium on some "standard" test system³³ whose equilibria have been determined reliably by some other method. This comparison is effective in showing whether systematic errors exist in the performance of still or in the determination of temperature, pressure, or composition.

The second test, which all vapor-liquid equilibrium data must satisfy to be valid, is the Gibbs-Duhem equation as given by classical thermodynamics.

Notable texts which give emphasis to the treatment of phase equilibria are the works of Denbigh³⁴ and the comprehensive treatment of Hala, et al.²⁹, which deals specifically with vapor-liquid equilibrium.

At equilibrium the following three requirements must be met³⁴:

$$T_{\text{liquid}} = T_{\text{vapor}}$$

$$P_{\text{liquid}} = P_{\text{vapor}}$$

$$\mu_{\text{liquid}} = \mu_{\text{vapor}}$$

From the requirement that the chemical potential of a component in the liquid phase must equal its potential in the vapor phase, and the definition of fugacity $d\mu = RT \ln f$, it is evident that the relationship $f_{\text{liquid}} = f_{\text{vapor}}$ must also hold.

Starting from the relationship $\mu_1 = \left(\frac{\alpha F}{\alpha N_1} \right)_{T,P,N_2}$, the definition of fugacity, and of the activity coefficient, one obtains the Gibbs-Duhem equation³⁴

$$\left[X_1 \left(\frac{\alpha \ln \gamma_1}{\alpha X_1} \right) = -(1 - X_1) \left(\frac{\alpha \ln \gamma_2}{\alpha X_1} \right) \right]_{T,P}$$

Dodge and Tbl³⁵ have extended this relationship to the more realistic case where pressure is varying as it must according to the phase rule for a binary, two phase isothermal system.

The essential point of the Gibbs-Duhem equation is that if one finds experimentally a relationship between γ_1 and X_1 , then there exists only one thermodynamically consistent relationship between γ_2 and X_2 . Thus if $\gamma_1 = \gamma_1(x)$ is known then $\gamma_2 = \gamma_2(x)$ can be obtained by an integration, or if both are known, then the two sets of data can be evaluated for consistency. Various integrated forms of the Gibbs-Duhem equation such as the Van Laar and Margules equations are discussed in the classic paper by Carlson and Colburn³⁶.

Recently Tierney³³ presented an attempt to make the evaluation of the constants in these integrated equations more objective by taking into account the random errors and statistical weights.

Another method for evaluating the thermodynamic consistency of vapor-liquid equilibrium data is the "equal-area test"²⁹

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dX_1 = 0$$

which also stems from the Gibbs-Duhem equation.

The use of the concept of the activity coefficient γ is very convenient, and it also gives an easily visualized measure of the non-ideality

of a system. The expression by which the activity coefficient can be computed from vapor-liquid equilibrium data is obtained as follows²⁹:

$$\gamma_1 = \frac{a_1}{X_1} \text{ by definition}$$

$$a_1 = \frac{f_{1L}}{f_{1L}^0} = \text{activity of component 1 in solution}$$

where f_{1L} = fugacity of component 1 in the solution

f_{1L}^0 = fugacity of pure component 1 as liquid at the temperature T and pressure P of the solution.

By the fugacity rule, $f_{1V} = (Y_1)(f_{1V}^0)$ for the vapor phase where f_{1V}^0 = fugacity of pure component 1 as vapor at T and P of the solution; but at equilibrium $f_{1V} = f_{1L}$, hence

$$\gamma_1 = \frac{Y_1 f_{1V}^0}{X_1 f_{1L}^0}, \text{ but } f_{1V}^0 = \phi_1 P, \text{ therefore } \gamma_1 = \frac{Y_1 \phi_1 P^*}{X_1 f_{1L}^0}$$

Y_1 = mole fraction of component 1 in the vapor phase

ϕ_1 = fugacity coefficient of component 1

X_1 = mole fraction component 1 in the liquid phase

P = total pressure.

Under conditions of low pressures, $(f_{1L}^0)_{T,P}$ becomes equal to P_1^0 . The vapor pressure of the liquid, and ϕ_1 tends toward unity²⁹. Hence the expression for the activity coefficient becomes

$$\gamma_1 = \frac{PY_1}{P_1^0 X}$$

* Upon evaluating f_{1L}^0 , the general equation for evaluating the activity coefficient becomes²⁹

$$\gamma_1 = \frac{Y_1 \phi_1 P}{X_1 P_1^0 \phi_1^0 \exp \int_{P_1^0}^P \frac{V_{1L} dP}{RT}}$$

Thus, for this case of the ideal vapor phase, a $\gamma = 1$ corresponds to Raoult's Law for ideal solutions and $\gamma_s > 1$ are denoted as positive deviations from ideality. Further evaluation of vapor phase imperfections in vapor-liquid equilibria is given in a recent paper by Black³⁷. Also, an extensive discussion of the correlation of activity coefficients with emphasis on the dilute regions is presented by Wehe and Coates³⁸.

CHAPTER II

DESCRIPTION OF APPARATUS

General Characteristics of the Equipment

Before going into the details of some of the components a brief, overall description will be given.

The equilibrium still designed and built for this investigation was of the mechanical recirculation type. The vapor was bubbled repeatedly through the liquid by means of a magnetic, piston pump. The vapor flow rate was indicated by a thermal flowmeter. The temperature was read on a Leeds and Northrup type K-3 precision potentiometer as the millivolt output from calibrated copper-constantan thermocouples. The pressure was indicated on a mercury manometer coupled to the still through a null point transmitter. The samples were hydrolyzed and analyzed by wet chemical methods. A Volhard⁴⁴ analysis was used for the bromide determination and a volumetric titration was used for the uranium analysis. For each run, the still was maintained under isothermal conditions for at least 12 hours.

Figure 7 shows a flowsheet for the entire equilibrium still assembly. Figure 8 gives an external view of the hood, the isothermal box in which the still is located, and some of the auxiliary piping of the vacuum and manometer manifolds. The hood in which the equipment is located is approximately 9 ft. long by 5 ft. wide by 9 ft. high. The constant temperature box, located inside of the hood, is 3 ft. wide by 2 ft. deep by 4 1/2 ft. high. The transfer box, used for emptying the vapor bulb into a fluorothene tube, can be seen in the center of the photograph. The manometer and instrument panels are at the extreme right.

In Figure 8, the still box is shown with the doors closed and with the valve holes plugged. The section on top of the box contains ductwork

Figure 7
Layout of Recirculation Type Vapor-Liquid Equilibrium Still

Figure 8
External View of Isothermal Box and Facilities in Hood

and the 400 cfm blower which recycles the air inside the box. For reasons of safety both the inside and outside of the box are covered with aluminum plate to reduce the possibility of the halogens contacting any organic matter. The actual construction of the box starting from the inside is as follows:

1/16-inch aluminum plate

1-inch layer of glass wool insulation

5/16-inch thick aluminum covered plywood

An asbestos board known as "marinite" was also used in the construction as a reinforcement in corners and around the edges of the two doors.

Figure 9 gives a view inside the constant temperature box which contains the equilibrium still. The vapor sample bulb is in the upper left hand corner. The magnetic piston pump and check valves are at the lower left. The equilibrium cell with the liquid sampler is at the center near the bottom of the photograph. The entire apparatus is constructed of nickel and Monel. Teflon is used for gasketing material. The valves are Monel bellows sealed with a Teflon seat; they were obtained from Hoke, Inc.

Magnetic Piston Pump

Because of the presence of the volatile uranium hexafluoride with its associated low-level radioactivity, leaks from the still into the surrounding air would constitute a hazard from the point of view of ingestion. Also loss of material would be objectionable because the depletion of material would not allow steady state operation. Similarly, leakage of air into the still was undesirable because the inerts would increase the pressure above that of the pure components. Also, moisture in the air would react chemically with the materials in the still to produce HF and other hydrolysis products.

Figure 9
Internal View of Still

Because of these stringent requirements, a conventional pump with either a stuffing box or a mechanical seal was not suitable because of the high probability of the seal leaking. Hence a completely sealed unit was required. For this purpose a magnetic piston pump patterned after one developed by Rosen³⁹ was built.

A single cylinder was used on the pump to reduce the gap between the magnet and the piston and to simplify the construction. The only difficulty experienced with the pump was occasional sticking of the check valves and the piston. Tapping the pump usually served to free these parts.

Calibration data obtained on pumping capacity versus discharge head for the piston pump are shown in Figure 10 with speed as parameter. For these performance checks, the volume of air pumped was determined by a wet test meter; the head was measured by a mercury manometer. The suction side of the pump was open to the atmosphere. Calculations showed that the pump was operating at very nearly the theoretical capacity of 13.85 cc/stroke. The 29 rpm speed was used on the pump on the equilibrium still; the low speed minimized the entrainment of liquid drops into the vapor phase. The vapor recycle rate in the still was about 500 std. cc/min.

Vapor Flowmeters

Since the still was of all metal construction with no flowmeters to permit visual observation, some device was needed to indicate that the pump was functioning properly. For this purpose an "audio" flow indicator was developed. The flow indicator consisted of a small microphone-amplifier-speaker setup. The sound of bubbling indicated that the pump

Figure 10

Performance Curves for Magnetic Piston Pump

was recirculating the vapors. This bubble sensing device was tested by bubbling air through water; the operation was very satisfactory. It was found possible, at low gas rates to count the bubbles from the sound produced when they disengaged at the surface of the liquid.

However, when this flow indicator was connected to the equilibrium cell, the sound of bubbling was somewhat obscured by the noise from the pump. The predominant sound was the clicking of the check valves. Hence, it was decided to install a more quantitative device. For this purpose a thermal flowmeter was chosen. Basically, this instrument measures the small temperature rise of the vapor stream as it passes through a heated section. A sketch of this meter, which was developed at the Oak Ridge National Laboratory, is shown in Figure 11.

A power of about one watt was put through the nichrome heating wire. The temperature difference, as indicated by the output from the thermopile, between the entering and leaving vapor was indicated on a recording potentiometer. The flowmeter was only used at the beginning and for periodic checks during the middle of run to verify that the vapor was being recycled. It was necessary to have the thermal flowmeter heater current on for about one-half a minute to given an indication of flow.

The thermal flowmeter was initially calibrated with air. Figure 12 shows the variation of the millivolt output with flow rate as determined with air. Previous tests on another similar flowmeter indicated that bromine pentafluoride and uranium hexafluoride gave outputs comparable to those for air. Hence, since precise values of the vapor flow rate were not required, the air calibration was used to approximate flows of the vapor in the still.

Figure II
Thermal Flowmeter ORNL - Mark I

Figure 12
Calibration of Thermal Flowmeter

Temperature Control and Indication

A precision mercury thermoregulator, with a variable set point, having a rated sensitivity of $\pm 0.03^{\circ}\text{C}$ was used as the temperature controller. Two electrical finstrip heaters were used to supply the necessary heat to the 400 cfm circulating air stream. The output from one heater could be changed by means of a variac; this was adjusted so that it supplied about 90 per cent of the required heat. The remaining power was supplied in an on-off fashion by the second heater which was actuated by the mercury controller. The heaters were located in back of the constant temperature box and were separated from the still piping by a baffle. The air stream flowed down through the still and then back up over the heaters. In practice, it was found that the box air temperature could be maintained constant to within $\pm 0.2^{\circ}\text{C}$.

A select grade 24-gage copper-constantan thermocouple wire was used for temperature measurement. The thermocouples were calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The calibration was accomplished by inserting the resistance thermometer together with the thermocouples into an oil bath in a glass dewar. The entire dewar assembly was then placed inside the constant temperature box and the oil bath was stirred. The potentiometric method was used for the calibration. This method involves placing a standard resistance in series with the platinum resistance thermometer. The current through the thermometer was adjusted to the recommended value of two milliamperes by means of a resistance box. A two volt battery supplied the current. A standard, precision resistor certified to $100.00 \pm .001$ ohms was used in the circuit. The potential drop across the standard resistor was measured,

and also across the platinum thermometer, using the K-3 potentiometer. The resistance of the platinum thermometer could then be computed from the relation

$$r_{pt} = r_{100} \times \frac{e_{pt}}{e_{100}} .$$

The thermocouples were calibrated only at the temperature levels corresponding to the isotherms to be run on the still. It was found that a correction of 0.1°C was to be added to the reference values given in the NBS-emf tables.

A distilled water-ice bath was used as a reference junction. Thermocouples were located both in the vapor and liquid phase of the equilibrium cell. The couples were located in wells made of $1/4$ -inch OD nickel tubing with a 0.035 inch wall.

The emf was determined using a Leeds and Northrup type K-3 precision potentiometer. A Leeds and Northrup galvanometer having a sensitivity of 0.001 millivolts/division was used with the potentiometer. For a copper-constantan thermocouple, ± 0.001 MV corresponds to $\pm 0.02^{\circ}\text{C}$ in the range 70 to 90°C .

Pressure Indication

The pressure in the still was indicated on an absolute, dual range well-type mercury manometer. The manometer had 1 mm divisions. A Booth Cromer⁴⁰ null point transmitter was used to isolate the reactive halogen compounds for the mercury in the manometer.

The pressure inside the still was continuously balanced with helium. For example, when the helium pressure on the manometer side of the transmitter was slightly greater than the pressure in the still, the relay automatically opened thus venting some helium through a needle. A

pressure differential of 0.5 mm Hg is sufficient to actuate the relay. An electrical contact for the relay circuit is located on the 3-mil thick nickel isolating diaphragm. The pressure transmitting system was checked periodically by applying helium pressure to the still. The helium pressure was then connected directly to one mercury column of the dual manometer. The balancing pressure was then read as usual on the other manometer. Over the range of 760 to 3800 mm Hg the two pressures agreed within ± 2 mm Hg as determined by spot checks over the interval.

Leak Testing

Before being placed in operation the still and connecting piping were degreased with acetone and leak tested. Final leak testing consisted of pressurizing the still to 60 psia with Freon 22 and then using the GE type H Halogen Leak Detector on all valves, welds, and flare connections. Finally the still was prefluorinated to stabilize the metal with a protective fluoride film.

Additional checking for leaks must be done at the beginning of each run to insure that the flare connections on the newly installed vapor bulb and liquid sample tube are tight. This can be done simply by either evacuating or pressurizing the connections and observing that there is no change in pressure over a 15 minute period. Also, observing the color change in moistened, starch-iodide paper from white to purple is very useful in pinpointing fluorine leaks. Normally, however, no difficulty is encountered with leaky flares, since the teflon gaskets used in the compression fittings make excellent seals.

Range of Operation for Equilibrium Still

It was necessary to design the still so that equilibrium data could be obtained at least in the range of 70 C to 90 C which encompasses the temperature variations involved in a distillation column separating the bromine pentafluoride-uranium hexafluoride binary at the standard operating pressure of 3 atmospheres.

The range of temperatures that can be investigated on the vapor-liquid bromine pentafluoride-uranium hexafluoride system is limited by the considerations of the appearance of a third (solid) phase and by the pressures involved. Since the triple point of uranium hexafluoride is 64.0°C at a pressure of 1137 mm Hg, it is necessary to operate a still at temperatures slightly above 64°C to insure that only a vapor and liquid phase will be present over the entire range of compositions. Hence, the first, or low temperature, isotherm chosen to be determined on the equilibrium still was at 70°C .

The mercury manometer used in this investigation to determine the pressure had an overall height of 13.5 feet; this was the maximum length which could be accommodated in the laboratory. The length of the mercury column was such that pressures up to 3800 mm Hg could be indicated on the scale. This value of 5 atmospheres corresponds to the vapor pressure of bromine pentafluoride at 94.5°C . Thus the upper limit of temperature for the particular binary system of interest in this investigation was fixed at about 94°C . Hence, the second, or high temperature, isotherm was chosen to be at 90°C . Other systems, with lower vapor pressures, could be investigated at temperatures up to about 130°C . The temperature limitation of 130°C comes mainly from the cement applied to the silicone

rubber gaskets used as a seal for the doors and from the fluorothene tubes used for taking the liquid sample. By venting one leg of the manometer one could extend the pressure range to 4560 mm Hg.

To summarize, the application of this equilibrium still is therefore limited to systems and conditions which satisfy the following requirements:

Mixtures do not severely corrode nickel or Monel

Temperatures in the range 25 to 130°C

Pressures less than 4560 mm Hg

CHAPTER III EXPERIMENTAL PROCEDURES

Brief Investigation of Entrainment

The presence of entrainment, resulting from excessive rates of bubbling of the vapor through the liquid, could vitiate the results. It was decided, therefore, to make a few tests to determine the extent of entrainment in a geometrically similar glass vessel. Air was pumped through a 0.349 molar uranyl nitrate solution using the magnetic pump. The air stream leaving the bubbler was passed through a refrigerated cold trap. The cold trap was followed by a millipore filter which quantitatively removes entrained particles having a diameter greater than 0.1 micron. The uranium content of the liquid condensed in the cold trap and held on the filter paper was determined fluorophotometrically. The data obtained are shown in Table 5. Evidently there was very effective de-entrainment since if even 0.1 cc of liquid were carried out by the air stream, then 8.3 mg of uranium would have been found.

From the data shown in Table 5 for run 2, it was computed that during a 12 hour run on the equilibrium still the entrainment could influence the analyses by less than 1/1000 per cent; this is a negligible amount.

The nickel equilibrium cell used on the still was built so that the vapor bubbled through the liquid after coming out of six holes 1/16 inch in diameter, drilled radially around the 3/8-inch O.D. sparge tube. Above the plane of the holes there was a horizontal plate to deflect the bubbles to the side to improve the contacting between the two phases.

Tests on Validity of Liquid Samples

It seemed desirable to conduct a few checks on the technique used to take liquid samples to determine if any change in composition took place

Table 5. Tests Simulating Entrainment in Still
(Air Sparge Through Uranyl Nitrate Solution)

Test No.	Duration of Run-minutes	Air Flow, Std. cc/min	Micrograms of U Collected		
			In Trap	On Filter	Total
1	37	3,000	24.4	60.0	84.4
2	90	750	4.4	1.2	5.6

Comments:

- a. Observation of the gas-liquid contactor at the high air rate (3,000 cc/min) indicated prohibitive amounts of entrainment; drops of liquid splashed up to heights ranging from about one to two inches. The second test at a low air rate showed only minor amounts of droplet carryover on the walls of vessel.

such as might be caused by flashing. A glass bulb having the same volume as the equilibrium cell on the still was filled half full with a binary mixture of known composition. Ethylene dichloride-toluene was chosen since the relative volatility of this mixture is similar to that for the bromine pentafluoride-uranium hexafluoride system. A liquid sample tube was fitted with two stopcocks to function as the two bellows valves on the actual still sampler. The procedure used was to first evacuate the sample tube. The vacuum valve was then closed and the valve connecting the equilibrium cell to the sample tube was opened. About five ml of sample was allowed to flow into the tube; the valve was then closed. The contents of the sample tube were then totally condensed (frozen) by placing a dewar of liquid nitrogen around the tube. The tube was then removed and the sample was subsequently analyzed by refractive index. The values for refractive index as a function of composition as determined by Jones et al.⁴¹, were used. The results of these tests on the liquid samples are summarized in Table 6.

It can be concluded that no bias or systematic change in composition occurs upon taking a sample. The differences are due to the limitations of the analysis.

Determination of Vapor-Liquid Equilibrium on an Organic Mixture

The final tests made on the equipment were to compare the performance of this equilibrium still with one which achieves circulation of the vapor by boiling and condensing. For this purpose, three runs were made on an organic test mixture. Table 7 gives a comparison of the results obtained on the ethylene dichloride-toluene system with those reported by Jones, et al.⁴¹, on a glass still. The pressure for the runs was slightly over

Table 6. Liquid Sampler Tests

<u>Composition in Mole Per Cent Ethylene Dichloride</u>		
<u>Original Solution*</u> <u>Before Sampling</u>	<u>Liquid Sample</u>	<u>Per Cent</u> <u>Difference</u>
21.9	22.0	+0.5
49.5	50.0	+1.0
50.0	49.7	-0.6
50.2	49.6	-1.2
67.5	67.5	0.0

*At 25°C and 1 atm.

Table 7. Vapor-Liquid Equilibrium for Ethylene Dichloride-Toluene

Mole Fraction Ethylene Dichloride in Liquid Phase	Mole Fraction Ethylene Dichloride in Vapor Phase		$\frac{Y_{\text{obs.}} - Y_{\text{lit.}}}{Y_{\text{obs.}}} \times 100$	Temperature °C
	X Observed	Y Observed Y Literature ⁴¹		
52.0	69.0	70.8	-2.5	92.8
49.5	68.6	68.3	+0.4	93.0
52.0	71.4	70.8	+0.9	92.7

1 atmosphere (767 to 779 mm Hg). The composition of the two phases was determined by refractive index to within ± 0.005 mole fraction on an Abbe refractometer at 25°C. From the three runs made, it was concluded that there were no inherent differences between the previously published results obtained on a glass equilibrium still with those obtained on the nickel recirculation still. The differences of -2.5, +0.4, and +0.9 per cent appear to be due to random errors principally from the analysis.

Hydrolysis and Analysis of Samples

First an evaluation of the purity of the two components used will be made.

The bromine pentafluoride was obtained from General Chemical Co. It was necessary to purify the material in a packed, nickel distillation column. A middle cut was taken consisting of about two-thirds of the charge. The more volatile impurity was primarily hydrogen fluoride and the less volatile was bromine trifluoride. The bromine pentafluoride was a colorless liquid at room temperature.

The uranium hexafluoride was obtained from Oak Ridge National Laboratory and was certified to be natural uranium hexafluoride with less than 0.01 weight per cent hydrogen fluoride impurity. As a precaution, the first liter of vapor was always discarded since the main impurity (hydrogen fluoride) is highly concentrated in the vapor phase. The uranium hexafluoride was a white solid at room temperature.

The purity of the components was substantiated by spectrographic analysis, wet chemical analysis, and by their vapor pressure. It can be concluded that their purity was greater than 99.6 per cent. Spectrographic

analysis of the solutions after having been in the still showed that nickel, aluminum, copper, and iron were the main impurities.

To apply conventional analytical techniques to a system such as bromine pentafluoride and uranium hexafluoride, it is advisable to first convert the sample to an aqueous solution for safety and convenience. This is done by a hydrolysis reaction in a closed system. These reactions proceed very vigorously.

The reaction of uranium hexafluoride with water proceeds as follows²⁵:

A yellow solution results. The solubility of UO_2F_2 in water at 25°C is 67.3 weight per cent²⁵. The presence of HF tends to decrease the solubility. The reaction of BrF_5 with water is discussed by Mellor⁴². The hydrolysis of BrF_5 was originally thought to be

However, according to Mellor, it was later demonstrated that the oxygen in the water was evolved as elemental oxygen; also, the liquid after hydrolysis has a red color suggesting the presence of free bromine. Hence, the reaction consistent with these observations is

A sufficient amount of hydrazine is added when a bromide analysis is required to reduce the bromine by the reaction (1/4 to 2 ml of 85 per cent hydrazine hydrate solution)

The size of the sample and hydrolysis bottle must be so chosen so that the gas pressure produced is not sufficient to rupture the bottle. Either glass or polyethylene bottles can be used for the hydrolysis.

A sketch of the hydrolysis rig is shown in Figure 13. Fluorothene grease was used on the stopper to improve the seal. The glass bottle was taped for safety. Approximately 400 ml of distilled water was used for the hydrolysis.

The fluorothene (monochlorotrifluoroethylene polymer) tube containing the interhalogen sample was kept in a dewar of liquid nitrogen for about 10 minutes to insure that there would be no loss of material due to volatilization when the plug was opened. This freezing operation also allowed one to insert the tube into the hydrolysis bottle in complete safety. Only after the sample starts to melt and drip into the water does the hydrolysis proceed rapidly.

The tube was allowed to remain undisturbed in the bottle for at least an hour. The hydrolysis assembly was then shaken manually for a few minutes; this shaking caused the tube to fall into the aqueous solution thus completing the hydrolysis of any material in the tube. After about a half hour, the solution in the bottle was poured into a volumetric flask. The bottle and tube were rinsed with distilled water. The final volume was made up to either 500 or 1000 ml. Approximately 30 mg of uranium and 100 mg bromine were used for each analysis. All analyses were performed in duplicate by the Analytical Laboratory of the Chemical Engineering Division. For uranium the volumetric method with a zinc reductor was used⁴³. The procedure 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:

Figure 13
Hydrolysis Bottle Assembly

The excess ceric ion is back titrated with ferrous ion $2\text{Ce}(\text{SO}_4)_2 + 2\text{FeSO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{Ce}_2(\text{SO}_4)_3$. Ferroin is used as the indicator. Fluoride ion is known to interfere with the analysis; hence the HF is removed by fuming with H_2SO_4 .

A standard Volhard analysis was used to determine the bromide content of hydrolyzed samples⁴⁴. The ionic reactors for the titration are as follows:

Excess thiocyanate is indicated as the red color of the complex with ferric ion in the acid solution.

In order to obtain estimates of the accuracy and precision of the hydrolysis and analytical techniques, standards were prepared. A sufficient number of standards were prepared so that the results could be subjected to a statistical analysis. The pure components and binary mixtures of known concentrations were hydrolyzed and analyzed. The standards covered the range of concentrations found in samples from the still.

The standards were prepared by first transferring a known amount of sample in a fluorothene tube; the weights were determined on an analytical balance to within ± 0.2 mg. After hydrolysis the volume was made up in a volumetric flask. The same techniques of hydrolysis, weighing, and volume determination were used on the equilibrium runs on the still. The pooled data obtained from the analytical standards are summarized in Table 8. Initially, some difficulty was encountered with a slight bias (inaccuracy),

Table 8. Summary of Results from Analytical Standards

Element Analyzed For	Component Hydrolyzed	σ_1 Standard Deviation of Percent Error For Any Given Analysis	Number of Analyses
Br	UF ₆ + BrF ₃	0.42	8*
Br	BrF ₅	0.60	13
U	UF ₆ + Br ₂	0.70	12
U	UF ₆	0.82	6

*Involves actually 16 analyses since each sample, both for the standards and for the unknowns from the runs, was run in duplicate. The average of these two determinations was the reported concentration.

Note: In the actual equilibrium runs, the samples from the vapor phase were subjected to an additional error as a result of the transfer step from the vapor bulb to fluorothene tubes. A statistical analysis made of 36 transfers showed a mean error of +0.011 gram. The standard deviation for any given transfer was ± 0.100 gram. Hence, the standard deviation of the mean was ± 0.017 gram. Therefore, there was no inaccuracy (loss of material) inherent in the transfer. Only random variations were present. In a 20 gram vapor sample the uncertainty of ± 0.100 gram corresponds to a ± 0.5 per cent error.

It was also observed that the standard deviation of the error for any given transfer for those vapor samples in the range $50 < Y \leq 100$ was only ± 0.038 gram. Thus bromine pentafluoride rich samples could be transferred more precisely than those which contained primarily uranium hexafluoride. The error in transfer is defined as the final weight of vapor sample collected in the fluorothene tube minus the weight of vapor initially in the vapor bulb.

but this was later rectified. Standards were analyzed both before and during the period of time when the equilibrium runs were in progress. The conclusions which can be drawn regarding the hydrolysis-analysis procedures are the following:

- a. The bromide does not interfere with the uranium analysis, and conversely the uranium does not interfere with bromide analysis
- b. The standard deviation of the error for any given uranium or bromide analysis is less than one per cent.

The Analytical Laboratory of the Chemical Engineering Division also have their own uranium and bromide standards prepared by more direct methods (no hydrolysis involved). They find an accuracy of about ± 0.5 per cent for the uranium and bromide analyses. Therefore, the hydrolysis operation does not introduce serious errors.

To increase the reliability of the calculations on the composition of samples in the range $X = 0$ to 30 per cent and $X = 70$ to 100 per cent, the technique used was to analyze for the component present in the smaller amount. For example, in the range $X = 70$ to 100 per cent, the uranium was analyzed. The bromine pentafluoride concentration was then obtained by subtracting the analyzed amount of uranium hexafluoride from the total sample weight which was known to within ± 0.2 mg. This method avoided the uncertainty inherent in subtracting two large numbers from each other. In the middle composition range, both the bromide and uranium could be analyzed for thus giving further checks on the analysis.

Operating Steps

The four basic steps in making a run on the still are as follows:

Charging material

Contacting vapor and liquid isothermally until equilibrium is attained

Recording temperature and pressure and taking samples of the two phases

Hydrolysis and analysis of samples.

To charge material, at the beginning of a series of runs, the still was first evacuated to remove any inerts. A cold trap refrigerated with liquid nitrogen was used to remove any condensable interhalogens thus preventing them from reacting with the oil in the vacuum pump. The cold trap was followed by a soda-lime plus limestone chemical trap for absorption of any residual halogens. With the mechanical vacuum pump the still could readily be evacuated to a pressure of 10 microns as indicated on a rotatable McLeod gage.

Both bromine pentafluoride and uranium hexafluoride were normally added as liquids from a nickel charge vessel which was fitted with a valve; to transfer the latter as liquid, it was necessary to have the lines heated above 65°C. The equilibrium cell was initially charged so that it was about one-half full of liquid; this corresponds to about 275 grams of material.

To change the composition from one run to the next, it proved to be more convenient to add the material directly as liquid to the evacuated vapor sample bulb from an inverted fluorothene tube fitted with a valve. Up to 50 grams could be added in this manner.

With the desired charge of material in the equilibrium cell, the next step was the approach to equilibrium conditions.

With the equilibrium still and box initially at room temperature, it was found that it required about one hour for the air temperature in the box to reach 70°C after the heaters and blower were turned on. At this time the temperature of the uranium hexafluoride-bromine pentafluoride mixture in the still was usually about 5°C below the final equilibrium value. In another hour, the temperature and pressure were slightly above their equilibrium values due to lag in the heaters (overshoot). After another five hours the still was in an isothermal condition and remained so until the end of the run. Thus about seven hours were required to reach a steady state.

Typical records of temperature and pressure as a function of time during the approach to equilibrium are shown in Figures 14 and 15. Initially, if the equilibrium cell contained solid material near room temperature, the temperature rose quite slowly; the rate of heat transfer was probably limited by the solid of uranium hexafluoride which has a low thermal conductivity. Then when a liquid film was formed at 65°C and the vapor pump was turned on to provide agitation, the rate of temperature rise increased despite the lower temperature differential between the air and the liquid.

After the isothermal conditions were attained, the still was run for at least another four hours before sampling the two phases. For some runs, the still was allowed to remain isothermally for times as long as one to three days. No significant differences could be detected

Figure 14
Typical Approach to Equilibrium of Temperature

Figure 15
Typical Approach to Equilibrium of Pressure

in the results. Hence, it can be concluded that equilibrium of temperature, pressure, and composition was achieved in the still.

The equilibrium temperature and pressure data were then recorded using the K-3 potentiometer and mercury manometer as described in the section on apparatus. The vapor circulating pump was then turned off.

The vapor sample was then taken by simply closing the inlet and exit valves to the vapor bulb thus isolating a portion of the vapor from the rest of the still. The liquid sample was taken by allowing liquid from the equilibrium cell to drain into a fluorothene tube. All of the valve manipulations were done by using extension handles inserted through 1/2 inch holes in the front of the constant temperature box. Tests showed that removing the plugs from the valve holes for a few seconds did not cause any observable temperature change inside the box.

After the equilibrium liquid and vapor samples were isolated as described above, the door of the box was opened. The vapor bulb was removed by loosening the two flare nuts. The liquid sample was first frozen by immersion in a dewar containing liquid nitrogen and then removed and plugged.

The vapor bulb and liquid tube were then weighed on an analytical balance. The vapor bulb was then attached to the fitting in the transfer box. The transfer box was heated to 90°C. The vapor from the bulb was then transferred into evacuated fluorothene tubes which were chilled with liquid nitrogen. About two hours were required for this transfer operation.

The vapor and liquid samples in the fluorothene tubes were then ready for the hydrolysis and analysis steps using the techniques discussed in Section 4.

Use of Fluorine

After the preliminary runs were made, it became evident that there was a small amount of corrosion taking place in the still. Reported corrosion rates of interhalogens in contact with Monel and nickel give very low values⁴⁵. The penetration rates are about 2 mils/year at 100°C. The low corrosion rates are due to the protective nickel fluoride film. However, these corrosion rates, when increased by the erosion of the moving piston against the cylinder, proved to be sufficient to make the data unreliable by producing unwanted components.

The probable corrosion reactions are:

Then the species BrF could be formed

Since the species BrF, Br₂, and BrF₃ have vapor pressures quite different from BrF₅, it is apparent that their presence would vitiate the results.

To overcome this problem, it was decided to add very small amounts of elemental fluorine to the still. This served to convert all the corrosion product species to BrF₅ as follows:

In the preliminary runs without fluorine, samples always showed a yellow color (suggesting BrF₃) or a reddish-orange (suggesting Br₂). Whereas, when the fluorine was present the samples were completely free of these colors. Only white solid and colorless liquid were present. Also, in

the absence of fluorine it was difficult to obtain reproducible values of vapor pressure or relative volatility. The addition of fluorine, therefore, insured that spurious results would not be obtained from the formation of bromine or bromine trifluoride. The amount of fluorine added was such that the final partial pressure of fluorine was usually in the range 5 to 20 mm Hg.

This "inert" pressure was subtracted from the total indicated pressure to obtain the true pressure due to the binary solution of bromine pentafluoride and uranium hexafluoride. The reported pressures are in mm Hg referred to the density of mercury at 0°C.

By extrapolating data on the vapor pressure of fluorine beyond the critical point with a $\log P$ versus $1/T$ plot, the ideal solubility can be computed by Raoult's Law which states that $P = P_1 X$

where P = partial pressure of fluorine in gas phase

X = mole fraction of fluorine in the liquid phase

P_1 = vapor pressure of fluorine at temp T (extrapolated above the critical point of fluorine).

This rather simple method of estimating the solubility of a gas in a liquid gives quite good results when applied to inert systems such as nitrogen in a nonpolar liquid⁴⁶. Since fluorine in bromine pentafluoride or uranium hexafluoride is an analogous system one can place some confidence in the predicted solubility.

At a temperature of 70°C and a partial pressure of fluorine of 20 mm Hg, one can compute that the concentration of fluorine in the liquid phase is 0.006 mole per cent. Additional confidence in the estimate of a very low solubility of fluorine in the liquid phase is gained from data on the

solubility of fluorine in chemically similar liquids such as HF·KF melts and SbF₅.⁴⁷ At temperatures in the range 39 to 100°C and fluorine pressures of 51 to 373 psia, the observed solubilities fell in the range 0.3 to 2.3 ml F₂ gas (STP) per gram of liquid. The behavior of fluorine, as evidenced by its low solubility, was stated to be similar to that of other inert gases in liquids and there was no evidence of abnormal solubility due to compound formation.

It is evident, therefore, that one is justified in neglecting the fluorine content of the liquid phase; hence, the liquid phase can be treated purely as a bromine pentafluoride-uranium hexafluoride binary solution. However, to obtain the true pressure due to the binary solution, it is necessary to subtract the partial pressure of the fluorine from the observed total pressure.

Safety Measures

To conclude the description of the various operations, the safety aspects of the experimental work will be mentioned briefly.

Uranium hexafluoride, bromine pentafluoride, and elemental fluorine are all powerful fluorinating agents. Bromine pentafluoride liquid when dropped on materials such as water, wood, or skin tissue reacts violently with the production of heat and light. Hence, it is necessary that protective clothing be worn during all operations such as charging materials, taking samples, hydrolysis, and removing cold traps. In these operations, there is always the possibility of leaks, in particular from the fracture of a fluorothene tube. Leather gloves, a leather jacket, and a plastic face shield were worn during the hydrolysis which was conducted in a well ventilated hood. Also, during the removal of fluorothene tubes containing

the halogen-bearing materials, a Mine Safety Appliance "lead hood" was worn. This hood completely covered the head and neck and furnished a supply of fresh air from a hose attached to the instrument air manifold.

During all operations the room air was monitored for radioactivity by the Radiation Safety group. The air count never exceeded a fraction of the allowable level. Any small release of material would be carried up into the filter system by the 1000 cfm of air which ventilated the hood in which the still was located. The glass doors in front of the hood were kept closed at all times except when it was necessary to gain access to the equipment.

Only two incidents in which some bromine pentafluoride and uranium hexafluoride fumes were released occurred during operation of the equipment. Both involved the fracture and ignition of a fluorothene tube containing a bromine pentafluoride rich mixture at 90°C. The still box and the ventilated hood confined and removed the fumes so that none of the material entered into the room air system. It is important that the fluorothene tubes be thoroughly cleaned, dried, and inspected for cracks or imperfections before contacting them with interhalogens at elevated temperatures.

CHAPTER IV
EXPERIMENTAL RESULTS

Typical Data and Calculations for a Run

A. Temperature

1. ice bath reference junction = 0.0°C
2. observed thermocouple emfs on K-3 potentiometer
vapor phase = 2.8635 millivolts
liquid phase = 2.8652 millivolts
average emf = 2.8644 millivolts
3. from NBS tables of standard emfs for a copper-constantan thermocouple⁴⁸
 $2.864 \text{ MV} = 69.0^{\circ}\text{C}$
 $2.908 \text{ MV} = 70.0^{\circ}\text{C}$
4. by interpolation from the NBS values
 $2.8644 \text{ MV} = 69.0^{\circ}\text{C}$ to nearest 0.1 degree
5. calibration of the thermocouples against a standard platinum resistance thermometer showed that 0.1°C should be added to value from the emf table to obtain the true temperature hence, 69.1°C is the equilibrium temperature.

B. Pressure

1. 1896 mm Hg reading on manometer
room temperature = 24°C
2. correction of pressure to 0°C
density of Hg at $0^{\circ}\text{C} = 13.5955 \text{ g/cm}^3$
density of Hg at $24^{\circ}\text{C} = 13.5364 \text{ g/cm}^3$
 $1896 \times \frac{13.5364}{13.5955} = 1888 \text{ mm Hg}$

3. correction for inert fluorine pressure; 8 mm Hg inert pressure observed in fluorothene tubes and vapor bulb in transfer apparatus with vapor sample frozen with liquid nitrogen.
4. true total pressure due to BrF_5 and UF_6 , referred to density of Hg at 0°C , is $1888 - 8 = 1880$ mm Hg

C. Vapor Sample

1. sample before transfer

gross weight of vapor bulb = 906.2872 grams

tare weight of vapor bulb = 888.0270 grams

net weight of vapor sample = 18.2602 grams

2. sample after transfer to fluorothene tubes

Tube 1

Tube 2

gross 330.4815

gross 322.4942

tare 314.1610

tare 320.5495

net 16.3205 grams

net 1.9447

16.3205

1.9447

3. total = 18.2652 grams vapor sample in fluorothene tubes.

4. samples in fluorothene tubes were hydrolyzed in water; the final amount of aqueous solution was 1000 ml in a volumetric flask.

5. uranium analysis of solution showed

1.558 $\frac{\text{mg U}}{\text{ml}}$

$$6. \quad 1.558 \frac{\text{mg U}}{\text{ml}} \times 1000 \text{ ml} \times \frac{\text{gU}}{1000 \text{ mgU}} \times \frac{352.07 \text{ g UF}_6}{238.07 \text{ g U}}$$

$$= 2.3040 \text{ grams UF}_6 \text{ in vapor sample}$$

$$7. \quad 18.2652 \text{ grams in sample}$$

$$\underline{-2.3040 \text{ grams UF}_6}$$

$$15.9612 \text{ grams BrF}_5 \text{ in sample}$$

$$8. \quad 1 - y = \text{mole fraction UF}_6 \text{ in vapor phase}$$

$$1 - y = \frac{\frac{2.3040}{352.07}}{\frac{15.9612}{174.916} + \frac{2.3040}{352.07}} = \frac{.006544}{.09125 + .006544}$$

$$1 - y = 0.0669 \cong 0.067$$

$$y = 0.933$$

$$y = 93.3 \text{ mole per cent BrF}_5 \text{ in vapor phase}$$

D. Liquid Sample

$$1. \quad \text{weights of sample and fluorothene tube}$$

$$\text{gross } 427.8272$$

$$\text{tare } \underline{408.4514}$$

$$\text{net } 19.3758 \text{ grams}$$

$$2. \quad \text{sample hydrolyzed in H}_2\text{O; final volume was 1000 ml}$$

$$3. \quad \text{uranium analyses of solution showed}$$

$$1.766 \frac{\text{mg U}}{\text{ml}}$$

$$4. \quad 1.766 \frac{\text{mg U}}{\text{ml}} \times 1000 \text{ ml} \times \frac{\text{gU}}{1000 \text{ mg U}} \times \frac{352.07 \text{ g UF}_6}{238.07 \text{ g U}}$$

$$= 2.6117 \text{ g UF}_6 \text{ in liquid sample}$$

$$5. \quad 19.3758 \text{ gram sample}$$

$$\underline{2.6117 \text{ gram UF}_6}$$

$$16.7641 \text{ grams BrF}_5$$

6. $1 - x$ = mole fraction UF_6 in liquid phase

$$1 - x = \frac{\frac{2.6117}{352.07}}{\frac{2.6117}{352.07} + \frac{16.7641}{174.916}}$$

$$1 - x = \frac{.007418}{.007418 + .09584}$$

$$1 - x = .0718 \approx .072$$

$$\therefore x = .928$$

x = 92.8 mole per cent BrF_5 in liquid phase

E. Relative Volatility α

$$\alpha = \frac{\frac{y}{x}}{\frac{1-y}{1-x}}$$

$$\alpha = \frac{\frac{.933}{.928}}{\frac{.067}{.072}}$$

$$\alpha = 1.08$$

F. Activity Coefficients

$$1. \quad \gamma_1 = \frac{P_y}{P_1^0 x}$$

2. P = total pressure = 1880 mm Hg

$$y = 0.933$$

$$x = 0.928$$

P_1^0 = vapor pressure of BrF_5 at 69.1°C

= 1893 mm Hg as computed from the equation¹⁰

$$\log_{10} P_1^0 = 6.4545 + 0.001101t - \frac{895}{t + 206}$$

where P_1^0 = mm Hg and $t = ^\circ\text{C}$

$$3. \quad \gamma_1 = \frac{1880 \times 0.933}{1893 \times 0.928} = 0.9985$$

$$\gamma_1 \cong 1.00$$

$$4. \quad \gamma_2 = \frac{P(1-y)}{P_2^0(1-x)}$$

$$P_2^0 = \text{vapor pressure of UF}_6 \text{ at } 69.1^\circ\text{C} = \text{mm Hg}$$

$$P_2^0 = 1334 \text{ mm Hg}^{49}$$

$$5. \quad \gamma_2 = 1.31$$

G. Correction of Observed Pressure to 70.0°C

$$1. \quad P = (\gamma_1)(x)(P_1^0) + (\gamma_2)(1-x)(P_2^0)$$

2. for the small increment of temperature from 69.1 to 70.0°C ,

one can express the corresponding change in pressure as

$$\Delta P = (\gamma_1)(x)\left(\frac{dP_1^0}{dT}\right)(\Delta T) + \gamma_2(1-x)\left(\frac{dP_2^0}{dT}\right)(\Delta T)$$

where for a given x , γ is assumed constant. The pressure at exactly 70.0°C will then be

$$P_{70.0} = P_{69.1} + \Delta P$$

$$3. \quad \gamma_1 = 1.00$$

$$\gamma_2 = 1.31$$

$$\Delta T = 70.0 - 69.1 = 0.9^\circ\text{C}$$

$$X = 0.928$$

$$\frac{dP_1^0}{dT} = \text{rate of change of the vapor pressure of BrF}_5 \text{ with temperature at } 69.6^\circ\text{C} = 56.9 \text{ mm Hg}/^\circ\text{C}^{10}$$

$$\frac{dP_2^0}{dT} = 41.2 \text{ mm Hg}/^\circ\text{C for UF}_6^{49}$$

$$4. \quad \Delta P = (1.00)(0.928)(56.9)(0.9) + (1.31)(0.072)(41.2)(0.9)$$

$$\Delta P = 47.5 + 3.5 = 51.0 \text{ mm Hg}$$

$$5. \quad P = 1880 + 51$$

$P = 1931$ = total pressure of $\text{UF}_6\text{-BrF}_5$ solution of composition

$X = 0.928$ if it were at exactly 70.0°C

The change from 69.1 to 70.0°C does not cause a significant change in the value of y .

Vapor Pressure of Pure Components

As mentioned in the literature survey, there are conflicting data (up to 17 per cent difference) between the published values of the vapor pressures of bromine pentafluoride in the range above 1 atmosphere.

Vapor pressure determinations on both pure components were therefore made using the isothermal vapor circulation equilibrium apparatus. The results obtained are indicated in Table 9. It is evident that the values are in agreement with the data of Long¹⁰ and Oliver²⁰; differences in the order of $\pm 1/2$ per cent are present. It is concluded, therefore, that the equation for the vapor pressure of bromine pentafluoride given by Ruff¹¹, cannot be extrapolated to pressures above 1 atmosphere. For positive pressures, the equation of Long¹⁰ must be used.

It is also interesting to note that if one extrapolates the equation $\log_{10} P_{\text{mm}}^{\circ} \text{Hg} = 7.9727 - \frac{1598.2}{T^{\circ}\text{K}}$ given by Rogers and Speirs¹² for the vapor pressure of bromine pentafluoride up to 40°C , to 70°C then the result obtained is also lower (by 3 per cent) than the value from the data of Ellis and Johnson. This tends to strengthen the conclusion that the results published by Ellis and Johnson on the vapor pressure of bromine pentafluoride in the range 40 to 100°C are too high. However, both of the published equations^{8,11,12} when extrapolated beyond their determined upper limit of 1 atmosphere, give results which are greater than the values obtained by Long¹⁰.

Table 9. Vapor Pressures of Pure Components

Temp °C	Component	Vapor Pressure - mm Hg		Per Cent Difference
		Observed	Previously* Published	
61.3	BrF ₅	1490	1492	-0.13
69.5	BrF ₅	1924	1916	+0.42
89.4	BrF ₅	3340	3335	+0.15
89.3	BrF ₅	3332	3326	+0.18
69.5	UF ₆	1350	1350	0.00
69.5	UF ₆	1352	1350	+0.15
89.6	UF ₆	2410	2397	+0.53

*Values for BrF₅ were computed from equation given by Long¹⁰ and values for UF₆ from equation of Oliver, et al.^{20,49}

Vapor Density Data

The weight of the saturated vapor sample was obtained for each composition under isothermal conditions. Knowing the volume of the vapor bulb, together with the observed weight, pressure and temperature, the composition of the vapor phase could be calculated if the compressibility factors were known.

Particularly in the middle composition range--from about 10 to 90 mole per cent bromine pentafluoride--this technique can be used advantageously since no chemical analyses is required. In the calculations of compositions, the chemical analyses were used rather than the analysis by vapor density. However, it is of interest to evaluate the agreement between the two approaches. This can be done best by deriving a relationship which would state that the mole fraction was some linear function of the weight, temperature, and pressure. This can be attempted as follows:

$$(1) \quad W = N_1 M_1 + N_2 M_2$$

where W = weight of vapor sample in vapor density bulb = grams

N_1 = gram moles of BrF_5

N_2 = gram moles of UF_6

M_1 = 174.916 = molecular weight of BrF_5

M_2 = 352.07 = molecular weight of UF_6

$$(2) \quad Y = \frac{N_1 \times 100}{N_1 + N_2} = \text{mole per cent } \text{BrF}_5 \text{ in vapor sample}$$

$$(3) \quad PV = Z(N_1 + N_2) RT \text{ gas law}$$

where Z = compressibility factor; assume the same Z for both

UF_6 and BrF_5

V = volume of vapor density bulb = liters = 1.031

P = observed pressure = mm Hg

$$R = \text{gas constant} = \frac{(\text{liter})(\text{mm Hg})}{(\text{g mole})(^{\circ}\text{K})} = 62.361$$

$$T = \text{observed temperature} = ^{\circ}\text{K}$$

by combining equations (1), (2), and (3) one gets:

$$(4) \quad \frac{WT}{P} = Y (K_1 - K_2) + K_2$$

$$\text{where } K_1 = \text{constant} = \frac{M_1 V}{RZ}$$

$$K_2 = \text{constant} = \frac{M_2 V}{RZ}$$

Hence by plotting $\frac{WT}{P}$ versus Y one should obtain a straight line if the assumptions used in the derivation were correct. A plot of the vapor density data obtained from the equilibrium runs is shown in Figure 16. It is apparent that the data can be fitted by two straight lines. Since the compressibility factor is in general a function both of the reduced conditions and composition a single linear correlation cannot be obtained.

Using unweighted least squares, the data were fitted to equations on an IBM-610 computer.

$$(5) \quad \frac{WT}{P} = - .03128 Y + 6.348 \text{ at } 90^{\circ}\text{C}$$

and

$$(6) \quad \frac{WT}{P} = - .03117 Y + 6.221 \text{ for the } 70^{\circ}\text{C points.}$$

A measure of the uncertainty in the above equations was obtained by computing the standard deviations of the constants. Corresponding to one σ , the values are ± 0.35 per cent for the intercept and ± 0.95 per cent for the slope.

The correlating plot or equations should be useful in obtaining rapid analyses of streams in a distillation column operating continuously on the uranium hexafluoride-bromine pentafluoride system. In the middle composition range, the composition of the sample can be determined to

Figure 16
Vapor Density of Saturated UF₆-Br F₅ Mixtures

about ± 1 per cent by vapor density. However, on either the uranium hexafluoride or bromine pentafluoride lean end of the diagrams, it is necessary to use chemical analysis because the small differences in weight cannot be determined with sufficient accuracy.

The vapor density data obtained for the 90°C and 70°C isotherms are shown in Tables 10 and 11 respectively.

From the value of the intercept K_2 , the average compressibility factor for the vapor, can be computed as

$$Z = \frac{M_2 V}{RK_2}$$

$$\text{At } 70^{\circ}\text{C}, Z = \frac{352.07 \times 1.031}{62.361 \times 6.221} = 0.936$$

Similarly at 90°C , $Z = 0.917$

Table 12 gives a comparison of the above observed compressibility factors with those predicted from various equations of state.

It is evident that there is excellent agreement between the values at Z obtained by the vapor density measurements and those computed from various equations of state. Also, in going from 70 to 90°C , with the resulting increase in pressure, the vapor phase becomes more non-ideal as predicted by equations.

In the range of reduced pressures from 0 to 0.05, at a reduced temperature of about 0.7, the plot of compressibility factor versus reduced pressure is essentially linear as shown by Hougen and Watson⁵². Using this fact, the fugacity of the pure component can be evaluated by integrating the equation (7) $\ln \frac{f}{P} = \int_0^P \frac{Z-1}{P} dp$, with the substitution $Z = m \frac{P}{P_c} + 1$ where the slope m is fixed by the value of Z determined herein at the temperature $T = 70^{\circ}\text{C}$.

Table 10. 90°C Vapor Density Data for Saturated UF₆-BrF₅ Mixtures

W grams	P mm	T °K	$\frac{WT}{P}$	Y
41.9388	2410	362.8	6.313	0.0
42.2323	2472	363.0	6.201	4.6
41.3955	2558	362.7	5.869	13.8
40.3580	2790	362.9	5.249	35.2
40.1094	2889	361.8	5.023	47.8
39.7564	2967	362.6	4.859	48.8
37.7283	3022	362.4	4.524	57.3
37.8720	2991	362.3	4.688	55.0
35.8240	3212	362.8	4.046	75.0
33.7671	3218	362.3	3.802	81.8
34.2314	3281	362.9	3.786	81.8
31.2517	3272	362.4	3.461	88.6
31.2653	3301	362.5	3.433	93.3
31.2653	3304	362.5	3.432	94.0
29.4820	3332	362.5	3.207	100.0
29.4290	3340	362.5	3.207	100.0

Table 11. 70°C Vapor Density Data for Saturated UF₆-BrF₅ Mixtures

W grams	P mm	T °K	$\frac{WT}{P}$	Y
24.5480	1352	342.7	6.222	0.0
23.1625	1380	342.6	6.088	4.2
24.0122	1429	342.5	5.755	14.8
24.1420	1564	343.1	5.296	28.0
24.1794	1569	342.8	5.282	30.7
23.8919	1582	342.9	5.178	32.0
23.0854	1683	342.6	4.699	50.2
23.3360	1708	342.9	4.684	50.4
22.4945	1731	342.8	4.454	55.9
22.2609	1778	342.7	4.290	63.8
21.2564	1836	342.9	3.970	72.2
20.5104	1854	342.8	3.792	79.4
19.5850	1870	342.7	3.589	82.8
18.2998	1885	342.6	3.325	89.1
18.2652	1880	342.3	3.326	93.3
18.3700	1888	342.5	3.332	93.7
17.9651	1904	342.5	3.231	94.3
17.9283	1896	342.7	3.240	94.9
18.2260	1902	342.5	3.281	94.3
17.7953	1913	342.6	3.187	96.8
17.9095	1915	342.8	3.206	98.6
17.6547	1924	342.7	3.145	100.0

Table 12. A Comparison of Compressibility Factors
for Saturated UF₆-BrF₅ Vapors

Temp. (°C)	Z Observed	Z BrF ₅		Z UF ₆	
		From Berthelot ⁵¹ Equation	From Generalized Reduced Properties ⁵¹	From Berthelot* Equation	From Published Equation ²⁴
70	0.936	0.940	0.932	0.951	0.928
90	0.917	0.913	0.908	0.928	0.924

$$*Z = 1 + \frac{9}{128} \left(-\frac{T_c}{T}\right) \left(-\frac{P}{P_c}\right) \left(1 - \frac{6 T_c^2}{T^2}\right)$$

Performing these operations one gets a value for the fugacity coefficient $\frac{f}{P} = 0.97$. Hence the fugacity differs from the pressure by only three per cent at conditions under which the vapor-liquid equilibria were measured. It is evident, therefore, that the approach used in this study involving the use of pressure rather than fugacity and of defining $\gamma_1 = \frac{P y}{P_{O1} x}$, which attributes the non-ideality to the liquid solution rather than to the vapor phase, is a reasonable approximation. For example, as shown in the following section, at either end of the equilibrium diagram activity coefficients of about 1.30 were observed which correspond to 30 per cent deviation from the ideal of $\gamma = 1$.

Two papers^{53,54}, dealing with generalized PVT correlations have recently appeared in the literature. The method of Kobe and Murti⁵³, is based on a Van der Waals type equation of state in which the constants are expressed as functions of the critical pressure and the ideal critical volume. Using this method, one obtains $Z_{\text{BrF}_5} = 0.957$ and $Z_{\text{UF}_6} = 0.963$ at 70°C.

70°C Isotherm

The data on the 70°C isotherm are given in Table 13. The activity coefficients were calculated from the equations (8) $\gamma_1 = \frac{P y}{P_{O1} x}$

$$(9) \quad \gamma_2 = \frac{P (1-y)}{P_{O2}^0 (1-x)}$$

The relative volatility α is defined by $\alpha = \frac{\frac{y}{x}}{\frac{1-y}{1-x}}$

The activity coefficients were correlated with composition by means of the thermodynamically consistent relationships

$$(10) \quad \gamma_1 = 10^{0.114 (1-x)^2} = 10^{A(1-x)^2}$$

$$(11) \quad \gamma_2 = 10^{0.114 (x)^2}$$

Table 13

VAPOR-LIQUID EQUILIBRIUM DATA FOR 70°C ISOTHERM: SYSTEM BROMINE PENTAFLUORIDE-URANIUM HEXAFLUORIDE

Mole Per Cent BrF ₅		Temp. °C t	Pressure mm Hg P	Relative Volatility α	Activity Coefficients	
Liquid x	Vapor y				BrF ₅ γ_1	UF ₆ γ_2
2.1	4.2	69.4	1380	2.04	1.44	1.00
9.3	14.8	69.3	1429	1.68	1.19	1.00
19.4	28.0	69.9	1564	1.62	1.17	1.02
22.5	32.0	69.7	1582	1.62	1.17	1.03
23.1	30.7	69.6	1569	1.47	1.08	1.05
40.0	50.2	69.4	1683	1.51	1.11	1.03
40.6	50.4	69.7	1708	1.49	1.10	1.05
46.1	55.9	69.6	1731	1.49	1.09	1.05
57.2	63.8	69.5	1778	1.32	1.03	1.12
67.5	72.2	69.7	1836	1.25	1.02	1.16
76.7	79.4	69.6	1854	1.17	1.00	1.21
78.2	82.8	69.5	1870	1.34	1.03	1.09
80.1	83.3	69.6	1887	1.24	1.02	1.18
88.0	88.4	69.4	1890	1.04	1.00	1.36
88.0	89.1	69.4	1885	1.11	1.00	1.28
92.4	93.0	69.5	1909	1.09	1.00	1.30
92.8	93.3	69.1	1880	1.08	1.00	1.31
93.2	93.7	69.3	1888	1.09	1.00	1.30
93.4	94.9	69.5	1896	1.31	0.97	1.09
93.8	94.3	69.3	1904	1.10	1.01	1.30
94.2	94.3	69.3	1902	1.03	1.00	1.37
96.2	96.8	69.4	1913	1.21	1.01	1.20
98.5	98.6	69.6	1915	1.06	1.00	1.35

which satisfy the Gibbs-Duhem equation

$$(12) \quad x \frac{d \ln \gamma_1}{dx} + (1-x) \frac{d \ln \gamma_2}{dx} = 0.$$

Equations (4) and (5) can be thought of as the Van Laar equations for the case where $A = B$. The Van Laar equation, as arranged by Carlson and Colburn³⁶, states that

$$(13) \quad \log \gamma_1 = \frac{A}{\left(1 + \frac{AX_1}{BX_2}\right)^2}$$

$$(14) \quad \log \gamma_2 = \frac{B}{\left(1 + \frac{BX_2}{AX_1}\right)^2}$$

One method of obtaining the "best" values for the constants A and B is to eliminate the composition variable X. One then gets the equation

$$(15) \quad (\log \gamma_1)^{1/2} = (A)^{1/2} - \left(\frac{A}{B}\right)^{1/2} (\log \gamma_2)^{1/2}$$

By plotting $(\log \gamma_1)^{1/2}$ versus $(\log \gamma_2)^{1/2}$, a linear relationship should result. This plot for the 70°C data is shown in Figure 17. From the slope of -1, it follows that $A = B$, and from the intercept, the constant A was evaluated as 0.114. This technique of obtaining the constants in the Van Laar equations was suggested by Snedeker⁵⁵.

The semi-log plot of activity coefficients versus composition is shown in Figure 18. The values of γ calculated from equations 10 and 11 were used to compute the smoothed pressure-composition curve shown in Figure 19 and the x-y curve in Figure 20. The smoothed total pressure for any given composition x was computed from the relationship

$$(16) \quad P = (\gamma_1)(x)(P_1^0) + (\gamma_2)(1-x)(P_2^0)$$

and the smoothed value of y corresponding to x was computed from equation (8).

Figure 17
Linear Plot of Activity Coefficients for 70°C Isotherm

Figure 18
Semi Log Plot of Activity Coefficient Versus
Concentration in Liquid

Figure 19
Pressure-Composition Diagram
Bromine Pentafluoride-Uranium Hexafluoride

Figure 20
Vapor-Liquid Equilibrium for the System
Bromine Pentafluoride-Uranium Hexafluoride

To permit a visual comparison over the entire range of compositions of the experimental points with the calculated values, the data points were corrected to exactly 70.0°C and then plotted in Figures 19 and 20. There is no evidence for an azeotrope in the vicinity of 90 mole per cent bromine pentafluoride.

By standard numerical methods the uncertainty in the intercept of the linear plot of the square root of logarithm of the activity coefficients was calculated to be ± 0.01 expressed as $\pm$ two standard deviations. Also the uncertainty in the slope is ± 0.095 as ± 26 . To attain a limiting value of $\gamma_2 = 1.42$, which is required to make $\alpha = 1$, it is necessary that the abscissa have the intercept $\sqrt{\log \gamma_2} = 0.39$. This value is, therefore, greater than four standard deviations away from the correlated value of 0.34. Hence, on a purely statistical basis, the existence of an azeotrope even in the limit is very improbable.

An observation of interest regarding the use of the $\sqrt{\log \gamma_1}$ versus $\sqrt{\log \gamma_2}$ method of finding the Van Laar constants A and B is that the experimentally determined values of γ should be expressed to three decimal places. In this investigation, the values of γ can be justifiably given to two decimal places. Thus any value in the range $1.000 \leq \gamma_1 \leq 1.004$ would be rounded off to 1.00. It is therefore possible that a slight reduction in the value of the constant B would result by this method. For example, rather than appearing on the abscissa, some points in the range $85 < X < 100$ would have their ordinates raised to values $0 < \sqrt{\log \gamma_1} \leq 0.047$.

90°C Isotherm

In agreement with the 70°C isotherm, the 90°C data showed positive deviations from ideality for the bromine pentafluoride-uranium hexafluoride system; no indications of an azeotrope were found. A summary of the 90°C phase equilibrium data is shown in Table 14. The activity coefficient data are plotted in Figure 21. The smoothed curves of γ versus x were computed from the relationships:

$$(17) \quad \gamma_2 = 10^{0.105 x^2} \quad \text{and} \quad (18) \quad \gamma_1 = 10^{0.105 (1-x)^2}$$

These equations were then used to evaluate γ in computing the temperature and composition correlations given in Figures 22 and 23.

The small change in the value of the constant in the equation $\gamma_1 = 10^A x^2$ from 0.114 at 70°C to 0.105 at 90°C is not very significant. The value of these constants can be checked by observing the fit with pressure-composition and vapor-liquid composition data. Correlating equations which involved two and three constants rather than one were also tried; the two and three constant correlations are discussed in the appendix.

If the change of A and therefore of γ_1 with temperature is real, one can compute the enthalpy change of mixing from the thermodynamic relationship³⁴

$$(19) \quad \left(\frac{\alpha \ln \gamma_1}{\alpha T} \right)_{P,X} = \frac{-\bar{\Delta H}_1}{RT^2} \quad . \quad \text{Where } \bar{\Delta H}_1 = \text{partial molar enthalpy of component one in solution} - \text{enthalpy of pure liquid at the same temperature.}$$

If γ decreases with temperature, then $\bar{\Delta H}_1$ must be a positive heat of mixing. Thus heat would be absorbed upon combining the two pure components as liquids.

Table 14. Vapor-Liquid Equilibrium Data for UF_6 - BrF_5 System: 90°C Isotherm

Mole Per Cent BrF_5		Temp. $^\circ\text{C}$ t	Pressure mm Hg P	Relative Volatility α	Activity Coefficients	
Liquid x	Vapor y				BrF_5 γ_1	UF_6 γ_2
2.1	4.6	89.8	2472	2.28	1.64	1.00
8.9	13.8	89.5	2558	1.65	1.18	1.01
25.6	35.2	89.7	2790	1.58	1.14	1.01
41.0	47.8	88.6	2889	1.32	1.04	1.10
42.6	48.8	89.4	2967	1.29	1.02	1.11
47.5	55.0	89.1	2991	1.35	1.05	1.08
50.7	57.3	89.2	3022	1.30	1.03	1.20
70.6	75.0	89.6	3212	1.25	1.01	1.13
79.8	81.8	89.7	3281	1.14	1.00	1.23
81.4	81.8	89.1	3218	1.03	0.97	1.34
88.2	88.6	89.2	3272	1.04	0.99	1.31
92.8	93.3	89.3	3301	1.08	1.00	1.33
93.6	94.0	89.3	3304	1.07	1.00	1.30

Figure 21
Semi Log Plot of Activity Coefficient Versus
Concentration in Liquid

Figure 22
Pressure - Composition Diagram
Bromine Pentafluoride-Uranium Hexafluoride

Figure 23
Vapor-Liquid Equilibrium for the System
Bromine Pentafluoride-Uranium Hexafluoride

By performing the integration at $X = 0$, one gets a value of $\bar{\Delta H}$ at infinite dilution equal to 256 cal/mole.

Calculated 3 Atmosphere Isobar

The isobaric data were calculated from the equation $P = (\gamma_1)(x)(P_1^0) + (\gamma_2)(1-x)(P_2^0)$. The vapor pressures P_1^0 and P_2^0 were computed at a temperature t together with the activity coefficients γ_1 and γ_2 for given composition. The calculation consisted simply in assuming a value of t and then checking to see if P came out to be exactly 3 atmospheres; the value of t from the first trial was then adjusted in the proper direction until the pressure was exactly 3 atmospheres. A linear temperature dependence of the correlating constant in the activity coefficient was assumed over the 20°C range.

Table 15 and Figures 24 and 25 summarize the results of the constant pressure calculations. For comparison, Raoult's Law predicts a relative volatility α of 1.40 at 90°C and an α of 1.42 at 70°C. It is evident that there is a considerable difference between the ideal relative volatilities and those computed from the equilibrium data.

Table 15. Summary of Calculations on 3 Atmosphere
Isobar

Mole Fraction BrF_5			
Liquid x	Vapor y	Temperature $^{\circ}\text{C}$	Relative Volatility α
0	0	87.7	$\lim_{x \rightarrow 0} = 1.80$
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	$\lim_{x \rightarrow 1} = 1.09$

Figure 24
Temperature-Composition Diagram
3 Atmosphere Isobar UF_6 - BrF_5

Figure 25
Vapor-Liquid Equilibrium for the System
Bromine Pentafluoride-Uranium Hexafluoride

CHAPTER V

DISCUSSION OF RESULTS

Comparison of Experimental Data with the Results of Ellis and Johnson⁸

The equilibrium data obtained in this investigation may be compared with the work of Ellis and Johnson⁸ by evaluating the vapor composition and total pressure for given values of liquid composition at 68°C. The total pressure and vapor composition were computed from equations (8), (16) and (10) with $A = 0.115$. For the comparison, the values of y and P for the 68°C isotherm of Ellis and Johnson were read directly from Figure 4.

The results of this evaluation are shown in Table 16. It is evident that over the entire range of compositions, the pressures found by Ellis and Johnson were greater than those found in this study. At $X = 90$, their reported pressure is 21.3 per cent larger than the value obtained in this study. Much of this difference in pressure is due to the higher values for the vapor pressure of bromine pentafluoride found by Ellis and Johnson.

A comparison of the limitations of the techniques of measurement in the two investigations is also of interest. Ellis and Johnson state that temperatures were indicated on a recorder and the values at various points agreed to within $\pm 1^\circ\text{C}$. Also they determined pressures on a 0-200 psi bourdon gage. The limit of error on the sonic analyzer, as determined by a check on one standard was about ± 0.5 per cent. It seems reasonable to conclude that the instruments used to indicate the temperature and pressure could be read to within $\pm 0.5^\circ\text{C}$ and ± 25 mm Hg respectively. The uncertainty in the measurement of temperature and pressure in the vapor

Table 16. Comparison of Observed Vapor-Liquid Equilibrium Data
With the Results of Ellis and Johnson⁸

Mole Per Cent BrF ₅ in Liquid X	Mole Per Cent BrF ₅ in Vapor Y		Relative Volatility α		Pressure: mm Hg P	
	This Study	Ellis and Johnson	This Study	Ellis and Johnson	This Study	Ellis and Johnson
10	16.3	20.0	1.75	2.25	1391	1420
30	40.4	48.0	1.58	2.15	1550	1740
50	58.7	67.5	1.42	2.08	1667	1970
70	74.9	80.5	1.28	1.77	1754	2140
90	91.2	90.0	1.15	1.00	1814	2200

Temperature = 68° C

recirculation equipment used in this investigation is estimated to be $\pm 0.1^{\circ}\text{C}$ and ± 6 mm Hg respectively.

However, the instruments themselves were capable of greater accuracy. Temperatures could be read to within $\pm 0.01^{\circ}\text{C}$ and pressures to within ± 1 mm Hg. At 68°C and 1500 mm Hg the uncertainties of $\pm 0.1^{\circ}\text{C}$ and ± 6 mm Hg correspond to relative errors of ± 0.15 per cent in temperature and ± 0.40 per cent in pressure.

From Table 16, it is also apparent that over most of the composition range the relative volatilities of Ellis and Johnson are significantly higher than those found in this investigation. For example, at $X = 10$, their value is 28.5 per cent greater. However, the most important difference is that, whereas Ellis and Johnson reported an azeotrope at $X = 90$ per cent bromine pentafluoride, no evidence was found for one in this work. By reference to Figure 4, it is to be noted that their claim for an azeotrope depends basically on an extrapolation of their data since no equilibrium determinations were made between $X = 90$ to 100 per cent bromine pentafluoride.

One advantage of the method of analysis of samples used in this investigation is that in the region of low relative volatility, the minor constituent can be analyzed for and the amount of the other component can be determined by subtracting from the total weight of the sample. It is possible that the sonic method of analysis could not detect the small differences in composition between the vapor and liquid phases in the bromine pentafluoride rich region. The uncertainties in the analysis of samples from the equilibrium runs in this work are as follows at three different levels of composition: $X = 10.0 \pm 0.1$,

$X = 50.0 \pm 0.5$, $X = 90.0 \pm 0.1$ where X = mole per cent bromine pentafluoride and the limits of error are given as approximately $\pm$ one standard deviation.*

Ellis and Johnson made no mention of activity coefficients in their paper or whether they had attempted to fit their data to thermodynamically consistent relationships. Because the values of Ellis and Johnson on the vapor pressure of bromine pentafluoride are believed to be in error, the two sets of equilibrium data cannot be put on the same basis. However, it is evident that they did find larger positive deviations from ideality than were found in this study.

To give a more quantitative comparison, an effort was made to compute activity coefficients from their 68°C pressure-composition plot (Figure 4). It was estimated that their activity coefficients would have limiting values of $\lim_{x \rightarrow 0} \gamma_1 = 1.26$ and $\lim_{x \rightarrow 100} \gamma_2 = 8.17$. Thus, the relationship of γ as a function of x for their data is not symmetrical and the limiting value of γ_2 is much greater than the value of 1.30 obtained in this study. At $x = y = 90$, a value of $\gamma_2 = 1.69$ was computed using the total pressure and vapor pressure given in Figure 4.

By examining the $\gamma - x$ data obtained in this study as shown in Figures 18 and 21, there is some evidence for the limiting value of γ_2 to be slightly greater than that of γ_1 . Since the $\lim_{x \rightarrow 100} \alpha = \frac{P_1^0}{\gamma_2 P_2^0}$, and using $P_1^0 = 1945$ and $P_2^0 = 1371$ at 70°C , it is apparent that for $\alpha \leq 1$ then $\lim_{x \rightarrow 100} \gamma_2 \geq 1.419$. Thus for an azeotrope to exist, it is necessary for the limiting value of γ_2 to be greater than 1.419.

*Refer to Table 8 for values of σ_i .

Finally, it may be remarked that the dispersion of the data for the 90°C isotherm of this study is twice that of the 70°C data as determined by deviations from the linear plot of $\sqrt{\log \gamma_1}$ versus $\sqrt{\log \gamma_2}$. However, an uncertainty of ± 0.02 , corresponding to two standard deviations in the intercept of the 90°C plot, is still insufficient to give rise to a correlation which would imply that the uranium hexafluoride be the more volatile component.

If the constant B in the Van Laar equation were evaluated by extrapolating the γ_2 -x curve (see for example, Figure 21) to $x = 100$ as is commonly done, then a value of $\lim \gamma_2 \cong 1.39$ ($B = 0.143$) would be obtained. This value of γ_2 , obtained in effect by giving weight to the end values at γ_2 , is to be compared to the symmetrical limiting value of 1.27 obtained from the $\sqrt{\log \gamma_1}$ versus $\sqrt{\log \gamma_2}$ plot which gives equal weight to each experimental point.

In either correlating method, however, the limiting value of γ_2 is considerably less than the value of γ_2 computed from the data of Ellis and Johnson. Also, either value of 1.27 or 1.39 is less than the value of $\gamma_2 = 1.419$ which is necessary to make the limiting value of the relative volatility α equal to one. Thus, the existence of the azeotrope for any x was not verified. Rather, the data obtained in this investigation indicate that α continually decreases as x increases but α always remains greater than one.

Comparison of Experimental Data with Solid Liquid Equilibria

It is also of interest to compare the condensed phase equilibrium data on the bromine pentafluoride-uranium hexafluoride system as shown in Figure 6 from the work of Fischer and Vogel¹⁴, to the vapor-liquid data

obtained in this study. This comparison can be made most conveniently by an evaluation of the activity coefficients.

Using the approach of equality of partial pressures^{14,32,52} (rather than fugacities since $P < 1$ atm) one can from the equilibrium at a temperature $t < 64^\circ\text{C}$ state that

hence, partial pressure UF_6 solid = partial pressure of UF_6 in solution.

Therefore, write $P_{2S}^\circ = \gamma_2 X_2 P_{2L}^\circ$ where

P_{2S}° = vapor pressure of solid UF_6 at t

γ_2 = activity coefficient of UF_6 in saturated solution

X_2 = mole fraction UF_6 in the solution

P_{2L}° = vapor pressure of supercooled UF_6 liquid at t

Standard state is pure supercooled, liquid UF_6 at temperature t . P_{2L}° is obtained simply by extrapolating the equation giving the vapor pressure of UF_6 as a function of temperature to the temperature t below the triple point of UF_6 .

Table 17 shows the results of these computations. In agreement with the conclusion stated in the paper¹⁴, the system shows only small deviations from ideality.

The major uncertainty in this computation of activity coefficients from the solid-liquid equilibria lies in the extrapolation of the equation for the vapor pressure of liquid uranium hexafluoride to temperatures below 64°C .

The positive deviations from ideality found in this study (see Figures 18 and 21) on vapor-liquid equilibrium were larger than those

Table 17. Activity Coefficients for Uranium Hexafluoride
Computed from Solid-Liquid Equilibria

t Temperature °C	X_2 Mole Per Cent UF_6 in Saturated UF_6 - BrF_5 Solution in Equilibrium with Solid UF_6	γ_2 Calculated Activity Coefficient of UF_6 in Solution
60	94	0.98
50	75	0.98
40	58	1.02
30	45	1.03
20	35	1.03
10	27	1.05
0	21	1.00
-20	13	0.86

computed from the condensed equilibria. However, the comparison is made at widely different temperatures. The values of γ_2 at 68°C calculated from the results of Ellis and Johnson at $x_2 = 34$ and $x_2 = 10$ are 1.20 and 1.69 respectively; these are much greater than average value of $\gamma_2 = 1.0$ indicated by the solid-liquid equilibrium data.

Comparison of Experimental Data with the Theory of Regular Solutions

The task of solution theory is to predict from some fundamental molecular parameters the values of γ , and thus make possible the estimation of vapor-liquid equilibria. Considerable progress has been made toward general methods of correlating and predicting phase equilibria.

One approach is that developed by Hildebrand⁴⁶ and Scatchard⁵⁶, and their co-workers known as the theory of regular solutions. The definition of a regular solution is one which has an ideal entropy of mixing. The theory then provides an estimate of ΔE ; when volume changes on mixing are negligible ΔE becomes equal to ΔH . Hence, the free energy change ΔF can be computed together with the activity coefficients. A convenient expression for γ derived from this hypothesis of a regular solution is as follows⁵⁷

$$(20) \quad \gamma_1 = e^{\frac{V_1 \phi_2^2}{RT}} \left[\frac{\Delta E_1}{V_1}^{1/2} - \frac{\Delta E_2}{V_2}^{1/2} \right] .$$

where ϕ_2 = volume fraction of component 2 in the liquid phase

V_1 = volume of liquid/mole of component 1

ΔE_1 = energy of vaporization/mole for component 1 - referred to zero pressure

γ_1 = activity coefficient of component 1.

It is of interest to compare the values of the activity coefficients obtained experimentally to those predicted by the above equation. First it may be noted that the equation for the predicted values of γ can be rearranged into the form

$$(21) \log_{10} \gamma_1 = C \phi_2^2 \text{ for a given temperature}$$

where C is a constant having the value

$$(22) C = \frac{0.4343 V_1}{RT} \left[\frac{\Delta E_1}{V_1}^{1/2} - \frac{\Delta E_2}{V_2}^{1/2} \right]^2.$$

Equation (21) has the same form as the equation used to correlate the experimentally determined values of γ which is

$$(23) \log_{10} \gamma_1 = A X_2^2.$$

The only difference is that equation (21) employs volume fraction and equation (23) mole fractions.

The volume fraction ϕ_2 can be computed from

$$(24) \phi_2 = \frac{X_2 V_2}{X_2 V_2 + X_1 V_1}$$

The following values for the parameters were used to compute the theoretical values of γ_1 and γ_2 :

	BrF ₅		UF ₆	
	70°C	90°C	70°C	90°C
V liter/g mole	0.0763	0.0790	0.0980	0.1014
ΔH_{vap} , Kcal/g mole	6.560	6.150	6.953	6.703
$\Delta E_{\text{vap}} = \Delta H_{\text{vap}} - RT$, Kcal/g mole	5.780	5.430	6.271	5.980

The term $\left(\frac{\Delta E_1}{V_1}\right)^{1/2}$ is commonly known as the "cohesive energy density" δ or the "solubility parameter." At 70°C, BrF₅ has the value 8.70 cal^{1/2}/cc^{1/2} and UF₆ has the value 8.00 cal^{1/2}/cc^{1/2}.

Table 18 gives a comparison between values of γ predicted by regular solution theory with those calculated from equations (10) and (11) which best fit the experimentally determined values of γ at 70°C.

From the comparison, it is evident that the general form of the function is predicted and that the theory predicts that there should be no azeotrope. However, over most of the composition range, the observed deviations from ideality were greater than those predicted.

A comparison of the observed and predicted temperature dependence of the activity coefficients may also be made. Table 19 gives a summary of the limiting values of γ at 70 and 90°C.

From the above calculations, it is evident that the theory of regular solutions predicts a small decrease in the activity coefficients as the temperature is raised from 70 to 90°C and that the data also indicate a similar trend. The change in the limiting values of γ is very small (about two per cent), over the 20°C range so that it is difficult to determine the magnitude of the temperature change precisely.

It is also interesting to observe that the theory predicts only a slight difference between the limiting values of γ_2 and γ_1 with $\lim_{x \rightarrow 1} \gamma_2 = 1.07$ and $\lim_{x \rightarrow 0} \gamma_1 = 1.06$. Assumptions involved in theory, other than the ideal entropy of mixing and no volume change, are spherical symmetry, a geometric mean potential interaction between unlike molecules, and no chemical, ionic, or dipole interactions. When two extra terms, which correct for non-ideal entropy of mixing⁴⁶ for molecules having widely different molar volumes, were incorporated, it was found that their contribution was negligible. This modified equation is⁴⁶

$$\ln \gamma_2 = \ln \phi + \phi \left(1 - \frac{V_2}{V_1} \right) + \frac{V_2 \phi_1^2 (\epsilon_2 - \epsilon_1)^2}{RT}$$

Table 18. A Comparison of Activity Coefficients at 70°C
With Those Predicted from Theory of Regular Solutions

Composition X Mole Fraction BrF ₅ in Liquid Phase	Activity Coefficients			
	γ_1 Calc.	γ_1 Pred.	γ_2 Calc.	γ_2 Pred.
0	1.30	1.06	1.00	1.00
0.3	1.14	1.02	1.02	1.01
0.7	1.02	1.01	1.14	1.03
1.0	1.00	1.00	1.30	1.07

γ calc = calculated from equations (10) and (11) which fit experimental data

γ pred = predicted value from theory of regular solutions

Table 19. A Comparison of the Limiting Values
of γ with Predicted Values

Temp. ($^{\circ}\text{C}$)	$x = 0$		$x = 1$	
	γ_1 Calc.	γ_1 Pred.	γ_2 Calc.	γ_2 Pred.
70	1.30	1.06	1.30	1.07
90	1.27	1.04	1.27	1.05

By combining the predicted change of γ_1 with temperature with the integrated form of equation (19) for $x = 0$ one obtains a value of 176 cal/g.mole for $\Delta\bar{H}$ of mixing at infinite dilution.

CHAPTER VI CONCLUSIONS

1. The vapor pressure of bromine pentafluoride, at temperatures above its boiling point, is given by the equation

$$\log_{10} P_1^0 = 6.4545 - 0.01101t - \frac{+895}{t + 206} \text{ where } P_1^0 = \text{mm Hg, } t = ^\circ\text{C}$$

as reported by Long¹⁰. The values for the vapor pressure of bromine pentafluoride predicted by this equation were checked to within ± 0.5 per cent at four temperature levels in the range 61.3 to 89.4°C. It is believed, therefore, that the values for the vapor pressure of bromine pentafluoride reported by Ellis and Johnson⁸ are in error by amounts ranging from ± 6 to ± 14 per cent over the range 60 to 90°C.

2. The compressibility factors of saturated vapor mixtures of bromine pentafluoride and uranium hexafluoride were found to be 0.936 at 70°C and 0.917 at 90°C. These values are in excellent agreement with the values predicted from Berthelot's equation of state and from generalized correlations in terms of reduced properties. It was found that measurement of the vapor density of saturated uranium hexafluoride-bromine pentafluoride mixtures could serve as a useful technique for the determination of composition to within ± 1 per cent.

3. To obtain reliable data on the vapor-liquid equilibria in the system bromine pentafluoride-uranium hexafluoride, it was found necessary to introduce elemental fluorine to the extent of about 10 mm Hg partial pressure to insure that extraneous chemical species such as Br₂, BrF, or BrF₃ were not formed. The binary vapor-liquid system bromine pentafluoride-uranium hexafluoride shows positive deviations from ideality. Contrary to the report of Ellis et al.^{8,9}, the system does not have an azeotrope.

Activity coefficients can be correlated as a function of composition by the symmetrical relationships of the form $\log_{10}\gamma_2 = AX^2$ and $\log_{10}\gamma_1 = A(1-X)^2$ where the constant A has the value 0.114 at 70°C. This value corresponds to a limiting value of the activity coefficient of 1.30. The three atmosphere isobar as computed from isothermal data at 70°C and 90°C has relative volatilities ranging from $\alpha = 1.80$ at $X \longrightarrow 0$ to $\alpha = 1.09$ as $X \longrightarrow 100$ per cent bromine pentafluoride. Comparisons made with published results on distillation of the binary, condensed equilibria, and the theory of regular solutions all indicate that the bromine pentafluoride-uranium hexafluoride shows small positive deviations from ideality with no azeotrope.

It is believed that the difference in results obtained in this investigation using a mechanical, vapor recirculation, equilibrium still as compared to the results of Ellis and Johnson using a static still⁸ can be explained at least in part by the fact that in this study fluorine was used whereas in the static still elemental fluorine was not present.

APPENDIX

Since the region in which there is a conflict of evidence in the system bromine pentafluoride-uranium hexafluoride is in the range of compositions $90 \leq x < 100$, where x = mole per cent bromine pentafluoride, an effort was made to obtain data in the extremely dilute region of $99.5 < x < 100$. In this region, the low uranium hexafluoride concentration results in a decrease in the precision of the uranium analysis. Because of this decrease in the reliability of the analysis together with increased sensitivity to any impurities, the five runs that were made in this low uranium hexafluoride region were not compiled with the other runs in Tables 13 and 14. As reported in Tables 13 and 14, ten equilibrium points were determined for $90 \leq x \leq 98.5$. All of these points indicated that bromine pentafluoride was the more volatile component, and that no azeotrope existed. The limiting value of the relative volatility α as $x \longrightarrow 100$ was found to be 1.09 as evaluated from a symmetrical Van Laar correlation.

Using this value of $\alpha = 1.09$, and letting $x = 99.90$ one can compute that $y = 99.91$. Hence, in terms of uranium hexafluoride concentration differences the per cent difference is $\frac{0.10 - 0.09}{0.10} \times 100 = 10$ per cent.

It was estimated that the uncertainty in the uranium analysis in this dilute range was ± 3 per cent. Hence, there seemed to be some chance of obtaining valid results even with only 0.01 per cent uranium hexafluoride present. The bromine pentafluoride content was obtained by subtracting the analyzed uranium hexafluoride from the total sample weight.

The results obtained are shown in Table 20. The mean value of the five determinations of the relative volatility is $\bar{\alpha} = 1.03$. The 90 per cent confidence limits on $\bar{\alpha}$, as computed from "Student's t " test⁵⁸ are

Table 20. Vapor-Liquid Equilibrium Data for the Bromine Pentafluoride-Uranium Hexafluoride System in the Dilute Uranium Hexafluoride Region

Mole Per Cent BrF ₅		Temp. °C T	Pressure mm Hg P	Relative Volatility α	γ_1	γ_2
Liquid x	Vapor y					
99.66	99.68	69.9	1932	1.06	1.00	1.33
99.76	99.75	69.5	1955	0.96	1.02	1.51
99.84	99.85	69.9	1931	1.07	1.00	1.32
99.91	99.93	87.9	3294	1.29	1.03	1.12
99.91	99.88	69.4	1946	0.75	1.02	1.93

$0.85 \leq \bar{\alpha} \leq 1.21$. Hence, this result is not inconsistent with the previously obtained result of $\alpha = 1.09$ as $x \longrightarrow 100$. If one computes the limiting value of $\alpha = \frac{\frac{y_1}{x_1}}{\frac{y_2}{x_2}}$, where the subscript 1 refers to bromine penta-

fluoride, from the value of the Van Laar constant $B = 0.96$ ($\lim_{x \rightarrow 100} \gamma_2 = 9.1$) for the one point at $x = 90$ from the data of Ellis and Johnson one gets

$\alpha = 0.19$. Hence, as before, one must conclude that the bromine penta-
 $\lim_{x \rightarrow 100}$
 fluoride-uranium hexafluoride does not exhibit an azeotrope at $x = 90$ per cent bromine pentafluoride.

APPENDIX II

It was suggested that the Redlich-Kister correlation also be tried to determine if a better fit of the data would result. The two constant equations involved in this system are⁵⁹

$$\begin{aligned}\log \gamma_1 &= X_2^2 \left[B + C(3X_1 - X_2) \right] \\ \log \gamma_2 &= X_1^2 \left[B + C(X_1 - 3X_2) \right] .\end{aligned}$$

The limiting behavior of the equations indicates that

$$\lim_{x \rightarrow 0} \log \gamma_1^* = B - C$$

$$\lim_{x \rightarrow 1} \log \gamma_2 = B + C$$

It was found that the constants which represent the data have the values

$$B = 0.1300$$

$$C = 0.0161$$

Figure 26 shows a comparison of the experimental results with the smooth curve calculated from the Redlich-Kister Equations. Three of the 70°C and two of the 90°C points are not included both because of experimental error considerations and because the points fall outside of the limits by an amount greater than three standard deviations. By comparing this to Figure 18 it is evident that the fit has improved slightly, particularly at $X < 0.5$. Since the important quantity α involves both γ_1 and γ_2 in the relationship $\alpha_1 = \frac{\gamma_1 P_1^0}{\gamma_2 P_2^0}$, an evaluation of the correlation may be made by comparing the observed relative volatility with the calculated value. Table 21 gives the results of this comparison for the isotherm at 70°C for which the most extensive data are available. For these data, from which three of the widely deviating points are omitted, the Redlich-Kister correlation gives a mean difference of -0.2 per cent between the observed

Figure 26
Semi Log Plot of Activity Coefficient Versus
Concentration in Liquid

Table 21. A Comparison of Two Correlations of the 70°C Data

Mole Percent BrF ₅ in Liquid x	Observed Relative Volatility α	Percent Difference $= \frac{\alpha_{\text{obs}} - \alpha_{\text{calc}}}{\alpha_{\text{obs}}} \times 100$	
		Redlich-Kister	Van Laar*
2.1	2.04	+10.3	+10.8
9.3	1.68	-6.0	-4.8
19.4	1.62	-4.9	-3.1
22.5	1.62	-3.1	-1.2
40.0	1.51	-2.0	+0.9
40.6	1.49	-2.7	0.0
46.1	1.49	+0.7	+3.4
57.2	1.32	-5.3	-3.8
67.5	1.25	-4.0	-3.6
76.7	1.17	-3.4	-5.1
78.2	1.34	+10.4	+7.2
80.1	1.24	+4.0	+2.4
88.0	1.11	-1.0	-4.5
92.4	1.09	+1.0	-3.7
92.8	1.08	0.0	-4.6
93.2	1.09	+1.8	-3.7
93.8	1.10	+2.7	-2.7
94.2	1.03	-2.9	-9.1
98.5	1.06	+2.8	-3.8

*Symmetrical

and calculated values of α . The standard deviation of the per cent difference for any given value of α is ± 4.7 per cent. Also, the standard deviation of the mean of the differences is ± 0.25 per cent. However, the previously used Van Laar correlation gave a mean difference of -1.5 per cent. Thus, comparing the values of 0.25 per cent to 1.5 per cent, it can be concluded that the Redlich-Kister correlation gives a better fit of the data.

A three constant Redlich-Kister correlation was also developed. The equations applicable to the 70°C isotherm are as follows:

$$\begin{aligned}\log \gamma_1 &= (1 - X)^2 \left[0.0882 + 0.1268x - 0.0240x^2 \right] \\ \log \gamma_2 &= (X)^2 \left[0.0248 + 0.1428x - 0.0240x^2 \right]\end{aligned}$$

Figure 27 shows the data points used in formulating the correlation together with the smooth γ -X curves computed from the three constant equations. The standard deviation of α from the calculated value is ± 2.8 per cent for any given value of the relative volatility for the seventeen data points. The use of the third constant is probably within the limits of the error variance of the data, hence its use is probably not justified over the simpler two constant correlation.

Figure 27
Semi Log Plot of Activity Coefficient Versus
Concentration in Liquid

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